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NOVEL PROCESSING COATING TECHNIQUES TOWARD

IMPROVED ELECTRO-CERAMICS

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by

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ABSTRACT

Novel coating processing techniques were utilized to improve the electrical performance of electro-ceramics. In the first part of this work, atomic layer deposition (ALD) coatings were used to encapsulate the BaTiO$_3$ multilayer ceramic capacitors and ZnO varistors against hydrogen and humidity exposure. In the second part, the Ni particles used in the manufacturing of MLCCs were coated by lithium carbonate to preserve their conductivity in oxidizing atmospheres. This method together with fast firing enabled us to sinter the MLCC in higher partial pressure of oxygen and, consequently, decrease the concentration of oxygen vacancies in them. In both parts, the applied methodologies were demonstrated to be effective in the improvement of electroceramic performance. In following, a brief description will be provided for every chapter in this dissertation for both the first and the second parts to provide a roadmap for readers.

Encapsulating of BaTiO$_3$ MLCCs and ZnO varistors against humidity and hydrogen exposure by ALD coatings

Hydrogen gas creates a highly damaging environment that degrades electrical properties in oxide based dielectrics and piezoelectrics. In the second chapter, the degradation resistivity due to hydrogen gas in a barium titanate X7R dielectric is studied for base metal electrode capacitors. The present paper is devoted to I-V measurements and the loss of resistivity in the electrode Schottky barriers. The DC degradation and asymmetries noted in I-V forward and reverse biasing conditions were assumed to be due to hydrogen ion interstitials, locally creating donor substitutions. Thermionic and field emission conductivity mechanisms are applied to model the I-V data; the conductivity is controlled by the Schottky barrier heights and hydrogen
ions localizing at the interfaces. Finally, a mechanism was proposed for resistivity degradation due to exposure to hydrogen gas. The proposed mechanism predicts the degradation should be reversible, and its validity was examined by recovery tests.

In the third chapter, the contributions of electrode interface, grain boundary, and grain to the total resistivity was differentiated by impedance spectroscopy (IS) tests and a 3RC model. It turned out that the largest contribution to total resistivity comes from electrode Schottky barriers, which control the major part of the degradation. Based on the IS analysis, the hydrogen diffusion coefficients of those three components were successfully calculated and compared with the diffusion coefficient in other systems. Determination of the hydrogen diffusion in grains and grain boundaries is important in understanding how hydrogen penetrates capacitors and can also be useful for applications that involve extreme environments. In this study, we also considered the kinetics and role of the metal electrode chemistry (Ag, Au, and Pt) and the thickness of active layers on the hydrogen degradation.

In chapters two and three, the degradative effect of hydrogen exposure was studied and documented. Next, ALD coatings were introduced as a solution to make a physical barrier between the electroceramic device and the degrading environment. In the chapter one, the encapsulating power of ALD coating has been reviewed. In addition, it was shown that the ALD techniques can coat the nanostructures (i.e. nanowires and nanoparticles) for both encapsulation or core-shell proposes.

In the fourth chapter under the title of “Evaluating the merit of ALD coating as a barrier against hydrogen degradation in capacitor components”, the encapsulating power of ALD coating was evaluated. Three ALD chemistries of ZnO, Al₂O₃, and HfO₂ with different thicknesses were coated onto BaTiO₃ capacitors, and their merit as hydrogen gas barriers at high
temperatures was evaluated by I–V and impedance spectroscopy which could monitor the degradation of resistivity. These experimental investigations provide the temperature of merit ($T_0$) and the proton (H-ion) diffusion coefficients of the ALD layers, which can be used to evaluate their barrier effectiveness. Transmission electron microscopy (TEM) analysis was applied to examine the ALD layers before and after the I–V tests and find out the physical dimensions, conformity, and structure (amorphous and crystalline) of the ALD layers. We determine that the failure of the barrier characteristics at elevated temperatures is due to crystallization. The diffusion coefficient associated with protons before and after crystallizations in ALD layers was determined. Within the chemistries investigated here, the most effective ALD layers are made of HfO$_2$ with an amorphous structure.

In the fifth chapter, the idea of using ALD coatings to protect electroceramics against hydrogen and humidity were tested in other electroceramics. Effectiveness of HfO$_2$ Atomic Layer Deposition coatings has been studied on ZnO varistors by I–V tests, impedance spectroscopy, and highly accelerated life test. Based on impedance spectroscopy analyses, the proton diffusion coefficient was measured to be 400 K times less in the coating. Transmission electron microscopy analysis shows that Atomic Layer Deposition films are continuous and conformal. After exposure to high temperature, partial crystallization was detected in the coating and increases proton diffusion coefficient by 150 times.

**Preserving the electrical conductivity of nickel nanoparticle by Li$_2$CO$_3$ coating to decrease the number of oxygen vacancies in MLCCs**

In the first try to preserve the electrical conductivity of Ni particles during sintering, the ALD coatings was coated on the Ni foils to study the behavior of these coatings at the sintering
conditions. Although many techniques have been applied to protect nickel (Ni) alloys from oxidation at intermediate and high temperatures, the potential of atomic layer deposition (ALD) coatings has not been fully explored. In the sixth chapter, the application of ALD coatings (HfO$_2$, Al$_2$O$_3$, SnO$_2$, and ZnO) on Ni foils has been evaluated by electrical characterization and transmission electron microscopy analyses in order to assess their merit to increase Ni oxidation resistance; particular consideration was given to preserving Ni electrical conductivity at high temperatures. The results suggested that as long as the temperature was below 850 °C, the ALD coatings provided a physical barrier between outside oxygen and Ni metal and hindered the oxygen diffusion. It was illustrated that the barrier power of ALD coatings depends on their robustness, thicknesses, and heating rate. Among the tested ALD coatings, Al$_2$O$_3$ showed the maximum protection below 900 °C. However, above that temperature, the ALD coatings dissolved in the Ni substrate. As a result, they could not offer any physical barrier. The dissolution of ALD coatings doped on the NiO film, formed on the top of the Ni foils. As found by the electron energy loss spectroscopy (EELS), this doping affected the electronic transport process, through manipulating the Ni$^{3+}$/Ni$^{2+}$ ratio in the NiO films and the chance of polaron hopping. It was demonstrated that by using the ZnO coating, one would be able to decrease the electrical resistance of Ni foils by two orders of magnitude after exposure to 1020 °C for 4 min. In contrast, the Al$_2$O$_3$ coating increased the resistance of the uncoated foil by one order of magnitude, mainly due to the decrease in the ratio of Ni$^{3+}$/Ni$^{2+}$.

Based on the previous chapter, Li$^+$ can be potential candidate to increase the ratio of Ni$^{3+}$/Ni$^{2+}$ and increase effectively the chance of electron hoping. In chapter seven, a new Ni electrode was manufactured from Ni nanoparticles, which coated by Li salts, namely Li$_2$CO$_3$, LiOH, and LiF with an innovative coating method. After the confirmation of a successful coating
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In chapter nine, by utilizing the novel coating together with fast firing techniques, the MLCCs were sintered in oxidizing atmosphere without losing their electrode conductivity. It demonstrated that the oxygen vacancy concentration decreased in the new MLCCs relative to conventional MLCCs, as illustrated by EELS analysis, as well as the color change of the samples. Due to the decline in oxygen vacancies, the dissipation factor was decreased by 60%. In
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In chapter ten, the effect of Li$^+$ doping by using HALT tests in both dried and humid environments as well as TSDC (thermally stimulated discharging current) was evaluated. The results suggested that Li doping does not affect the electrical properties of multilayer ceramic capacitors, and the reliability is not limited by the strategies of Li$_2$CO$_3$ coating. So we see that the main goal to establish an approach to customize multilayer BaTiO$_3$-Ni structures at high oxygen activities and H$_2$-free atmospheres were successful, with no unforeseen limitations with Li-addition.
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1 Review on the Diffusion Process and the Encapsulating Property of Atomic Layer Deposition Coatings

1.1 Introduction

Coatings have found wide applications due to the fact that they offer a dual property. For example, most materials cannot simultaneously provide both high hardness with good abrasion resistance and high fracture toughness. This is due to the fact that, generally, materials with high hardness have a crystal structure with few slip systems to avoid deformation, while materials with high fracture toughness need a large amount of plastic deformation, which requires a crystal structure with many slip systems [1]. Inevitably, many industrial applications need a material with dual property, which cannot be found in a single material. The fulfilment of the dual property is the main drive of utilizing coatings. In the above example, the high fracture toughness can be provided by using low carbon steels as the core, and the high hardness can be obtained by utilizing ceramic coatings around the core [2].

One of the main applications of coatings is protecting the core against harsh environments. One may think that in order to protect the core, there is a need for thick coatings produced in conventional methods. For example, the oxidation of nickel metal and its alloys has been studied for a long time [3,4], and many coating techniques have been suggested to protect them from oxidation, such as electrochemical plating [5], cladding and hardfacing [6,7], and organic films [8]. The minimum thickness in these techniques is in the range of several ten micrometers. The functional graded coating is a more intricate generation of these coatings, where the reinforcements gradually change through the thickness of the coating, and thickness could be several millimeters [9–12]. These types of coating have found applications in aerospace
industries [13]. Despite the conventional techniques, which lead to thick coatings, recently a new type of coating with thicknesses on orders of a nanometer has been developed [14–16]. For example, 2D materials [17,18] were coated on Ni foils with a thickness of one atomic layer (less than 2 nm), and it was shown that despite their nanoscale thickness, they could effectively protect Ni metals from oxidation at high temperatures. It was illustrated that boron nitride 2D coatings can preserve the substrate up to 850 [19] or even 1100 °C [18] with 5 nm thickness. The same protection was reported by graphene on Ni substrates up to 650 °C [20]. Morrow et al. [21] reviewed the diffusion barrier of graphene. Atomic layer deposition (ALD) is another new technique that has been widely used as a diffusion barrier on the various materials [18,22–37].

The introduction of atomic layer deposition techniques goes back to 1965, by Shevjakov et al. [38]. It took until the 1990s before ALD coatings found their way into some industrial applications. Perhaps one of the most successful applications of ALD coatings was their replacement of the SiO$_2$ gate oxides in transistors [39]. Conventionally, SiO$_2$ was the ubiquitous gate oxide, but the need for miniaturization and low energy consumption led to the development of a new gate oxide with high dielectric constant through a careful ALD technique. Nowadays, ALD coatings have a wide range of applications, such as the fields of microelectronics, catalysts, electroluminescence, and nanotechnology [40–42]. One of the main applications of ALD coating is its use as a diffusion barrier on the various materials [18,22–36,43]. ALD coatings have been demonstrated as an effective barrier due to the fact that they provide a continuous and conformal layer all around the object. The ALD encapsulating feature comes from the nature of their layer-by-layer growth process, as will be explained later.

In this review paper, first the nucleation and growth mechanism of ALD coating was briefly explained, and then the application of ALD coatings as a protecting layer on both bulk
and nanostructures against harsh environments was discussed. At the end, the limitations of ALD encapsulation would be reviewed.

1.2 Deposition process of ALD coatings

1.2.1 Coating Growth

The nature of the deposition mechanism of ALD coatings has been studied and is well understood [44–46]. Two gases (or precursors) are involved in the deposition process, and every gas reacts with the substrate separately. As such, the first precursor is injected to the ALD chamber with a duration, called the dose time, and then the chamber is purged with nitrogen gas. In the second half-cycle, the second precursor is injected and purged out in the same manner. A single atomic layer is deposited in every cycle, and the depositing reaction should be self-terminating. This means that the reaction should stop after depositing one layer of atoms.

In order to further explain the deposition process, we use an example of alumina deposition. Among the materials grown by ALD, the Al₂O₃ deposition is one of the simple systems that has been repeatedly studied [47–49]. The fundamentals of the deposition process in other systems is similar that of the Al₂O₃ systems. Trimethylaluminum (TMA) and water vapor are often used as the precursors [50]. One can think of the TMA molecule as an aluminum atom surrounded by three branches of methyl (CH₃), and its chemical formula is Al(CH₃)₃, as schematically shown in Figure 1.1. The recipe for ALD deposition can be varied for different ALD systems. Some of the effective variables are vacuum pressure, chamber geometry, precursor chemistry, and deposition temperature. For example, in our lab, we use 150LE, Kurt J. Lesker Co. system; at 200 °C and 750 mTorr, we use 0.03 second of dose time for TMA, followed by 10 seconds of purge time by nitrogen gas and then 0.1 second of dose time for water.
vapor, followed by another 10 seconds of nitrogen purging [51]. In the first half-cycle, TMA reacts with the hydroxide on the surface and loses one or two of its methyl ligands and produces CH$_4$ as a by-product. The first half reaction can be written as:

$$ Al - OH^* + Al(CH_3)_3(g) \rightarrow Al - O - Al - (CH_3)_2^* + CH_4 $$

Eq.1.1

where the asterisks indicate the surface species. This reaction proceeds until there is no accessible hydroxide left. Thus, one atomic layer of $Al(CH_3)_2^*$ or $Al(CH_3)^*$ would be deposited on the surface in the first half-cycle. The reason for having one layer is that TMA can react only with hydroxide, and after the reaction, the surface will be terminated by $-CH_3$, with which the other TMA molecules cannot react, as schematically illustrated in Figure 1.1. In the second half-cycle, all $-CH_3$ species on the surface will be replaced by hydroxide based on the following reaction:

$$ Al - CH_3^* + H_2O(g) \rightarrow Al - OH^* + CH_4(g) $$

Eq.1.2

After the second half-cycle, the surface will be terminated to hydroxide again, and Eq.1.1 can be repeated. The process is shown schematically in Figure 1.1. The alumina ALD coating has an amorphous structure, as reported in numerous works [51] and also suggested by the schematic illustration. Most of the ALD coatings are amorphous; however, they can be crystalline in as-deposited state in a higher deposition temperature, thicker thickness, or higher chemical purity [52]. For example, TiO$_2$ [53] and SnO$_2$ [54] ALD coatings have a crystalline structure when they are deposited above 250 °C. However, below 200°C, they are deposited in a fully amorphous structure.
Figure 1.1 Schematic of the growth process of ALD coatings. The Al-O bonds are showing the reactions between the precursors and the substrate in each growth cycle. The image shows the termination of the TMA-cycle, where the surface is covered with CH₃. The dotted box shows an Al vacancy.

In order to have a realistic image of the growth in ALD coatings, it should be noted the idea of growing one perfect layer after another is not true. There are many factors, such as steric hindrance, desorption, or residual precursors that can introduce impurities, holes, and uneven growth fronts [44,45]. The most common residue is carbon or hydrogen atoms. Despite of all these shortcomings, one can manage to deposit a flawless coating by optimizing the recipe and coating conditions. For example, Ritala et al. [55] was able to deposit a thick layer of 300 nm of Al₂O₃ on the top of non-flat silicon wafer, as shown in Figure 1.2 (a). Also, they showed that the ALD process can proceed until it fills the empty space between nano-pillars on the surface, as illustrated in Figure 1.2 (b).
The capability of ALD coating to grow on substrates with high aspect ratio provides a continuous and conformal sealing on the substrate against the outside atmosphere. As will be illustrated later, this feature of ALD makes it a suitable candidate to provide a hermetic sealing compared to the use of other techniques. For example, Kohandehghan et al.[56] used both magnetron sputtered and ALD TiN coatings to protect silicon nanowire against contraction/expansion due to Li diffusion. The directional deposition flux in magnetron sputtering caused a heterogeneous coating, due to shadowing effects, while the ALD technique provided a conformal and homogenous coating. However, there are some reports of using magnetron sputtering for the deposition of vapor-barrier coatings [57,58].

The other alternative technique for providing an encapsulating coating is MOCVD (Metal-organic chemical vapor deposition). It has been utilized to prevent copper [59–62] or aluminum [63] diffusion in interconnects. MOCVD is similar to ALD in the sense that both use metal-organic precursors; however, their growth mechanisms are fundamentally different. In MOCVD, the deposition temperature should be high enough so that the precursors are decomposed on the top of the substrate and then they transfer to the surface. The average deposition temperature in MOCVD is 450 °C to 850 °C [64]. However, in ALD, the precursor decomposition should occur exclusively on the substrate surface and, as a matter of fact, the deposition temperature should be low enough to prevent the precursor decomposition in the gas phase. Thus, the ALD deposition temperature on average is in the range of 60 °C to 450 °C. Thus, the conformity and the thickness control in ALD coating is better than in MOCVD due to step-by-step self-terminating growth nature of ALD coatings [64]. In addition, the ALD provides extra parameters (i.e. dose time and purge time), which can be manipulated to obtain a better coating. For examples, the dose and purge time in the second cycle can be elongated to minimize
the amount of impurities in the coatings [65]. By providing more time in the second-half reaction, one can make sure that all the ligands react with the second precursor, while in MOCVD, both half-reactions happen at the same time so that the time parameters cannot be manipulated to control the impurities. Or, in the case of coating porous substrates or nanoparticles, the dose time can be manipulated to ensure the full coverage of the surface in every cycle. Nevertheless, one of the disadvantages of ALD coatings is their low growth rate, which will be discussed in section 5.

![SEM micrographs of alumina ALD coating on silicon substrate](image)

Figure 1.2 SEM micrographs of alumina ALD coating on silicon substrate (Reprinted with permission from Ref. [40]).

### 1.2.2 Nucleation process

The deposition of ALD coating needs an initial nucleation, in which the first layer of the atoms will be deposited on the substrate surface. Langereis et al. [66] studied the nucleation and the growth of ALD coatings by in situ ellipsometry. As long as the cation precursor (e.g. TMA in the above example) can make a bond with the atoms on substrates and deposit the first layer of cations, ALD coatings can be nucleated. Surfaces having an oxide layer on the top make an excellent substrate for ALD nucleation. Thus, one can easily coat oxide substrates as well as
metallic substrates with ALD, due to their oxide layer on the top. As shown in Figure 1.3 (a), the ALD coatings can even be deposited on noble metals, such as Pt. The deposition is likely due to the fact that there is a thin layer of oxide even on noble metals (a single atomic layer of oxygen is enough), which can provide the necessary oxygen for ALD’s nucleation. The versatility of ALD to coat different surfaces provides a unique capability to encapsulate devices. As illustrated in Figure 1.3 (b), the HfO$_2$ seamlessly coats both Pt electrode and ZnO varistor; it was demonstrated that the ALD coating can solve the degradation problem due to exposure to humidity in ZnO varistors [67].

![Figure 1.3 HAADF and TEM micrographs of the HfO$_2$ ALD coatings on (a) Pt electrode and (b) both the Pt electrode and the ZnO varistor.](image)

However, if the substrate does not have any oxygen atoms on the surface (e.g. some polymers), the ALD deposition can be challenging. George [44] has reviewed the techniques by which one is able to deposit ALD coatings on polymers. One solution can be to keep repeating the first cycle until precursor molecules trap inside the polymer chains at the top of the substrate and provide a start point for ALD deposition.
The nucleation problems will be studied in more detail in section 4, but it is worth pointing out that the nucleation of ALD coating on carbon nanotubes provides an interesting example [68]. A bundle of carbon nanotubes after 50 ALD cycles is presented in Figure 1.4. The defected areas with dangling covalent bonds are the only sites able to react with precursor molecules and provide the first nuclei for the ALD film growth. Since the ALD coating grows only around the nuclei, the final structures would be so-called semi-spherical patches on carbon nanotubes, as shown in Figure 1.4. Obviously, the defectless area did not provide any nucleation site in the entirety of the coating process. However, the nucleation sites can be artificially created by the functionalization [69] of carbon nanotubes by ozone [70] (covalent) or NO₂ [71] (non-covalent) treatments.

Zhang et al. [72] have introduced a new technique for coating carbon nanotube. They coated carbon nanotube by ALD-TiO₂ at the low temperature of 60 °C; due to physisorption (i.e. physical adsorption due to van der Waals forces between the precursor molecules and the substrate atoms [45]) at low temperature, a continuous layer of TiO₂ would form on carbon nanotubes. At this step, the bonds between the coating and the substrate were mostly van der Waal. Then, after annealing the coated carbon nanotubes at 450°C, a crystalline TiO₂ with C-O-Ti bonds can be formed.
1.3 ALD coatings as a diffusion barrier on bulk substrates

As mentioned earlier, the encapsulating capability of ALD coatings comes from their layer-by-layer growth nature, which results in a continuous and conformal layer on the substrate, and also from their versatility to nucleate on various surfaces. Due to these features, ALD coatings have already been identified as diffusion barriers in a number of applications [18, 22–36, 43], such as hindering copper diffusion to dielectrics in the back-end copper interconnects [26, 73, 74], or as a gas diffusion barrier on Kapton and PEN (Polyethylene Naphthalate) polymers [27].

The degradation due to humidity is a typical concern in many applications; it is demonstrated that the degradation can be prevented by ALD coatings [28, 30, 32, 34, 36]. For example, it has been shown that a 10nm alumina ALD coating can reduce the water vapor transmission rate by three orders of magnitude [27, 28]. Humidity also degrades the organic light emitting diode (OLED) by forming black spots in them [75]. One popular remedy to save OLED
in ambient atmosphere is to coat them with ALD coatings [29,76–79]. Elrawemi et al. have studied and modeled the water vapor permeability through ALD coatings on flexible photovoltaic modules [80,81].

We showed that humidity can degrade the electrical resistance of multilayer ceramic capacitors by increasing leakage current [82,83]. Then we illustrated that amorphous HfO$_2$ and Al$_2$O$_3$ ALD coatings can prevent the degradation by hindering the proton diffusion into these devices [51]. The ALD coatings had the minimum thickness of 10 nm, but they could increase the onset of the resistance degradation from 160°C for the uncoated capacitors to 310°C.

The open volume is generally larger in amorphous structures than crystalline ones, and consequently, one may expect that the diffusion coefficients of degrading agents would be higher in amorphous structures. Then, the question becomes how the amorphous ALD coatings with several tens of nanometers thickness can perform as a diffusional barrier. This question will be answered by studying the diffusion of humidity as an example.

Humidity is incorporated to oxide ceramics by the following reaction,

$$ H_2O(g) + V_0 + O'_0 \rightarrow 2[OH]_0 $$

the final product is hydroxide. Norby et al. [84] have reviewed the hydroxide diffusion in oxide ceramics. The hydrogen ions (also known as protons) diffuse in oxide ceramics by making bonds from one oxygen to another. It is worth pointing out that the exposure to hydrogen gas produces the same species as the exposure to water vapor, since hydrogen gas would ionize to protons, which bond to oxygen atoms and form [OH]$_0$ [83].

The enthalpy of hydrogen and oxygen bonds determines the activation energy for proton diffusion [85]. Since this bond is strong, the activation energy for proton diffusion in most oxides is high. For example, the activation energy was reported to be 1.25 eV for crystalline Al$_2$O$_3$.
However, the activation energy in ceramics with perovskite structures is much smaller due to octahedron oscillations (also known as octahedral tilting), which cause the momentary $O - H \cdots O$ bonds to form [84,88–90]. This momentary bond causes the original O-H bond to become weak and break with less activation energy. For example, the activation energy for proton diffusion for BaZrO$_3$ [91–93], SrTiO$_3$ [94], and CaTiO$_3$ [94] was reported as 0.17-0.45, 0.50, and 0.42 eV, respectively. In the ceramic capacitors, the dielectric is BaTiO$_3$ with perovskite structure, and the activation energy for proton diffusion is reported to be 0.50-0.52 eV [82,88]. Thus the higher activation energy for proton diffusion in Al$_2$O$_3$ is due to the lack of octahedron oscillations; this is one of the reasons that the Al$_2$O$_3$ coating can be a good barrier against proton diffusion (i.e. humidity).

However, the above mechanism is not the main reason that the ALD Al$_2$O$_3$ coating can be an effective diffusional barrier. We measured the activation energy for proton diffusion in amorphous coatings of HfO$_2$ and Al$_2$O$_3$ as 2.3 and 2.4 eV [51], and this activation energy is much larger than their crystalline counterparts with activation energy of 0.91 [95] and 1.25 eV [86,87], respectively. Beyer [96] has observed the same increase in the activation energy for proton diffusion between amorphous and crystalline silicon. The activation energy increased from 0.48 eV in the crystalline structure to 2.2 eV in amorphous structure [97].

Due to the randomness of the amorphous structure, there are some sites in which the diffusing ion (e.g. proton) has a higher coordination number and is able to make more bonds, so that these sites have much higher activation energy than do the others, as schematically presented in Figure 1.5 (a). Kirchheim [98,99] showed the activation energies of the interstitial sites for proton diffusion have a bell distribution (i.e. it follows Fermi-Dirac statistic), as schematically
shown in Figure 1.5 (b). The sites at the end of the distribution can act as a trap and restrain the diffusing atoms. This is why the activation energy is high in amorphous structures.

![Figure 1.5 Schematic of (a) potential trace of a proton in an amorphous structure, (b) Fermi-Dirac distribution of interstitial activation energies, where the colored area is the traps filled with protons.](image)

However, there are a limited number of traps with a high activation energy, and they can be filled with the diffusing atom so that the other atoms do not fall in these traps (or fall in the traps, which have a lower activation energy). This causes the activation energy to decline by increasing hydrogen concentration. This phenomenon can be explained by the plot in Figure 1.5 (b); at the beginning of hydrogen exposure, the protons may fall to the trap with activation energy as high as $G_0$, but after several hours of exposure, the maximum activation energy would decline to $G_1$. Beyer has traced a decline in the activation energy by increasing proton concentration, and his work will be discussed in section 5 [96]. That being said, the trap occupation also follows the Fermi-Dirac statistics and this makes the estimation of activation energies complicated [98].
One may conclude that despite the common perception that amorphous materials should provide a high diffusion rate, protons have lower diffusion rates in amorphous materials specifically in low concentrations. We measured the proton diffusion coefficient in amorphous Al$_2$O$_3$ and HfO$_2$ ALD coating as $2.0 \times 10^{-16}$ and $2.8 \times 10^{-17}$ cm$^2$s$^{-1}$ at 150°C, respectively [51], while we measured the diffusion coefficient in BaTiO$_3$ as $1.3 \times 10^{-9}$ cm$^2$s$^{-1}$ at the same temperature [82]. The diffusion coefficients were seven and eight orders of magnitude lower in the ALD coatings. This is why the ALD coatings, despite their thin thicknesses (e.g. 10 nm), can be an effective diffusional barrier. 150°C was selected since it is the maximum operation temperature for ceramic capacitors. In the same work [51], we showed that the onset temperature of hydrogen degradation increases from 160 °C for the uncoated sample to 250, and 310°C for Al$_2$O$_3$ and HfO$_2$ coated samples, respectively.

In order to make a comparison between amorphous and crystalline ALD coatings, we coated BaTiO$_3$ capacitors with crystalline ZnO ALD coatings. The protection power against hydrogen gas declined, and the onset temperature of degradation was measured to be 210 °C. As demonstrated in Ref. [51,52], the crystalline ZnO coating is made of the columnar grains of ZnO. The grain boundaries and crystalline structure are the main reasons for the increase in the diffusion coefficient of degradative ions, as will be discussed in section 5.

The ALD coatings have been used as oxidation barrier on a variety of materials such as copper [100], titanium alloys [101,102], silicon carbide [103], nickel [104], and calcium [105]. For example, the formation of Ni oxide layer on the Ni foils can be avoided by ALD coatings up to 850 °C [104]. The average of NiO layer formed on the Ni foil after the exposure to 900°C is 1.95 µm. However, it was shown that by applying Al$_2$O$_3$, HfO$_2$, SnO$_2$, and ZnO 25-nm-thick ALD-coatings around the foils, the thickness of the NiO layer can be decreased to 0.260, 0.647,
It can be concluded that the Al₂O₃ and ZnO coatings showed the maximum and minimum protection against nickel/oxygen diffusion, respectively.

The TEM micrograph and the EDS (energy dispersive spectrometry) map of the Al₂O₃-coated foil after exposing to 900°C suggested that the ALD coating is buried under the NiO layer, as presented in Figure 1.6. The diffusivity of Ni atoms in the substrate is high enough at 900°C to pass through the ALD coating and form NiO on the top of the ALD coating. Also, oxygen can diffuse into the ALD coating and form a NiO layer below the ALD coating. However, the coating could still preserve its shape and continuity during these diffusion processes. At this point, the ALD coatings cannot provide any physical barrier against the outside atmosphere.

![Figure 1.6 TEM micrograph and EDS map of the alumina ALD coating after exposed to 900 °C.](image)

At the temperature of 1100 °C, all the above-mentioned ALD coating will be dissolved into the NiO layer [104]. The cations in the ALD coatings can dope the NiO film and change the
physical properties of the Ni foil. For example, the electrical resistance of the ZnO-coated foil is three orders of magnitude lower than the Al₂O₃-coated foil after exposure to 1100 °C. This huge difference is due to the fact that Zn²⁺ cations can increase the chance of electron hopping between Ni³⁺ and Ni²⁺, while Al³⁺ cations decrease the number of Ni³⁺ and, consequently, decrease the chance of electron hopping [104].

The above example demonstrates the broad meaning of protection in the context of preservation. If one wishes to prevent the NiO formation on the Ni substrate at high temperatures (i.e. below 850°C), the best choice will be Al₂O₃ coatings, and the worst one will be ZnO coating, since the Al₂O₃ coating has a robust chemical compound and makes a stable physical barrier between the Ni substrate and atmosphere with a low diffusion coefficient, while the ZnO coating with as-coated crystalline structure cannot provide an effective diffusional barrier. On the other hand, for the purpose of electrical conductivity preservation, the ZnO coating works the best, and the worst choice is the Al₂O₃ coatings, since, as discussed above, Zn²⁺ can dope the NiO film and significantly decrease the electrical resistance.

Although the dissolution of ALD coatings into the substrate means the termination of their diffusional barrier, this unfortunate phenomenon can be utilized to dope the substrate or to manufacture nanopowders and nanowires with a unique structure [106–108], as will be discussed in section 4.4.

1.4 ALD coatings on nanostructures

One of the big advantages of ALD coating is that it can provide continuous and conformal coating around nanostructures (e.g. nanopowders and nanowires) and provide a dual property, which is otherwise impossible to obtain from either the core or the shell [109], for
example, increasing the oxidation resistance of metal nanopowders [110,111] or improving the charge collection efficiency in TiO$_2$ nanowires [112].

Several methods were developed to coat nanoparticles and nanowires in the layer-by-layer fashion, such as fluidized bed reactors [113,114], rotary ALD reactors [68], and high-speed and continuous spatial ALD reactors [115]. Due to their versatility, ALD can be considered as a suitable technique to coat nano-substrates, among other viable techniques (e.g. Sol-Gel nano-coating) [116,117].

### 1.4.1 Physical or chemical barrier applications of ALD coatings

One of the popular applications of ALD coatings as a shell is protecting the core against harsh environments. As pointed out before, the encapsulating ability of ALD coatings, together with both chemical inertness and low diffusion coefficient of amorphous ceramics, provides a physical and chemical barrier against outside environments [118].

TiO$_2$ particles have been used in paper, paint, and plastic industries as a white pigment material. TiO$_2$ in outdoor applications can be degraded when exposed to small amounts of H$_2$SO$_4$ in acidic rains [109]. It is shown that the ALD-SiO$_2$ coating with thickness of 2 nm can decrease the dissolution of TiO$_2$ particles from ~60% (for the particles without coating) to less than 1% after a 24-hour exposure to 5.0 M H$_2$SO$_4$ solution. However, the ALD-Al$_2$O$_3$ coatings did not show any significant protection, and the TiO$_2$ dissolution was ~30% after the same exposure [119]. The superior passivation capability in the former coatings comes from the inertness of SiO$_2$ oxides and the strong covalent bond between silicon and oxygen. The bond dissociation energies of Al-O and Si-O are respectively 512 and 798 kJ/mol [120]. In addition, SiO$_2$ has a unique macromolecular structure, in which Si cannot be easily replaced by other cations [121].
The agglomeration of nanoparticles at high temperatures is a diffusion process, where the atoms move from the surface of particles to their joint with the adjacent particles. The driving force for this reaction is surface reduction, which is the main reason for densification during sintering processes [122,123]. However, there are some applications for which the agglomeration of particles at high temperature is not desirable. One can effectively hinder the interdiffusion of particles by applying ALD coating as a diffusional barrier around them. For example, an annealing process at 700°C is necessary for FePt nanoparticles for obtaining the desired intermetallic phases since this temperature is high enough to cause the particles to agglomerate. The 11-nm-thick ALD-Al₂O₃ coating around these particles could prevent their interdiffusion up to 730°C; however, above this temperature, the ALD coating crystalized, and the nanoparticles started to agglomerate [124]. By applying the same idea, Park et al. [125] increased the agglomeration temperature of ZnO nanoparticles from 350°C to 450°C by applying a 0.1nm to 0.2nm thick ALD-TiO₂ coating. They showed that due to the ALD coating, the annealing temperature can be increased and this promote the photoelectrode efficiency of solar cells using ZnO nanoparticles. Wang et al. [126] coated Fe₃O₄ nanoparticles with ALD-Al₂O₃ to prevent their agglomeration during synthesizing of carbon nanotubes at 750°C. By maintaining the size of the Fe₃O₄ particles, they could grow longer carbon nanotubes with a more uniform diameter than the carbon nanotubes grown with the uncoated particles.

In another study, the TiO₂ nanoparticles, coated with 10 nm of ALD-Al₂O₃, were sintered at 1400°C [127]. The relative density of the coated particles declined from 97% for the uncoated particles to 90% for the coated particles after the sintering process. In addition, the grain size (~5 µm) of the coated particles was considerably smaller than for the size (~1 µm) of the uncoated particles. This study is a good example for showing the restraint of the particle interdiffusion.
during the sintering process due to the diffusional barrier nature of ALD coatings. However, the formation of aluminum titanate (Al$_2$TiO$_5$) due to the interdiffusion of the coating and the substrate was verified by XRD.

Another important area where ALD coatings are promising is in enhancing the oxidation resistance of metal nanoparticles. This can be found an application in electroceramic cofiring with metallic electrodes, such as solid oxide fuel cells [128,129], piezoelectrics devices [130,131], or multilayer ceramics capacitors [132,133], where one is interested in preserving the electrical conductivity of the electrodes in an oxidizing atmosphere. Hakim et al. could increase oxidation-resistance of iron nanoparticles from slightly above room temperature to 430 °C, as shown in the plot of Figure 1.7, where the mass gain versus temperature for uncoated, 30 cycle, and 50 cycle coated particles are shown. This plot also provides some insight into the failure of ALD coatings, which will be discussed in the next section.

We used Li$_2$CO$_3$ coating to preserve the electrical conductivity of Ni particles at 1330 °C [134]. The Li$^+$ cations dope the newly-formed NiO phase and increase the chance of electron hopping, as discussed in the previous sections. This, consequently, decreases the electrical resistance of the Ni electrodes by five orders of magnitude after sintering in an oxidizing atmosphere.
1.4.2 Application of ALD coatings in batteries and supercapacitors

Due to the excellent conformity of ALD coating, two types of applications in solid full cells [135], ion batteries [136,137], and supercapacitors [138] can be found for the ALD coatings. First, they can be utilized to prevent the capacitance degradation due to the diffusion of deteriorating species. Second, they can provide a layer with high dielectric constant on the materials with large surface area and improve the electrical properties of devices [139]. For example, both carbon nanotube [140] and carbon particles with a large amount of porosity [141] have a large surface area, and coating them with ALD-Al$_2$O$_3$ doped with Zn$^{2+}$ [142] or V$_2$O$_5$ [143] can provide supercapacitors with large capacitance (e.g. 540 F/g [141]). However, the focus of this review is the former application. It was demonstrated that the ALD coating can hinder the degradative reactions between electrodes and electrolytes in supercapacitors at high-voltage operation or prevent the capacity degradation during their cycle-life [144,145].

MoO$_3$ has high specific capacity, which make it a potential candidate for anode materials in lithium ion batteries. However, due to the 100% expansion and contraction in the

Figure 1.7 Thermogravimetric results of coated/uncoated iron nanoparticles with the average size of 50 nm in air (Reprinted with permission from Ref. [110]).
charge/discharge cycle, which led to cracking and eventually crushing of MoO$_3$ particles, their application is limited due to the high rate of capacitance degradation [146,147]. Riley et al. [148] coated MoO$_3$ particles on the electrode so that a continuous layer of ALD-Al$_2$O$_3$ would be formed on both particles and electrode, which increased the adhesion of the particles to the electrode. The MoO$_3$ particles would experience the same expansion/contraction and, consequently, had the same degradation rate, but since the ALD coating held them toward the electrode, they would keep their electrical conductivity in a larger number of cycles. In other words, ALD coatings were used as a binder to keep the particles and electrode together.

Silicon was proposed as the replacement of the conventional carbon anodes, since silicon can store more Li ions due to the intermediate phase of silicon and lithium [149,150]. However, due to charging and discharging, the silicon undergoes the cycle of expansion/contraction, which causes the development of cracks and deterioration of the electrode [151]. Some studies suggested that the degrading process can be arrested by applying ALD coatings around the nanowires [152–155]. Nguyen et al. [156] argued that the improvement of the life time of the silicon nanowire is due to protecting patches (these patches look like those shown in Figure 1.4); they hinder the excessive reactions at defective areas on silicon nanowire. However, others reported the enhancement of crack resistance in the nanowires is due to the application of ALD coatings, which can act as a shield around the nanowire and retard the radial expansion [56] or due to the deactivation of the initial spots (e.g. small pinholes and nanoscale cracks) for crack propagation [157]. The improvement of mechanical properties by utilization of ALD coatings will be reviewed in the next section.
1.4.3 Improvement of mechanical properties of nanostructures by applying ALD coatings

As discussed before, the ALD technique has the versatility to nucleate on numerous surfaces and deposit a continuous layer. These features make it suitable to be used as a binder between nanostructures (e.g. nanoparticles and nanowires). One can think of the final structure as a composite, where the reinforcements are nanostructures (e.g. nanoparticle and nanowires) and the matrix is the material deposited with ALD. Thus, the coatings improve the mechanical properties of the nanostructure and make them more durable in a harsh environment.

NTF (nanoparticles thin films) is an alternative layer of oppositely charged nanoparticles on polymeric or glass substrate [158]. They will be able to provide dual property of both particles, but since the bonding between particles is weak, they are not mechanically stable. Dafinone et al. [159] used the idea of using ALD coating as a binder between nanoparticles to increase the mechanical properties and abrasion resistance of NTFs. They reported that both young module and hardness increase four times by applying 15 cycles of Al₂O₃-ALD coating. The schematic and micrographs of NTFs before and after the ALD process is shown in Figure 1.8.
Mohseni and Scharf [160] showed that both wear resistance and thermal conductivity of porous carbon-carbon composites can be improved by filling the porosity with ALD coatings. In addition, it is shown that the interface thermal resistance between ALD coatings and the substrate can be very low [161]. Therefore, one can design a composite (as explained at the beginning of this sections and schematically presented in Figure 1.9) for the heat dissipation applications made of carbon nanotube and ALD coatings. The CNTs can have a thermal conductivity as high as 3000 W/mK [162], seven times higher than the conductivity of copper. The CNTs provide the high thermal conductivity within the composite, and the ALD coating provides the low interface thermal resistance. In the conventional CNT composites, in which
polymers were used as a matrix, the large interface thermal resistance between the matrix and the CNTs is a major drawback in the total conductivity of these composites [163].

As pointed out in the explanation of Figure 1.4, the challenge of using carbon nanotubes as substrate is that the ALD coating may not form a continuous film on the carbon nanotube without functionalization, as reported in several works [68,164]. Due to the inertness of carbon nanotubes, the nucleation and growth of the ALD coating is limited to the defected areas with dangling bonds. However, there are some cases in which, due to high density of the defects, the ALD coating forms a continuous layer without any pretreatment [165,166]. Brieland-Shoultz et al. [167] used ALD-Al$_2$O$_3$ to coat carbon nanotube forests to improve their mechanical properties. They were able to tune the Young’s modulus (up to three orders of magnitude increase) and mechanical strength (up to one order of magnitude increase) of carbon nanotubes by controlling ALD coating thickness. On the other hand, Cavanagh et al. [68] reported that the carbon nanotubes bundles can be coated with a rotary ALD reactor after functionalization with NO$_2$, and they noticed that the ALD coating did not make any strong bond with the ALD coating (in the contrast of Brieland-Shoultz’s report [167]) and, as a matter of fact, the coating could even slide along the nanotubes. By comparing the two works, it appears that the mechanical strength of the coated carbon nanotubes depends on the following: the type of bonds between ALD coatings and carbon nanotube substrates (i.e. covalent or non-covalent) [69], the arrangement of carbon nanotubes (i.e. forest [167] or bundle [68]), and the thickness of ALD coatings. As mentioned before, the type of functionalization can determine the bonding between the ALD coating and substrate.

In the case of carbon nanotube forest (Brieland-Shoultz’s work [167]), ALD can make a matrix for carbon nanotubes and bind them to each other. As illustrate trough Figure 1.9 (a) to
(c), the growth of ALD coating can fill the empty space between CNTs and eventually make a monolithic matrix. This, and having a covalent bond between carbon nanotubes and ALD coatings, were the reasons that the Brieland-Shoultz’s group was able to increase the mechanical strength of the carbon nanotube forest tenfold by applying the 40 nm ALD-Al₂O₃ coating [167].

![Figure 1.9](image)

Figure 1.9 Schematic and SEM micrographs of carbon nanotube forest during the ALD-Al₂O₃ deposition in three steps of a) as grown, b) 13 nm coating, and c) 51 nm coating. The composite-like structure was obtained at step c, where the empty space between carbon nanotubes fill with ALD coating. (Reprinted with permission from Ref. [167])

### 1.4.4 Interdiffusion of ALD coatings and substrates

As mentioned in the previous section, at high temperatures the ALD coating can interdiffuse into the substrate, which cannot be necessarily considered as a failure. This phenomenon
can be used to dope the substrate or change the chemical phase of the substrate and make new materials.

Wang et al. [168] demonstrated that the idea of doping the nanostructures by ALD coating is plausible by forming an Al\(^{3+}\) doped ZnO film as a shell on ZnO nanowires as a core. They deposited a coating of Al\(_2\)O\(_3\) and ZnO layers with the ratio 1:20 and then annealed at 500 °C for one hour to obtain the doped shell.

Yang et al. [169] applied the idea of coating-substrate interdiffusion to manufacture the Zn\(_2\)TiO\(_4\) nanowire with annealing the TiO\(_2\)-coated ZnO nanowire at the temperature range between 700 °C to 800 °C. The final structure was the interconnected bricks of Zn\(_2\)TiO\(_4\). The effective processing variables were found to be TiO\(_2\) shell thickness, reaction temperature, and reaction time. No voids were found in the final structures of Zn\(_2\)TiO\(_4\). This may be due the same interdiffusion rate of TiO\(_2\) and ZnO. By using the same idea, the nanowire of ZnGa\(_2\)O\(_4\) [170] and CoSi\(_2\) [171,172] were produced by annealing of ZnO/Ga\(_2\)O\(_3\) and Si/Co core-shell nanowires, respectively. Mato [108] reviewed the possibilities of utilizing ALD coatings and post-heat-treatments in the manufacturing of nanoscale structures.

In some other studies, the multilayers of ALD coatings (e.g. the alternative layer of ZnO and Al\(_2\)O\(_3\)) were used. Utilizing the multilayer coatings makes the interdiffusion process more complex and can provide a technique to produce a porous nanostructure due the different diffusion rates of the layers. This practice was proven to be effective in producing porous spinel [173,174]. Guder et al. [175] deposited alternative layer of ZnO and Al\(_2\)O\(_3\) ALD coatings on ZnO nanowire or Si substrate. Then the samples were exposed to the temperature range between 700 °C to 800 °C. The final structure was the crystalline ZnAl\(_2\)O\(_4\) spinel with Kirkendall voids due the different interdiffusion rates of Al\(_2\)O\(_3\)-in-ZnO and ZnO-in-Al\(_2\)O\(_3\). They could even
design the amount and geometry of the porosity by manipulating the number and the thickness of layers in the ALD coating. This unique structure can be used in optical and electroluminescence applications.

1.5 Limitations and the nature of barrier power in ALD coatings

A suitable ALD coating with a low diffusion coefficient can effectively encapsulate substrate against the deteriorating species. However, there are some limitations, which will be explored in this section.

One may consider the processing time of ALD techniques as a drawback. A typical cycle takes 20 seconds for bulk substrates [51] and can be 5 minutes per cycle for nanoparticles [114,176]. However, considering the fact that the ALD coating is usually most effective in the range of 10 nm to 20 nm, it makes the processing time reasonably short (50 [51] and 470 [176] minutes for the bulk and powder substrates, respectively, for a 15 nm thick-coating). Thicker ALD coatings, due to their higher chance of cracking and crystallization, are not necessarily providing better protection. As will be discussed next, two competing parameters, resilience against cracking and crystallization vs. diffusional barrier, determine the encapsulation power of ALD coatings.

1.5.1 Cracking and crystallization of ALD coatings

Most of the ALD coatings are made of ceramic with low fracture toughness. Thus, cracks can initiate and grow easily in them; the cracks provide an easy pass for the degrading ions and decrease the encapsulating power of ALD coatings. Since the encapsulating coatings are usually used in high-temperature applications, the strain, due to the difference in the thermal expansion of the coating and the substrate, is the main reason for cracking. Miller et al. [177] have
developed a technique to measure the mechanical properties (e.g. fracture toughness and critical strain) of ALD coatings. They illustrated that the mechanical properties decline by the coating thickness. For example, the critical strain (the maximum strain before failure) increases from 0.88% in 125 nm thick alumina ALD coating to 5.08% in the 5 nm thick coating [177]. Jen et al. [178,179] also showed that the thinner ALD coating have higher fracture toughness (i.e. higher resilience to cracking).

The other reason for the decline in the encapsulating power of ALD coatings in high temperature is the amorphous-crystalline transformation. As mentioned earlier, the ALD coatings with amorphous structures have a higher activation energy for the diffusion of degrading ions (e.g. proton and oxygen ions) than do the ALD coatings with crystalline structures. So one can expect that the amorphous-crystalline transformation causes the encapsulation power to decline. In addition, the temperature of this transformation decreases by the thickness of ALD coatings [52]. Regarding these two above facts, one may conclude that the thinner ALD coatings have more resilience against the decline in the encapsulating power due to crystallization at high temperatures.

We illustrated that the HfO$_2$ and Al$_2$O$_3$ ALD coatings develop a semi-crystalline structure with columnar grains during long exposure to 300 and 350 °C, respectively [51]. The as-coated and semi-crystalline structure of HfO$_2$ are shown in Figure 1.10. The newly formed columnar grain, shown by A, B, and C in Figure 1.10.b, and grain boundaries can provide a free path for protons to pass through the ALD coatings. We measured the proton diffusion coefficient in both amorphous and semi-crystalline coatings, and the results are presented in Table 1.1. The activation energy declines by going from an amorphous structure to semi-crystalline in both Al$_2$O$_3$ and HfO$_2$. This trend suggests that the crystallinity makes proton transfer easier, and this
is why the diffusion coefficient increases by three orders of magnitude, as presented in Table 1.1. This observation is in concert with the diffusion mechanisms in amorphous and crystalline structure, explained in section 3. In addition, the activation energy and the diffusion coefficient in BaTiO$_3$ are given in Table 1.1, as a reference of barrier power of the ALD coatings. It can be concluded that although the proton diffusion coefficient in ALD coatings increases due to crystallization, it is still several orders of magnitude lower in the semi-crystalline coating than that in BaTiO$_3$. However, we could measure a notable change in the leakage current of the ALD-HfO$_2$ and ALD-Al$_2$O$_3$ coated BaTiO$_3$ capacitors after the crystallization transformation [51].

![Figure 1.10. TEM micrographs of ALD-HfO$_2$ coatings (a) before and (b) after exposure to 350 °C. A, B, and C are newly-formed columnar grains after the heat treatment. The insets are the SAD (selected area diffraction) patterns from the coatings and are clearly indicative of (a) amorphous and (b) crystalline structures (Reprinted with permission from Ref. [51]).](image)

The above observation, plus the comparison between crystalline and amorphous ALD coatings on Ni substrate [104], indicates that the barrier power in amorphous ALD coatings is
higher than that in the crystalline ones, mainly due to the grain boundaries and the columnar grains, which provide a path for rapid diffusion [51,67,81].

Table 1.1 Activation energies and coefficients for proton diffusion in different materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Activation Energy (eV)</th>
<th>Diffusion coefficient at 150 °C* (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaTiO₃ (cubic perovskite)</td>
<td>0.50-0.52 eV [82,88]</td>
<td>1.3×10⁻⁹</td>
</tr>
<tr>
<td>Al₂O₃ (amorphous)</td>
<td>2.4 [51]</td>
<td>2.0×10⁻¹⁶</td>
</tr>
<tr>
<td>Al₂O₃ (semi-crystalline)</td>
<td>2.0 [51]</td>
<td>1.1×10⁻¹³</td>
</tr>
<tr>
<td>HfO₂ (amorphous)</td>
<td>2.3[51]</td>
<td>2.8×10⁻¹⁷</td>
</tr>
<tr>
<td>HfO₂ (semi-crystalline)</td>
<td>1.9 [51]</td>
<td>4.6×10⁻¹⁴</td>
</tr>
</tbody>
</table>

* 150 °C was selected because it is the maximum operation temperature for ceramic capacitors

1.5.2 Diffusional barrier of ALD coatings

As reported in many studies [180–184], the diffusional barrier of amorphous ALD coatings increases exponentially with thickness up to a certain limit, at which the growth of the diffusional barrier will stop. Carcia et al. [181] argued that the thickness of the ALD coatings can be related to the number of traps in the ALD coatings so that in the small thickness (i.e. below 5 nm), the number of the traps is not high enough to provide a significantly high diffusional barrier. Their argument strongly supports the model introduced in section 3, based on which the activation energy of sites follows the Fermi-Dirac statistic. Statistically speaking, in order to have sites with high activation energy (i.e. traps), the number of sites (i.e. the statistical sample) should be large enough. Obviously, the number of sites depends on the thickness of the ALD coatings. So the activation energy of traps should increase by thickness, when the statistical sample is growing. As both models suggest, there should be a certain thickness in which the activation energy of traps will not change significantly by increasing the number of sites. This is why the encapsulation power vs. thickness reach to a plateau especially in low exposure temperatures (i.e. below 100 °C), in which the effect of cracking and crystallization is absent
Klumbies et al. [184] tested the encapsulation power of ALD-$\text{Al}_2\text{O}_3$ coatings in the thickness range of 15 nm to 100 nm at 38°C. The encapsulation power increases exponentially up to 25 nm, but it was almost constant from 50 nm to 100 nm. In other similar reports, this limit has been found to be 10 nm [181,183] and 20 nm [182].

The nature of the diffusional barrier in ALD coatings can be illustrated by the TGA (thermogravimetric analysis) results in Figure 1.7, where 30-cycle and 50-cycle thick ALD coatings were compared with the uncoated powders (every cycle on average is equivalent to 1.6 angstrom [110]). The slope of the weight gain (i.e. the oxidation) is sharp for the uncoated particles. The 30-cycle (4.8 nm) coating pushed back the onset of oxidation from room temperature for the uncoated particles to 400 °C, but the slope of the weight gain is relatively sharp after 400 °C. On the other hand, the particles with the 50-cycle (8.0 nm) coating did not show a significant weight-gain up to 430°C and even after holding for 200 minutes. One can argue that, since the test was conducted in air, there was an unlimited source of ambient oxygen. The fifty-minute exposure time during ramping to 400 °C was enough to fill all the traps at the 30-cycle coating, and after that, the oxygen could pass through the coating at a fairly high rate (i.e. a catastrophic failure as explained later). However, the 50-cycle coating still had enough traps after the heat treatment, ramping to 430 °C and holding for 200 minutes, to prevent the oxygen diffusion, as shown in Figure 1.7.

It is worth comparing this case with the classical diffusion theory, where $x = \sqrt{Dt}$ (x is mean diffusion distance, D diffusion coefficient, and t exposure time). If D was constant, one would expect the failure time (t) to increase by the square of the coating thickness (which is equivalent to x). However, the results in Figure 1.7 suggest that the ALD coating does not follow this classical equation, since the equation suggests only 2.7 folds increase in the failure time by
increasing the thickness from 4.8 nm to 8.0 nm. If this estimation were true, the particles with the 50-cycle coating would fail shortly after exposing it to 430°C especially regarding the fact that the diffusion coefficient will increase exponentially by temperature, while the experimental results suggest that the 50-cycle coating can hold back the weight gain by more than 200 minutes. This large difference is due to the fact that the diffusion coefficient (D) is much lower in the 8.0 nm coating than that in the 4.8 nm coating.

In the thin ALD coatings (e.g. below 10 nm thickness), where the chance of cracking or formation of columnar grains is small at high temperatures, the diffusional barrier is the dominate parameter in determining the protection power of ALD coatings. Thus, the above study is a good example to study the diffusional barrier effect.

The exposure time is another factor in the encapsulation power. As mentioned before in Section 3, one can expect that the diffusion coefficient in amorphous ALD coating to increase by exposure time, since the traps were filled, and the diffusion of other atoms needs less activation energy. For example, Beyer [96] showed that the activation for proton diffusion decreases from 2.2eV to 1.4 eV in amorphous silicon, when the proton concentration increases from 0.1 at.% to 14 at.%. In other words, the proton diffusion coefficient declines by four orders of magnitudes from $6.1 \times 10^{-25}$ cm$^2$/s to $2.1 \times 10^{-21}$ cm$^2$/s.

As another example, Carcia et al. [27] coated polyester substrates with 25nm of Al$_2$O$_3$, 20nm of ZrO$_2$, and 25nm of alternative layers of Al$_2$O$_3$ and ZrO$_2$. The ALD coatings were exposed to 60 °C and 85% relative humidity for 2000 hours, and the proton concentration was measured by the coulometric sensor embedded beneath the substrate. In all three coatings, there was a catastrophic failure, meaning the concentration of protons increase exponentially during the failure. This behavior can be well explained by the model in Section 3. When most of the
traps with the high activation energies are occupied with protons after a long exposure, there is nothing to stop the proton diffusion. So a large number of protons pass through the ALD coatings readily and cause the catastrophic failure. It should be noted that since the exposure temperature is low, both crystallization and cracking of the ALD coatings are unlikely. Thus the ALD coatings failed merely due to the lack of a diffusional barrier.

For the preservation of Ni foil from oxidation at high temperatures (e.g. 700 °C) [104], it was clearly demonstrated that there is an optimum thickness for the maximum protection against oxygen. As discussed before, the amorphous thicker layers have a higher diffusional barrier by offering more traps for oxygen ions. On the other hand, the thick coatings have lower fracture toughness [178,179] or tendency for crystallization [52], which both cause the encapsulation power to decline (as discussed in the previous section). Thus, an optimum thickness between 15 nm to 35 nm was found for HfO$_2$, SnO$_2$, ZnO, and Al$_2$O$_3$ ALD coatings for having the maximum encapsulation [104]. Baumert et al. [185] arrived at the same conclusion in that a 10 nm of alumina ALD coating has the optimum thickness for protecting silicon film against humidity.

In order to obtain the maximum protection power, one should find the optimum thickness of ALD coatings, where both the diffusional barrier and the crack resistance and/or the resilience against amorphous-crystalline transformation would be maximum. The optimum thickness depends on chemical compound and as-coated structure of ALD coatings, type of degrading ions, exposure time and temperature, substrate, and heating rate [104,180–190].

1.6 Summary

In this review, we present numerous examples of utilizing ALD to improve the physical properties of the substrate in harsh environments. Due to the nature of layer-by-layer growth of
ALD, it is able to provide continuous and conformal coatings with high aspect ratio, which cannot be obtained with other coating techniques. This, together with versatility of the nucleation on various surfaces, provides a hermetic sealing between the substrate and outside environment at low temperatures.

Since most of the ALD coatings have an amorphous structure (or can be deposited in the amorphous structure in low temperatures), the diffusion coefficients of the deteriorating ions (e.g. hydrogen or oxygen) in the ALD coatings are several orders of magnitude lower than those in the substrates with crystalline structure. This is why the thin ALD coating can provide an effective diffusional barrier. However, the diffusion coefficient of ALD coatings may increase by cracks, amorphous-crystalline transformations, or long time exposure to high concentration of the deteriorating ions. As discussed in detail, finding the optimum thickness for having the maximum barrier power is important.

In addition, due to the layer-by-layer growth of ALD techniques, they can be used to coat nanostructures (e.g. nanopowders and nanowires). As illustrated by numerous examples in this paper, the final core-shell structures have the capability to improve physical properties, or increase the durability of the nanostructures in a harsh environment. Furthermore, the interdiffusion of substrate and ALD coating during annealing at high temperatures can provide a unique structure, which cannot be obtained with standard techniques.
2 Electrical Characterization and Analysis of the Degradation of Electrode Schottky Barriers in BaTiO$_3$ Dielectric Materials due to Hydrogen Exposure

2.1 Introduction

The literature review in the previous chapter suggested that ALD coating can hinder the proton diffusion and prevent the insulation resistance degradation due to hydrogen exposure. However, before evaluating the effectiveness of ALD coatings, the degradation process itself would be studied and effective mechanisms would be explored in this chapter.

Exposure to a hydrogen atmosphere typically induces degradation in the insulation resistance or associated dielectric properties, as has been investigated in several dielectric oxide systems based on TiO$_2$ [191], SrTiO$_3$ [192], BaTiO$_3$ [193,194], and Pb(Zr,Ti)O$_3$ [195,196]. Two possible scenarios have been previously suggested for the resistivity degradation. The first suggests that due to reducing atmosphere, oxygen may be lost from dielectrics and give free electrons to conduction band, which causes reduced resistivity; this reaction is well known and used in thermochemical defect chemistry investigations at high temperatures. However, this scenario was ruled out by Aggarwal et al. [195] for the temperatures below 400 °C, which is the interest of this study. The second scenario considers the hydrogen undergoing ionization, followed by incorporation as an interstitial ion to produce free electrons based on the following reaction, decreasing the resistivity.

\[ H_2(g) \rightarrow 2H_i + 2e^- \] (2.1)
Although there is a debate on whether the protons make bond to oxygen ions in perovskite oxides [195–197] or if they can exist as ‘free proton’ [198], most researchers support a hypothesis that protons bond to oxygen [88] by the following reaction:

\[
H_i + O^x_0 \rightarrow [OH]_o
\]  
(2.2)

Another important gas species, reported as a degrading agent, is humidity. In closed systems, water vapor can react with oxygen vacancies and decompose to OH\(_-\), basically behaving similarly to hydrogen gas [199], by the following reaction [88]:

\[
H_2O(g) + V^+_O + O^x_0 \rightarrow 2[OH]_o
\]  
(2.3)

Concern for H\(_2\) and H\(_2\)O atmospheres is based on the evolving challenges of packaging electronics in modules for power electronics [200] that operate at 150°C and above, but other cases are also noted to have similar issues, as outlined above. Within closed systems, a hydrogen source can be out-gassing from incompletely cured polymers, such as epoxies, or from other components, such as electrolytic capacitors, and aqueous based ultra-capacitors [201] as possible sources. Considering these cases, the vulnerability of all components in the system should be assessed. The objective of this investigation is to assess the sensitivity of BaTiO\(_3\) dielectrics and understand the nature of dielectric changes due to hydrogen gas at different temperatures. To do so, different electrical tests, namely, leakage current vs. voltage (I-V) were utilized to study the effect of hydrogen on Schottky barriers.

### 2.2 Experimental Procedures

The X7R322N BaTiO\(_3\) powders from Ferro Co. with X7R formulations co-doped with Y\(_2\)O\(_3\)-MnO, were tape casted into layers with thickness of 50 and 20 µm and cut to the 1 × 1
inch squares. The electrodes patterns, $4 \times 5$ rectangles with the dimensions of $2 \times 4.5$ mm, were printed with a homemade nickel ink (made with Shoei Chemical Ni powder) on the two of squares with 20-µm thickness. The two tapes were aligned so that every printed rectangle had an overlap area of $2 \times 3.5$ mm with an extent of 1 mm in each tape in the length direction., see the “exposed electrodes” face in Figure 2.1(a). After alignment, those 20 µm layers were stacked with six 50-µm squares on the top and the bottom and were then laminated and cut to separate rectangles with a pair of buried electrodes. Next, the samples were sintered at 1300 °C for 2 hours in $10^{-10}$ atm of oxygen partial pressure, followed by a reoxidation at 800 °C in $10^{-8}$ atm of oxygen partial pressure for 8 hours. The final prototyped capacitors had one active layer with 18 µm thickness. To make sure hydrogen would be exposed in the same way to the active layer in all the samples, they were cut along the electrode on one side, as shown in Figure 2.1 (a), and hydrogen effects could be noted over relatively accelerated conditions. An SEM (scanning electron microscope) micrograph of exposed electrodes of the prototyped structures is shown in Figure 2.1 (b).
Electrical measurements: Leakage current-voltage (I-V) was executed in the temperature interval of 100 to 230 °C at two atmospheres of forming gas (5% hydrogen and 95% nitrogen) and ambient atmosphere (air). For convenience, the forming gas atmosphere is called hydrogen atmosphere from now on. The systems used in the experiments were HP4284A LCR meter (Hewlett-Packard, Santa-Clara, CA), HP4140B PA meter (Hewlett Packard). A furnace with a sealed stainless steel box with 4 samples fixtures was used to heat the samples up to 230 °C. A pipe was connected to the box to supply reducing gas into a sample chamber with adjustable rates from 0 to 500 cc/min. A K-type thermocouple was placed inside the box to make sure the true temperature would be measured during the tests. Microstructural characterization was performed with Hitachi S-3000N SEM (Tokyo, Japan) and JEOL-2010 field emission TEM (Tokyo, Japan).
2.3 I-V measurements and Schottky barriers

The I-V curves for the BME (Base Metal Electrodes) capacitors are measured under different atmospheres at 180 °C and shown in Figure 2.2 (a); as can be seen, the hydrogen gas causes slight increases in leakage current at voltage extremer. This difference between the air and hydrogen atmospheres can be more significantly increased by raising temperature and voltage. The temperature effect is shown in Figure 2.2 (b). The hydrogen ion diffusion begins to show resistivity degradation around 150 °C, and after that, leakage currents increase abruptly with temperature. As seen, the difference of the leakage currents is notable at 180 °C, so this temperature was selected to study the hydrogen effect.

![Figure 2.2 a) Saturated leakage current vs. DC voltage (I-V curves) in air and hydrogen atmospheres at 180 °C b) the saturated leakage current at 45 V vs. temperature.](image)

The other major variable that controls the deteriorating of the leakage current is the magnitude of the applied DC bias. The DC bias was applied to a sample for a time over 1000s, and immediately after that, the I-V test was executed; this procedure was done under the different DC biases at 180 °C in air atmosphere. After that, the same set of tests were executed on the same sample at the same temperature, but this time under the hydrogen atmosphere. The
DC bias and I-V results are shown and contrasted in Figure 2.3. There is no degradation observed for the case of the DC bias in the ambient air atmosphere, Figure 2.3 (a) and (c). However, there is an insulation resistance degradation in the case with hydrogen atmosphere, Figure 2.3 (b) and (d).

Figure 2.3 Leakage current vs. time at different DC bias in (a) air and (b) hydrogen atmosphere. Saturated leakage current vs. DC voltage in (c) air and (d) hydrogen atmosphere.
In an ideal Schottky barrier, in which there is no insulation gap between semiconductor and electrode and no interface states, the difference between metal work function ($\phi_m$) and semiconductor affinity ($\chi$) is the Schottky barrier height ($\phi_B$) [202,203], as shown in Figure 2.4:

$$\phi_B = \phi_m - \chi$$

(2.4)

A Schottky barrier potential is different in forward and reversed bias. As an example, as the electrons move from dielectric to metal electrode, $J_{D\rightarrow M}$ is called leakage current in forward bias. When the current is reversed, $J_{M\rightarrow D}$ is called leakage current in reverse bias. As seen in the Figure 2.4, the barrier height is smaller for forward bias than for reverse bias, which shown by the internal bias $\Psi_b$ and Schottky barrier $\phi_b$ respectively. This causes current $J_{D\rightarrow M}$ to be larger than $J_{M\rightarrow D}$ at the same but opposite-sign voltage. $\Psi_b$ gets shorter by applied forward bias, but $\phi_b$ roughly remains constant under bias [202,204].

![Figure 2.4 The schematic of an ideal Schottky barrier and three conduction mechanisms (TE: thermionic emission, TFE: thermionic-field emission, FE: field emission) by which an electron can pass across the barrier.](image)
It has been shown in Figure 2.3 (b) that the leakage current starts to increase under the bias voltage roughly around $10^2$ seconds when exposed to the hydrogen atmosphere, while nothing is noted in the air atmosphere experiments. Furthermore, all the leakage currents are an order of magnitude larger under the hydrogen than air. It is likely that hydrogen acts as an ionized interstitial donor (Eq. (2.1)) and reduces resistivity; however, resistivity degradation due to hydrogen ionization cannot explain asymmetric curves in Figure 2.3 (d). The other degradation mechanism is that the dissolved bulk ionized hydrogen can easily undergo electromigration and pile up at the cathode and reduce depletion layer thickness ($w_D$), according to following equation for an ideal Schottky barriers [202]:

$$w_D = \sqrt{\frac{2\varepsilon_s}{qN} (\Psi_b - V - \frac{kT}{q})}$$

(2.5)

where $\varepsilon_s$ is the semiconductor permittivity, $q$ electron charge, $N$ the number of donors, $V$ applied voltage, $k$ Boltzmann’s constant, $T$ absolute temperature. Decreasing the $w_D$ raises the chance of electron tunneling and having the insulation effectiveness of the barriers reduced. Thus, the higher concentration of H-ion ($N$) leads to the shorter Schottky barrier width, and then higher leakage current.

The I-V tests under the hydrogen atmosphere, which result in the observations of asymmetric curves in Figure 2.3 (d), can now be well explained by Schottky barriers. Under the positive bias, let’s say an electric field from left to right, hydrogen donors pile up by electromigration in the front of right hand side electrode and decrease its barrier height, while the left electrode Schottky barrier ends up with less hydrogen donors. After the DC degradation, when the positive voltage is applied in I-V test, the electrons experience two major barriers: on
the right electrode, a reverse bias Schottky barrier ($\phi_{bR}$) with more hydrogen, and on the left electrode, a forward bias Schottky barrier ($\Psi_{bL}$) with less hydrogen. In the negative applied voltage, the forward and reverse biases exchange their places, and electrons would experience $\phi_{bL}$ and $\Psi_{bR}$, respectively. One can argue since $\phi_b$ is always higher than $\Psi_b$ (Figure 2.4), the reverse-bias barrier is the dominant barrier, and due to the degradation, $\phi_{bL}$ is larger than $\phi_{bR}$. So there is higher leakage current in the negative applied voltage than the positives in Figure 2.3. It is worthwhile to note that there are no asymmetries in I-V results in air, because $\phi_{bL}$ and $\phi_{bR}$ are equal to each other.

2.4 Thermionic Emission and Field Emission through Schottky barriers

Electrons can pass across Schottky barriers with two mechanisms. Since it has been concluded in previous sections that the reverse bias barriers are more dominant than forward bias ones, here the reverse bias mechanisms would be just considered. The first well known mechanism is thermionic emission (TE), in which the electrons can pass over the barrier, as schematically represented in Figure 2.4. The temperature dependence of the leakage current ($J_{TE}$) due to TE increases as follows [202]:

$$J_{TE} = A^*T^2\exp\left(-\frac{q\phi_b}{kT}\right)$$

(2.6)

where $A^*$ is the effective Richardson constant.

The second mechanism is field emission (FE) and is due to electron tunneling through the barrier. FE takes place at low temperatures and high electric fields, while TE takes place at high temperature and low electric field. There is an intermediate mechanism between FE and TE, called thermionic field emission (TFE). TFE is the mixture of TE and FE; the electron energy
can be raised by TE to the higher portion of the barrier, which has a lower thickness, and the chance of tunneling is higher, and then it passes through the barrier by FE [202].

To study those respective cases, the samples were placed in the furnace with air atmosphere, and the temperature was ramped from 185 to 230 °C with 15 °C interval steps. At every temperature, the voltage increased from 5 to 305 V, and during sixty-second time intervals, the leakage current was measured every second at each voltage. The saturated leakage current, i.e. the one that measured at 60th second, is given vs. voltage at different temperature in Figure 2.5 (a). As shown, the leakage current increases by increasing temperature and voltage, and it passes through all three possible conduction mechanisms.
Figure 2.5 (a) Leakage current vs. voltage at different temperature, the redrawn curves (b) in the form of Eq. (2.6) for TE mechanism, and (c) in the form of Eq.(2.9) for FE mechanism; the black solid lines are the fitted lines. The curves in (c) are redrawn in (d) for the whole range.

At low voltages up to 95V, since the resultant graphs based on Eq. (2.6) are linear, as shown in Figure 2.5 (b), one can conclude that the dominant conductivity mechanism is TE. For comparison, that type of graph is drawn for the high voltage of 305 V, and it departs from being linear, as illustrated in Figure 2.5 (b). The line slopes are equivalent to the Schottky barrier height ($\phi_b$) and are 1.21±0.01, 1.14±0.02, 1.09±0.01, and 1.05±0.02 eV for the applied voltage of 5, 35, 65, and 95V, respectively. As the results suggest, the barrier height is reduced by
increasing voltage, and it can be due to the fact that there are some dopants and oxygen vacancies in samples; at high voltage, they have the chance to move toward electrodes and reduce the barrier height. The amount of ionic impurities in front of the electrode will be discussed later.

It is recalled that the difference between nickel work function (5.01 to 5.10 eV) [205,206] and electron affinity of BaTiO$_3$ (3.9 eV) [207] can roughly be a good guide to check the validity of measured barrier heights. Based on Eq. (2.4), the barrier height should be between 1.11 to 1.20 eV, if there is an ideal Schottky barrier with pure BaTiO$_3$. The barrier heights are in good agreement with the earlier work [208]. However, later it will be shown that the barrier height can be really small (around 0.2 eV) by introducing hydrogen gas to samples. Therefore, there are several factors, such as concentration of impurities, contact property between metals and dielectrics, interfacial alloys, and electrode roughness, which affect the reported value for the barrier heights [209–211]. By increasing voltage, the conduction mechanism changes from TE to TFE. There is no straightforward equation for the mixed cases, so this case is not able to be modeled.
The other possible conduction mechanism would be field emission (FE). There are several equations that can be used to relate the leakage current to voltage, depending on whether there is an interfacial oxide layer between electrode and dielectric. Based on TEM analysis on BME dielectrics used in the present work, no intermediate oxide layer was detected between dielectric and electrode, as shown in Figure 2.6. Thus, the following equation may be used for $J_{FE}$ [202]:

$$J_{FE} = A^* \left( \frac{E_{00}}{k} \right)^2 \left( \frac{\phi_b + V}{\phi_b} \right) \exp \left( - \frac{2q\phi_b^{3/2}}{3E_{00}\sqrt{\phi_b + V}} \right)$$

(2.7)

where $A^*$ is basically the effective Richardson constant ($A^*$), considering quantum-mechanical tunneling and reflection coefficients. $E_{00}$ is given by:
\[ E_{00} = \frac{q\hbar}{2} \sqrt{\frac{N}{m^*\varepsilon_s}} \]

(2.8)

where \( m^* \) is the effective mass in dielectric and \( \hbar \) is Planck’s constant divided by \( 2\pi \). Eq. (2.7) can be rewritten in following form

\[ \ln \left( \frac{J_{FE}}{\phi_b + V} \right) = \ln \left( A^{**} \left( \frac{E_{00}}{k} \right)^2 \frac{1}{\phi_b} \right) - \left( \frac{2q\phi_b^{3/2}}{3E_{00}} \right) \frac{1}{\sqrt{\phi_b + V}} \]

(2.9)

Based on the thermionic results, \( \phi_b \) has a value from 1.09 to 1.21 eV. So \( \phi_b \) variation is still small compared to applied voltage, and \( \phi_b \) s, showed in bold font in Eq. (2.9), can be roughly equal to a constant (e.g. 1.1 V). Then, the leakage currents in Figure 2.5 (a) can be cast into the format of Eq. (2.9); the resultant curves are given in Figure 2.5 (c). All the curves can be fitted by a line, with respect to Eq. (2.9), and thereby can be used for the FE portion of the leakage current. The linearity of curves in Figure 2.5 (c) is only limited to the FE portion of leakage currents, to verify that the whole range was drawn in Figure 2.5 (d). As can be seen, the curves are not linear in the TE and TFE portions of the data.

Despite these limitations across the whole range, \( E_{00} \) was calculated, and then in turn relate it to the impurity concentration in front of Schottky barriers (N) by Eq. (2.8). One is not interested in the exact value of N (i.e. the number of protons), as one anticipates lock variations, but one is interested in relative trends.

The thermionic emission (TE) fitting based on Eq. (2.6), and field emission (FE) fitting based on Eq. (2.9), can provide tools to track the changes of Schottky barrier height (\( \phi_b \)) and impurity concentration (N) in different temperatures and atmospheres. The forward bias Schottky
barriers vs. voltage are shown in Figure 2.7 (a). The primary data were similar to the ones that were shown in Figure 2.5 (a), and the barrier heights were calculated from the primary data by using Eq. (2.6). The same test has been executed twice and shown as “first measurement” and “second measurement” in Figure 2.7 (a). The results suggest that the barrier height is reduced by voltage and time (the difference between the first and second measurement). The reduction amounts and their dependence on time suggest that some impurities (such as oxygen vacancies) can migrate and pile up in front of the electrode due to the high voltage and high temperature. The change of impurities is traceable, thanks to fitting the primary data by Eq. (2.9). The ratios of impurity concentration (N) to the initial concentration (N_0) are shown in Figure 2.7 (b) at two different temperatures and atmospheres. N/N_0 will be called as N* from now on. N* was measured for 90 minutes at 185 °C in air at every 30 minutes; after that, the “first measurement” test shown in Figure 2.7 (a) was executed, and then another N* measuring at 185 °C, which is shown at 150th minute as point (1). Following, the “second measurement” test and another N* measuring at 185 °C, shown as point (2), was done. The results indicate that N* is constant at 185 °C in air in the first 90 minutes. After the “first measurement”, it increased to 1.3, and after the “second measurement”, to 2.0. This trend proves that the impurities in front of the electrode are constant at 185 °C, i.e. no significant electromigration; however, N* would be changed at the higher temperature, as suggested by “first measurement” and “second measurement”. A similar trend has been found in thermal stimulated depolarization current [212,213]and earlier oxygen vacancy studies [214,215]. For comparison with constant N* in the first 90 minutes in air at 185 °C, N* was presented in hydrogen atmosphere at 230 °C. Since protons can diffuse readily to the devices at high temperature, N* increases abruptly in the first 90 minutes.
It would also be informative to see the change of the barrier height with hydrogen. To do this, the maximum applied voltage was decreased from 305 V to 45 V to decrease the driving force for the oxygen vacancy electromigration. The results are shown in Figure 2.7 (c). The atmosphere was air in the first three hours; as it can be seen, the barrier height was almost constant, with slightly decline in respect to voltage. During the fourth hour, the forming gas was applied, and then up to the sixth hour, the measured data could not be successfully described by Eq.(2.6), so no barrier height was reported. The hydrogen ion concentration reached a steady state condition at the sixth hour, and the measured data could be again fitted by Eq.(2.6). There was massive reduction in the barrier height, as illustrated in Figure 2.7 (C). Also it is shown for the degraded sample (the measurement after 6th hour) that the barrier height decreases with voltage and reaches zero for the voltage above 21 V.
A further analysis can be extracted from the primary leakage currents to assess the relation between the onset voltage of tunneling ($V_{FE}$) and temperature. A comparison between the value of $E_{00}$ and $kT$ can be a criteria, based on which, when $E_{00} \ll kT$, TE is the dominant mechanism for the leakage current, and when $E_{00} \gg kT$, FE is dominant. Regarding Eq. (2.8), one should note that $E_{00}$ itself is a function of impurity donor concentration (N) and temperature. When the temperature is high, the average of electron energy is high, so that a large number of electrons can pass the barrier due to TE. When the impurity concentration (N) is high, there is a shorter depletion layer ($w_D$) according to Eq.(2.5) and consequently a higher chance of tunneling, so that the number of electrons, which can pass the barrier due to FE, will increase. The relation between temperature and the onset tunneling voltage ($V_{FE}$) in air shows in Figure 2.7 (d). As seen, $V_{FE}$ is increased by temperature.

The degradation mechanism can be thought of as, when the devices are exposed to hydrogen gas, protons are introduced to the active layer, and they accumulate in front of
electrodes. That causes the chance of tunneling through depletion region to be increased and eventually manifests as the resistivity degradation. Since protons are mobile defect, the degradation should be reversible by simply shifting from hydrogen atmosphere to air.

2.5 Recovery Study

To assess the reversibility of the resistivity degradation due to hydrogen exposure, I-V tests were executed at 200 °C in air for the first thirty minutes, then hydrogen atmosphere was applied from the 30th to 135th minute, and then the air atmosphere was applied again. The saturated leakage currents for the different voltages are shown in Figure 2.8. The leakage current was constant and small in the first thirty minutes in air at each voltage. Then it started to increase abruptly in the first 45 minutes after exposure to hydrogen gas due to the above mechanisms of the degradation of electrode Schottky barrier. The high rate degradation is followed by a lower rate of degradation. This behavior is seen in all applied voltages, but is more pronounced by increasing voltage. At 135th minute, the recovery process is begun by applying air. The recovery follows the same pattern as the degradation, a fast recovery with high decrease rate in the leakage current and then the second recovery with a much slower rate. The fast degradation happens because of H-ion accumulation in front of electrodes which causes a large decrease in the resistivity of their Schottky barriers. The recovery has the high rate as well at the beginning due to the dilution of the accumulated H-ions.
2.6 Conclusions

This study provides insights into the dominant role of the electrodes that control the resistance degradation due to hydrogen exposure, and the vulnerability of these interfaces to the absorption of H-ions. This work investigates and exploits the semiconductor materials physics to track the changes in I-V behavior under different measurement conditions. Conditions are identified to separate out the degradation influence of oxygen vacancy controlled conditions and the effects of Hydrogen exposure. Based on the findings, a mechanism was proposed. It suggests that the exposure of the devices to hydrogen gas causes protons and free electrons to be incorporated in them and decrease the overall resistivity. Since the protons are mobile defects, they can accumulate in front of electrodes. This accumulation was traced by monitoring FE conductivity, and its side effects were demonstrated as an asymmetry in I-V curves and a decrease in barrier heights, monitored by TE conductivity. Eventually, it was shown the whole process is reversible, as can be inferred from the proposed mechanism, through recovery tests.
3 Analysis of the Degradation of BaTiO$_3$ Resistivity due to Hydrogen Ion Incorporation: Impedance Spectroscopy and Diffusion Analysis

3.1 Introduction

In the previous chapter the mechanisms, which are responsible for the degradation of MLCCs due to exposure to hydrogen gas was explored. In this chapter, the impedance spectroscopy was utilized to measure the diffusion coefficient of protons in BaTiO$_3$ MLCCs. This technique will be used in chapter 4 and 5 for measuring the diffusion coefficients in ALD coatings and ZnO varistors.

Diffusion of hydrogen ions into electronic materials can cause the degradation of their electrical insulation properties. The piezoelectric degradation of Pb(Zr,Ti)O$_3$ (PZT) due to hydrogen cations is well known and has been studied by many researchers [195,216–218]. For example, PZT can be used as an actuator in hydrogen internal combustion engines as a better replacement for port injections, but because of hydrogen degradation, they fail frequently [219,220]. Furthermore, hydrogen can be undesirable in ferroelectric random access memory; hydrogen ions tend to bind with oxygen atoms and hinder ferroelectric hysteretic switching in PZT [195]. Hydrogen can also decrease resistivity and change capacitance in PZT [196]. Furthermore, the perovskite oxides (ABO$_3$) coated on a silicon wafer should be annealed at 450 $^0$C in the reductive atmosphere, containing hydrogen gas, to prevent SiO$_2$ formation at the interface [221]. One concern is that hydrogen ions may diffuse to the perovskite layer and degrade its resistivity [197].
On the other hand, hydrogen diffusion in some of the perovskite oxides (e.g. CaTiO$_3$ or BaZrO$_3$) can be considered a desirable phenomenon. Since perovskite is one of the most stable crystal structures, it can be used as a separator material in electrochemical cells [88,222].

Numerous techniques can be found in literature for measuring hydrogen diffusion in perovskite oxides. Those techniques can be as simple as exposing samples to hydrogen and watching the color change from the exposed surface toward the virgin area [223] or using more advanced techniques, such as impedance spectroscopy [88,224], thermal desorption studies (TDS) [193], quasi-elastic neutron scattering (QENS) [225], or proton nuclear magnetic resonance (NMR) [219]. The reported diffusion coefficient for the same material can be different in different papers. Those differences can be due to the fact that some perovskite oxides change their crystal structure by temperature [88]. Some instrumental differences can lead to measuring different diffusion coefficients; for example, in the impedance techniques, the electrodes can act as a catalyst and facilitate hydrogen ionization [226], so one may measure rates with different electrodes.

Impedance spectroscopy has been proven to be a powerful technique to differentiate between the contributions of different components in total impedance [227]. There are several methods to analyze the measured data in impedance spectroscopy tests [228]. For simple systems, the method of equivalent circuit is popular [214,229]. The objective of this work is to use the impedance changes and the equivalent circuit analysis to provide a more detailed understanding of resistivity changes and infer routes for H-ion diffusion into the microstructure.
3.2 Experimental Procedures

The X7R322N BaTiO$_3$ powders from Ferro Co. with X7R formulations co-doped by Y$_2$O$_3$-MnO were tape casted into layers with a thickness of 50 and 20 µm and cut into 1 × 1 inch squares. For buried base-metal electrode (BME) samples, the electrodes patterns, 4 × 5 rectangles with the dimensions of 2 × 4.5 mm, were printed with a homemade nickel ink (made with Sheoi Chemical Ni powder) on the two layers with 20-µm thickness. The two tapes were aligned so that every printed rectangle had an overlap area of 2 × 3.5 mm with an extent of 1 mm in each tape in the length direction, see the “exposed electrodes” face in Figure 3.1. After a satisfactory alignment, those 20 µm layers were stacked with six 50-µm squares on the top and the bottom and were then laminated and cut into separate rectangles with a pair of buried electrodes. Next, the samples were sintered at 1300 °C for 2 hours in 10$^{-10}$ atm of oxygen partial pressure, followed by reoxidation at 800 °C in 10$^{-8}$ atm of oxygen partial pressure for 8 hours. The prototyped capacitors had one active layer with 18 µm thickness and can be a representative of typical MLCCs used in electronic industries. To make sure hydrogen would be exposed in the same way to the active layer in all the samples, they were cut along the electrode in one side, as shown in Figure 3.1 as “exposed electrodes”.

![Figure 3.1 schematic of cut capacitors.](image)
The other type of sample was monolithic structures, sometimes called k-squares. They were made by stacking tape casted BaTiO$_3$ layers to get a 550 µm thickness, then laminated and cut to 7×7 mm thickness with Universal M360 laser cutter. Next, these were sintered in the above mentioned process. Then the samples were washed, first with acetone, and then isopropanol, for 10 min in an ultrasonic bath, followed by drying in an oven at 120 °C for 20 minutes. Next, the Ag, Pt, and Au electrodes with the same area as BME samples were applied to both sides of the samples with Quorom EMS 150 Sputter Coater. The thickness of the electrodes were 100 nm. To make sure the electrodes are in the center and face each other, a label was cut with the laser cutter to a 7×7 mm square, with a circle in the middle and an area of 5 mm$^2$, and used as a mask in the electrode sputtering.

Impedance spectroscopy was executed with SR-830-DSP Lock-in connected to homemade charge measurement hardware. An HP4284A LCR meter (Hewlett-Packard) was used to measure impedance at 1 kHz. A PSU constructed furnace, inside which was a sealed stainless steel box with 4 sample fixtures, was used to heat the samples up to 255 °C. A pipe was connected to the box to blow in reducing gas into the sample chamber with adjustable rates from 0 to 500 cc/min. Forming gas (5% hydrogen and 95% nitrogen) was used to expose the samples to hydrogen gas. For convenience, the forming gas will be referred to as hydrogen atmosphere from now on. A K-type thermocouple was placed inside the box to make sure the true temperature would be measured during the tests.

To be sure about the precision of electrical measurements, the hardware was tested with NIST traceable air gap standard capacitors from HP. In addition, the 1 nF standard capacitor was tested with Solartron ModuLab XM as well and there was an excellent match between the results of these two systems.
TEM samples were prepared by FEI-Quanta-200 FIB (Oregon, USA). TEM micrographs were done by Philips 420.

### 3.3 Impedance Spectroscopy

Impedance spectroscopy has previously been applied to base metal capacitors to assess interfacial changes under typical time dependent breakdown, re-oxidation, and ambipolar diffusion for dielectric /piezoelectric based materials [214,230,231]. Here, in a similar way, the effects of H-ion degradation. The impedance measurements were made between frequencies 0.01 and $10^5$ Hz at 0.1 V and across a temperature range of 215 and 255 °C. 3RC model was applied to interpret the raw Cole-Cole plots in Figure 3.3 (a). A 3RC model was chosen, because there are three components in every capacitor (electrode and grain boundary Schottky barriers, and bulk grains), which have separate contributions to total resistivity and capacitance. Plus, the quality of the fitting with an average of $R^2=0.98$ between measured data and fitting curves provides another support for using the 3RC model. Furthermore, the 3RC model was used to successfully interpret the raw data for the same type of capacitors in other works [214,229]. However, if core-shell is the dominated structure in capacitors, it may limit 3RC model [229]. A transmission electron microscopy (TEM) diffraction contrast analysis was executed on the samples in order to search for the core-shell structure. As shown in Figure 3.2, core-shell is not the dominant structure in the current samples. The calculated activation energies for grain (0.78±0.05 eV), grain boundary (1.12±0.02 eV), and electrode (1.15±0.04 eV), based on an Arrhenius relationship, are also comparable to similar studies [214,229].

The respective microstructural contribution to each impedance element was inferred through the guidance of the previous works. The differentiation between bulk grains and
Schottky barriers is relatively easy; grains have the highest slope in \(1/C_i\) vs temperature (where \(C_i\) is capacitance of \(i^{th}\) element) curves [214,229]. Those curves are shown in Figure 3.3 (b), and the steepest slope belongs to grains.

![Figure 3.2 TEM micrograph of sintered BaTiO₃ dielectric microstructure. Grains have domain structures and, in some cases, \(\{111\}\) growth twins; average grain size is about 0.5 microns.](image)

Figure 3.3 (c) shows the resistivity of the three components; the electrode-dielectric interface has the highest resistivity in all temperatures. Considering the fact that there are many grain boundaries in the active layer, but their combined resistivity is still less than electrodes, one can conclude the electrode barrier height should be much higher than that of the grain boundaries, as schematically shown in Figure 3.4. Electrodes have Schottky barriers, and the grain boundaries have back-to-back Schottky barriers in the capacitors. One can consider an impedance element, which includes in parallel one ideal resistor and one ideal capacitor, for
every grain, grain boundary, and electrode in Figure 3.4. Then all similar types of impedance are added together and make one of the RC’s in the 3RC model.

![Graphs showing impedance spectroscopy results](image)

Figure 3.3 (a) Imaginary impedance ($z''$) vs. real impedance ($z'$) at different temperatures for the BaTiO$_3$ single layer capacitor structure, (b) $1/C_i$ vs temperature, and (c) resistivity vs. temperature based on the 3RC model and Cole-Cole graphs in (a).

The samples were then exposed to a hydrogen atmosphere at 245°C, and the impedance spectroscopy was executed repeatedly for five hours; between every IS, the impedance was measured for 15 minutes at 1 kHz by LCR meter. As shown in Figure 3.5 (a), there is a good match between both curves from the experimental data, obtained by LCR meter, and the ones from 3RC model. That match can be another support for the validity of the 3RC model. The
Cole-Cole plots are shown in Figure 3.5 (b) in relation to the changes with hydrogen exposure. The total impedance reduces as the hydrogen ions enter the dielectric as interstitial donors, as would be anticipated from prior studies [196,232,233].

Figure 3.4 A schematic of electrode and grain boundary Schottky barriers in the capacitor active layer under no external fields.

As shown in Figure 3.5 (c), the maximum reduction in the resistivity occurs at the electrodes and with much less amplitude in grain boundaries; the resistivity reduction in the grain component is almost negligible. Hydrogen ions may decrease BaTiO$_3$ resistivity with two mechanisms. First, hydrogen gas (H$_2$) can be ionized according to Eq. (2.1), and as a donor gives free electrons to conduction band, so absorbing hydrogen generally decreases resistivity.

\[ H_2 \rightarrow 2H^+ + 2e^- \]

(3.1)

More importantly, hydrogen ions can pile up in the interfaces (electrode-dielectric or grain boundary) and reduce the depletion width, causing Schottky barriers to have lower resistance [204][83]. There is an order of magnitude reduction in the electrode resistivity that is much higher than the grain boundary reduction, which can be due to the fact that the largest contribution to the total resistivity comes from electrodes, and its reduction would be the largest portion of resistivity reduction and main cause of the total resistivity degradation. The proposed mechanism for hydrogen ion diffusion and distribution is schematically shown in Figure 3.6.
This is analogous to observations by Opitz et al. [234] with tracer oxygen diffusion, which has been proposed to account for reoxidation kinetics. The hydrogen gas dissociates into 2H\(^+\) cations and easily migrates along the electrode-dielectric interfaces and grain boundaries, and later diffuses into the grains.

![Figure 3.5](image_url)  
Figure 3.5 (a) Measured and calculated impedance at 1 kHz vs exposure time to hydrogen gas. (b) Imaginary impedance ($Z''$) vs real impedance ($Z'$) at different exposure time at 245 °C. The result of 3RC model, separated to ideal (c) resistors and (d) capacitors vs. time based on data on the Cole-Cole plots in (b).
3.4 Diffusion Coefficient

To describe the hydrogen diffusion into the samples, the boundary conditions should be correctly defined, then the concentration distribution can be calculated by the second Fick's Law [235].

The active layer was defined as a one dimensional system along the electrodes, started from the exposed surface toward the inside of the sample, as shown in Figure 3.1 and Figure 3.6. This modelling approach makes sense, since the amount of hydrogen in the active layer affects the amount of measured resistivity in impedance spectroscopy tests, and the closest way for hydrogen ions enter to the active layer is through the exposed surface. This experimental set up is similar to that used by Donnelly and Randall for calculating oxygen diffusion in BaTiO₃ and lead oxide volatility in PZT piezoceramics [224,231,236].

![Figure 3.6 Schematic of hydrogen diffusion in BME capacitors. The red ink shows the hydrogen cations. The difference between diffusion rates in electrode interfaces, grain boundaries, and grains are drawn proportionally.](image)

The system may be considered as semi-infinite media with the following boundary condition at the exposed surface:

$$\frac{dN(t)}{dt} = \alpha(C_0 - C_s)$$

(3.2)
where \( C_0 \) and \( C_S \) are concentration of hydrogen in atmosphere and on an exposed surface, respectively; \( N \) is the total hydrogen concentration in the active layer, and \( \alpha \) is a proportionality constant [237]. In other words, Eq. (3.2) simply shows that the entering rate of total hydrogen ions inside the active layer is proportional to the concentration difference between atmosphere and surface.

Next, the measured resistivity should be related to hydrogen ion concentration at the electrode. The impedance tests and 3RC model indicate that the electrode contribution to the total resistivity and its reduction by time are experimentally accessible, see Figure 3.5 (c). Inverse of resistivity or conductivity (\( \sigma \)) can be related to leakage current density (J), and then J can be related to hydrogen concentration through thermionic and field emission conductivity mechanisms for electrode Schottky barriers, which was studied in chapter 2. Here, for simplicity, a Taylor series is used to relate the conductivity (\( \sigma \)) to the hydrogen concentration. Just the first four terms of the Taylor series are used, and later it will be shown that the third and fourth terms are too small and negligible. The Taylor series would be as:

\[
\sigma = A + BN + CN^2 + EN^3
\]

(3.3)

where A, B, C, and E are constant and \( N \) is the proton concentration in front of electrodes.

Now the second Fick's equation in semi-infinite media for the boundary condition in Eq. (3.2) may be solved as:

\[
N(t) = \left( \frac{C_0}{h} \right) \left[ \exp(h^2Dt)erfc(h\sqrt{Dt}) - 1 + \frac{2}{\sqrt{\pi}}h\sqrt{Dt} \right]
\]

(3.4)

Where: \( t \) is time, \( D \) diffusion coefficient, and \( h = \frac{\alpha}{D} \).
The proof of Eq. (3.4) is given in Ref. [237]. Now, Eq. (3.3) and (3.4) can be used to relate resistivity (the inverse of conductivity) to time; on the other hand, there are resistivity-time curves, resultant from impedance spectroscopy tests for the electrode contribution. For example, see Figure 3.5 (c). By using a least square method and a Matlab code, one would be able to fit the curves with the equations and find the amount of A, B, C, E, \( \alpha \), and D. The best fitting curve for the electrode resistivity vs. time, shown in Figure 3.7 (a), is labeled as “Electrodes”. C and E were calculated \( 2.12 \times 10^{-20} \) and \( 8.28 \times 10^{-32} \). Considering the fact that N is not larger than 100 ppm as shown in Figure 3.7 (a), one can be eliminated both C and E coefficients, and Eq. (3.3) would be:

\[
\sigma = 4.35 \times 10^{-9} + 7.15 \times 10^{-5} N
\]

(3.5)

The fitting has R-square of 0.9915 based on Eq. (3.5).
Figure 3.7. (a) Hydrogen concentration vs. time for BaTiO$_3$ buried layer capacitor at 245 °C at three RC components. (b) Distribution of hydrogen impurities along the electrode-BaTiO$_3$ interface at every 1.5 hours after exposing to hydrogen gas. (c) Diffusion coefficients of hydrogen at three RC components vs inverse of temperature.

The diffusion coefficient for electrodes at 245 °C is shown in Table 3.1. Based on the Figure 3.6, one can assume the same governing equation and boundary conditions as electrodes for grains and grain boundaries. By using their resistivity, resultant from impedance spectroscopy, diffusion coefficient in these components at 245 °C can be found. The curve
fittings for grains and grain boundaries are shown in Figure 3.7 (a), and R-squares are 0.998 and 0.991, respectively. Those curves were again obtained based on the linear relation between conductivity and hydrogen concentration. The diffusion coefficients are shown in Table 3.1. Since the diffusion coefficients are highest at the electrode-dielectric interface, the hydrogen can diffuse rapidly through that interface. The second highest diffusion coefficient belongs to the grain boundaries, and the minimum with much lower value to grains. Thus, the schematic drawing in Figure 3.6 is a reasonable representative of the diffusion regime, discussed by Mehrer [238]. Since electrode has the highest diffusion coefficient, it is not surprising that the highest hydrogen ion concentrations are calculated in front of electrodes. However the concentrations are small and in the order of ppm.

Table 3.1 Diffusion behavior of BaTiO$_3$ capacitor in electrodes, grains, and grain boundaries.

<table>
<thead>
<tr>
<th></th>
<th>Diffusion coefficient (D) at 240 $^\circ$C (cm$^2$s$^{-1}$)</th>
<th>$D_0$ pre-exponential factor (cm$^2$s$^{-1}$)</th>
<th>$E_A$ activation enthalpy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrodes</td>
<td>$6.35 \times 10^{-8}$</td>
<td>0.8788</td>
<td>0.73</td>
</tr>
<tr>
<td>Grain Boundaries</td>
<td>$5.32 \times 10^{-8}$</td>
<td>1.2779</td>
<td>0.76</td>
</tr>
<tr>
<td>Grains</td>
<td>$1.80 \times 10^{-8}$</td>
<td>$2.02 \times 10^{-3}$</td>
<td>0.52</td>
</tr>
</tbody>
</table>

By knowing the diffusion coefficients (D) and h in Eq. (3.4), one can calculate the estimated distribution of hydrogen ions along the electrode-BaTiO$_3$ interface (x), shown in Figure 3.6, by using Eq. (3.6):

$$\frac{C(x,t)}{C_0} = erfc \left( \frac{x}{2\sqrt{Dt}} \right) - \exp(hx + h^2Dt) \, erfc \left( \frac{x}{2\sqrt{Dt}} + h\sqrt{Dt} \right)$$

(3.6)
where $C(x,t)$ is the concentration of hydrogen in respect to position ($x$) and time ($t$). For clarification, Eq. (3.7) shows the relation between $N(t)$ and $C(x,t)$.

$$\frac{dN(t)}{dt} = -D \frac{\partial C(x=0,t)}{\partial x}$$

(3.7)

In the other words, one can think of $N(t)$ as the area under the $C(x,t)$ curves, shown in Figure 3.7(b).

The amount of hydrogen increases rapidly in the first several micrometers of the interface, as seen in Figure 3.7(b). For example, there is a rapid increase of hydrogen concentration in front of the electrode in the first 1.5 hours. However, the rate of proton concentration increase is reduced by passage of the time; for example, there is not much difference between the curves for 9 and 10.5 hours. This rapid increase manifests itself in a large drop in the electrode resistivity in Figure 3.5 (c) and is the key to explain the fast resistivity degradation in the capacitors, as discussed in the previous chapter.

The same impedance tests were repeated at 275 and 305 $^\circ$C, and then by the above mentioned procedure, the diffusion coefficients for the electrodes, grain boundaries, and grains were calculated. Since diffusion is a thermally activated process, there is an Arrhenius relationship between $D$ and $T$ as follows [83]:

$$D = D_0 \exp \left(\frac{-E_A}{kT}\right)$$

(3.8)

where $k$ is Boltzmann’s constant, $T$ temperature, $D_0$ pre-exponential, and $E_A$ activation enthalpy. The log of the calculated diffusion coefficients vs. reciprocal temperature is shown in Figure 3.7
(c). As seen, the diffusion coefficient is highest for the electrode interface at every temperature. Diffusion coefficients in grain boundaries are slightly lower, but in grains are much lower than in electrodes. From Figure 3.7 (c), one can obtain the pre-exponential factor \(D_0\) and activation enthalpy \((E_A)\) for hydrogen diffusion in the three components, as shown in Table 3.1. The rate of hydrogen successful jump from one oxygen atom to another, shown by \(\omega\), may be written as [238,239]:

\[
\omega = \nu_0 \exp \left( -\frac{S_a}{k} \right) \exp \left( -\frac{E_a}{kT} \right)
\]

(3.9)

where \(\nu_0\) is an attempt frequency, and \(S_a\) entropy of activation. \(S_a\) and \(E_a\) are related to activation energy \((G_a)\) by:

\[
G_a = E_a - TS_a
\]

(3.10)

Since \(D\) is proportional to \(\omega\), one can expect that there would be a relation between \(D_0\) and \(E_a\). Obtaining that relationship is complicated for hydrogen and needs a quantum mechanical approach [238]. For example, Kreuer [88,222], by using quantum molecular dynamics, successfully calculated the bulk hydrogen diffusion coefficient in several perovskite oxides. For comparison to the present chapter, \(E_a\) and \(D_0\) for several perovskite oxides for diffusion in bulk (grains) are given in Table 3.2. As seen, both \(E_a\) and \(D_0\) would change with different constituent atoms, dopant, or dopant concentration, but the range stays between \((0.17 \text{ to } 0.63 \text{ eV})\) and \((3 \times 10^{-5} \text{ to } 3.47 \times 10^{-2} \text{ cm}^2/\text{s})\), respectively. The reported \(E_a\) and \(D_0\) in Table 3.1 for grains lie within those bounds. Moreover, Norby [84], by considering \(E_a\) in around 35 perovskite oxides \((\text{ABO}_3)\),

69
found the following empirical relationship between electronegativity difference of A and B \( \Delta X_{B-A} \) with \( E_a \):

\[
E_a (eV) = 4.15 \Delta X_{B-A} - 1.87
\]

(3.11)

Although there is a large scattering in the reported data that they used to find Eq. (3.11), and the equation does not take the dopant concentration into account, it is a good guide for a rough estimation for \( E_a \). Plus, the reported activation energies by Norby [84] cover the range of 0.21 to 1.87 eV, which almost contain the reported activation energy in Table 3.2. [94] [91] [92] [93]

<table>
<thead>
<tr>
<th>Oxide</th>
<th>crystal structure</th>
<th>( D_0 ) (cm(^2)/s)</th>
<th>( E_a ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba(Zr(<em>{0.9}Y</em>{0.1}))O(_3)</td>
<td>Cubic</td>
<td>2.34\times10^{-3}</td>
<td>0.43 [88]</td>
</tr>
<tr>
<td>Sr(Ti(_{0.95}S_{0.05}))O(_3)</td>
<td>Cubic</td>
<td>7.41\times10^{-4}</td>
<td>0.42 [88]</td>
</tr>
<tr>
<td>Ba(Ti(_{0.95}S_{0.05}))O(_3)</td>
<td>Cubic</td>
<td>1.95\times10^{-2}</td>
<td>0.64 [88]</td>
</tr>
<tr>
<td>Pb(Zr,Ti)O(_3)</td>
<td>Cubic</td>
<td>-</td>
<td>0.44 [196]</td>
</tr>
<tr>
<td>CaTiO(_3)</td>
<td>Cubic</td>
<td>1.48\times10^{-3}</td>
<td>0.42 [94]</td>
</tr>
<tr>
<td>SrTiO(_3)</td>
<td>Cubic</td>
<td>1.12\times10^{-3}</td>
<td>0.5 [94]</td>
</tr>
<tr>
<td>Ba(Zr(_{0.9}I_{0.2}))O(_3)</td>
<td>Cubic</td>
<td>2.2\times10^{-4}</td>
<td>0.45[91]</td>
</tr>
<tr>
<td>Ba(Zr(_{0.5}I_{0.5}))O(_3)</td>
<td>Cubic</td>
<td>1.1\times10^{-4}</td>
<td>0.62 [91]</td>
</tr>
<tr>
<td>Sr(Ce(<em>{0.9}Y</em>{0.1}))O(_3)</td>
<td>non-cubic</td>
<td>8.32\times10^{-3}</td>
<td>0.63 [88]</td>
</tr>
<tr>
<td>Ba(Ce(<em>{0.85}Y</em>{0.15}))O(_3)</td>
<td>non-cubic</td>
<td>3.47\times10^{-2}</td>
<td>0.6 [88]</td>
</tr>
<tr>
<td>BaZrO(_3)</td>
<td>Cubic</td>
<td>3\times10^{-5}</td>
<td>0.17-0.20 [92] [93]</td>
</tr>
<tr>
<td>Ba(Zr(<em>{0.8}Y</em>{0.2}))O(_3)</td>
<td>Cubic</td>
<td>5\times10^{-2}</td>
<td>0.47 [92]</td>
</tr>
</tbody>
</table>

Norby and his coworkers [84] briefly reviewed the hydrogen diffusion in grain boundaries; they speculate that the activation energy should be higher in grain boundaries than in grains. There is not yet a comprehensive study on the hydrogen diffusion in the grain boundaries.
and electrode-dielectrics interface in perovskite oxides to compare with the diffusion coefficients in the present chapter. However, they can be rationalized by comparison to the studies on other systems. Naundorf [240] reviewed grain boundary diffusion and proved that diffusion in grain boundaries is similar to diffusion in amorphous materials. Kirchheim [98,241] shows that there is a spectrum of enthalpies in amorphous Pd-Cu-Si alloy with a Gaussian distribution due to the disordered structure of amorphous materials.

One can extend the logic in Naundorf’s [240] and Kirchheim’s [98,241] research to the present study. Since there is a spectrum of enthalpies at interfaces and grain boundaries, and hydrogen ions prefer to go to the lower level energy, they fill the lower enthalpy level first; this is why the activation enthalpy $E_a$ is higher at the electrode-BaTiO$_3$ interfaces and grain boundaries than in grains (see Table 3.1). Especially in low hydrogen concentration, that enthalpy spectrum can make a large difference [98]. All in all, the diffusion coefficients in interfaces and grain boundaries due to having larger $D_0$ are higher than the diffusion coefficients in grains, as shown in Figure 3.7.

### 3.5 Impact of different parameters on resistivity degradation

Now, by knowing the impedance spectroscopy results and hydrogen diffusion in those RC components, one would be able to check the validity of 3RC model and get a better understanding about hydrogen diffusion by manipulating some parameters in the impedance tests. Two parameters of electrode chemistry and active layer thickness were changed and then checked to determine whether the 3RC model would be able to justify the new results.
3.5.1 The impact of active layer thickness

The active layer in BME samples increases from 18 to 500 µm in k-square samples. Although the electrode materials and area remains same, the resistivity components in 3RC model increase 5.8, 7.7, and 13.2 times in electrode (E), grain (G), and grain boundary (GB) components, respectively. There is an increase in G and GB resistivity, because the number of grains and GB Schottky barriers increase. The E resistivity increases as well, because the increase in GB and G resistivities leads to a larger voltage drop, and that means less voltage difference at electrode Schottky barriers and eventually less leakage current due to a less contribution of Field Emission conductivity [83].

The resistivities of electrode, grain boundary, and grain extracted from impedance tests by the 3RC model are shown in Figure 3.8 for BME and k-square samples. K-square results are normalized with the above mention factors, so that every RC component’s curve starts from the same place. As can be seen, the amount of degradation is higher in every BME component than in k-square’s. Since the active layer is thinner in BME when exposed to the same hydrogen atmosphere, the accumulation of hydrogen ions would be higher in a small portion of BME samples than in k-square ones. The higher hydrogen concentration manifests in higher reduction in resistivity. For instance, the BME electrode shows much higher degradation than the k-square, mostly because that hydrogen concentration in front of the k-square electrode is less accumulated. Since the diffusion coefficient in grain boundary is almost as high as in an electrode interface, as shown in Figure 3.7 (c), the grain boundaries can be a free path for hydrogen atoms and move them away from the electrode to the inside of active layer in k-squares; regarding the higher thickness of k-square samples, that leads to less hydrogen
concentration in front of the electrode. In short, hydrogen ions reach higher concentration in BME electrode, and this is why they are degraded more.

3.5.2 The impact of electrode materials

In the case of an ideal Schottky barrier at the electrode interface, in which there is no gap between semiconductor and electrode and no interfacial states to pin the Fermi Level, the difference between metal work function ($\phi_m$) and semiconductor affinity ($\chi$) is the Schottky barrier height ($\phi_B$) [202]:

$$\phi_B = \phi_m - \chi$$

(3.12)

So in principle, different electrode metals with different work functions can change the height of Schottky barriers in the absence of pinning. Work function depends on surficial parameters, such as surface cleanliness and surface crystal plane, so one may find different values for work function of a metal [242,243]. Three electrodes of Ag, Au, and Pt are selected with work functions of 4.26 [244], 5.40 [245], and 5.64 eV [206] in polycrystalline form. The advantages of using those electrodes are, first, their work functions were well studied and known; second, they all could be easily coated on BaTiO$_3$ k-square samples with the same method (sputtering) to make sure their quality is somewhat similar; third, regarding BaTiO$_3$ electron affinity, 3.9 eV [207], the Schottky barriers are different enough to make tangible changes in IS results [246].
The impedance tests were executed on the three samples, and the results are shown in Figure 3.9. As was expected, a much smaller curve was obtained for virgin sample with silver electrode than the samples with Au and Pt electrode in Figure 3.9 (a). As a matter of fact, Ag electrode Schottky barrier is negligible. Pt electrodes shows the largest resistivity, and Au electrode have the second largest resistivity, as expected from electrode work functions and Eq. (3.12).

In regard to the impact of resistivity changes in the presence of hydrogen gas with different metal electrode chemistries, there is a 35% reduction in Pt electrode resistivity, while resistivity reduces by 29% in an Au electrode. It can be concluded that Pt electrode is a better catalyst for hydrogen ionization, given in Eq. (2.1), than Au. This conclusion is in agreement with earlier observations of Han and Ma [226]. They studied the hydrogen influence on SBT
(SrBi$_2$Ta$_2$O$_9$) remanent polarization; based on their results, Pt can pump much more hydrogen to SBT than Au.

All the samples show the same grain resistivity in Figure 3.9 (b), since they all have the same thickness. The grain boundary resistivity of Pt is slightly higher than Ag and Au at the beginning of the exposure; it is due to the higher Schottky barrier in the Pt-BaTiO$_3$ interface, which leads to a higher voltage drop at interface. However, hydrogen degradation reduces electrode resistivity, which causes a voltage drop decrease at the interface, so that all grain resistivities would be same after the 2$^{nd}$ hour of exposure.

The obvious conclusion from Figure 3.9 is that the RC contribution for electrodes has been chosen correctly, since it was illustrated that electrode resistivity contribution would experience the maximum change by changing the electrode metals.

![Figure 3.9](image)

Figure 3.9. Impedance result of the k-square samples with silver, platinum, gold electrodes at 245 $^\circ$C. (a) Cole-Cole plot before and after exposing to hydrogen for 10 hours, and (b) calculated resistivity vs. time for electrode, grains, and grain boundary for each sample.
3.6 Conclusions

In this chapter, the resistivity degradation of BaTiO$_3$ due to hydrogen gas was studied by using impedance spectroscopy. Since there are three main contributors to samples’ resistivity (electrode, grain boundary, grains), a 3RC model was found to be the best model to fit the Cole-Cole plots, resultant from the impedance tests. Plus, some techniques have been illustrated to differentiate between RC’s.

The electrode interfaces have the largest contribution to the resistivity of BME samples when the samples are exposed to hydrogen gas; the largest resistivity reduction also happen at these interfaces.

Moreover, hydrogen diffusion coefficients could be successfully calculated, assuming the right boundary conditions and relating measured resistivity to hydrogen concentration at grain, grain boundary, and electrode interface. The pre-exponential factor (D$_0$) and activation enthalpy (E$_a$) were respectively measured $2.02 \times 10^{-3}$ cm$^2$/s and 0.52 eV for grains, which are in a good agreement with other reports. The diffusion coefficients at electrode interfaces and grain boundaries are larger than grains. The results were rationalized by findings in other systems. The resultant diffusion coefficients can be useful in fuel cell studies, where people are interested in measuring hydrogen diffusion coefficient in perovskite oxides.

Finally, the effective parameters in impedance measurement are manipulated and show how they affect hydrogen diffusion. In short, the geometry of the active layer influences the degradation; there would be more proton accumulation in BME capacitors than in k-square ones. Electrode chemistry can also affect the total resistivity and the rate of degradation.
4 Evaluating the Merit of ALD Coating as Barrier against Hydrogen Degradation in Capacitors Components

4.1 Introduction

In the two previous chapters, the degradative effects of hydrogen exposure was explored and a strategy was introduced to measure the diffusion coefficient of protons in BaTiO$_3$ MLCCs. In the present chapter, the possibility of utilizing ALD coatings as a diffusional barrier to prevent the degradation was explored and discussed.

Hydrogen gas exposure to a BaTiO$_3$ based dielectric material can dramatically decrease resistivity. This is believed to be associated with H$^+$ ions (protons) accumulating in interfacial regions, and in the case of n-type doped semiconductors, makes the Schottky barriers more conductive. This could be a potential problem in packaging modules for power electronics [201], as outgassing of hydrogen or related gases will raise the activity of H$_2$ in the sealed modules. This can gradually impact capacitors and other interfacial controlled devices that control voltage and current, such as varistors and positive temperature coefficient of resistance (PTCR) components, inducing early lifetime failures of the components and possibly catastrophic system failures [191–193,195]. The resistivity degradation of multilayer BaTiO$_3$ MLCCs has been studied by a number of other reports [82,83]. In contrast to those oxygen vacancy controlled time dependent break down processes [214,215,247], the effects of H$^+$ has been rarely considered. In our recent investigations of the effects of H$^+$, it was demonstrated that there are major changes that significantly reduce the electrode Schottky barrier width, especially
at the electrode interfaces, as determined by combined *in-situ* impedance spectroscopy and I-V analysis [82,83].

The objective of this investigation is to determine if there is a potential for effective use of atomic layer deposition (ALD) coatings to limit the insulation degradation due to hydrogen gas on base metal electrode (BME) BaTiO$_3$ capacitors [44,45,248]. ALD coatings have already been identified as diffusion barriers in a number of applications [18,22,23][24], such as prohibiting copper diffusion to dielectrics in the backend copper interconnects [26,73], or as a gas diffusion barrier on Kapton and PEN (Polyethylene Naphthalate) polymers [44]. The effectiveness of ALD as a diffusion barrier is significant for those polymers; for example, it has been shown that a 10nm alumina ALD can reduce the water vapor transmission rate by 3 orders of magnitude [27,28]. The gas barrier property of oxides is due to the strong bond between hydrogen and oxygen, which considerably increases activation enthalpy for proton diffusion in oxides. [85]. Norby et al. [84] have reviewed hydrogen diffusion in different oxides.

ALD consists of two half reactions that conformally coat a layer with atomic precision on a surface [249–251]. For example, ALD reactions for alumina are made of two half reactions [127]:

$$Al - OH^* + Al(CH_3)_3 \rightarrow Al - O - Al - (CH_3)_2^* + CH_4$$

$$Al - CH_3^* + H_2O \rightarrow Al - OH^* + CH_4$$

(4.1)

where the asterisks indicate the surface species. Both reactants, namely, Trimethylaluminum (TMA), $Al(CH_3)_3$, and water are in a gas phase. Both reactions are self-terminating, i.e., after the first atomic layer, the reactions stop automatically and are exothermic enough to continue spontaneously. These features are essential in ALD reactions [252].
ALD coatings have several features that make them a unique technique for coating barrier layers. Since the ALD reactions can be separated into two independent and self-terminating half-reactions, the coatings have high aspect ratio, which leads to a conformal, and continuous coating, with an even thickness all around samples [44,252].

In this chapter, it has been shown that ALD coating can be deposited on BaTiO$_3$. Their barrier properties were studied while the samples were exposed to hydrogen gas with I-V tests and impedance spectroscopy to measure the temperature of merit ($T_0$) and diffusion coefficient in ALD layers. Diffusion coefficient in ALD coating can be a quantitative criterion to show how effective an ALD layer is against hydrogen or find applications in the study of oxide layer degradation due to exposing to hydrogen gas in MOS (metal–oxide–semiconductor) devices [253,254]. TEM analysis has also been executed to study the structure of the layers before and after exposing to hydrogen gas at high temperature.

4.2 Experimental Section

Model capacitor structures were fabricated with typical cofired methods [255]. The X7R322N BaTiO$_3$ powders from Ferro Co. with X7R formulations co-doped by Y$_2$O$_3$-MnO were tape casted into layers with a thickness of 50 and 20 µm and cut into 1 × 1 inch squares. The electrodes patterns, 4 × 5 rectangles with the dimensions of 2 × 4.5 mm, were printed with a homemade nickel ink (made with Shoei Chemical Ni powder) on the two of squares with the thickness of 20-µm. The two tapes were aligned so that every printed rectangle had an overlap area of 2 × 3.5 mm with an extent of 1 mm in each tape in the length direction. Thus, the activation. After a satisfactory alignment, those 20 µm layer were stacked with six 50-µm squares on the top and the bottom and then were laminated, cut to separate rectangles, and
sintered at 1300 °C for 2 hours in $10^{-10}$ atm of oxygen partial pressure. After that, the samples were reoxidized at 800 °C in $10^{-8}$ atm of oxygen partial pressure for 8 hours. The final products were test capacitor structures, which had one active layer with 18 µm thickness, can be a representative of typical MLCCs. To make sure hydrogen would be exposed in the same way to the active layer in all the samples, they were cut along the electrode, as shown in Figure 3.1 (a), and hydrogen effects could be noted over relatively accelerated conditions.

<table>
<thead>
<tr>
<th>Table 4.1 ALD recipes for ZnO, Al₂O₃, and HfO₂ coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal-Precursors</td>
</tr>
<tr>
<td>Precursor dose time (s)</td>
</tr>
<tr>
<td>0.015</td>
</tr>
<tr>
<td>Purge time (s)</td>
</tr>
<tr>
<td>Water dose time (s)</td>
</tr>
<tr>
<td>Purge time (s)</td>
</tr>
<tr>
<td>Temperature</td>
</tr>
<tr>
<td>Growth rate</td>
</tr>
<tr>
<td>Base pressure</td>
</tr>
</tbody>
</table>

Before the ALD process, the samples were placed in an ultrasonic bath of acetone for 5 minutes, followed by another 5 minutes in isopropyl alcohol, and dried in an oven for 20 minutes at 120 °C to make sure all the surface contaminations were removed. Then they were coated with an ALD system (150LE, The Kurt J. Lesker Co.) with the recipes shown in Table 4.1. The samples were coated with 220, 440, 660, and 880 cycles. The schematic of ALD coated sample is shown in Figure 3.1 (b). In this chapter, the number of cycles instead of thickness will be used. Since every cycle takes roughly 20 seconds, the number of cycles represents the processing time for ALD coatings. One can convert the cycles to the thickness by the average growth rates,
reported in Table 4.1. (However, it would demonstrate thickness does not play a fundamental role in barrier property of the coatings.)

Before and after ALD coating the sample, capacitance and loss were measured by HP4284A LCR meter (Hewlett-Packard) at 1 V to make sure that their electrical properties did not change before and after ALD.

![Figure 4.1 schematic of (a) cut capacitors, (b) ALD coated capacitor from left view.](image)

The I-V tests were used to assess the merit of the coatings in the forming gas atmosphere (4% hydrogen and 96% nitrogen) in the temperature interval of 150 to 300 °C. A furnace with sealed stainless steel chamber inside was used to heat samples. Forming gas could be blown inside the box, and temperature could be measured accurately with a K-type thermocouple embedded inside the box. The temperature was ramped with 10 °C step, each sample was charged by HP4140B PA meter (Hewlett Packard) to 15 V for 60 seconds, and leakage current was recorded per second and then discharged for another 60 seconds. This process was repeated three times at each temperature to make sure stable numbers were being measured. The final leakage current was measured for each temperature, roughly after 25 minutes of being at that temperature. Two samples without coatings were tested in air and forming gas as references for no degradation and complete degradation states, respectively. Forming gas would be called hydrogen atmosphere from now on.
Impedance spectroscopy was executed by using SR-830-DSP Lock-in connected to homemade charge measurement hardware to measure the proton diffusion coefficient in ALD layers. The impedance tests were executed in the frequency range of 10 kHz to 0.01 Hz with ac voltage of 0.1 V at temperatures of 235, 245, and 255 °C.

TEM samples were prepared by FEI-Quanta-200 FIB (Oregon, USA). TEM micrographs were done by JEOL-2010 field emission TEM (Tokyo, Japan).

4.3 **HALT tests for coated and uncoated MLCCs**

The saturate leakage currents vs. temperature for samples without coating are shown in Figure 4.2 (a) in air and hydrogen atmosphere. As described in previous chapter, hydrogen ions cause a resistivity degradation in BaTiO₃ capacitors. As shown in Figure 4.2 (a), the leakage current difference between the two typical samples in air and hydrogen atmosphere becomes obvious around 160 °C. Those curves are shown in the other graphs of Figure 4.2 and can be used as the indicators of two extreme conditions, from no protection to full protection against hydrogen gas damage.

Figure 4.2 (b) shows the results of the I-V test for the samples coated with 220 to 880 cycles of Al₂O₃. As long as the measured leakage current for the coated samples is close to the leakage currents for the uncoated sample in air, it would be assumed that the ALD coating is fully protecting the samples against hydrogen gas, and the first departure from the ‘air’ curve would be considered as the failure of the coating against hydrogen. Thus, one would be able to define a temperature, below which the samples are fully protected against hydrogen, would be called temperature of merit (T₀) in this chapter. T₀ is shown in Table 4.2 for Al₂O₃ coatings. The highest T₀ is 270 °C and has been obtained at 660 cycles, while T₀ is 260 °C for 880 cycles. Plus,
the fact that the measured leakage current is much higher for 880 cycles at 300 °C than 660 or even 440 cycles, suggests that the thicker coatings do not necessarily provide better protection, and rather, there is an optimum thickness. This phenomenon would be discussed more by using TEM analysis.

Table 4.2 Temperature of merit (T₀) in terms of °C for Al₂O₃, HfO₂ coatings

<table>
<thead>
<tr>
<th>Oxide</th>
<th>110</th>
<th>220</th>
<th>440</th>
<th>660</th>
<th>880</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>-</td>
<td>200</td>
<td>250</td>
<td>270</td>
<td>260</td>
</tr>
<tr>
<td>HfO₂</td>
<td>290</td>
<td>310</td>
<td>310</td>
<td>310</td>
<td>310</td>
</tr>
</tbody>
</table>

The leakage currents for the samples with HfO₂ coatings are given in Figure 4.2 (c) and T₀ in Table 4.2. As can be seen, there is not much difference between 220 to 880 cycle coatings up to 300 °C. To find out how high T₀ is, the maximum temperature was extended to 350 °C, and the sample with 110 cycle thickness was also tested. It can be seen in Table 4.2 that all the thicknesses above 110 cycles have T₀ of 310 °C. The sample with 110 cycle coating has T₀ of 290 °C. As found for Al₂O₃ coatings, the lowest leakage current at 350 °C is for the sample with 660 cycles. However, the differences are not as large as with the Al₂O₃ coatings.

The ZnO ALD was, comparatively, not as good a barrier against hydrogen ions under the deposition conditions used here. The 660 and 880 cycle coatings change the sample resistivity before and after ALD coating. The best results were acquired in 440 cycles, which has been compared with Al₂O₃ and HfO₂ 440 cycles in Figure 4.2 (d). The T₀ would be 230 °C for ZnO coating, which is the lowest among other ALD coatings. HfO₂ shows the best barrier property against hydrogen gas.
Figure 4.2. Saturated leakage current vs. temperature for samples (a) without coating in air and hydrogen atmosphere, (b) with Al₂O₃, and (c) HfO₂ coatings at various cycles (d) with different ALD coatings of 440 cycles.

It should be pointed out that since the different components have different growing rates as shown in Table 4.1, after 440 cycles, they have different thicknesses. As will be demonstrated later, the thicknesses are 40, 48, and 57 nm for Al₂O₃, HfO₂, and ZnO respectively. As mentioned in the experimental section, the number of cycles is representative of processing time. So Figure 4.2 (d) basically shows that by spending of same amount of processing time, one can
obtain much better gas barrier by using HfO$_2$ instead of the other compounds. Number of cycles is suitable variable to compare different ALD coatings, since one of the ALD disadvantage is mentioned to be a time consuming process and it draws this conclusion that by using more stable compound one would be able to obtain a better barrier layer by spending the same processing time.

Furthermore, the coating thickness does not have a fundamental contribution to the barrier property of ALD coatings; as shown in Figure 4.2 (c), the leakage currents do not change below $T_0$ for the coating with cycle number, higher than 110. This is true for Al$_2$O$_3$ coating with the cycle number, higher than 220. Thus, the comparison of the ALD coatings with 440 cycles is quite reasonable.

Boiling and melting temperatures can be a criterion of the bond strength of chemical compounds. Since the atomic bonds will break during evaporation, higher boiling temperature means stronger bond between atoms. So one would be able to compare the ALD coating stability with each other by knowing their boiling temperatures. The ZnO, Al$_2$O$_3$, and HfO$_2$ have boiling points of 1975 [256], 2980 [257], and 5100 $^\circ$C [258], respectively. So HfO$_2$ is the most stable oxides among the others. One can arrive to the same conclusion by comparing their melting points, or their bond dissociation enthalpy. Hf-O, Al-O, and Zn-O have the bond dissociation enthalpy of 801, 502, 250 kJ/mol [259], respectively.

This is possibly why HfO$_2$ is the best barrier coating among the others. Yesibolati [260] demonstrated that HfO$_2$ can be used as an effective surface passivation. Huang showed that HfO$_2$ shows better stability and barrier property than Al$_2$O$_3$ [261]. On the contrary, ZnO has the lowest boiling point, which is the least stable structure and having the minimum barrier property among the others.
4.4 TEM analyses of the coated MLCCs

Figure 4.3 shows the TEM micrograph of Al₂O₃ coatings with 220, 660, and 880 cycles along with the energy dispersive spectroscopy (EDS). ALD coatings, as expected, are continuous, and conformal, as shown in Figure 4.3 (a) in a low magnification. The ALD layers of 220, 660, and 880 cycles have been shown in higher magnification in Figure 4.3 (b) to (d). Their thicknesses are respectively measured between (17, 20), (57,63), and (75, 79) nm for the 220, 660, 880 cycles, which suggested the average growth rate of 0.9 Å per cycle. Since the original samples were made by sintering of BaTiO₃ powder and they have rough and porous surfaces, the fluctuation in thickness was expected. Furthermore, it was proven that Al₂O₃ layers are amorphous by SAED (selected area electron diffraction) patterns. The gold layers, shown in Figure 4.3, were coated on the samples during the sample preparation process.
Figure 4.3 TEM micrographs from samples with Al₂O₃ ALD coating with thickness of (a) and (b) 880 cycles (80 nm), (c) 660 cycles (60 nm), and (d) 220 cycles (20 nm) (e) elemental analysis vs distance cross the layers shown in (d); the arrow shows the path and the direction of the line analysis.
The EDS analysis was executed across the layers in Figure 4.3 (d), and the result for Au, Al, and Ba vs distance are shown in Figure 4.3 (e). It proves the layers are labeled correctly in Figure 4.3 (d).

The ALD coating is effective because both precursors are in gas phase; they can diffuse to the sample and fill the interconnected porosities and the empty space between grains and electrode interfaces. An example of a BaTiO$_3$ grain, enclosed with ALD coating, can be found in Figure 4.3 (a), where the arrow is pointing. As a matter of fact, the precursor diffusion is not limited to the surface grains; they can diffuse inside the capacitors and fill the open interconnected porosities. For example, during TEM analysis, a hole 4.8 µm beneath the surface and near to electrode was found partially filled with alumina. That can be considered as an advantage for ALD coatings, because precursors can fill the holes near the surface and form a continuous coating on the top of the surface, providing a true sealing for the samples against hydrogen gas.

The next insight that can be found by TEM analysis is why ALD coatings fail after $T_0$. Figure 4.4 shows the 80 nm Al$_2$O$_3$ layer after the I-V test. As seen in Figure 4.4 (a), some portion of ALD layer is crystallized and surrounded by an amorphous structure. The crystallized part looks like a nucleus in the early state of growth. Figure 4.4 (b) shows a bigger crystallized region, with the grain boundary between crystallized and amorphous area. It looks like a fully grown columnar grain, which reach the upper and lower interfaces. One can see the primary and the final states of grain crystallization from the amorphous region through Figure 4.4 (a) and (b).
Figure 4.4 TEM micrographs from the sample with 880 cycles of Al₂O₃ ALD coating after the I-V test, (a) nucleus in the state of growing (b) well devolved crystallized grain with boundaries with amorphous region, (c) mismatch or cracks in ALD layer because of crystallization.

Figure 4.4 (c) shows the crack-like features due to the internal stress of ALD coating, caused by the crystallization. However the dominant faults were grain boundaries between
crystallized and amorphous regions. These features offer an easy path for hydrogen ions to diffuse into the capacitors, and this is the main reason for ALD layer failure after $T_0$.

Those grain boundaries were much less in 660 cycle ALD layer, so it may be the reason that the leakage current is much higher in 880 cycle than 660 and 440 cycle at 300 °C, as shown in Figure 4.2(b). Since the leakage current is also slightly higher for 880 cycle than 660 and 440 cycle in HfO$_2$ layers at 350 °C, as shown in Figure 4.2(c), one can conclude, based on those curves, that the coatings with 880 cycles are less stable than the 660 and 440 cycles in both Al$_2$O$_3$ and HfO$_2$ at high temperatures. In other words, the thicker coatings become crystallized more easily in high temperature than the thinner ones, and above $T_0$, the total proton diffusion mostly depends on the crystallization percentage and the number of grain boundaries, and not on the layer thicknesses. Jen et al. [178] have shown thinner Al$_2$O$_3$ ALD coatings are more mechanically robust against cracking than the thicker ones.

The TEM micrograph of the HfO$_2$ coated samples with 880 cycle coating before and after I-V tests along with SAED patterns is shown in Figure 1.10. It suggests exposure to high temperature, 350 °C, introduces crystallized portion and grain boundaries to HfO$_2$ layers, too.

There is an obvious region with coarse Moiré fringes, which is the sign of two crystallized planes that translate or/and rotate against each other [262] in Figure 1.10 (b), shown with ‘A’. There are other regions with less obvious fringes, labeled as ‘B’ and ‘C’. They may result from a crystallized and amorphous planes that sit on top of each other. This explanation can be supported by SAED pattern, which was shown in insets. Having both patterns of donut-shape and points indicates the coexistence of crystallized and amorphous regions in the microstructure, shown in Figure 1.10 (b).
The other feature is Fresnel-contrast, the result of two neighbor regions with different inner potentials, when the image is out of focus [263]. This contrast can be seen in the borders of regions B and C and can be the sign of grain boundaries, which connect the top of ALD layer to the bottom. These types of faults can provide a free path for protons to pass ALD layer and diffuse inside BaTiO₃. Although one should be wary not to mistake the artifact for a real feature in TEM micrographs, there is a considerable change before and after exposure to high temperature, so that it rules out the artifact effect. As a conclusion, the same mechanism as the Al₂O₃ failure, which is crystallization due to exposing to high temperature, is the reason of HfO₂ failure.

Since ZnO has the weakest bond strength, and we observe the minimum T₀ among the tested ALD coatings, it is expected to have the maximum amount of crystallization and faults.
The TEM micrograph of ZnO ALD layer as coated is shown in Figure 4.6. The ALD layer is still conformal and continuous, but due to large amount of crystallization and faults, the layer fails to protect the capacitor against hydrogen gas. As mentioned above, the grain boundaries provide a free path for hydrogen diffusion. The layer in Figure 4.6 has thickness between 112 and 115nm, and the growth rate in average would be 1.3 Å per cycle.

![Figure 4.6 TEM micrographs from the sample with 880 cycles of ZnO ALD coating as coated in two different magnifications.](image)

4.5 Measuring diffusion coefficient of hydrogen ions in ALD coatings

In the previous chapter, the proton diffusion coefficients were found for BaTiO$_3$ BME capacitors in bulk, grain boundaries, and electrode interfaces. Considering there is a linear relation between proton concentration of capacitors and their conductivity (inverse of resistivity) [88,224,231,264] at a constant temperature, one would be able to find the proton diffusion
coefficient in ALD layers by measuring conductivity changes of the coated capacitors during hydrogen exposure. To find the diffusion coefficient, the diffusion system should be first defined.

In order to degrade the samples, protons need to pass through ALD coating and arrive to the capacitor active layer, see Figure 3.1 (b). Since they diffuse in just one direction, and ALD layer is thin so that the proton diffusion reaches steady state quickly, one can define the diffusion system in one direction and apply Fick's first law to find diffusion coefficient. Since it has been proved that the ALD layers can act as a gas barrier (Figure 4.2), it is assumed that BaTiO$_3$ has a higher diffusion coefficient than ALD layer, and there is no hydrogen accumulation beneath ALD layer at the BaTiO$_3$ and ALD interface.

A virgin sample, coated with 95nm HfO$_2$, was exposed to hydrogen for seven hours while impedance spectroscopy test was executed once in every hour. The entire test was repeated at three temperatures of 235, 245, and 255 °C. The resultant Cole-Cole plots are shown in Figure 4.7 (a). It has been shown that Cole-Cole plots of BME BaTiO$_3$ capacitors can be best fitted by 3RC model [82,215,229]. Since the electrode has the largest loss of resistance due to hydrogen exposure among the other RC’s (grains and grain boundaries) [82], it would be more sensitive to proton concentration. Therefore, the electrode conductance was extracted from the Cole-Cole plots and shown in Figure 4.7 (b) at different time and temperatures. As seen, the data can be fitted by a line with R-squares above 0.99.

From our earlier work in measuring proton diffusion coefficients for BaTiO$_3$ capacitors, it was shown that there is the following relation between conductivity ($\sigma$) and proton concentration ($N$) at 245 °C [82]:

$$\sigma (S) = 4.35 \times 10^{-9} + 7.15 \times 10^{-5}N (ppm)$$
By using Eq. (4.2), the diffusion flux \( J \) can be obtained and then by replacing it in Fick's first law, the diffusion coefficients can be calculated at 245 °C. The diffusion coefficients can be obtained in the same way for other temperatures and other ALD coatings; the coefficients for virgin (as produced) \( \text{HfO}_2 \) and \( \text{Al}_2\text{O}_3 \) layers along bulk \( \text{BaTiO}_3 \) [82] are shown in Figure 4.7 (c). As seen, the diffusion coefficient at 245 °C in \( \text{BaTiO}_3 \) is approximately 3000 and 1000 times higher than \( \text{HfO}_2 \) and \( \text{Al}_2\text{O}_3 \) coatings, respectively. The activation energy in \( \text{HfO}_2 \) and \( \text{Al}_2\text{O}_3 \) layers are 2.3 and 2.4 eV in contrast to 0.5±0.01 eV in \( \text{BaTiO}_3 \). So protons need to pass a higher barrier to jump from one oxygen atom to another in \( \text{HfO}_2 \) and \( \text{Al}_2\text{O}_3 \), while in \( \text{BaTiO}_3 \), due to octahedron oscillation and momentary \( O-H \cdots O \) bonds, the activation energy is much smaller [84]. This explains why those ALD layers can make a good hydrogen gas barrier.

If the \( \text{HfO}_2 \) and \( \text{Al}_2\text{O}_3 \) are extrapolated, they intersect with \( \text{BaTiO}_3 \) at 376 and 348 °C, which theoretically means that they lose their barrier properties at those temperatures. However, the \( \text{Al}_2\text{O}_3 \) and \( \text{HfO}_2 \) layers start to crystallize at 260 and 310 °C, and this structural change means they lose their barrier property, far below than those extrapolated temperatures. This is also why the reported diffusion coefficient at 255 °C in Figure 4.7 (c) deviates from the Arrhenius equation. To show the effect of crystallization, two virgin samples, coated with 95nm \( \text{HfO}_2 \) and 80nm \( \text{Al}_2\text{O}_3 \), were annealed at 350 and 300 °C for one hour at air. Then the same diffusion measurement tests were executed, and the results are shown in Figure 4.7 (c) as ‘\( \text{HfO}_2 \ C’ \) and ‘\( \text{Al}_2\text{O}_3 \ C’ \). There is an approximately 50 and 100 times increase in diffusion coefficients in annealed samples at 245 °C, which can be due to the grain boundaries [86,87][95].

The activation energy for the hydrogen diffusion process in the present materials is given in Table 4.3, along with some related other materials for comparison. The activation enthalpies
(H), and especially pre-exponential factors (D₀), are given in crystallized Al₂O₃ and ZrO₂ for comparison with amorphous counterparts. H and D₀ of HfO₂ were not found in literatures, but ZrO₂ is an adequate replacement, since they have the exact same crystal structure and oxidation state and very close atomic radius and crystal parameters [265]. As suggested by data in Table 4.3, H and especially D₀ for amorphous structure are much higher than the crystallized structure for the same chemical compound. However, those large pre-exponential factors were expected in amorphous structures, as Faupel et al. [266] have reported that D₀ can be in the range of 10⁻¹¹ to 10⁻¹⁹ cm²/s for amorphous alloys.

The concentration of protons can influence the H and D₀ as well. To show an example, the proton activations for amorphous and crystallized silicon [96,97] are given in Table 4.3. The amount of H and D₀, respectively, decreases from 2.2 eV to 1.4 eV and 10³ cm²/s to 10⁻⁴ cm²/s by increasing proton concentration from 0.1 to 14 at.% in amorphous silicon. Considering the proton concentration is in the order of ppm in this work [82], the data in Table 4.3 for ALD layers are physically reasonable. In short, since D₀ is related to entropy of migration, one can expect proton migration in amorphous structure will produce more entropy than the order crystals and make D₀ larger in amorphous structures. In the case of enthalpy (H), there is a spectrum of enthalpies in amorphous structures due to the fact that the interstitial sites are not similar and have different amount of enthalpies. Protons like to fill lower level of enthalpies at first, so that enthalpies are high at low proton concentration, and then they decrease by increasing proton concentration [98,240,241].
Figure 4.7 (a) Cole-Cole plots for BaTiO$_3$ capacitor ALD coated with 95 nm of HfO$_2$ at 235, 245, and 255 °C before and after 7 hours exposure to hydrogen, (b) electrode conductance of the Cole-Cole plots extracted by 3RC model vs time at different temperatures, (c) Proton diffusion coefficient at 235, 245, and 255 °C for ALD coatings of virgin HfO$_2$, Virgin Al$_2$O$_3$ and crystallized HfO$_2$ and Al$_2$O$_3$. For comparison diffusion coefficients in bulk BaTiO$_3$ are given [82].

Now, the difference of activations for amorphous and partially crystallized structures in this work can be explained. $D_0$ is smaller in partial crystallized structures, because the structure gets partially ordered, and it would reduce the average amount of entropy for proton migration. Less disordered structure leads to smaller $D_0$. One can arrive at the same conclusion by comparing $D_0$ of amorphous and crystallized compounds in Table 4.3. For example, $D_0$ for amorphous Al$_2$O$_3$ from $8.0 \times 10^{12} \text{ cm}^2/\text{s}$ decreases to $2.4 \times 10^{-3} \text{ cm}^2/\text{s}$ for fully crystallized Al$_2$O$_3$. It
goes down to $7.7 \times 10^{10}$ for partial-crystallized Al$_2$O$_3$ in our work. Apparently, the amount of ordering in partially crystallized structures is not as much as in crystallized ones, since $D_0$ is still much higher than in crystallized structures.

$H$ (i.e. activation energy for diffusion) is decreased as well in partial crystallized structures, because grain boundaries can offer a wider space for proton diffusion than amorphous structures and protons need less activation enthalpies to jump. Compare the data in Table 4.3. The enthalpy decrease is the main reason that partially crystallized structures have higher diffusion rates than amorphous ones.

Table 4.3 Activation enthalpy ($H$) and pre-exponential factor ($D_0$) for amorphous and crystallized materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Activation Energy (eV)</th>
<th>$D_0$ (cm$^2$/s)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Al$_2$O$_3$ (crystallized)</td>
<td>1.24–1.25</td>
<td>$2.4 \times 10^{-3}$</td>
<td>[86,87]</td>
</tr>
<tr>
<td>ZrO$_2$ (crystallized-monoclinic)</td>
<td>0.91</td>
<td>$2.4 \times 10^{-7}$</td>
<td>[95]</td>
</tr>
<tr>
<td>Si (crystallized)</td>
<td>0.48</td>
<td>$2.3 \times 10^{-4}$</td>
<td>[97]</td>
</tr>
<tr>
<td>Si (amorphous)</td>
<td>1.4–2.2*</td>
<td>$10^{-4}$–$10^{3}$*</td>
<td>[96]</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (amorphous)</td>
<td>2.4</td>
<td>$8.0 \times 10^{12}$</td>
<td>present study</td>
</tr>
<tr>
<td>HfO$_2$ (amorphous)</td>
<td>2.3</td>
<td>$7.2 \times 10^{10}$</td>
<td>present study</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (partially crystallized)</td>
<td>2.0</td>
<td>$7.7 \times 10^{10}$</td>
<td>present study</td>
</tr>
<tr>
<td>HfO$_2$ (partially crystallized)</td>
<td>1.9</td>
<td>$2.0 \times 10^{9}$</td>
<td>present study</td>
</tr>
</tbody>
</table>

* Both activation energy and pre-exponential factor decrease by increasing hydrogen concentration

The above mentioned technique may be used as a quantitative method to evaluate the quality or the stopping power of ALD coatings at different temperatures for comparison between different ALD coatings.
4.6 Conclusions

The stopping or barrier power of ALD coating is mostly determined by their chemical composition; as can be seen, there is a huge difference in performance between ZnO, Al₂O₃, and HfO₂. The Al₂O₃ and HfO₂ ALD coatings have amorphous structure and are both effective barriers, up to the crystallization temperatures that are associated with T₀. It was illustrated that the results of I-V tests can be supported by TEM analysis. The Al₂O₃ and HfO₂ ALD coatings are continuous, conformal, and amorphous below T₀, and they show a high barrier performance, as predicted from I-V results. TEM analysis shows that the grain boundaries, formed at temperatures above T₀, cause a reduction in the barrier performance.

The activation of the proton diffusion was measured in the amorphous and partially crystallized structures. The proton diffusion coefficients in ALD are much smaller than the one in BaTiO₃ and this the main reason that the ALD coatings can stop protons, although their thickness is on order of nanometer. Measuring a lower activation enthalpy (H) in the partially crystallized structures suggests that grain boundaries have higher diffusion coefficient than amorphous structures. Both temperatures of merit (T₀) and diffusion coefficients, respectively, resultant from I-V and impedance spectroscopy tests, can be used as a characterization method to assess the quality and stopping power of ALD coatings.
Evaluation of Atomic Layer Deposition Coating as Gas Barrier against Hydrogen for ZnO Varistors

5.1 Introduction

In the previous chapter, it was demonstrated that the ALD coating can prevent the insulation resistance degradation in BaTiO$_3$ MLCCs. This idea would be tested on another device, ZnO varistors, in this chapter. Since the varistors are connected to the circuits in parallel to protect them from the surcharges, their insulation resistance is important for energy efficiency concerns.

Varistors or variable resistors are passive components, which are used in protection against voltage surges, that shunt the excess charge to ground [267–270]. The design is typically around ceramic materials based on ZnO with dopants and sintering aids added to control the nature of the controlled breakdown process and minimize the leakage in the stand-by operational condition [270,271]. The grain size and the grain boundary compositions are critical and are back-to-back Schottky barriers controlling these conditions [267,269,272,273]. There is a concern about the packaging of varistor components at the atmosphere in which they are exposed to humidity or hydrogen gas [83]. The source of hydrogen gas could, for example, be the outgassing of corrosive atmospheres from incompletely cured epoxies and or electrolytic capacitor seal failure [200,274,275].

There have been earlier studies on the atmosphere sensitivity to varistors, such as the work of Sonder et al.[276] who have studied systematically the effects of reducing atmosphere on the resistivity degradation of ZnO varistors. In their case, a reductive agent of CO and different percentage of oxygen and inert gas at the interval temperature of 150 to 800 °C were
considered. It was found that ZnO varistors can be degraded by annealing at 260 °C in a CO/CO\textsubscript{2} atmosphere, and showing resistance can decrease from $10^{10}$ to $10^{4} \Omega$ after 33 hours of exposure to CO/CO\textsubscript{2}. In addition, there are additional reports of resistivity degradation of ZnO varistors due to hydrogen gas exposure [275,277]. It will be shown in this report that the leakage current can increase from $10^{-8}$ to $10^{-4}$ A at 170 °C after one hour exposure to a hydrogen gas.

ALD (Atomic Layer Deposition) coatings demonstrate a good gas barrier property [18,22,23,44] on various substrates, which makes them promising to hinder the degradation process. In this chapter, the effect of exposure of ZnO varistors to forming gas (4% hydrogen and 96% nitrogen) and humidity has been studied, and the application of ALD coating as a gas barrier layer has been evaluated. In addition, the proton diffusion coefficient has been measured for both ZnO varistor and HfO\textsubscript{2} ALD layers to demonstrate effectiveness as gas and humidity barriers for ZnO based varistors.

5.2 Experimental sections

A commercial ZnO, purchased from Eaton's Cooper, varistor was cut to 15×15×1.4 mm and grinded up to 1200 grit sandpaper, then a circular Pt electrode with area of 5 mm\textsuperscript{2} was sputtered to the center of both sides of the samples. The impedance spectroscopy was applied, by SR-830-DSP Lock-in connected to a charge measurement system (the test was conducted in Material Characterization Lab of Pennsylvania State University), to trace the degradation in grain and grain boundaries at 135, 155, and 175 °C, when they were exposed to forming gas (4% hydrogen and 96% nitrogen) for 3 hours.

HfO\textsubscript{2} ALD coating was applied around the devices by using 150LE, The Kurt J. Lesker Co. and the precursor of TDMAH, tetrakis (dimethylamino) hafnium (IV) (C\textsubscript{8}H\textsubscript{24}N\textsubscript{4}Hf), and
water. The dose times of the precursor and water were 0.15 and 0.03 s, followed by the purge time of 10 seconds at the temperature of 200 °C and the pressure of 400 mtorr. The growth rate was measured 1.3 Å/cycle.

Another set of tests was leakage current measurement to monitor the amount of resistivity degradation. The varistors with different coating thicknesses were exposed to forming gas in the interval of 80 °C to 290 °C; for every 20 °C increment, they were held for 30 minutes, while the leakage current was measured every second under applied voltage of 5V. A Highly Accelerated Life Test (HALT) was executed by Temperature Humidity Chamber (Blue M, Illinois, USA) at the temperature of 90 °C and humidity of 85% for 120 hours, under 100 V applied voltage on the coated and uncoated samples. TEM samples were obtained by FEI Helios NanoLab 660 FIB/FESEM. The TEM analysis was executed by JEOL 2010F.

5.3 Impedance spectroscopy analyses and HALT tests

Impedance spectroscopy analysis is an effective method to monitor the relative changes in resistivity and capacitance in grain and grain boundary microstructures. The impedance data ($Z'$, $Z''$) are presented in the complex plane in the form of Nyquist or Cole-Cole plots, noting the changes with the experimental variable of different exposure times in Figure 5.1 (a). Since every impedance spectroscopy took 45 minutes specifically the low frequency measurements (i.e. below 1 Hz), the impedance of the samples decreased during the tests. This decline causes the curvature at the end of the plots. It was found that the Cole-Cole plots can be fitted well with the two impedance element equivalent circuit shown in Figure 5.1 (b), the electrode contribution is negligible in the ZnO varistor, and the largest contribution comes from grain boundary barriers. The approach of this research is consistent and builds on the analysis of Andres-Verges and West
[278], where the grain impedance can be approximated with a pair of ideal capacitor and resistor. The capacitor is the representative of the transient charge storage in grains and the resistor the bulk resistivity of ZnO crystals. For the grain boundary circuit representation, another element, CPE (constant phase element [227]), is added to consider the inhomogeneity over all the grain boundaries [279].

Figure 5.1 (a) Cole-Cole plots for ZnO varistor exposed to forming gas at 135 °C with different exposure time; (b) Equivalent circuit; (c) Resistance of grains and grain boundaries vs. gas exposure time at 135 °C; (d) Proton diffusion coefficients vs. reciprocal temperature in the grain boundaries of ZnO varistors, virgin HfO₂ ALD layers and crystallized HfO₂ ALD layers.
The resistance of grains and grain boundaries under different hydrogen gas exposure times is shown in Figure 5.1 (c). The resistance of the grain boundaries at the beginning of the exposure is 100 times higher than the resistance of grains at the end of exposure. While the GB (grain boundary) resistance decreases an order of magnitude, the grain resistance is essentially invariant under the gas exposure conditions used here. The change in GB resistance can be related to proton concentration acting as a donor dopant reducing the interfacial grain boundary resistance [275].

The change in GB resistance can be used to determine the diffusion of hydrogen into the grain boundaries, by defining appropriate boundary conditions and solving Fick’s law, one can estimate diffusion coefficient of protons at 135 °C in grain boundaries [82]. One of the boundary conditions can be concluded from the fact that the entering rate of total hydrogen ions \( \frac{dN(t)}{dt} \) to the device is proportional to the concentration difference between atmosphere \((C_0)\) and surface \((C_S)\), which can be represented as:

\[
\frac{dN(t)}{dt} = \alpha(C_0 - C_S)
\]

where \(\alpha\) is a proportionality constant.

The other boundary conditions are obtained based on the assumption that the diffusion system is semi-infinite. Here, we need to consider an additional assumption, which is that the Pt electrode is not a barrier against proton diffusion. Regarding the hydrogen diffusion coefficient in Pt [280,281] and ZnO [275,282–284], the diffusion coefficient in Pt is several orders of magnitude higher than the diffusion coefficient in ZnO in the temperature interval of the present work. So the above mentioned assumption is valid.
The same impedance spectroscopy tests were executed at 155 and 175 °C, and the calculated diffusion coefficients are shown in Figure 5.1 (d). One can find the best line that passes those three points, and find the activation enthalpy for proton diffusion, as 0.88±0.02 eV, which is fairly close to the reported values of 1.21[283] and 0.91 eV [275] for proton diffusion in ZnO. However, it is reported as 0.17 eV [282] elsewhere. Nickel [284] has thoroughly studied the proton diffusion coefficient in single and polycrystal ZnO thin films. He argued that the activation enthalpy can depend on temperature and reported 0.75 eV for ZnO poly crystals at 155 °C. It should be noted that the resultant diffusion coefficients in the present study are for the grain boundaries of ZnO ceramics, which was doped with Bi and Sb. See the supplementary information for SEM micrograph.

![Figure 5.2](image.png)

Figure 5.2 (a) Leakage current vs. temperature for ZnO varistors coated with various thickness of HfO; ALD in forming gas and 5V applied voltage; the Air and Hydrogen curves are representative of minimum and maximum degradation. (b) Leakage current vs exposure time for uncoated and coated varistors with different thickness of ALD layers at temperature of 90 °C, humidity of 85%, and under 100 V applied voltage.

The changes of leakage currents in the coated and the uncoated varistors were considered after exposure to forming gas, which are presented in Figure 5.2 (a). The uncoated samples were tested in forming gas and air as indicators of maximum and minimum degradation and shown as
“Hydrogen” and “Air”. It is observed that the leakage of all the coated varistors is as good as that of their performance in ambient air conditions up to \( \sim 250 \, ^\circ \text{C} \). It means that the ALD coatings can fully protect varistors against forming gas up to a critical temperature, no matter how thick they are. The other observation is that the critical temperature is \( 140 \, ^\circ \text{C} \) for the uncoated varistor, and it can increase to \( 250 \, ^\circ \text{C} \) by applying of 10 nm of HfO\(_2\) ALD coating.

The stability of a varistor under humidity testing and also the effectiveness of ALD coatings were studied; some data is shown in Figure 5.2 (b). The ALD layers can fully protect the varistors during the Highly Accelerated Lifetime Time (HALT) test, but the leakage current increases three times in the uncoated varistor at the end of the test. As water vapor is incorporated to ZnO ceramics by following reaction, the final product is hydroxide.

\[
H_2O(g) + V_\text{O}^- + O_\text{O}^x \rightarrow 2[OH]_O
\]

(5.2)

Both hydrogen and humidity lead to a similar final product, and there is an excess of donors to be incorporated in the grain boundaries, which lowers the insulation resistance, which degrades the varistor performance.

5.4 TEM analyses

To investigate the failure of ALD coating after \( 250 \, ^\circ \text{C} \), TEM analysis was executed on ALD layer before and after exposing to high temperature. The TEM micrographs are shown in. The ALD layer is continuous, and amorphous before exposing to high temperature, see Figure 5.3 (a) and (b). On the other hand, the ALD layer, after exposing to high temperature, is not flawless and shows Moiré fringes in TEM micrographs, as presented in Figure 5.3(c). The fringes are the sign of two crystallized planes that translate or/and rotate against each other [262].
So the ALD layers are crystallized and cannot stop hydrogen as effectively as before crystallization. If the ALD layers had not become crystallized, they could have protected the varistors for a long time, with the maximum protection as demonstrated in the HALT test; there is no leakage increase even after 120 hours exposure at 90 °C.

Figure 5.3 TEM micrographs of HfO: ALD layer with thickness of 40 nm on ZnO varistors (a), (b) before, and (c) after exposing to 290 °C.
5.5 Conclusions

The true barrier power of HfO$_2$ can be seen through both Figure 5.1 (d) and Figure 5.2. The former shows that the proton diffusion coefficient is 400 thousand times higher in ZnO varistors than the ALD coating [51], the exposure to high temperature and partial crystallization increase the diffusion coefficient by 150 times but that is still much smaller than the diffusion coefficient in ZnO varistors. Obviously, the low proton diffusion coefficient is the cause of the low leakage current of coated samples in Figure 5.2. As shown in TEM micrographs, the ALD coating is conformal and continues with very low diffusion coefficient and can offer an effective gas barrier, even though its thickness is in the range of nanometer.

In the cases of both humidity and hydrogen gas exposure, the ALD coatings provide adequate protection and offer an effective solution to future packaging of passive components in circuits that operate under extreme environments.
6  Study on the Behavior of Atomic Layer Deposition Coatings on Nickel Substrate at High Temperature

6.1  Introduction

The ALD applications as an encapsulating layer was reviewed in chapter one. In previous two chapters, it was demonstrated that they can hinder the insulation resistance degradation in BaTiO$_3$ MLCCs and ZnO varistors due to hydrogen or humidity exposure. The successful examples of utilizing ALD coatings as a diffusional barrier, presented in these chapters, resulted in the preliminary idea of evaluating their protection power in preventing Ni particles from oxidation. This idea was explored in this chapter. For the sake of simplicity in the experimental procedures, the Ni foils instead of Ni particles were coated by ALD coatings. The goal in this chapter is to provide a basic understanding about the behavior of ALD coatings at high temperatures (e.g. above 900 °C).

The oxidation of nickel metal and its alloys has been studied for a long time [3,4]. Many coating techniques have been suggested to protect metals from oxidation, such as electrochemical plating [5], cladding and hardfacing [6,7], and organic films [8]. Recently, new coating techniques have been tried to preserve Ni from oxidation [14–16]. For example, graphene [17] and 2D BN [18] were coated on Ni foils, and it is shown that despite their thin thickness, they can effectively protect Ni metals from oxidation at high temperature in air. However, there is a temperature limit for effective protection against oxidation; graphene and 2D BN are both degraded at 650 [20] and 850 [19] °C, respectively.

Atomic layer deposition (ALD) is another new technique that has been widely used as a diffusion barrier on the various materials [18,22–24,26–28]. ALD coatings have been
demonstrated as an effective gas barrier, due to the fact that they provide a continuous and conformal layer all around the object. The ALD encapsulating feature comes from the nature of their layer-by-layer growth process [44,45]. In spite of their potential to protect Ni metal from oxidation, the behavior of ALD coatings on Ni metals at high temperatures has not been thoroughly studied. Since many chemical compounds can be deposited by the ALD process [45], there are a number of potential candidates to preserve Ni from oxidation at high temperature.

The effective coating in order to protect nickel from oxidation has many applications [285], from turbine blades [286] to Ni foil passivation for growing piezoelectric films [287] and multilayer applications, such as Ni electrodes being used in co-fired capacitive devices, and multilayer piezoelectrics with lead free chemistries [130,131,288] and solid oxide fuel cells [128,129]. As a model system, nickel and BaTiO₃ cofiring has been studied many times and underpins a multibillion dollar passive component industry [132,133,289–291]. A technique that can keep the Ni electrode metallic (i.e. preserve the conductivity of the Ni electrode) during the cofiring process in air or relatively oxidized atmospheres is very attractive for increasing performance and reducing manufacturing costs [292].

In this research, two measures were considered to kinetically limit the oxidation of the Ni metal. The key solution is the application of ALD coatings around Ni metal to make a physical barrier between Ni metal substrate and atmospheric oxygen. The second one is the fast heat treatment of Ni metals with fast heating and cooling rates. Thus, the Ni metal is exposed to high temperature a shorter amount of time. The fast heat treatments can be useful in sintering of Ni particles, in which Ni particles need to be exposed to high temperature for a short duration.

An ALD coating suitable for the present purpose, besides having small diffusion coefficient of oxygen, should have a good mechanical stability (i.e., no cracking due to strain) to
remain continuous and conformal at high temperature, e.g. 1000 °C. As observed in the previous work [51], the barrier power of the ALD coatings against hydrogen gas [82,83] and humidity [67] decreases due to cracks and crystalline defaults. The source of strain for cracking can be the difference of thermal expansion between substrate and coating [178,179,293].

In order to make a complete introduction, it should be pointed out that the ALD coatings can be dissolved in the Ni foil substrate above some critical temperature. This phenomenon will be demonstrated later in this chapter. So, the dissolution of ALD coating should be considered as the second mechanism, by which ALD coating collapses and cannot provide a physical barrier between the Ni foil and outside atmosphere.

These factors make the selection of ALD coatings a critical part of this study. Conventionally, HfO₂ [260] and Al₂O₃ [22] coatings are well-known gas barriers with amorphous structure. In addition, SnO₂ [54] and ZnO [51] coatings can be a potential candidate, since they can have a crystalline structure, and their cations provide 2+ oxidation state (Sn has the possibility of both 2+ and 4+ oxidations [294]). The influence of oxidation state would be illustrated at the end of this chapter.

In this chapter, the behavior of ALD coating on Ni metals at high temperature was investigated and specifically determine how the electrical resistance of the coated Ni foils would be affected during a heat treatment.

6.2 Experimental procedures

Ni foils with purity of 99.5%, obtained from Alfa Aesar, were cut to 7×10 mm pieces, and two holes with diameter of 0.5 mm were drilled into some of them, as shown in Figure S 6-1. The foils were cleaned in an ultrasonic bath of acetone for 5 minutes, followed by another 5
minutes in isopropyl alcohol, and dried in an oven for 20 minutes at 120 °C. Then, they were coated with the Al₂O₃, HfO₂, ZnO, and SnO₂ in the ALD system (Cambridge System, Savannah 200). The process recipes are shown in Table 4.1.

Table 6.1 ALD recipes for ZnO, Al₂O₃, SnO₂, and HfO₂ coatings

<table>
<thead>
<tr>
<th>Metal-Precursors</th>
<th>ZnO</th>
<th>Al₂O₃</th>
<th>SnO₂</th>
<th>HfO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>DEZ*</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TMA**</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDMA-Sn†</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDMAH††</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precursor dose time (s)</td>
<td>0.015</td>
<td>0.03</td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>Purge time (s)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Water dose time (s)</td>
<td>0.015</td>
<td>0.1</td>
<td>0.1</td>
<td>0.03</td>
</tr>
<tr>
<td>Purge time (s)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Temperature</td>
<td>200 °C</td>
<td>200 °C</td>
<td>200 °C</td>
<td>200 °C</td>
</tr>
<tr>
<td>Growth rate</td>
<td>1.3 Å/cycle</td>
<td>0.9 Å/cycle</td>
<td>1.1 Å/cycle</td>
<td>1.1 Å/cycle</td>
</tr>
<tr>
<td>Base pressure</td>
<td>300 mtorr</td>
<td>750 mtorr</td>
<td>400 mtorr</td>
<td>400 mtorr</td>
</tr>
</tbody>
</table>

*Diethylzinc    **Trimethylaluminum     †Tetrakis(dimethylamino)tin(IV)       ††Tetrakis (dimethylamido) hafnium (IV)

To study the oxidation behavior of the foils during the heat treatments, two platinum wires were passed through those holes, shown in Figure S 6-1, and the samples were suspended in a tube furnace, by which temperature was increased at the rate of 4 °C/min to 900 °C in air, and DC resistance was measured during heating. Since the resistance due to formation of the Ni oxide film is much higher than the contact resistance and the other resistivities, the formation of NiO oxide layer can be traced online by monitoring the resistance of the foils.

A fast-heating furnace [295], which was able to heat up and cool down at the rate of 100 and -50 °C/min, was used to study the effect of the heat rate on the oxidation of the foils. The fast heat treatments were designed to investigate the effect of sintering condition on the ALD coating on Ni substrate. So, obviously, there was a need to assess the conductivity of Ni foils after a real sintering process. Based on the other studies on sintering Ni particles [296–299], the
heating schedule of 1020 °C for 4 minutes was selected, and then it was confirmed that Ni particles could be successfully sintered with it. This heat treatment would be used as a criterion to evaluate the merit of the ALD coatings to preserve Ni conductivity during sintering of Ni particles.

Impedance spectroscopy tests were executed by Solartron Module Lab XM on the foils after the fast sintering to estimate the thickness of the oxide layers or the effectiveness of ALD coatings. The test was executed at the voltage of 1V and the range of 0.1 Hz to $10^5$ Hz. To make sure that there is a good contact between the probe and the foils, a circular area with diameter of 3 mm on both sides of foils was sputtered by gold with thickness of 50 nm. After that, the foil was placed in a fixture and the impedance spectroscopy test was executed at room temperature.

The Transmission Electron Microscopy (TEM) samples and cross sections were prepared by FEI Helios NanoLab 660. TEM analyses were done by FEI TALOS F200X and JEOL-2010 field emission TEM, equipped to Energy Dispersive X-ray Spectrometer (EDS) and electron energy loss spectroscopy (EELS) systems.

### 6.3 Nickel oxidation

The resistance of the uncoated Ni foil as a function of temperature during heating, at the rate of 4 °C/min in air, is shown in Figure 6.1 (a). The resistance is small at temperatures below 710 °C, but it starts to increase abruptly around 710 °C. As shown in Figure S 6-2 in Supporting Information, the diffusivity of oxygen in NiO start to increase abruptly around 700 °C, and that causes an abrupt growth of NiO film, which is manifested as a rapid increase in the resistance. Nowotny and Sadowski [300] used a similar method to measure the diffusion coefficient of
oxygen in NiO. Thus, the DC resistance measurement during heating can offer a strong tool to monitor the thickness of NiO film.

From now on, the temperature in which the resistance of Ni foil passes $10 \, \Omega$ is called the critical temperature ($T_0$). By obtaining $T_0$ for the coated foils, one can judge the effectiveness of the ALD coatings on hindering oxygen diffusion. In other words, $T_0$ shows how protective a coating is against oxygen diffusion for ALD coating with similar chemistry (at the end of this chapter, it will be shown that the ALD coatings can be dissolved in the NiO foil and affect the conductivity mechanism; thus, this test is only valid for comparison of the ALD coatings with a similar chemistry).

To further study the nature of $T_0$, a Ni foil was heated up to 700 °C, and just before increasing resistance, it was cooled down. The maximum measured resistance was 4 Ω. The TEM analysis was performed on this foil and compared with an untreated foil. Figure 6.1 (b) shows the TEM micrograph of the untreated foil. As seen, an oxide layer can neither be observed nor detected with the EDS in the scale shown in this micrograph. On the other hand, there is an oxide layer with minimum thickness of 500 nm on the foil, heated to 700 °C, as presented in Figure 6.1 (c) and (d). One can argue that this thickness (i.e. $\sim$500 nm) is the minimum sensitivity limit of our in-situ measurement since the rise in resistance is high enough at this thickness so that our setup would be able to detect it. In addition, for clarity, it should be noted that the resistance difference between the coated foils and the uncoated foil before the heat treatments was too low, so that their difference is in the margin of error of this technique. As suggested here, and will be supported later, the NiO film should be thicker than $\sim$500 nm in order to measure a resistance above $10 \, \Omega$ for both coated and uncoated foils.
Figure 6.1. (a) Resistance of nickel foil vs temperature. TEM micrograph from (b) nickel foil without any heat treatment, (c), (d) nickel foil, heated up to 700 °C with heating rate of 4 °C/min at different magnifications.

The second conclusion of the above TEM analysis is that Ni foils can tolerate some oxidation without a significant increase in resistance. The resistance below 10 Ω can be considered low in the context of the present study. So, eventually, this study narrows down to finding methods to hinder the growth kinetic of the NiO film to keep the resistance of Ni foils low. However, later, it will be shown that the doping of the NiO film with the suitable cations can offer another mechanism to lower the resistance.
In the rest of this chapter, the fast heating rate and ALD coatings are explored to see their relative effectiveness in hindering the elevation of resistance during heat treatments.

### 6.4 ALD coatings and fast heat treatments

Figure 6.2 (a) presents the effect of HfO$_2$ ALD coating on the elevation of resistance at the heating rate of 4 °C/min. $T_0$ has been increased from 710 °C to 820 °C from the uncoated foil to the one coated with 35 nm of HfO$_2$, and then it decreased to 755 °C in the thickness of 50 nm. Based on the previous discussion, the higher critical temperature ($T_0$) means a coating with higher potential to preserve Ni conductivity. So the barrier power of HfO$_2$ coatings increases up to 35 nm and then decreases. Figure 6.2 (b) shows the critical temperatures for HfO$_2$, Al$_2$O$_3$, ZnO, and SnO$_2$ coatings with different thicknesses. As is illustrated in this plot, the same trend has been noted in all the ALD coatings. The increase of critical temperature ($T_0$) by thickness is due to the fact that the thicker layer can provide a more effective barrier against oxygen diffusion, as previously reported [51]. On the other hand, the thicker ALD coatings are more susceptible to cracking, which provides an easy path for diffusion, as demonstrated by Jen et al [178,179]. So there is a critical thickness in which both diffusion barrier and mechanical stability (i.e., no cracking due to thermal strains) are high enough to provide the maximum protection. The highest $T_0$ (i.e., the most effective barrier) was found to be 850 °C for the foil, coated with 35nm of SnO$_2$. The second highest $T_0$, 835 °C, belongs to ZnO with thickness of 25 nm.
The second approach to hindering the formation of NiO film is fast heat treatments. By heating and cooling quickly, the exposure time to high temperature is shorter, and the NiO film is thinner. For example, the resistance of a nickel foil, heated up to 800 °C with rate of 100 °C/min and then immediately cooled down with the rate of -50 °C/min, was 2Ω. Thus, $T_0$ can be increased from 710 °C at the heating rate of 4 °C/min to above 800 °C by utilizing the fast heat treatments. As explained in the Introduction, the fast heat treatment can be used for sintering Ni particles, in which the Ni particles are exposed to high temperature for a short duration of time. The study of the behavior of the coated Ni foils during these heat treatments can provide insights on the behavior of the ALD coating on Ni particles.

For the foils subjected to the fast heat treatment, the in situ resistivity measurements were not technically available. So their resistance was measured by impedance spectroscopy after the heat treatments. Impedance spectroscopy can provide information about electron hopping and NiO film thickness.
Figure 6.3 (a) shows the impedance vs frequency for the foils, heated to 900, 1000, and 1100 °C at the rate of 100 °C/min. For all the foils, impedance (Z) increased by decreasing frequency and eventually reached a plateau at some critical frequencies. To explain this behavior, the Ni foil can be thought of as two impedance elements of Ni metal and NiO film, which connected in series. The impedance of Ni metal is negligible, so the total impedance is correlated to the impedance of NiO film. Since electron hopping between Ni$^{3+}$ and Ni$^{2+}$ is the dominant conductivity mechanism in the NiO film [301,302], the impedance is increased by decreasing frequency linearly in log scale and eventually, when the frequency is low enough, the hopping will not be an effective conductivity mechanism, and impedance becomes constant vs frequency. This type of behavior was observed in many other systems, in which the electron hopping is a dominant conductivity mechanism. The electron hop between percolative clusters and the impedance decrease by increasing frequency [303–307]. The constant impedance, shown as $Z_0$, can be reliable criteria for evaluating the thickness of NiO film and the effectiveness of hopping mechanism. Snowden and Saltsburg [308] observed the same linearity and plateau for impedance spectroscopy of nickel oxides. The $Z_0$ was measured for the foils with different ALD coating, heated to 900, 1000, and 1100 °C, and the results were shown in Figure 6.3 (b) along with the $Z_0$ of the uncoated foil. At 900 °C, the $Z_0$ was 6 Ω, 70 Ω, 370kΩ, and 901 kΩ for Al$_2$O$_3$, HfO$_2$, ZnO, and SnO$_2$, respectively. The difference of those points are not recognizable in the scale of the plot in Figure 6.3 (b). The $Z_0$ of the uncoated foil was 13.5MΩ, so all the ALD coating could decrease the resistance considerably, and the Al$_2$O$_3$ coating seemed the best candidate for doing that. However, by raising the maximum temperature to 1000 and 1100 °C, the impedance of the Al$_2$O$_3$-coated foil significantly increased even more than the uncoated foil. The impedance of the
HfO$_2$-coated foil considerably increased as well, but it did not pass the impedance of the uncoated foil. The least impedance growth was detected in ZnO and SnO$_2$-coated foils. This behavior would be explained by the result of TEM analyses.

In order to evaluate how effective ALD coatings are after a real sintering schedule, the coated Ni foils were exposed to the designed sintering schedule, explained in the Experimental section, and then the impedance spectroscopy was performed on them; the results are shown in Figure 6.3 (c). The lowest resistivity or maximum protection was obtained for the ZnO-coated foil. All the ALD coatings show a level of protection; however, again the anomaly is the foil coated with Al$_2$O$_3$.

Figure 6.3 (d) shows the result of impedance spectroscopy on the SnO$_2$-coated foils with different thicknesses after the sintering heat treatment. The maximum protection has been found for the coating with 15 nm thickness. This outcome can be contrasted by the data in Figure 6.2 (b), which illustrate that the maximum protection at the slow heating rate is obtained for the SnO$_2$ coating with 35 nm thickness. As mentioned before, there is balance between mechanical stability (i.e. no cracking due to strain) and diffusion barrier of ALD coatings, which results in an optimum thickness. By increasing heating rate, the importance of the mechanical stability is promoted over the diffusion barrier, and the thinner coatings are more mechanically stable, according to Jen et al. [178,179]. So the optimum thickness will be smaller in fast heating rate than the optimum thickness in slow heating rate. This phenomenon has been observed in other studies. For example, Li et al. [19] demonstrated that the oxidation resistance of 2D BN coating depends on heat treatments.
Figure 6.3 (a) Total impedance ($|Z|$) vs frequency for the uncoated foils, heated to 900, 1000, and 1100 °C; (b) Impedance at low frequency ($|Z_0|$) vs temperature for different ALD coatings. $|Z|$ vs frequency for the coated foil with (c) different ALD coating and (d) SnO$_2$ coating with different thicknesses.

As indicated by the data in Figure 6.3, the resistance (i.e., impedance at low frequency) values for the coated foils exposed to the sintering heat treatment are not low enough to serve as an electrode; one may expect that electrodes have a resistance below 10 Ω after sintering, while the measured resistances were on the order of MΩ. However, the two-orders-of-magnitude decrease in resistance, as shown in Figure 6.3 (c), indicates a significant potential in the ALD coatings to reduce the Ni foil resistance. So it would not be trivial to investigate the evolution of the ALD coatings during ramping to high temperature by TEM analyses.
6.5 TEM Analyses

6.5.1 TEM Imaging

In order to investigate the behavior of the ALD coating during the heat treatments, the STEM (scanning transmission electron microscopy) micrographs of the Al₂O₃-coated foil heated to 700, 900, and 1100 °C at the rate of 100 °C/min together with as-coated foil, are presented in Figure 6.4. It can be seen that the ALD coating remains on the top of the foil without any discontinuity or major defect until 700 °C. However, at 900 °C, Ni atoms diffuse through the ALD coating, and the ALD layer is buried under the Ni substrate, as shown in Figure 6.4 (c). At 1100 °C, the ALD layer is dissolved in the foil. The different regions, detected by EDS analyses, are labeled in the micrographs.

Since the Al₂O₃ coated foil seems to be at a transition point at 900 °C, it was studied more carefully, and more TEM micrographs are presented in Figure 6.5. The first observation is that the ALD layer is crystallized due to the presence of Moiré fringes [262] in Figure 6.5 (a). In addition, the x-ray diffraction (XRD) pattern with grazing incidence diffraction geometry shows an extra wide peak at 68 °, which was absent in the diffraction pattern with conventional Bragg-Brentano geometry. The extra peak is well matched with one of the corundum peaks. The XRD pattern unambiguously showed Ni and NiO phases in the foil. The XRD pattern is shown in Figure S 6-3 of Supporting Information.
In order to bury the ALD layer, Ni atoms need to pass though the ALD layer. Their diffusion path can be clearly illustrated by the bright field STEM micrographs, in which the Al₂O₃ coating appears bright and the Ni atoms dark. The dark narrow line passing through the ALD layer are the cracks or grain boundaries, which provide easy pass for Ni atoms. This explanation can be further supported by EDS maps of the ALD coating presented in Figure 6.5.
The EDS Ni map shows some thin lines of Ni in the ALD layer, indicating that Ni concentration in these lines is above the detection limit of the EDS instrument. These lines are detected with different contrast in the counterpart of HAADF micrographs. In addition, some parts of the Al₂O₃ layer started to dissolve in surrounding NiO phase. Figure 6.5 (d) shows some parts of the ALD coating, where the border between the ALD coating and NiO phase is fuzzy, in the right-hand side of the micrograph. In comparison to the border in left-hand side, one may conclude that the ALD coating is in the early stage of the dissolution process. Figure 6.5 (e) is the dark field TEM micrograph. The micrograph was formed by selecting one of the bright spots in the diffraction pattern, shown in the inset. The fact that the grain on the top is bright and the other NiO grains are dark demonstrates that the bright grain has different crystal orientation from the rest of the grains. This grain is shown in the Figure 6.5 (b) with an arrow. It may be concluded that the Ni diffuse through the coating and then re-nucleate on the top of it in the different crystal orientation. This is why ALD coating seems to be buried under the Ni substrate. In addition, as is indicated by EDS maps, oxygen can pass through the ALD coating and oxidized Ni underneath it.
Figure 6.5 (a) TEM, (b) STEM Bright Field, (c) EDS maps and HAADF (d) HAADF, and (e) TEM dark field micrographs of the nickel foil coated with 25 nm of Al₂O₃ and heated to 900 °C.

Figure 6.6 shows the STEM micrograph of the HfO₂ and SnO₂ coatings after exposure to the same heat treatment (heating to 900 °C at the rate of 100 °C/min and immediately cooling down at the rate of -50 °C/min). The HfO₂ coating is buried under the NiO substrate, as was the case for the Al₂O₃ coating. The EDS map of the HfO layer is presented in Figure S 6-4 in Supporting Information. Figure 6.6 (c, d) show the SnO₂-coated foil after the same heat treatment. The SnO₂ coating disappeared, and the EDS analyses did not show any peak for Sn.
However, one should bear in mind that the detection limit of STEM-EDS was reported 1-2 wt%\cite{309} in average working conditions. The SEM micrographs of the ZnO-coated foil, presented in Figure S 6-5, did not show any sign of the ALD coating after the same heat treatment either.

Two scenarios can be thought of for the disappearance of ZnO and SnO\textsubscript{2} ALD coating. Either the ALD coatings were evaporated during the heat treatment, or they were buried under the Ni film and dissolved into it before 900 ⁰C. The former scenario does not seem the dominant mechanism, since it does not provide any explanation for the decrease of resistance in both SnO\textsubscript{2} and ZnO coated foils. In addition, Varela et al. \cite{294} demonstrated that the SnO\textsubscript{2} evaporation is limited above 1200 ⁰C, and Badev et al. \cite{310} showed that the weight loss of ZnO nanopowder is less than 0.4 wt.\%, even after one hour holding at 900 ⁰C. So the second scenario is more likely, and both SnO\textsubscript{2} and ZnO dissolved into NiO film. This conclusion will be further supported by EELS data.

Since all the foils were exposed to the same heat treatment (i.e. heating to 900 ⁰C by the fast heat treatment), the thicknesses of NiO film can be an indicator of how effective the ALD coating is to hindering the mass transfer of Ni and oxygen atoms. The thickness of NiO films was 0.260±0.135, 0.647±0.167, 1.16±0.24, and 1.32±0.26 µm for the foils coated with Al\textsubscript{2}O\textsubscript{3}, HfO\textsubscript{2}, SnO\textsubscript{2}, and ZnO. The FIB cross section of the uncoated foil, exposed to the same heat treatment, showed that the thickness of the NiO film was 1.95 µm, as illustrated in Figure S 6-6 in Supporting Information. One can conclude that all the ALD coatings offer some level of diffusion barrier against oxygen; the Al\textsubscript{2}O\textsubscript{3} coating has the highest barrier power and ZnO the lowest.
6.5.2 EELS analyses

The foil, coated with Al₂O₃, showed an abnormal increase in the impedance after exposing to 1020 °C for 4 minutes. As shown in Figure 6.3(c), its impedance is even higher than the impedance of the uncoated foil. On the other hand, the Al₂O₃ coatings can hinder oxygen diffusion even more effectively than the other ALD coatings (e.g. the ZnO-coated foil), as suggested above. One may expect that the foil with less oxygen diffusion has a thinner NiO film and, consequently, should have lower impedance than that of the other foils. However, the reason for the large impedance of the Al₂O₃-coated foil can be explained by the study of NiO defect chemistry.

Nickel oxide has the possibility of non-stoichiometric defects with Ni vacancies ($V''_{Ni}$) [308,311,312], whose concentration depends upon the amount of oxygen exposure to the Ni metal during oxidation [313,314]. It was reported that the non-stoichiometric solubility can be $\text{Ni}_1-\alpha\text{O}$ with $0<\alpha<0.2$ [315]. The $V''_{Ni}$ species introduce negative charge to the system, and at the
same time, the charge neutrality should maintain in the oxide. Thus, some of Ni ions change their oxidation state from 2+ to 3+ to electronically compensate for the extra negative charge. The larger ratio of Ni$^{3+}$/Ni$^{2+}$ increases the chance of electron hopping in NiO and decreases its resistance.

The EELS point analysis was done on the uncoated, 25nm-Al$_2$O$_3$-coated, and 25nm-ZnO-coated foils after heating to 1100 °C. The raw data are presented in Figure 6.7 (a - c). The points were on the top, 1/3, 2/3, and the bottom of the NiO films. The ratio of the height of L$_2$ edge over L$_3$ edge after the background subtract is equal to the Ni$^{3+}$ concentration over Ni$^{2+}$ concentration [313,316,317]. This ratio was calculated as \( \frac{L_2\text{-base line}}{L_3\text{-base line}} \) and is shown as L* in Figure 6.7 (d). The results suggest that there is a high concentration of Ni$^{3+}$ on the top of the film, and it decreases toward the interface of Ni and NiO in all three samples. This is due to the fact that the excess of oxygen causes more \( V''_{Ni} \) in NiO [314], and oxygen ions diffuse inside the foil from the top to the bottom, so that there is a gradient of oxygen concentration across the NiO films. As a result of this oxygen gradient, Ni$^{3+}$ has the maximum concentration at the top of the foil and decreases toward the interface. This observation matches well with the Volenik et al. [314] work on nickel oxidation and Tyuliev and Sokolova [313] EELS analyses regarding Ni$^{3+}$ concentration at NiO surfaces. Thus, EELS provides a powerful tool to trace the concentration of Ni$^{3+}$, which has a direct influence on conductivity due to electron hopping between Ni$^{2+}$ and Ni$^{3+}$. It should be noted that EELS analyses are more suitable for detecting atoms with low concentration than EDS analyses, since they are able to provide a higher signal-to-noise ratio [318]. This is especially true for the atoms with low atomic mass [309].
Now, one can hypothesize that in the Al\textsubscript{2}O\textsubscript{3} coating, Al\textsuperscript{3+} is dissolved into NiO film and then, to maintain charge neutrality, the system would decrease the concentration of Ni\textsuperscript{3+}. This decreases the chance of hopping between Ni\textsuperscript{3+} and Ni\textsuperscript{2+} and increases impedance, as shown in Figure 6.3 (c). This hypothesis can be supported by the curve of Al\textsubscript{2}O\textsubscript{3} in Figure 6.7 (d). The fact that the NiO film of the Al\textsubscript{2}O\textsubscript{3}-coated foil has lower L* on the top than that of the uncoated foil suggests a lower concentration of Ni\textsuperscript{3+} in the presence of Al\textsuperscript{3+}. In contrast, the ZnO curve is above both the uncoated and the Al\textsubscript{2}O\textsubscript{3}-coated foils, especially on the top of the NiO film. This is due to the fact that both Ni\textsuperscript{3+} and Ni\textsuperscript{2+} can be replaced by Zn\textsuperscript{2+}. If Ni\textsuperscript{2+} is replaced by Zn\textsuperscript{2+}, the number of the total 2+ charges is constant, and the charge neutrality is maintained. However, if Ni\textsuperscript{3+} is replaced by Zn\textsuperscript{2+}, more Ni\textsuperscript{3+} should be created due to the charge neutrality. This is the reason that the L* is higher in the ZnO-coated foil, and this can thereby contribute to their low resistivity. It is worth mentioning that L* of all three foils have almost the same values at the Ni-NiO interface, indicating Ni\textsuperscript{3+}/Ni\textsuperscript{2+} ratio is same when Ni and NiO is at equilibrium. In addition, Muto et al. [317] found the ratio of L\textsubscript{2}/L\textsubscript{3} 0.25 for stoichiometric NiO. Their finding matches well with the L* in Figure 6.7 (d) at the interface. This can support the validity of our EELS analyses.

Due to the lattice charge neutrality, required during ionic diffusion, the charge balance of cations with 4+ state would limit their diffusivity in the NiO grains. So Hf\textsuperscript{4+} [319] and Sn\textsuperscript{4+} [294,320] have small diffusion coefficients in NiO crystal. One can argue that since the ions with 4+ states do not effectively diffuse into the NiO crystal structure, they cannot change the ratio of Ni\textsuperscript{2+}/Ni\textsuperscript{3+}; this is why the resistance of the HfO\textsubscript{2}-coated foil does not significantly rise in comparison to Al\textsuperscript{3+} in the plot of Figure 6.3 (b and C). However, Varela et al. [294] argue that the oxidation state of Sn changes from 4+ to 2+ in SnO\textsubscript{2} above 1000 °C. If this is the case, Sn\textsuperscript{2+} can decrease the resistance of NiO film in the same mechanism, which was explained for Zn\textsuperscript{2+}. 

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This explanation can justify the one-order-of-magnitude decline in resistance by going from HfO$_2$ coatings to SnO$_2$ coatings in Figure 6.3 (c) and why the graph of SnO$_2$ and ZnO coated foils sit next to each other.

![Figure 6.7 EELS spectra of nickel L$_{2,3}$ edges, taken from nickel foil (a) uncoated and coated with (b) Al$_2$O$_3$ and (c) ZnO ALD on top, 1/3, 2/3, and the bottom of NiO film after exposure to 1100 °C. (d) L*, which is $\frac{L_3-\text{base line}}{L_2-\text{base line}}$ versus normalized width of the NiO film.](image)

Now one can explain the impedance of the coated foil, reported in previous section in Figure 6.3 (b). The Al$_2$O$_3$-coated foil has the lowest impedance at 900 °C since the Al$_2$O$_3$ coating can effectively prevent the oxygen diffusion. The thickness of NiO film was 0.26 µm and, consequently, the impedance was 6 Ω. However, at temperature above 900 °C, the Al$_2$O$_3$ coating would be dissolved in the NiO film and significantly increase the impedance. On the other hand, the ZnO coating cannot hinder oxygen diffusion as effectively as the Al$_2$O$_3$ at 900 °C. This is
why the NiO film on the Ni foil was 1.32 µm, and its impedance was measured 370 kΩ. However, at temperature above 900 °C, the impedance did not increase abruptly, due to the fact that the Zn²⁺ doping increased L* and prevented the impedance surge. Both observations can be compared with the uncoated foil. At 900 °C, the NiO film thickness was 1.95 µm. So both ALD coatings provide some level of protection against oxygen at 900 °C. At temperatures above 900 °C, the coating would be dissolved in the NiO film and after the dissolution, the L* and hopping mechanism would determine the conductivity of the foils. This is why the impedance of Al₂O₃-coated foil is even higher than the uncoated foil in both Figure 6.3 (b) and (c), but the impedance of ZnO-coated foil is several orders of magnitude lower.

Considering all the above observations, it seems the most effective approach in order to preserve the conductivity of Ni foils at the temperature above 900 °C is encouraging the hopping conductivity through suitable doping system, rather than keeping a physical barrier against oxygen diffusion. For example, doping with ‘1+’ oxidation state ions with small ionic radius effectively increases the ratio of Ni³⁺/Ni²⁺ [321]. Alkali metals, especially lithium, seem promising elements. We demonstrated the feasibility of using Li⁺ to reduce the impedance of Ni particles after sintering in other work by the authors [134,322].

6.6 Conclusions

The conductivity preservation of the coated Ni foils during heating to high temperatures can be divided into two parts, before and after the dissolution of the ALD coating.

Before the dissolution of ALD coatings, the mechanism that keeps the resistance low is the physical barrier between the foil and atmospheric oxygen. This barrier limits the oxygen diffusion and the formation of NiO film. As shown for the foils heated to 900 °C, thinner NiO
film results in lower resistance. In this regime, the governing factors are mainly the robustness of ALD coatings (for example, one can compare the micrographs of the SnO$_2$ coating with the Al$_2$O$_3$ coating at 900 °C), coating thickness, and heating rate. A suitable barrier layer needs both diffusion barrier and mechanical stability (i.e. no cracking) at high temperature. The diffusion barrier will be increased by thickness, while the mechanical stability will be decreased by thickness [51]. Thus, there is an optimum thickness at which the barrier power is maximum, as shown in Figure 6.2 (b) for the low heating rate. The increase of heating rate can change the balance between diffusion barrier and mechanical stability, since the mechanical stability becomes more important than the diffusion barrier. So the optimum thickness shifts to thinner coatings, as demonstrated for the SnO$_2$ coatings in Figure 6.3 (d).

After the dissolution of coatings, the cation diffusivity and its oxidation state are critical parameters in the Ni foil conductivity. Changing doping cations from Al$^{3+}$ to Zn$^{2+}$ can decrease resistance from 931 MΩ to 4 MΩ, according to the plot of Figure 6.3 (c). Thus, at temperatures above 900 °C, which is necessary for sintering Ni particles, the most effective approach to preserving conductivity of Ni electrodes is choosing a suitable doping system. These findings enable the electroceramic industries to sinter their devices in higher partial pressure of oxygen without losing the conductivity of their electrode. As a result, the device would have less oxygen vacancies and consequently lower energy loss.

6.7 Supporting Information
The diffusion coefficients of oxygen in NiO is plotted in Figure S 6-2 based on Nowotny and Sadowski’s study [300]. As seen, the oxygen diffusivity increase abruptly around 700\(^\circ\) C.

Figure S 6-2 Diffusion coefficient of oxygen in NiO. The Dotted line shows 700 \(^\circ\)C, at which diffusion coefficient start to significantly increase.
Figure S 6-3 (e) XRD pattern from the Al₂O₃-coated foil with 25 nm thickness, heated to 900 °C with the rate of 100 °C/min; C stands for Corundum.
Figure S 6-4 HAADF micrograph and EDS maps of the HfO₂ coated foil after heating to 900 ° C.
Figure S 6-5 SEM micrographs of the ZnO coated foil after heating to 900 °C. The top carbon layer is deposited during the sample preparation.

Figure S 6-6 SEM micrographs of the uncoated foil after heating to 900 °C.
7 Coating Ni Particles to Preserve Their Conductivity during Sintering in Oxidizing Atmosphere

7.1 Introduction

In the previous chapter, the possibility of using ALD coatings against Ni oxidation was studied. The result suggested that the ALD coating would start to dissolve into the Ni substrate at 900 °C. The dissolved cations would dope the newly-formed NiO layer on the top of the foil. It was concluded that an effective strategy to preserve the Ni conductivity is that to dope the NiO films with Li\(^+\) cations to encourage the electron hopping by increasing the ratio of Ni\(^{3+}\)/Ni\(^{2+}\).

Nickel electrodes have been widely used in electroceramics, such as co-fired capacitive devices, solid oxide fuel cells [128,129], and are now being considered for multilayer piezoelectrics with lead free chemistries [130,131,288]. Among these devices, the nickel and BaTiO\(_3\) multilayers [132,133,289–291], and especially the Ni electrode [292,296,298,299,323–325], have been studied extensively. The technology of cofiring BaTiO\(_3\) and Ni was first introduced by Herbert [326] in 1963 and revolutionized the dielectric industry in the late 1980s [132]. The introduction of Ni electrodes instead of platinum or palladium alloys had the advantage of cost reduction. However, to prevent Ni electrodes from oxidizing, a reducing atmosphere on the order of pO\(_2\)=10\(^{-10}\) atm was necessary [214]. This atmosphere results in the introduction of high number of oxygen vacancies in BaTiO\(_3\), which decreases its insulation properties and the life time of its capacitors [132,290]. In addition, reducing atmospheres of
$10^{-10}$ atm requires a hydrogen gas mixture as a reducing agent, which has been reported to cause resistivity degradation in electroceramic devices [51,67,82,83].

The oxygen vacancies increase the amount of leakage current and decrease the lifetime of a capacitor due to their migration and piling up in front of cathode [214,215]. Many material engineering design strategies and processes have been practiced to limit this phenomenon, such as different types of acceptor dopants and co-doping with an amphoteric dopant, grain and core shell design, and also post-reoxidation processes [132]. All of the above strategies limit the electromigration across a dielectric layer, but relative to air fired dielectrics, a significant concentration of oxygen vacancies would remain in dielectrics [132,247,327–330]. The idea in this work is rather different; a method to preserve the Ni electrode conductivity during sintering in less reducing atmospheres e.g. $P_{O_2} = 10^{-4}$ atm was explored. Consequently, the resultant device would have less oxygen vacancy concentrations, to increase the insulation resistance and improve lifetime performance.

The typical Ni particles that are sintered in oxidizing atmosphere arrive to a microstructure, which is the mixture of Ni and NiO grains. These NiO grains significantly increase the total resistance of the electrode. One way to decrease the total resistance is to decrease the resistivity of the NiO. Depending on the amount of oxygen in atmosphere during Ni oxidation, NiO has the possibility of being non-stoichiometric (i.e. Ni$_{1-x}$O) due to the presence of Ni vacancies [308,311–314]; where $\alpha$ can be within $0<\alpha<0.2$[315]. The Ni vacancies introduce negative charge to the system, which would be compensated by changing the oxidation state of some Ni ions from 2+ to 3+. The mixture of Ni$^{3+}$ and Ni$^{2+}$ enables electron hopping between those ions [301,302]; this is the dominant conductivity mechanism in NiO.
In the previous work [104], it has shown that when the Ni foils with ALD (atomic layer deposition) Al$_2$O$_3$ or ZnO coatings are exposed to temperatures above 900 °C in air, the coatings would be dissolved into the Ni substrate. It was demonstrated that Al$^{3+}$ decreased the ratio of Ni$^{3+}$/Ni$^{2+}$ and discouraged electron hopping; as a result, the foil resistance would be 1 GΩ. On the other hand, Zn$^{2+}$ reduced the resistance to 2 MΩ, due to the larger ratio of Ni$^{3+}$/Ni$^{2+}$ by adding Zn$^{2+}$ to the system. According to the law of charge neutrality, discussed in previous work [104], one can come to the conclusion that alkali metals with 1+ oxidation state can significantly increase Ni$^{3+}$/Ni$^{2+}$ and decrease resistivity even more than Zn$^{2+}$. Among alkali metals, Li$^+$ would be the best candidate, since it has the closet ionic radius to Ni ion, and it is expected to have the highest diffusion coefficient in NiO crystals. Li$^+$ and Ni$^{2+}$ ionic radius are respectively 76 and 69 pm [331]. In addition, Some authors have reported the decrease in NiO resistivity due to Li$^+$ doping [321,332].

In this study, ALD technique was replaced with a much simpler technique. The coating was provided from the deposition of dissolved Li salts on Ni particles. This technique has a predecessor [333–335], called hydro-coating, which includes a piece of metal in a solution. The metal piece was heated, and the dissolved compound would precipitate on the metal. We employed this idea and used it to deposit Li chemical compounds on Ni nanoparticles.

The Ni nanopowders were coated with the different Li chemical compounds in order to find out which chemical provide a better conductivity preservation. Then the coated particles were sintered at different schedules and partial pressure of oxygen, and then their resistance was measured to evaluate the merit of Li$^+$ doping in preserving electrical conductivity of Ni electrode after sintering.
7.2 Material and methods

In order to coat Ni particles with Li chemical compound, the compound was first dissolved in deionized water, and then Ni particles were added; next, the mixture was heated to evaporate the liquid, while it was mechanically stirred in the entire evaporation process. The mixing setup consisted of a mechanical stirrer, a beaker, and a heater, as shown in Figure S 7-1. A detailed discussion, which enables the coating processes and explains the effective parameters, can be found under Supporting Information, entitled “S1. Effective parameters in the coating process.” In addition, the process are schematically shown in the graphical abstract.

Three Li compounds of Li$_2$CO$_3$, LiF, and LiOH, with the saturation concentration of 1.32 [336], 0.13 [337], 11.14 [338] grams per 100 gram water at room temperature, were tested with our coating processes. The Li chemical compounds were bought from Alfa Aesar in powder form with 99.9+% purity. The Ni powders were supplied courtesy of JFE Mineral Company and Shoei Chemical, with the average particle size of 300 nm and purity of 99+%.

10.9 molar percent of Li$^+$ from those three compounds was used to coat 6 grams of Ni powder. In order to compare different Li compounds, the mole of Li$^+$ should be considered instead of the mole of chemical compound. Next, the coated Ni particles were mixed with 1 gram of the 15 wt.% ethyl cellulose solved in dihydro terpineol. The final product was a liquid mixture with a high viscosity, commonly referred to as “electrode ink”. Then the ink was painted by a brush on a piece of 1 cm by 0.5 cm alumina sheet and dried at 120 °C for 20 minutes. As it was shown by SEM imaging in Figure S 7-7 in Supporting Information, the thickness of NiO layer, formed on the top of the painted layer is on the order of several micrometer, while the thickness of the layer is on order of 1 to 2 mm. Because of this and the way that the resistance
was measured, the thickness uniformity of the painted sheets is not important in the present experiments.

The alumina sheets were sintered at two temperatures of 1020 and 1330 °C for 3 minutes, with the heating and cooling rate of 100 °C/min and -50 °C/min in air. This high heating rate was obtained by a homemade fast-heating furnace [295]. The 1020 °C-3min and 1330 °C-3min were selected, since they are suitable for sintering low-firing and BME (base metal electrode) BaTiO₃ powders, respectively. The resistance of the sheets was measured at 1 kHz and 1 V by a two-electrode probe, connected to Keysight Technologies E4980AL LCR meter. The probes were placed on the top of the sheets with 0.5 cm distance from each other. As pointed out above, a continuous layer of NiO would be formed on the top of the sheet and hinder the electron flow between the probes. The existence of this NiO layer cause the measured resistance increase dramatically; thus, measuring the resistance of electrodes is a suitable method to assess the formation of NiO layer. As it will be showed later, there are many other factors, involved in the resistance of the electrodes. However, the comparison of measured resistances is still a valid method to evaluate the success of our coating technique since the conductivity preservation is the ultimate goal of this study. For further information on resistance measurement, readers can consult with “S4. Resistance measurement” in Supporting Information.

Different weight percent of 3.4, 6.5 (equivalent to 10.9 molar%), 12.3, and 17.3 wt%, were added to the Ni powder and sintered in atmospheres with different pO₂ (partial pressure of oxygen). pO₂ was manipulated with mixing nitrogen and oxygen; the oxygen flow varied from 0.001% to 1%. The nitrogen source has the purity of 99.999%. The source of oxygen was the cylinders with 0.1% and 1% oxygen balanced with nitrogen. The carbon dioxide gas had the purity of 99.99%.
The SEM micrographs and FIB cross sections were obtained by FEI Helios NanoLab 660 FIB/SEM. The TEM (transmission electron microscope) samples were prepared by the same FIB system. The TEM analysis was done by FEI TALOS F200X. The TGA (thermogravimetric analysis) tests were done by TA Instrument SDT Q600.

### 7.3 Coating process

As explained in Supporting Information at “S1. Effective parameters in the coating process”, a successful coating process needs a good mixing of Ni particles in the Li salt solutions and an effective growth and nucleation on the surface of Ni particles during water evaporation. Figure 7.1 shows comparative examples of a low quality coating and a successful coating process. Figure 7.1 (a) shows the Li$_2$CO$_3$ particles, which nucleate independently of Ni particles and form separated particles. They are the elongated particle with a dark contrast. On the other hand, Figure 7.1 (b,c,d) shows a successful coating process, in which Li$_2$CO$_3$ deposited on Ni particles. The reason for the failure of the former mixture was the low quality of the Ni surface that could be due to surface contamination during storage and age of the Ni particles after opening containers, as discussed in Supporting Information. In the case of the latter mixture, by using the fresh Ni particles with clean surface, the Li$_2$CO$_3$ was deposited on Ni particles. The number of Li$_2$CO$_3$ particles, which were able to nucleate and grow separately, could be the indicator of how successful the coating process was. In the comparison of Figure 7.1 (a) and (b), there are no or few Li$_2$CO$_3$ particles in Figure 7.1 (b), which is the indicative of a successful coating. On the other hand, Figure 7.1 (a) is a representative of unsuccessful coating, in which many Li$_2$CO$_3$ particles can be detected.
Figure 7.1 SEM micrographs of Ni particles, coated with 6.5 wt.% Li$_2$CO$_3$ (a) illustrating an unsuccessful coating process, in which most of the lithium carbonates nucleate independently; (b), (c), (d) illustrating a successful coating process, in which the majority of lithium carbonates deposited on Ni particles.

7.4 The Li salt coatings

Figure 7.2 (a) and (b) shows SEM micrographs of LiF and LiOH coated particles, respectively. Figure 7.2 (c) is a reference for the no-coating state and can be compared with the coated particles, shown in Figure 7.1 (d) and Figure 7.2 (a, b). All the compounds showed a fairly good deposition, after the coating process.
The resistance of sheets containing LiF, LiOH, and Li$_2$CO$_3$ with 10.9 mol% of Li$^+$, after sintering at 1020-3 in air, was measured as 120, 20, and 1 kΩ, respectively. If those values were compared with the resistance (250 kΩ) of the sheet without any Li$^+$ additive, it would be obvious that all the Li chemical compounds offer some level of conductivity preservation.

Both LiOH [339] and Li$_2$CO$_3$ [340] decomposed to Li$_2$O and produced some types of reducing atmospheres at high temperature, but LiF did not. This might be the reason of the high resistance of the LiF-coated particles after sintering.

As suggested by Kim and Lee [340], the Li$_2$CO$_3$ decomposition in presence of carbon would produce a reducing atmosphere of CO/CO$_2$. According to Ellingham diagram, if the ratio of CO/CO$_2$ was larger than 0.05, it would prevent Ni from oxidation at the sintering temperatures.
(e.g. 1020 and 1330 °C). Later, it would show that the Li$_2$CO$_3$ decomposition can linger until the end of the sintering processes at atmosphere with less oxygen, thereby offering additional oxidation resistance locally. Although LiOH coated particles also showed promising results, since the resistance of Li$_2$CO$_3$ coated particles was lower, Li$_2$CO$_3$ was selected as the main Li chemical compound and was the focus for further investigations.

### 7.5 The effect of coating vs conventional mixing

In a sense, the coating process is a mixing process, by which one can place Li$_2$CO$_3$ around the Ni particles. It would be informative to compare the conductivity preservation in the mixture of Li$_2$CO$_3$ particles and Ni particles, produced by the conventional mixing process, with the Li$_2$CO$_3$-coated Ni particles. The mixture was obtained after ball milling the Ni and Li$_2$CO$_3$ powders in ethanol medium for 24 hours. In order to demonstrate the homogeneity of the mixture, its microstructure is presented in Figure 7.3 at two different magnifications. The microstructure of the coated particles is shown in Figure 7.1 (b to d). The mixture was comparable with the coated particles since both have the same 6.5 wt.% of Li$_2$CO$_3$. The resistance after sintering at 1020-3 in air were measured 16 and 1 kΩ for the sheets, made of the mixture and the coated particles, respectively. This observation showed that the coating process was a vital part of the conductivity preservation process, and the coated particles cannot be replaced by a well-distributed mixture of two powders.
Figure 7.3 SEM micrographs of Li$_2$CO$_3$-Ni mixture at two different magnifications.

7.6 The effect of Li concentration and sintering atmosphere

Before running any characterization tests, the color of Ni sheets after sintering can be a first indicator of the severity of oxidation and Ni ion stats. As reported by other authors [133,308,314], the color of NiO can be varied from light green to dark gray. When the NiO has stoichiometric composition, due to its band gap, it has high absorption in the red and violet region of the light spectrum, so that it appears as a green color. On the other hand, when NiO is non-stoichiometric due to free charge carriers (holes), it appears as shiny gray. However, later it will be shown that a layer of carbon can form on the top of the sheets in high weight percentage of Li$_2$CO$_3$ and makes the color deep black. So one can produce a color spectrum from light green to deep black by changing partial pressure of oxygen and Li chemical compound concentration. The color difference and the resistance of the sheets were discussed in more detail in Supporting Information at “S2. The influence of oxygen flow on the color and the resistance of the sheets”.

Table 7.1 shows the resistance of the sheets with different weight percent of Li$_2$CO$_3$, sintered at different schedules and oxygen flow. In order to keep the loss in electronic devices
low, the resistance of electrode should be as low as possible. If one uses an arbitrary criterion that $50\Omega$ is the maximum acceptable resistance for an electrode, then Table 7.1 can be better understood. In other words, every combination of $\text{Li}_2\text{CO}_3$ weight percentage, oxygen flow, and sintering program, which ends up to a sheet with a resistance below $50\Omega$, is worthy to be explored for making a device. Based on this criteria, the conditions in Table 7.1 are color coded to green (which means the condition is worthy of further investigation) and red (which means the condition definitely cannot be used in electroceramics manufacturing).

The first conclusion that can be drawn from this table is that the resistance of Ni electrode is low enough without the help of $\text{Li}_2\text{CO}_3$ at oxygen flow of $0.001\%$, equivalent to $\text{pO}_2$ of $10^{-5}$ atm, for both sintering schedules. According to the Ellingham diagram, $10^{-5}$ atm of oxygen should provide enough oxygen for the formation of NiO phase in equilibrium condition. However, the fast sintering processes that have been utilized in this study, did not kinetically allow Ni to be considerably oxidized; consequently, the resistance values remained low. A photograph of the sheets at different oxygen flows was given in Supporting Information in Table S1.

**Table 7.1** the resistance of sheets with different wt.% of $\text{Li}_2\text{CO}_3$ in two sintering schedule and at different oxygen flow*

<table>
<thead>
<tr>
<th>Sinter. Prog.</th>
<th>Oxygen %</th>
<th>0 wt.%</th>
<th>3.4 wt.%</th>
<th>6.5 wt.%</th>
<th>12.3 wt.%</th>
<th>17.3 wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020-3</td>
<td>0.001</td>
<td>5Ω</td>
<td>1Ω</td>
<td>2Ω</td>
<td>1Ω</td>
<td>1Ω</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>220kΩ</td>
<td>3Ω</td>
<td>4Ω</td>
<td>5Ω</td>
<td>5Ω</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3MΩ</td>
<td>30Ω</td>
<td>97Ω</td>
<td>150Ω</td>
<td>200Ω</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>250kΩ</td>
<td>4kΩ</td>
<td>1kΩ</td>
<td>470Ω</td>
<td>213Ω</td>
</tr>
<tr>
<td>1330-3</td>
<td>0.001</td>
<td>1Ω</td>
<td>1Ω</td>
<td>1Ω</td>
<td>2Ω</td>
<td>2Ω</td>
</tr>
<tr>
<td></td>
<td>0.02</td>
<td>140kΩ</td>
<td>1Ω</td>
<td>1Ω</td>
<td>8Ω</td>
<td>10Ω</td>
</tr>
<tr>
<td></td>
<td>0.04</td>
<td>160kΩ</td>
<td>3kΩ</td>
<td>2kΩ</td>
<td>100Ω</td>
<td>43Ω</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>282kΩ</td>
<td>77kΩ</td>
<td>67kΩ</td>
<td>11kΩ</td>
<td>5kΩ</td>
</tr>
</tbody>
</table>

* The table is color coded to green color, conditions with low resistance, and red color, conditions with too large resistance.
By increasing the flow of oxygen to more than 0.001%, the resistance of pure Ni sheets considerably increased for both sintering programs. So there was a need for Li$_2$CO$_3$ to keep the resistance low at higher oxygen flow. At oxygen flow of 0.02%, for instance, the resistance was significantly decreased by applying Li$_2$CO$_3$ coatings in both sintering programs. But there was not a tangible difference in resistance of the sheets with different amount of Li$_2$CO$_3$.

By increasing the amount of oxygen flow, the resistance difference between the sheets with different weight percentages of Li$_2$CO$_3$ became more obvious. In the case of 1020-3 sintering program with 0.1% oxygen flow, the resistance increased by increasing the amount of Li$_2$CO$_3$. This is due to the fact that Li$_2$CO$_3$ decomposed to Li$_2$O and CO$_2$ during the course of the sintering processes. The decomposition started around 760 °C as will be illustrated in the next section and, theoretically, the Li$_2$CO$_3$ would be able to lose 58% of its original volume according to Eq. 7.1. This amount of volume loss has been verified by TGA in the next sections.

\[
\text{Li}_2\text{CO}_3(l) \rightarrow \text{Li}_2\text{O}(s) + \text{CO}_2(g)
\]

Eq. 7.1

If all the Li$_2$CO$_3$ decomposed, one should expect a 7.48 vol% loss in the sample with 3.4 wt.% Li$_2$CO$_3$. However, the volume loss increased to 27.2 vol% in the sample with 17.3 wt.% Li$_2$CO$_3$. Figure 7.4 shows SEM micrographs of the cross section of the sheets with 3.4 and 17.3 wt.% of Li$_2$CO$_3$ after sintering at 1020-3 in air. The air atmosphere was selected since the volume loss due to the decomposition was more pronounced (as will be illustrated by TGA in the next section). The sheet with 3.4 wt.% had random porosity, as was expected to be seen in the sintered materials. In the sheet with 17.3 wt.%, the porosities (i.e. empty spaces due to the volume loss) were formed along the grain boundary. This volume loss decreased the connectivity of the grains and increased the resistance. The shape of the porosity suggests that the most of the
Li$_2$CO$_3$ was at the grain boundaries before decomposition. As will be discussed later, Li$_2$CO$_3$ residues reside at grain boundaries.

The percentage of porosity in micrographs of Figure 7.4 seems less than the above calculated volume loss. This is due to the fact that some of the volume loss could be compensated by interdiffusion of Ni grains during the course of sintering.

As for the second reason of resistance increase by Li$_2$CO$_3$ percentage, one can argue that since the conductivity of both Li$_2$CO$_3$ [341] and Li$_2$O [342] is low and on the order of $10^{-7}$ Ω·cm$^{-1}$, they can decrease the total conductivity. However, it should be noted that the resistance would be on the order of kΩ or even MΩ if the coated particles were not used as can be confirmed in Table 7.1 by comparing the “0 wt.%” column with other columns.

As will be shown in the next section, the volume loss increases by increasing oxygen percentage. Thus, the volume loss is negligible at 0.02% oxygen flow so that the resistance differences in Table 7.1 are negligible vs Li$_2$CO$_3$ percentage in the rows of “0.02%” oxygen.

Figure 7.4 The SEM micrograph from the FIB cross section of the sheets with (a) 3.4 and (b) 17.3 wt.% lithium carbonate, sintered at 1020-3 in air. The “Pt layer” in (a) was coated to protect the top surface against FIB milling.

On the contrary of the previous trend, the resistance decreased by increasing Li$_2$CO$_3$ percentage in air at sintering schedule of 1020-3. This was due to the fact that the Ni oxidation
would be the main reason for resistance increase rather than the amount of porosity in high percentage of oxygen flow (air has ~21 vol% oxygen).

Increasing the sintering temperature from 1020 °C to 1330 °C aggravate the discontinuity problem due to the weight loss by having more grain interdiffusion. However, the Ni oxidation was more pronounced at higher temperature due to the increase in the kinetic of NiO formation. Thus, the same trend (increasing Li$_2$CO$_3$ causes decreasing resistance) was observed in both the 0.04% oxygen and air at sintering program of 1330-3. In other words, increasing Li$_2$CO$_3$ percentage in 1330-3 schedule prevents a significant rise in the resistance values by oxygen flow. For example, one can compare the column of “3.4 wt.\%” with “17.3 wt.\%” at 1330-3 program in Table 1. The resistance of the sheets with 3.4 wt.\% Li$_2$CO$_3$ increased from 1 Ω to 77 kΩ by increasing oxygen flow, while for the sheets with 17.3 wt.\% Li$_2$CO$_3$, the resistance only increased to 5 kΩ. One can find the same trend in other columns.

The oxygen flow and the maximum temperature during sintering had a cumulative effect on the resistance increase. This is why an acceptable resistance was obtained at 0.1% oxygen in 1020-3, but the oxygen flow would have to decrease to 0.04% in 1330-3 to obtain an acceptable resistance. Thus, it is expected that increasing both temperature and oxygen flow increase the amount of NiO phase and consequently raise the resistance of the sheets. However, to make a complete argument, it is worth mentioning that this is not always the case. For instance, the resistance does not follow this general trend in the column of “0 wt.\%” for the uncoated Ni particles at the sintering program of 1020-3. This is due to the fact that the Ni$^{3+}$/Ni$^{2+}$ ratio may change by oxygen flow and affects the resistance. For more information, readers are encouraged to consult the Supporting Information, “S2. The influence of oxygen flow on the color and the resistance of the sheets”.

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A series of SEM micrographs, shown in Figure 7.5, illustrates the evolution of the sheet microstructure by increasing the amount of Li$_2$CO$_3$ at 1330-3 with 0.02% oxygen flow. 0.02% oxygen flow was selected, since it could depict the microstructure evolution more obviously than the conditions with higher oxygen flow. All micrographs were taken at the same magnification, so the grain sizes, shown in micrographs, are comparable. Figure 7.5 (a) shows the sheet without Li$_2$CO$_3$; there is a NiO layer around every grain, and it forms a continuous network of NiO grain boundaries all over the sheet. Furthermore, in the Supporting Information under the section of “S3. Nickel oxidation during sintering”, it was demonstrated by FIB cross sections that a continuous NiO layer formed on the top of the sheet with thickness of 1.5µm. In addition, the evolution of Ni particles during sintering in air was systematically studied in Supporting Information; it was concluded that due to the oxidation of Ni particles, both densification process and grain growth would be considerably hindered in comparison to Ni particles, sintered in Nitrogen.

Adding Li$_2$CO$_3$ can effectively break down the network of oxide layers, as suggested by the micrographs of 3.4 wt.% Li$_2$CO$_3$ and 6.5 wt.% Li$_2$CO$_3$ in Figure 7.5 (b) and (c) and consequently the grain size would be much larger. In addition, the FIB cross section on the sheet with 6.5 wt.% Li$_2$CO$_3$, presented in Figure 7.5 (d), shows the NiO layer on the top of sheet disappeared (or at least it is not detectable in the present magnification). For confirmation, one can compare Figure S 7-7 with Figure 7.5 (d).

Li$_2$CO$_3$ has been used as sintering aid due to its low melting temperate and providing liquid phase sintering in many systems [343,344]. The Li$_2$CO$_3$ coating melts and surrounds the Ni grains in the early stage of sintering of the coated particles. In addition, Li$_2$CO$_3$ will decompose and provide reducing atmosphere, which hinders the formation of NiO phase during
the sintering process. The Li$_2$CO$_3$ decomposition will be studied in the next section. The disappearance of both the NiO layer and network of NiO boundaries, as mentioned above, supports the idea that the presence of a reducing gas, produced during the Li$_2$CO$_3$ decomposition, limits the formation of NiO phases. In addition, Beyer et al. [345] proved the existence of CO gas during the decomposition of Li$_2$CO$_3$ in the presence of carbon in argon atmosphere. Also, they showed that the CO convert to CO$_2$ in air atmosphere. Their finding match well with the TGA results in this study in the next section.

The residue of Li$_2$CO$_3$ can be found at the grain boundary as a thick layer, as shown in Figure 7.5 (b) and (c). The layer has a depth of 5µm inside the sheet as shown in Figure 7.5 (d). However, some of the Li$_2$CO$_3$ residues are detected with black contrast and will be studied next.

![SEM micrographs of the sheet with (a) 0, (b) 3.4, (c) 6.5 wt.% Li$_2$CO$_3$, sintered at 1330-3 in 0.02% oxygen. (d) FIB cross section of the sheet, presented in Figure (c).](image)
By increasing the amount of Li$_2$CO$_3$ to 12.3 and 17.3 wt.%, carbon flakes would appear on the surface, as shown in Figure 7.6 (a) and (b). As seen, the amount of carbon flakes increase by increasing Li$_2$CO$_3$ percentage. The carbon flakes are the byproduct of the Li$_2$CO$_3$ decomposition. The decomposition of lithium carbonate is shown in Eq. 7.1 without the interference of residual carbon. However, the presence of carbon may cause the Boudouard reaction ($CO_2(g) + C(s) \rightleftharpoons 2CO(g)$) to convert CO$_2$ gas to CO. The CO volume percentage increased by temperature, as reported by Holleman and Wiberg 75 and 100 vol% at 750 and 1000 °C [346], respectively. Thus, as suggested by Kim and Lee [340], the decomposition reaction would be as follows in the presence of carbon:

$$Li_2CO_3(l) + C(s) \rightarrow Li_2O(s) + 2CO(g)$$

*Eq.7.2*

The source of carbon in the present samples was the residue of the organic materials used in making the inks [133,347]. In addition, the secondary reaction:

$$2C(s) + O_2(g) \overset{Ni}{\leftrightarrow} 2CO(g)$$

*Eq.7.3*

can occur during the decomposition process. If there was insufficient oxygen during the sintering process, according to Le Chatelier's principle, the reaction would be driven to the left to compensate the lack of oxygen and some carbon produced on the top of the sheet as a byproduct. It is a well-known that Ni plays an important role as a catalyst in the reverse reaction [348–350]. EDS analyses confirmed that the dark layer on the top of the sheets was carbon as presented in Figure S 7-8 and Ref. [322]. Furthermore, The difference between the decomposition process in
air and nitrogen was studied with TGA in the next section, and it was shown that the peak for the weight loss due to the decomposition reaction could be pushed back by 267 °C from 819 °C in air to 1086 °C in nitrogen at heating rate of 20 °C/min. Thus the carbon flakes are the byproduct of the Li₂CO₃ decomposition and they will be disappear either by decreasing the percentage of Li₂CO₃, as presented in Figure 7.5 (b,c), or increasing the oxygen flow, as presented in Figure 7.4(b). As shown in Figure 7.6 (c), a FIB cross section on the area covered with carbon flakes shows that under the carbon layer, there is a similar structure of Li₂CO₃ residue to the one presented in Figure 7.5 (d) for the sheet with 6.5 wt.% Li₂CO₃. However, the residues appear with dark contrast. If the understanding of the decomposition process is correct, one can increase the amount of oxygen flow in the sintering process to force more carbon to convert to CO/CO₂ gas and probably get rid of the top carbon layer. The oxygen flow was increased from 0.02% to 0.04% and every other parameter kept constant. The micrograph of the resultant sheet is presented in Figure 7.6 (d). As expected, the surface carbon was decomposed. The micrograph is similar to the ones presented in Figure 7.5 (b) and (c) for the sheets with 3.4 and 6.5 wt.% Li₂CO₃, except for the fact that Li₂CO₃ is detected with a dark contrast. Based on those two above observations, one may conclude that the microstructure of the sheets did not change by increasing Li₂CO₃ from 6.5 wt.% to 17.3 wt.%; the only difference is that there is more carbon in the sample, which did not decompose during the sintering condition. The carbon would be found in two forms: in the residue of Li₂CO₃ at grain boundaries and as the carbon flakes on the top of the sheets. As Figure 7.6 (c) shows, the carbon can be found in both the top layer and the residues below the surface. The other study showed that those Li₂CO₃ residues have the mixture of Li, O, and C [322].
The residue at the top of the sheet with 6.5 wt.% Li₂CO₃, presented in Figure 7.5(c), loses all its carbon and is detected as a bright contrast. However, even in this sheet, there are some black spots below the surface, as presented in Figure 7.5 (d). This suggests that since the residues below the surface exposed to less amount of oxygen, they possess more carbon than the residue on top. Furthermore, the same phenomena was observed in the sheet were sintered in 0.04% oxygen flow as well. A mixture of the Li₂CO₃ residues with and without carbon were found at grain boundaries. Their micrograph along with EDS-line-scan are presented in Figure S 7-8. In conclusion, the amount of carbon in the residues depend on the amount of oxygen exposure during sintering.

![SEM micrographs of the sheet](image)

Figure 7.6 SEM micrographs of the sheet with (a) 12.3, (b) 17.3 wt.% Li₂CO₃, sintered at 1330-3 in 0.02% oxygen; (d) FIB cross section of the sheet, presented in Figure (b). (d) SEM micrograph of the sheet with 17.3 wt.% Li₂CO₃, sintered at 1330-3 in 0.04% oxygen. The “Pt layer” in (c) was coated to protect the carbon layer against FIB milling.
The sintering conditions in this study produced a mixture of Ni and NiO grains, as discussed in Supporting Information under “S3. Nickel oxidation during sintering”. One may consider two mechanisms for the preservation of Ni conductivity. First, Li$_2$CO$_3$ can be decomposed and provide reducing atmosphere during sintering and eventually decrease the number of NiO grains. Second, Li$^+$ can incorporate into NiO phases and increase the chance of electron hopping by increasing Ni$^{3+}$/Ni$^{2+}$ [312,321,322]. The influence of these mechanisms was observed in the measured resistances and the SEM micrographs as well as in the color change in the sheets (Table S2) in Supporting Information.

7.7 The trace of Li$_2$CO$_3$ decomposition

As mentioned above, the Li$_2$CO$_3$ decomposition can hinder the formation of NiO grains. In this section, this composition will be studied in detail. Figure 7.7 (a) shows the TGA results of Li$_2$CO$_3$ powders in air at different heating rates. Their weight loss (i.e. decomposition) follows Eq.1. The onset of weight loss is 732, 744, and 763 °C for heating rates of 10, 40, and 100 °C/min. The melting temperature of Li$_2$CO$_3$ was reported at 720 °C [351]. Based on Eq.1, the weight loss can be calculated as 59 wt.%, which matches well with experimental measurement of 59±1 wt.%. The other effective parameter in Li$_2$CO$_3$ decomposition is the atmosphere of heat treatment. As the TGA data in Figure 7.7 (b) suggests, the decomposition of Li$_2$CO$_3$ is the same in air and nitrogen. But the decomposition can be considerably hindered by using carbon dioxide. This phenomenon can be well explained by Eq.1. The air and nitrogen is neutral, since they do not change the balance of the left and right side of the equation. However, applying CO$_2$
atmosphere forces the reaction to shift to the left, according to Le Chatelier's principle, and
hinders the Li$_2$CO$_3$ decomposition.

The electrode ink was tested with TGA in air, nitrogen, and carbon dioxide. The results
are shown in Figure 7.7 (c), which presents the weight derivation in respect to time vs.
temperature. As shown, six peaks can be detected. (1) and (2) belong to evaporation of dihydro
terpineol and the decomposition of ethyl cellulose, since the boiling point of the former is 205
$^\circ$C, and the decomposition peak of the latter is between 300 and 352 $^\circ$C, at different atmospheres
[352]. Peak (3) belong to Ni oxidation, which is absent in both nitrogen and carbon dioxide
atmosphere. Peak (4), (5), and (6) are Li$_2$CO$_3$ decomposition in air, nitrogen, and carbon dioxide.
The onset points of weight loss for Peak (4) and (5) are close; they are, respectively, 744 and 751
$^\circ$C. However, peak (4) reached maximum at 819 $^\circ$C, but peak (5) reached maximum at 1086 $^\circ$C.
Both decomposition processes followed the same chain of reaction. First, Li$_2$CO$_3$ decomposed
and produced CO$_2$ gas, and then, based on the Boudouard reaction, CO$_2$ converted to CO [346].
However, in the nitrogen atmosphere due to the lack of oxygen, Eq. 3 would be driven to the left.
This caused the carbon deposition on the Ni particles and increased the weight of the sample.
This is why the peak of the weight loss was pushed back to 1086 $^\circ$C in Nitrogen atmosphere.

Peak (6) is shifted to 1235 $^\circ$C. In addition, the onset temperature of the peak is 1208 $^\circ$C
while it was 744 and 751 $^\circ$C for peak (4) and (5) respectively. The push back of the onset
temperature suggests that applying CO$_2$ atmosphere hinders the first reaction (i.e. Eq.1) in the
decomposition process. This conclusion can be further supported by the TGA results of Li$_2$CO$_3$
powders in Figure 7.7 (b), where the Li$_2$CO$_3$ powder loses 35% weight in both nitrogen and air,
while the loss is less than 2% in carbon dioxide.
It is worth noting that the carbon redeposition was not detected for the Li$_2$CO$_3$ powder in nitrogen atmosphere. As shown in Figure 7.7 (b), the graphs of TGA tests in air and nitrogen atmosphere lay on the top of each other, indicating no mass gain due to carbon redeposition in nitrogen atmosphere. This is mainly due to the fact that there is neither Ni in the system to act as catalyst nor residual carbon to encourage CO gas formation through the Boudouard reaction. So the decomposition reaction will occur exactly as shown in Eq.1 in both air and nitrogen.
In order to trace the decomposition process, a series of sheets, heated up to 700, 850, 1000, 1150 °C and without holding, cooled down to room temperature at 0.04% oxygen flow. Figure 7.8 shows the microstructure evolution of the sheet during the sintering process.

At 700 °C, there are random small black spots on Ni particles, as presented in Figure 7.8(a). They are due to the carbon redeposition due to CO gas. However, the CO gas was produced due to burning of organic materials instead of the Li₂CO₃ decomposition. The Li₂CO₃ decomposition is expected to start at 763 °C according to TGA results of Li₂CO₃ powder in Figure 7.7 (b). This carbon redeposition was detected by TGA tests in nitrogen as a small peak between peak (2) and (4) in Figure 7.7 (c), labeled as (*). Since carbon deposition did not occur in CO₂ atmosphere, this peak would disappear in CO₂ atmosphere. Due to the unlimited sources of CO₂ gas, Boudouard reaction \((\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO}(g))\) would be driven to the left and consume all the residual carbon [322,346]. This is why no weight gain due to carbon deposition was detected in the TGA result at CO₂ atmosphere.

By increasing temperature to 850 °C, the onset of Li₂CO₃ decomposition has passed, and there will be more CO production and, consequently, more deposited carbon; the carbon layer became almost continuous, as shown in Figure 7.8 (b). By increasing temperature, the carbon layer became thicker, and the sheet surface was buried under a thick layer of carbon at 1000 °C, as shown in Figure 7.8 (c). Since the Li₂CO₃ decomposition peak was at 1086 °C, the maximum deposited carbon was observed in Figure 7.8 (c). However, at 1150 °C, most of the lithium carbonate was decomposed, i.e., the source of CO/CO₂ gas was depleted. So the reaction for carbon redeposition, Eq.4, shifted to the right and consumed the deposited carbon. This is why the carbon layer starts to disappear around 1150 °C, as illustrated in Figure 7.8 (d). The carbon
redeposition in Figure 7.8 is comparable with the TGA results for the nitrogen gas in Figure 7.7(c).

Figure 7.8 SEM micrographs of the coated particles, heated to (a) 700, (b) 850, (c) 1000, and (d) 1150 °C in 0.04% of oxygen flow.

7.8 Conclusions

In this study, an innovative coating method to coat Ni particles with three Li compounds (Li₂CO₃, LiOH, and LiF) was presented. The optimal coating parameters was found, and all three compounds were successfully coated on Ni particles as confirmed by SEM micrographs. Next, the coated particles were sintered in air under the 1020-3 schedule and the particles coated with Li₂CO₃ showed a consistent ability to preserve Ni conductivity by reducing the resistance from 250 kΩ for the uncoated particles to 1 kΩ. In addition, the coating process was a vital part of the
conductivity preservation, where one cannot simply mix the two powders and expect to have the same amount of resistance reduction.

The conductivity of the Ni sheets was systematically tested as a function of Li$_2$CO$_3$ weight percentage, sintering program, and the oxygen percentage during sintering. The results showed that increasing the oxygen flow and maximum temperature have a cumulative effect on the resistance increase. However, the Li$_2$CO$_3$ percentage showed a dual effect. In the sintering program of 1020-3, the resistance decreased by decreasing Li$_2$CO$_3$, since its decomposition caused volume loss and introduced discontinuity between Ni grains. On the other hand, in the sintering program of 1330-3, the resistance decreased by increasing the percentage of Li$_2$CO$_3$, since the Ni oxidation is the main cause of resistivity increase, and the larger percentages of Li$_2$CO$_3$ can provide a better preservation.

The microstructure of the sheets after sintering showed that the residues of Li$_2$CO$_3$ would settle between Ni grains. In addition, it was observed that the amount of carbon in the residues was correlated to the amount of oxygen flow and the percentage of Li$_2$CO$_3$. It is suggested that the Li$_2$CO$_3$ melts during sintering and is pushed into grain boundaries from the coarsening of Ni grains. At the same time, the Li$_2$CO$_3$ started to decompose. The decomposition yielded CO, which invoked a reducing atmosphere, and subsequently decreased the amount of NiO phase. The decomposition process and the carbon deposition was studied by TGA and SEM imaging. The other mechanism is the diffusion of Li$^+$ inside the NiO grains and the decrease of their resistivity due to an increase in the Ni$^{3+}$/Ni$^{2+}$ ratio. The effect of this ratio increase can be seen in the color change of the sheets in Table S2 in Supporting Information.

In this research, it was demonstrated that the Ni coated particles are able to be sintered at 0.02 or 0.04% oxygen flow and still retain a low resistance, while the uncoated Ni particles,
sintered in the same condition, have resistances on the order of kΩ or even MΩ. Thus, the coating technique demonstrated in this work could potentially provide a sintering condition in which electroceramics can be sintered in a higher partial pressure of oxygen with a negligible increase in the electrode resistivity. The utilization of the coated Ni particles in electroceramic manufacturing can effectively untangle the problem of oxygen vacancies. Conventionally, electroceramics were manufactured in heavily reducing atmosphere (e.g. pO₂=10⁻¹⁰ atm) to prevent Ni oxidation. By introduction of this new electrode, the partial pressure of oxygen can be increased by six orders of magnitudes and consequently the formation of oxygen vacancies would be suppressed effectively.

7.9 Supporting Information

S1. Effective parameters in the coating process

The schematic of the coating setup was shown in Figure S 7-1. During the water evaporation, the Li compound reached its saturation concentration and started to nucleate and grow on the surface of Ni particles. If this is the coating mechanism, one should be cautious about the three following phenomena. The discussion below is not a comprehensive and systematic study on the coating process, which is not the scope of this study. This is rather the observations and recognition of the effective parameters for obtaining an optimum condition for the coating process.
1. **Dissolution of the Li salts and wetting of Ni particles:** All particles of the Li salts should be dissolved in water at first, and then the solution needs to wet all the Ni particles. In order to make sure of this, the mixture is stirred for one hour at 40 °C at high speed stirring, followed by adding Ni particles and another hour of mixing.

An effective stirring is important in this process. The intensity of stirring is increased by choosing a propeller with a diameter close to the diameter of the beaker, placing the propeller close to the bottom of beaker, and off-centering the propeller axis.

The dissolution of the Li salts particles before adding Ni particles is important. Thus one should make sure the initial salt concentration is below the saturation of the salt solutions. For example, for manufacturing 17.3% Li$_2$CO$_3$ coated particle, 1.038 gram of Li$_2$CO$_3$ was dissolved in 200 CC of water (i.e. the concentration was 0.523 grams of Li$_2$CO$_3$ per 100 gram water), which was below the saturation (1.32 grams per 100 gram water). The saturation concentrations of Li compounds were given in the main text.
2. **Nucleation and growth of Li compound:** The surface quality of Ni particle is highly important in nucleation. We have experience both with using old Ni particles, whose surface was not clean due to storage condition, and also with using fresh Ni particles, which had just came out of packaging. The latter showed far better coating than the former. An example of failed and successful coating was presented in the main text.

The rate of nucleation and growth depends on the temperature of heater at the evaporation process. A temperature around 300°C was selected to evaporate the water.

The Li compounds can nucleate on the beaker wall or without any surface. Because of that, one needs to make sure before reaching the saturation concentration, which is the onset of the nucleation process, there is a complete wetting between Ni particles and the solution to increase the chance of nucleation on Ni particles. In addition, the Ni particles should be evenly exposed to the saturated solution during the entire of deposition process. Considering all of that, the saturation concentration of chemical compound is an important factor in a homogenous nucleation, as it would be explained in the next part.

3. **Li compounds:** a suitable Li compound for the coating process should be dissolved into water, yet it should have low saturation concentration. In this way, the Li compounds would be able to be deposited homogeneously during the course of the evaporation process. For example, LiNO$_3$ is not a good candidate, since it has the solubility of 60.08 grams per 100 grams water [353]. Let say that the Li compound should be 1 gram in the coating process. Thus, when the LiNO$_3$ solution reaches saturation during evaporation process, there is only $\sim$1.7 CC of the solution remaining, and with that much liquid, an effective stirring is impossible. On the other hand, Li$_2$CO$_3$ is a good candidate, since it
has the solubility limit of 1.32 grams per 100 grams of water at 20 °C [336]. In this way, when the Li$_2$CO$_3$ reaches the saturation, there is still ~75.8 CC of the solution remaining, and that much liquid provides an effective mixing during the course of Li$_2$CO$_3$ deposition. In addition one can manipulate the saturation concentration by modifying the solvent. Lu et al.[336] showed that the solubility of Li$_2$CO$_3$ can be decreased by an order of magnitude by adding 50 vol% ethanol into the water. Ethanol was used to decrease the saturation concentration of Li compounds, so that the deposition process started at 150 CC to 200 CC of the solution for the processes of the powders with different Li$_2$CO$_3$ weight percentage.

S2. The influence of oxygen flow on the color and the resistance of the sheets

The color of Ni sheets can be representative of Ni oxidation state and the severity of oxidation. In order to demonstrate the influence of Ni$^{3+}$ concentration on color and resistivity, a series of sheets with uncoated Ni particles has been sintered at 1020-3 in pure nitrogen, 0.001%, 0.1%, 0.5%, 1% of oxygen flow, and air. The photos of the sheets after the sintering, with their resistivity, are presented in Table S 7-1. The one sintered in air has been exposed to a large amount of oxygen, which produced a high number of Ni vacancies and, as a result, increased the concentration of Ni$^{3+}$. This is why it appears as shiny dark gray and has low resistance when compared to other NiO sheets. By decreasing the amount of oxygen to 1, 0.5, or 0.1% of oxygen flow, the Ni sheets would be exposed to the right amount of oxygen to produce stoichiometric NiO, which have the green color and high resistance. The green color goes from light to dark from 1% to 0.1%. At 0.001%, there is a region with a metallic color, surrounded by greenish gray, and at the corners, the color turns to faint dark green. The color change from light green to
dark green in the sheets may simply depend on the amount (thickness) of NiO on the top of the sheets. Ni oxidation is studied in more detail in the next section. In the case of pure nitrogen, the sheet has a metallic color and low resistivity, indicating a negligible amount of oxidation, which would be later confirmed by the TGA tests. Voleník et al. [314] have a similar observation with Ni oxidation. As was discussed in the main text, resistance above 50Ω is not acceptable for electrodes. So most of the sheets in Table S 7-1 are not suitable to be considered as an electrode, but it is worth illustrating the influence of Ni$^{2+}$/Ni$^{3+}$ ratio on the color and resistance of the sheets, as well as their resistance. Based on the reported resistance in Table S 7-1, one can conclude that using a more reducing atmosphere during sintering Ni particles does not necessarily decrease the resistance of the sheets. For example, the sheets sintered in air have one order of magnitude lower resistance than the sheet sintered in 0.1% oxygen ($pO_2 = 10^{-3}$).

<table>
<thead>
<tr>
<th>Pure nitrogen</th>
<th>0.001% of O$_2$</th>
<th>0.1% of O$_2$</th>
<th>0.5% of O$_2$</th>
<th>1% of O$_2$</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>50mΩ</td>
<td>0.6Ω</td>
<td>3MΩ</td>
<td>30MΩ</td>
<td>80MΩ</td>
<td>250kΩ</td>
</tr>
</tbody>
</table>

In a sense, Li$_2$CO$_3$ has a similar effect as oxygen. By increasing Li$_2$CO$_3$, the number of Ni$^{3+}$ increased due to charge neutrality and, as a result, resistance decreased and the color changed from green to shiny gray and dark black, as shown in Table S 7-2. Those sheets were sintered at 1020-3 in 0.1% of oxygen. The color of nonstoichiometric NiO is the shiny gray,
which is the color of the sheets with 3.4 and 6.5 wt.% Li$_2$CO$_3$. The deep black color in the sheets with 12.3 and 17.3 wt.% Li$_2$CO$_3$ is due to the top carbon layer. The formation of the carbon layer was explained in the main text.

Table S 7-2 the photo of the sheets with different amount of Li$_2$CO$_3$ sintered at 1020-3 at 0.1% oxygen along with their resistance

<table>
<thead>
<tr>
<th>No Li$_2$CO$_3$</th>
<th>3.4 wt.% Li$_2$CO$_3$</th>
<th>6.5 wt.% Li$_2$CO$_3$</th>
<th>12.3 wt.% Li$_2$CO$_3$</th>
<th>17.3 wt.% Li$_2$CO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3MΩ</td>
<td>30Ω</td>
<td>97Ω</td>
<td>150Ω</td>
<td>200Ω</td>
</tr>
</tbody>
</table>

S3. Nickel oxidation during sintering

Having a clear image about sintering of Ni particles is vital for understanding the effects of Li$_2$CO$_3$ coatings. The sintering of the uncoated Ni particles at two atmospheres of air and nitrogen was systematically studied here.

The pure Ni sheets were heated to 850, 950, 1050, 1150, 1300, and 1400 °C without holding to cool down. Their micrographs are presented in Figure S 7-2. The average grain sizes were roughly measured as 0.3, 0.4, 0.7, 2.1, 4.7, and 9.5 μm at 850, 950, 1050, 1150, 1300, and 1400 °C, respectively. The micrographs of Figure S 7-2 are not shown in the same magnification, so one should consider the scale bar of each image for the comparison of grain sizes. The evolution from Ni particles (Figure 2 (c)) to a densified sheet can be followed in these micrographs. From 850 °C to 1400 °C, there is a typical sintering process and grain growth. However at 1150 (the transition can be seen at 1050 °C as well), the grain boundaries start to stand out of the sheet. That is due to the fact that the shrinkage rate of grain boundaries is smaller.
than in grains, and in some point during the sintering process, this difference causes the middle of the grain to go down and the grain boundary to stand up. In order to show the height difference, a FIB cross section was performed on the sample exposed to 1150 °C and 1400 °C, and the micrographs are shown in Figure S 7-5. Both micrographs show that the grain boundary surrounds the grain like a wall. Since the sintering process is more progressed at 1400 °C than 1150 °C, the amount of shrinkage and, consequently, the height difference, are larger at 1400 °C. The maximum height difference was measured 0.8 and 4μm for the samples, heat treated at 1150 and 1400 °C, respectively, as illustrated in Figure S 7-5 (d).
Figure S 7-2 SEM micrographs of the sheets with the uncoated Ni particles, heated to (a) 850, (b) 950, (c) 1050, (d) 1150, (e) 1300, and (f) 1400 °C in air.
Next, it would be informative to compare these sheets with similar sheets that were heat treated at 700 and 850 °C in nitrogen. Their micrographs are shown in Figure S 7-5. The average grain sizes are 2.1 and 11.8 µm for the sheets heated to 700 and 850 °C, respectively. As supported by SEM micrographs (Figure S 7-5 (c)) and FIB cross section (Figure S 7-5(d)), the sheets with pure Ni particles reached the full densification at 850 °C. Thus, the Ni particle reached densification at lower temperature and had larger grain in reducing atmosphere since the interdiffusion of Ni grains was much faster than interdiffusion of NiO grains, as suggested by Jo et al. [299]. The other observation is that in nitrogen-sintering, there was no sign of the network of NiO grain boundaries, which observed in the air-sintering. This is due to the fact that during
sintering in the nitrogen atmosphere, the shrinkage rate of grain boundary is higher than the grain and it causes the grain boundaries to go slightly down and the grains to stand up, as illustrated in Figure S 7-5(d). So, the conclusion is that the network of NiO grain boundaries can be a sign of existence of oxidizing atmosphere during sintering and its absence is a sign of a reducing atmosphere. This conclusion was used in the main text, when the reducing atmosphere due to the Li$_2$CO$_3$ decomposition was discussed.

The TGA tests of Ni particles in air and nitrogen, shown in Figure S 7-5, suggest that the Ni particles start to gain weight (i.e. oxidizing) at 360 °C. Since the weight vs. temperature curve in air has two different slopes, first very steep and then much lower at 710 °C, it suggests that the oxidation is severe in the first stage and then slows down. The dotted line in Figure S 7-5 is the calculated maximum weight gain.
The other observation is that some metallic Ni grains were found at the bottom of FIB cross-sections of the Ni sheets that were heated to 1150 and 1400 °C, as shown by bright contrast at Figure S 7-6 (a) and (b). A TEM sample was prepared from that bottom area, and it was proven by EDS (energy dispersive spectroscopy) that the bright contrast is actually Ni grains. Figure S 7-6 (c) shows the STEM micrograph at the bottom of the sheet heated to 1150 °C. The NiO grains are colored; the microstructure shows the mixture of Ni and NiO grains. The Ni grains have the average diameter above 1 µm, while the largest Ni particle is 700 nm in Figure 2 (c), and the average grain size is 300 nm. This suggests that some of the Ni particles at the depth
of ~10 µm below the sheet surface did not oxidize during the heat treatment and eventually interdiffused at high temperature.

There are several explanations for this observation, but only one of them can explain all the above observations. There is a large interface between the Ni particles and air in the first stage of heat treatment in air; thus, oxygen can freely come inside to the sample and expose all the Ni particles. This is why the oxidation rate is high in the first stage. However, after 710 °C, the particles start to inter-diffuse and make a barrier (i.e. a semi-continuous surface on top) against arriving air inside the sample. At the same time, some of Ni particles are oxidized, use some of the oxygen, and provide less oxidative atmosphere for other Ni particles. So some of the Ni particles are not oxidized, and this is why even at 1400 °C, some metallic Ni grains can be detected at the depth of 10 µm. It should be noted that the heating and cooling rates are 100 and -50 °C/min, which helps in hindering the Ni oxidation.

![Figure S 7-5 Weight percentage of pure Ni particles vs temperature at heating rate of 100 °C/min in two atmosphere of air and nitrogen. The dotted line shows the maximum calculated weight gain.](image)

Figure S 7-5 Weight percentage of pure Ni particles vs temperature at heating rate of 100 °C/min in two atmosphere of air and nitrogen. The dotted line shows the maximum calculated weight gain.
Figure S 7-6 SEM micrographs of FIB cross section in the sheet with the uncoated Ni particles, heated to (a)1150 and (b)1400 °C in air; STEM micrograph with EDS oxygen mapping from the bottom of the cross section, shown in Fig. (a).

The FIB cross section of the sheets with Ni particles, which were sintered at 1330-3 and 0.02% oxygen, are presented in Figure S 7-7. Figure S 7-7 (a) shows a network of NiO grain boundaries at the top of the sheet, which is the indicator of oxidizing atmosphere and Ni oxidation, as discussed above. The cross section at line 1 and 2 in Figure S 7-7 (a), is presented in Figure S 7-7 (b) and (c), respectively. The SEM micrographs with the SEM-EDS results suggest that the layer with the dark contrast is a continuous layer at the top of the sheet, with the average thickness of 1.5 µm. This observation matches well with the mechanism explained above regarding Ni particle oxidation. Above ~700 °C, a semi-continuous layer formed on the top of the sheet, as can be implied by Figure S 7-4 (a), and only the top layer of the sheet was
oxidized during the rest of the sintering process through oxygen diffusion. The number of oxide grains is much smaller in the depth of this sheet, since the amount of oxygen is much lower in the surrounding gas, so that less Ni phase is sacrificed to preserve the other Ni grains.

![SEM micrographs of the sheet with the uncoated Ni particles, sintered at 1330-3 in 0.02% oxygen flow; (a) the surface of the sheets; two FIB cross sections at line (b) 1 (c) 2, as shown in Fig. (a).](image)

Figure S 7-7 SEM micrographs of the sheet with the uncoated Ni particles, sintered at 1330-3 in 0.02% oxygen flow; (a) the surface of the sheets; two FIB cross sections at line (b) 1 (c) 2, as shown in Fig. (a).

By increasing the amount of oxygen to 0.04%, one can find the Li$_2$CO$_3$ residues in both dark and bright contrasts, as presented in Figure S 7-8. The EDS-line-scans confirm that some of the residues have carbon and some do not.
Figure S 7-8 (a) SEM micrograph of the sheet with 17.3 wt.% Li$_2$CO$_3$, sintered at 1330-3 in 0.04% oxygen along with EDS line-scan on line1 and line2, which the data are shown in (b) and (c), respectively.

S4. Resistance measurement

As explained in Material and methods in the main text, the 2-point probe technique was used to measure the resistance by placing two electrodes on the top of the sheets. By some simplification and ignoring the contact resistances, the equivalent circuit for the system can be the schematic circuit, shown in Figure S 7-9. As illustrated in the equivalent circuit, the electron can take path 1 or path 2 from anode to cathode. In path 1, electrons pass through the NiO film on the top of the sheet without entering to Ni substrate. In path 2, the electron perpendicularly
pass the NiO film and enter to the Ni substrate and then pass the NiO film for the second time and goes into the cathode. In reality the electron transfer can happen through both paths, but considering the fact that the resistivity of the NiO film is much larger than the Ni substrate, it would be reasonable to assume that most of the charge transfer occur through path 2. Especially, in the present study, one is interested to the cases with the resistance less than $50\Omega$, which means very thin NiO films. Thus, in the resistance measurements, one measures a mixture of NiO film resistance (which electrons pass perpendicularly) and Ni substrate resistance.

![Figure S 7-9 equivalent circuit of resistance measurement.](image-url)
8 Preserving nickel electrode conductivity during sintering process using lithium carbonate coatings

8.1 Introduction

In the previous chapter, it was demonstrated that Li$_2$CO$_3$ can coat the Ni particles and the resistance of the coated particle was decreased by five orders of magnitude. In this chapter the mechanisms behind this decline would be explored.

Nickel electrodes have been frequently used in electroceramic devices, such as co-fired capacitive devices, multilayer lead free piezoelectrics [130,131,288] and solid oxide fuel cells [128,129]. To protect Ni from oxidation, a heavily reducing atmosphere e.g. $P_{O_2} = 10^{-10}$ atm should be used [214]. This atmosphere introduces a large number of oxygen vacancies to the system, which reduce the insulation resistance properties and also the life time of devices [132,290]. In addition, to obtain an atmosphere with an oxygen partial pressure in order of $10^{-10}$ atm, hydrogen gas should be used as a reducing agent. It was demonstrated that hydrogen can diffuse into electroceramic devices and degrade their insulation properties [51,67,82,83]. In order to avoid these shortcomings, one solution is to sinter the devices in less reducing atmosphere, e.g. $P_{O_2} = 10^{-4}$ atm, without using hydrogen and, on the other hand, using some measurements to preserve Ni electrode conductivity. In the previous chapter, it was illustrated that the resistance of Ni electrode can be kept as low as 1 $\Omega$ by coating Li$_2$CO$_3$ around Ni particles after sintering at $P_{O_2} = 10^{-4}$ atm, while the resistance of the uncoated particle was 140 k$\Omega$ after sintering under the same conditions. Although the Li$_2$CO$_3$ coatings show promising potential in preserving Ni particle conductivity, the mechanism behind the conductivity preservation still needs to be explored.
Two mechanisms were speculated as being responsible for the conductivity preservation in this study. First, the lithium carbonate can decompose in the course of the sintering process and produce CO gas in the presence of carbon [134,340]. CO gas is a reducing agent and can decrease pO$_2$ locally. The source of carbon is the organic materials used in making the electrode paste [133,347]. The second mechanism is to dope the NiO phase in the electrodes with Li$^+$ in order to increase the Ni$^{3+}$/Ni$^{2+}$ ratio and encourage electronic polaron hopping between them [302,315]. Depending on the amount of oxygen, nickel oxide has the possibility of non-stoichiometric defects with Ni vacancies ($V_{Ni}''$) [308,311–314]. $V_{Ni}''$ introduces negative charge to the lattice, which would be compensated by changing the oxidation state of some Ni ions from 2+ to 3+. The mixture of Ni$^{3+}$ and Ni$^{2+}$ enables electron hopping between those ions [301]. Thus, one can argue that the conductivity of NiO phases can be manipulated by changing the Ni$^{3+}$/Ni$^{2+}$ ratio through doping. In the previous work [104], it was illustrated that the resistance of Ni foils after a heat treatment in air can be changed from 1 GΩ doped with Al$^{3+}$ to 2 MΩ doped with Zn$^{2+}$. An EELS (electron energy loss spectroscopy) analysis showed that the ratio of Ni$^{3+}$/Ni$^{2+}$ in the Zn$^{2+}$-doped foil is larger than the Al$^{3+}$-doped foil. If this is the case, Li$^+$ will be a good candidate to dope the NiO phase, since Li$^+$ doping can disturb charge neutrality more and increase the Ni$^{3+}$/Ni$^{2+}$ ratio more effectively. In addition, among the alkali cations, Li$^+$ has the closest ionic radius to Ni ions, and it is expected to have the highest diffusion coefficient in NiO crystals. Li$^+$ and Ni$^{2+}$ ionic radius are 76 and 69 pm [331]. In addition, the other authors have reported the decrease in NiO resistivity due to Li$^+$ doping [321,332].

In the previous chapter, a simple and innovative method to coat Li$_2$CO$_3$ on Ni particles was introduced, and it was illustrated that the coating is able to effectively preserve Ni electrode conductivity. In this chapter, a systematic study on microstructures of Ni electrodes during
decomposition and the atom distribution in the Ni electrodes was executed to explore the mechanisms that are responsible for conductivity preservation.

### 8.2 Experimental Section

To coat Ni particles with Li$_2$CO$_3$, the compound was dissolved into deionized water, and then Ni particles were added and stirred to make sure of the full wettability of Ni particles. Next, the mixture was heated to evaporate the liquid, while it was mechanically stirred during the entire process. The solution reached saturation, and the chemical compound started to deposit on Ni particles. More detail about the coating process is given in Supporting Information and in the previous chapter.

The Li$_2$CO$_3$ was bought from Alfa Aesar in powder form, with 99.998 % purity. The Ni powder was the courtesy of JFE Mineral Company and Shoei Chemical, with the average particle size of 300 nm and purity of 99+. If it did not specify in the text, 17.3 wt% of Li$_2$CO$_3$ was used for coating Ni particles.

6 grams of the coated particles were mixed with 1 gram of the 15 wt.% ethyl cellulose solved in dihydro terpineol. The final product was a liquid mixture with a high viscosity, commonly referred to as “electrode ink”. Then the ink was painted on a piece of 1 cm by 0.5 cm alumina sheet and dried at 120 °C for 20 minutes. After that, the alumina sheets were exposed to different heat treatments at different atmospheres. The heating and cooling rates were 100 °C/min and -50 °C/min, obtained by a homemade fast-heating furnace [295]. The sintered particles were referred as “sheet” in this study. The nitrogen and carbon dioxide gases have the purity of 99.999% and 99.99%, respectively. The source of oxygen was the cylinder with 0.1% oxygen balanced with nitrogen.
The electrical resistance measurement was executed by a two-probe method and was explained elsewhere [134]. The SEM (scanning electron microscope) micrographs and TEM (transmission electron microscope) samples were obtained by FEI Helios NanoLab 660 FIB/SEM. The TEM analysis was done by FEI TALOS F200X and TECNAI G20, equipped with EELS (electron energy loss spectroscopy). The TGA (thermogravimetric analysis) tests were done by TA Instrument SDT Q600.

### 8.3 Lithium carbonate decomposition

Lithium carbonate decomposed into Li$_2$O and CO$_2$ around 763°C, based on TGA (thermogravimetric analysis) tests in Supporting Information. Subsequently, CO$_2$ would be converted to CO in the presence of carbon [340,345]. The next reaction in low partial pressure of oxygen and the presence of Ni as a catalyst could be the CO decomposition to oxygen and carbon [134]. In Supporting Information, it was demonstrated that the peak of the maximum weight loss in TGA tests due to the decomposition reaction can be pushed back from 819 °C in air to 1086 °C in nitrogen and 1235 °C in carbon dioxide. Also, the results suggest that the decomposition rate of pure Li$_2$CO$_3$ powders would be significantly different in CO$_2$ and nitrogen atmosphere. The effect of sintering atmosphere was discussed in more details in Supporting Information. For instance, applying CO$_2$ atmosphere during sintering could hinder the first reaction (i.e. producing CO$_2$ gas) in the chain of the decomposition process; due to the extra CO$_2$ gas, the reaction would be reluctant to proceed to the right and produce more CO$_2$ gas, based on Le Chatelier's principle. In other words, Li$_2$CO$_3$ can be preserved in CO$_2$ atmosphere up to 1235 °C. Thus, one may conclude that the Li$_2$CO$_3$ decomposition can be manipulated by applying different sintering atmosphere.
The lithium carbonate decomposition was investigated by heating the coated particles to 900 °C and cooling down without holding at five different atmospheres of CO₂, pure nitrogen, 0.02% oxygen, 0.04% oxygen, and air. The SEM micrographs of the FIB cross section of these sheets are presented in Figure 8.1. The microstructure of the sheet, exposed to 900 °C in CO₂, is presented in Figure 8.1 (a). Based on the discussion above, this micrograph can represent the mixture of Ni and Li₂CO₃ in the early stage of sintering, as if there is no Li₂CO₃ decomposition. As shown in the micrograph, the Li₂CO₃ without decomposition is able to melt and surround all Ni grains; one can consider that as a liquid phase sintering, in which one compound gets melted at the beginning of sintering and surrounds the grains of the second powder [343,344]. In addition, since there is an unlimited source of CO₂ due to blowing CO₂ gas into the chamber, all the residual carbon would be eliminated by \( CO_2(g) + C(s) \rightarrow 2CO(g) \) in the early stage of sintering [354].

Figure 8.1 (b) shows the micrograph of the sheet, sintered under pure nitrogen. There is a thick layer of carbon on the top of the sheet. In the absence of an unlimited source of CO₂ gas and the presence of residual carbon, Li₂CO₃ decomposed to CO. In the next set of reactions, due to the lack of oxygen, CO decomposed and redeposited carbon on Ni particles at the top of the sheet based on Eq.8.1 [349,354,355]. More evidence is provided elsewhere [134] and also in Figure S 8-3, presented the TEM analyses of the carbon layer.

\[
2C(s) + O_2(g) \xrightarrow{Ni} 2CO(g)
\]

Eq.8.1

Now, oxygen would be added to the scenario and increased to 0.02 and 0.04 vol.% and, eventually, air; the microstructure of the sheets is presented in Figure 8.1 (c) to (e), respectfully. The thickness of the carbon layer on the top of the sheets, sintered in nitrogen, 0.02, and 0.04
vol.%, were measured 2.29, 2.0, and 1.6 µm on average, and it disappeared in air. This suggests that the carbon re-deposition decreases by increasing oxygen and, eventually, it becomes zero in air. That observation fits well with the explanation of Eq.8.1, in which it is suggested that increase in the amount of oxygen drives the equilibrium to the right and prevents carbon re-deposition.

The other observation is that, by increasing the amount of oxygen from pure nitrogen to air, the amount of weight loss increases and as a result, the space between individual Ni grains would increase. The trend of this phenomenon can be traced in Figure 8.1 (b) to (e). There is a small number of the isolated Ni grains on the top of the cross section in Figure 8.1 (c); their number increased by increasing the oxygen flow from 0.02 to 0.04% oxygen, and they overcame the entire cross section in air, as shown in Figure 8.1 (d) and (e). This is due to the fact that the Li$_2$CO$_3$ can lose up to 59% of its original weight during the decomposition process. On the other hand, the system can simultaneously compensate some of the weight loss by the carbon re-deposition. Increasing the oxygen flow would hinder the carbon re-deposition process and weight loss would be manifested as the empty space between the grains. To verify this explanation, the amount of Li$_2$CO$_3$ decreased from 17.3 wt.% to 3.4 wt.% in the coating process, and the resultant particles heated to 900 °C in air. The cross-section of this sheet is presented in Figure S 8-5. It can be seen that the empty space between grains decreased significantly due to the decrease in the Li$_2$CO$_3$ percentage and, consequently, the weight loss. Furthermore, a similar conclusion can be reached from TGA tests in Supporting Information.

Now, the importance of Figure 8.1 (a) can be better appreciated. Since CO$_2$ prevented Li$_2$CO$_3$ decomposition and eliminated residual carbon, Figure 8.1 (a) shows the ideal case of neither the Li$_2$CO$_3$ decomposition nor the carbon re-deposition; the Li$_2$CO$_3$ coating only melted
and enclosed Ni grains. In the mixture of oxygen and nitrogen gas, on the other hand, Li$_2$CO$_3$ did the same thing, but it was simultaneously decomposed. However, the decomposition is not necessarily a harmful process, since it produces CO gas and limits the NiO phase formation during the sintering process, as will be discussed in more details later.

Figure 8.1 The SEM micrographs of FIB cross section of the sheets with 17.3 wt.% of lithium carbonate, heated up to 900 °C at (a) carbon dioxide, (b) nitrogen, (c) 0.02% oxygen (c) 0.04% oxygen, and (d) air.
A detailed study on the Li$_2$CO$_3$ decomposition and carbon re-deposition vs. temperature at 0.04% oxygen flow is given in Supporting Information.

8.4 Li$^+$ effect and distribution

The second mechanism for reducing resistivity is the Li$^+$ doping effect, as discussed in the introduction. In order to illustrate the Li$^+$ contribution, two sheets with similar microstructure were selected. The first sheet was made of coated particles and sintered at 1330°C for 3 minutes at 0.04% oxygen, and the other one was made of uncoated particles and sintered in the same program but at 0.02% oxygen. Their microstructures are presented in Figure 8.2 (a) and (b); there is NiO layer on the top of both sheets, with the minimum thickness of 2.0 and 1.3 µm, respectively. Both sheets have a similar microstructure, in the sense that both have a NiO layer on top. Although the NiO layer is thicker on top of the sheet with Li$_2$CO$_3$, its resistance was measured as 43Ω, while the resistance of the sheet without Li$_2$CO$_3$ was measured as 140kΩ [134]. A four orders of magnitude decrease in resistance in the sheets with a similar microstructure comes from the Li$^+$ doping effect. The microstructure of the coated particles were further investigated in the Supporting Information (Figure S 8-1).

The other observation in Figure 8.2 (a) is that the final microstructure of coated particles is a mixture of Ni and NiO grains with some black islands; that type of microstructure was also noted in the previous chapter. Figure 8.3 shows one of the islands in its matrix together with its EDS (energy dispersive spectroscopy) analysis. As Figure 8.3 (a) shows, the matrix is made of Ni and NiO grains, and the island is made of a mixture of oxygen, carbon, and lithium and would be called LiCO area. The EDS map of Figure 8.3 (a) is shown in Supporting Information. The
map shows that there is a mixture of Ni and C at the border of the island, suggesting the interdiffusion of the island and the matrix.

Figure 8.2 SEM micrographs of FIB cross section in the sheets, made of (a) coated particles and sintered in 1330 °C for three minutes at 0.04% oxygen (b) uncoated particles and sintered in the same sintering program but at 0.02% oxygen.

Figure 8.3 (b) shows the LiCO area in a higher magnification, and its EDS maps are presented in Figure 8.3 (c-e). The EDS analysis suggests that there is not a detectable amount of Ni in LiCO region, and the amounts of oxygen and carbon are not uniformly distributed in the LiCO region. In order to quantitatively show the distribution of carbon and oxygen, an EDS line-scan and the molar ratio of carbon over oxygen, based on EDS data, are presented in Figure 8.3 (f) and (g), respectively. The line-scan data come from the line, shown in Figure 8.3 (b) and labeled as ‘EDS line scan’. Three regions are detectable: carbon-rich, Li$_2$CO$_3$, and carbon-depleted. These three areas can be located, based on Figure 8.3 (g), where some areas are above, below, or on the line of 1/3 molar ratio of carbon over oxygen. Since we are certain that the atoms in LiCO region are limited to Li, C, and O (the existence of Li would be demonstrated by EELS later), one can argue that all the plausible solid phases are Li$_2$O, Li$_2$CO$_3$, and pure carbon.
By considering the cooling rate of -50 °C/min in the heat treatments and eutectic reaction at 705 °C in Li$_2$O and Li$_2$CO$_3$ phase diagram [356], one can argue that the LiCO area is made up of non-equilibrium phases of Li$_2$O and Li$_2$CO$_3$, with some rich carbon areas due to the carbon re-deposition.
Figure 8.3 (a), (b) STEM-Dark Field micrographs of the Ni sheet with 17.3 wt.% Li$_2$CO$_3$ sintered in 1330-3 in 0.04% of oxygen flow. The EDS map of (c) carbon, (d) oxygen, and (e) nickel from the area, shown in figure (b). (f) intensity (g) molar ratio of carbon over oxygen vs distance on the line, showed in figure (b). The EELS line scan 1 and 2 are the lines, where EELS analysis in Figure 8.4 (a) and (c) were done.

The LiCO islands were separated from each other and made a small portion of the microstructure, while the matrix (i.e. the continuous phase) was made of Ni-NiO grains, as shown in Figure 8.2 (a) and Figure 8.3 (a). So the most of the electron conductivity happened through the matrix, whose conductivity was determined by Li$^+$ concentration and Ni$^{3+}$/Ni$^{2+}$ ratio.

Two sets of data, Li$^+$ distribution and Ni$^{3+}$/Ni$^{2+}$ ratio, can be provided by EELS analysis. Figure 8.4 (a) presents the intensity of Li$^+$ edge vs. distance on the line, labeled as ‘EELS line-scan 1’ in Figure 8.3 (a). The intensities suggest that the Li$^+$ concentration is maximum at the border of the LiCO island and decrease with distance from it. By passing the Ni-NiO grain boundary, the intensity becomes considerably low, indicating Li$^+$ concentration is negligible in Ni grains. To verify this conclusion, four spectrums of EELS analysis at different points are shown in Figure 8.4 (b). As discussed in literatures, Li K-edge can be shifted from 54.7 to 61 eV for different Li bonding [357–359], and Ni has its M$_{2,3}$ edge at 68 eV [357]. As can be seen, two edges can be detected at 58.5 and 65 eV in spectrum (1), (2), and (3), which are collected from
NiO grain. The place of these points are marked in Figure 8.4 (a). The spectrum (1) to (3) can be a signature for Ni, Li, and O coexistence. The concentration of Li was related to the intensity of the edge at 58.5 eV. As illustrated in spectrum (4), Li\(^+\) edge becomes negligible in the Ni grain and the Ni M\(_{2,3}\) edge shift from 65 eV back to 68 eV.

The other set of experiments is core-loss EELS and collecting Ni energy loss at 845 and 874 eV. The ratio of the intensity of the second edge over the intensity of the first edge, shown by R in this chapter, is equivalent to the Ni\(^{3+}\) concentration over Ni\(^{2+}\) concentration \([313,316,317]\). So one would be able to trace Ni\(^{3+}/Ni^{2+}\) ratio by EELS analysis, as demonstrated in the previous chapter. The significance of Ni\(^{3+}/Ni^{2+}\) in Ni conductivity was discussed in Introduction and chapter 6 and 7.

Figure 8.4 (c) presents R vs. distance; the EELS data were collected on the line, labeled as ‘EELS line-scan 2’ in Figure 8.3 (a). A comparison between Figure 8.4 (a) and (c) suggests that the ratio of Ni\(^{3+}/Ni^{2+}\) increased by increasing Li\(^+\) concentration except near the island, where Li concentration exponentially increased, while R ratio reached a plateau at 0.45. This upper limit can be justified as the state in which all of the Ni\(^{2+}\) ions has been converted to Ni\(^{3+}\) to compensate the charge offset due to Li\(^+\) introduction. On the other hand, there is a lower limit for R, where stoichiometric NiO with minimum Ni\(^{3+}\) was tested. The lower limit of R was reported as 0.25 by the authors [104] and Muto et al. [317] As can be seen, every point in the curve of Figure 8.4 (c) is above the lower limit. One may conclude that Li\(^+\), even in low concentration, can effectively increase Ni\(^{3+}\) in the entire NiO grain. Three typical spectra were selected from the line scan in Figure 8.4 (c) and are presented in Figure 8.4 (d). Spectrum (1) is a typical spectrum, which can be found near the LiCO island and since the Ni is diluted by carbon and lithium, its edge intensity is low. By going away from the island, the spectrum evolved to (2) and (3), and
the edge intensity increased due to increase of Ni concentration. However, as explained above, the interest of this research is the R and Ni$^{3+}$/Ni$^{2+}$ ratio.

Now, one can have a complete image of the electron conductivity in the sheets. The conductivity occurred through the continuous matrix of Ni and NiO grains. Electrons can easily transfer through Ni metallic grains, and when they reach the Li doped NiO grains, the electrons can still pass them without much increase in resistivity through the polaron hopping process. This mechanism can justify the decline in the resistance of the sheets, shown in Figure 8.2, from 140kΩ to 43 Ω.

![Figure 8.4](image)

Figure 8.4 (a) The intensity of Li edge and (c) the ratio of second edge over the first edge in Ni spectra (shown as R) vs distance along with the image, where the analysis was executed. Typical spectrums in line scan of (a) and (c) are shown in (b) and (d) respectively.
8.5 The effect of lithium carbonate decomposition on conductivity preservation

The influence of Li$^+$ is shown in the previous section specifically by comparing the two cases in Figure 8.2. It would be informative to repeat the same experiment with and without the effect of Li$_2$CO$_3$ decomposition. In order to do so, CO$_2$ gas was utilized during sintering. As suggested previously, CO$_2$ can preserve Li$_2$CO$_3$, and at the same time, burn out all residual carbon. Thus, without the residual carbon, the sintering atmosphere would be CO$_2$ gas (with a purity of 99.99%) without any reducing agents (i.e., CO). The coated particles were sintered at 1330 °C for 3 minutes in CO$_2$ gas and, afterward, their resistance was measured as 1.2 kΩ, while the resistance of uncoated particles was measured as 80 kΩ. One can argue that this decrease in resistance is only due to the Li$^+$-doping effect.

One can argue that the coated particles sintered at CO$_2$ atmosphere can be compared with the coated particles sintered in 0.02% oxygen balanced with nitrogen. The atmosphere with 0.02% oxygen possessed a higher oxygen content than the CO$_2$ atmosphere since the CO$_2$ gas only had a 0.01% impurity comprised of oxidizing agents. In addition, the resistance of uncoated particles, after sintering in the CO$_2$ and 0.02% oxygen, were measured as 80 and 140 kΩ, respectively. Thus, the 0.02% oxygen atmosphere is more oxidizing than the CO$_2$ atmosphere.

Next, the coated particles were sintered in the 0.02% oxygen atmosphere, and their resistance was measured as 10Ω. This value is two orders of magnitude less than the 1.2 kΩ resistance of the CO$_2$-sintered sheet. Furthermore, the FIB cross section of the CO$_2$-sintered sheet, presented in Figure S 8-4, showed a thick NiO layer of 1.5 µm on the top of the sheet. However, this layer would be negligible in 0.02% oxygen with the average thickness of 0.1 µm.
as shown in Figure S 8-3 (The effect of the Li$_2$CO$_3$ decomposition on NiO layers were further investigated in the previous chapter). It can be concluded that although 0.02% oxygen is more oxidizing than the CO$_2$ atmosphere, the coated particle would have less NiO phase and consequently less resistance due to the decomposition of Li$_2$CO$_3$ and the production of CO gas.

8.6 Conclusions

Coating Ni particles with Li$_2$CO$_3$ can preserve the electrical conductivity of the resultant electrode in more oxidative atmospheres during sintering which can offer significant improvements in electroceramic processing and electrical properties by limiting the concentration of oxygen vacancies. In this study, the underlying mechanisms in the process of conductivity preservation were explored and understood. Two mechanisms of Li$^+$ doping and Li$_2$CO$_3$ decomposition were introduced, and their effects on conductivity preservation were studied independently. It was shown that the Li$_2$CO$_3$ melted and flowed around the Ni grains; at the same time, it decomposed into CO gas. The CO acted as a reducing agent and could hinder the NiO formation. In addition, a layer of carbon on the sheets was the result of CO gas existence; its thickness was found to be dependent on oxygen percentage and temperature. It was demonstrated that by applying CO$_2$ gas during the sintering process, the reducing effect of CO gas could be eliminated and, as a result, the resistance increased from 10Ω to 1.2 kΩ in the same concentration of Li$^+$. 

The final microstructure of the sheets was a matrix of Ni and NiO grains with islands of residual Li$_2$CO$_3$. The distribution of ions were mapped for this microstructure. The Ni$^{3+}$/Ni$^{2+}$ ratio, which controls electron hopping and resistivity reduction in NiO phases was also
measured. Two similar microstructures, with and without Li$^+$, were selected, and it was shown that the Li doping effect can decrease the resistance from 140 kΩ to 43 Ω.

Both previous observations suggested that the Li$^+$ doping effect and the production of CO gas were both relevant in preserving the electrical conductivity. The CO gas, as a reducing agent, decreased the amount of NiO phases and hence the oxidation of metallic Ni, while the Li$^+$ doping decreased the resistance via increasing the Ni$^{3+}$/Ni$^{2+}$ ratio. The combination of both mechanisms resulted in a five-orders-of-magnitude decrease in the resistance of the sheets.

### 8.7 Supporting Information

A schematic of the setup, used in this study, is presented in Figure S 7-1. The setup up was made of a mechanical stirrer, beaker, and heater. 1.21 grams of Li$_2$CO$_3$ powder were added to 200 ml of deionized water and stirred to obtain the full dissolution. Next, 6 grams of Ni particles were added. After making sure of full wetting between Ni particles and solution, the liquid was evaporated during stirring. When the solution became saturated, the Li$_2$CO$_3$ started to nucleate and grow on Ni particles. This method was successful for coating Li$_2$CO$_3$ and other lithium chemical compounds on Ni particles, as explained in previous work [134].

**The Microstructure of sheets after sintering at 1330-3 in 0.04% oxygen**

The microstructure of the sheet, after exposing to 1330 °C for three minutes in 0.04% oxygen, is shown in Figure S 8-1. This heat treatment is suitable for sintering BME (base metal electrode) BaTiO$_3$ powders. The Li$_2$CO$_3$ residue with black contrast can be detected at the grain boundaries. The FIB cross section illustrated in Figure S 8-1 (b) and (c) shows the grain boundary can be as deep as 1.1 µm. There is a continuous layer of NiO on the top of the sheet with minimum thickness of 1.9 µm. The FIB cross section is comparable with the cross section,
presented in Figure 8.2 (a); both taken from the same sample, but different places. Based on the EELS analysis, one can expect that the top NiO layer was doped with Li$^+$ and had high ratio of Ni$^{3+}$/Ni$^{2+}$. The Li$^+$ doping caused the resistance of the sheet to be considerably decreased, as discussed in the text.

![SEM micrographs of the sheet](image)

Figure S 8-1 SEM micrographs of the sheet, made of coated particles and sintered at 1330 °C for three minutes in 0.04% oxygen. (a) is the top view of the sheet. (b) and (c) are the milled hole and the FIB cross section.
TEM analyses

The micrograph of LiCO island in the Ni-NiO matrix, together with its EDS maps, is presented in Figure S 8-2. The Ni and O maps show the coexistence of Ni and NiO grains in the matrix. The carbon map shows that the carbon goes beyond LiCO island, and there is mixture of Ni and carbon at the border.

Figure S 8-2 HAADF micrographs and EDS maps of the LiCO island in the Ni/NiO matrix.
A TEM sample was prepared from the coated particles, sintered at 1330°C for 3 minutes in 0.02% oxygen. The EDS maps suggest that the layer on top of the sheet is made of carbon, due to the fact that the carbon map shows strong signals on the top of the sample, and the other maps do not show a significant signal. Since the carbon layer is softer than the Ni substrate, some of it is milled away during the TEM sample preparation; however, there is enough material left to demonstrate the top layer is made of carbon.

Figure S 8-3 HAADF micrographs and EDS maps from the top layer of the sheet, made of coated particles and sintered at 1330 °C and 3 minutes in 0.02% oxygen flow.
Sintering at CO$_2$ atmosphere

The SEM micrograph of the coated particle, after sintering at 1330 °C for 3 minutes in CO$_2$ gas, is presented in Figure S 8-4. As discussed in chapter seven, the microstructure, shown in Figure S 8-4(a), is an indicator of Ni oxidation during sintering. In addition the FIB cross section in Figure S 8-4(c), shows a NiO layer on the top of the sheet with 1.5 µm thickness.

Figure S 8-4 SEM micrographs and FIB cross section of the coated particle, sintered at 1330 for 3 minutes in CO$_2$ gas. (a) is the top view of the sheet. (b) and (c) are the milled hole and the FIB cross section.
Supporting Figures

Figure S 8-5 SEM micrograph of FIB cross section from the sheet with 3.4 wt.% lithium carbonate, exposed to 900 °C in air.
9 Decreasing Oxygen Vacancies in Multilayer Ceramic Capacitors by Preservation of Electrode Conductivity in Oxidizing Sintering

9.1 Introduction

Nickel electrodes have been being widely used in electroceramic industries; particularly, the nickel and BaTiO₃ system has been studied many times [132,133,289–291]. The technology of cofiring of BaTiO₃ and Ni was first introduced by Herbert [326] in 1963 and provided the foundation to revolutionize the dielectric industry in 1980s [132]. The introduction of Ni electrode instead of platinum or palladium had the advantage of major cost reduction, the ability to increase the layer count, and reduce the dielectric layer thickness. But to be useful as an inner electrode, the Ni electrode had to remain metallic, and thereby a reductive atmosphere in the order of \( P_{O_2} = 10^{-10} \) atm [214] should be used. However, the reductive atmosphere heavily introduces oxygen vacancies to BaTiO₃ and reduces its insulation resistance and also the life time of capacitors [132,290]. Obtaining a reducing atmosphere on this order requires using hydrogen as a reducing agent. H⁺ ions can also degrade the resistance of multilayer ceramic capacitors and increase their leakage current [51,67,82,83].

The quality of capacitors is evaluated by their dissipation factor, DF, (also known as loss tangent), their insulation resistance, and their reliability.

Conventionally, the DF of MLCCs is too high, due to the large number of oxygen vacancies introduced during sintering at \( P_{O_2} = 10^{-10} \) atm. In order to decrease the oxygen vacancies, a post-reoxidation process, an annealing at relatively oxidizing atmosphere, will be executed. However, one should be cautious and not cause too much oxidation in Ni electrode and lose their conductivity. So, in other words, the reoxidation processes is finding the optimum
point between the lowest dielectric conductivity due to oxygen vacancies and the highest Ni electrode conductivity to minimize DF. The friction due to reorienting dipoles can be ignored, as long as the dielectric material and its microstructure do not change.

The nickel and BaTiO$_3$ multilayers, and especially the Ni electrode itself, [296,298,299,323,360–362] have been studied in detail. As mentioned above, one common practice is to reduce the amount of oxygen vacancies by post-reoxidation process. This technique is based on the fact that the oxygen ions have a lower diffusion rate in NiO ($D_{\bar{V}_O} = 0.0164\exp(-11276.6/T))$ [300] than oxygen vacancies in BaTiO$_3$ ($D_{\bar{V}_O} = 5700\exp(-23780.6/T))$ [363] at temperature of 700 $^\circ$C or higher (both diffusion coefficients are in cm$^2$/s). So the Ni oxidation will be the slowest reaction, and the BaTiO$_3$ can be partially reoxidized without too much oxidation of the Ni electrodes. However, Weiss [364] argued that, because of the geometry of MLCCs, the BaTiO$_3$ between electrodes can never reach the fully oxidized state.

The idea in this work is rather different than the previous approaches. The MLCCs was cofired in a less reducing atmosphere at $P_{O_2} = 10^{-4}$ atm instead of $10^{-10}$ atm to introduce lower number of oxygen vacancies in the first place and eliminate the need of using hydrogen gas. But to preserve Ni conductivity, two methodologies would be used. First, the fast firing technique was utilized to conclude the sintering process faster and hinder the Nickel oxidation kinetically. Mostaghaci and Brook [365] showed that fast sintering can promote densification over grain growth [365]; this promotion eventually causes a faster densification in comparison to traditional sintering processes, and the sintering can be executed in a shorter period of time. Second, it was demonstrated in the previous paper that the Ni particles, coated with Li$_2$CO$_3$, can reduce the
resistance of Ni particles from 140 kΩ to 1 Ω in a less reducing atmosphere (e.g. \(P_{O_2} = 10^{-4}\)) [134]. The \(Li_2CO_3\) decomposing locally produces reducing atmosphere with CO/CO\(_2\) gases, and simultaneously the Li ion dopes the new-formed NiO phases and reduced their resistivity [322]. In order to evaluate the merit of this approach, the coated Ni particles were utilized in manufacturing MLCCs, and their electrical properties would be compared with the MLCCs without coated Ni particles and the conventional MLCCs.

9.2 Experimental procedures

The preparation process of multilayer ceramic capacitors included tape casting, screen printing, and pressing; this was a standard process in the electroceramic field and explained elsewhere [82]. However a new binder system (i.e. poly-propylene carbonate) [366] was utilized in this study. The green samples were burnt out with heating rate of 2 \(^0\) C/min to 210 \(^0\) C and holding for 5 minutes. Next, the samples were fast fired at 1300, 1330, and 1360 \(^0\) C for three minutes with heating and cooling rate of 100 and -50 \(^0\) C/min at different oxygen flow from 10 ppm to 200 ppm. These high heating rates were obtained by utilizing a homemade fast-heating furnace [295]. Two types of Ni electrode, uncoated and coated, were used in this study. The preparation process of Ni inks, used for printing electrodes, was explained elsewhere [134]. 3.4 wt.% \(Li_2CO_3\) was used during the preparation of the coated Ni particles. In this paper, the fast-fired MLCCs with the coated and uncoated Ni particles, referred as the Coated and Uncoated samples, respectively. In order to put these samples in contrast with the conventionally manufactured MLCCs, some samples were sintered at 1300\(^0\) C for two hours with ramping rate of 4 \(^0\) C/min at pO\(_2\)=10\(^{-9}\) atm. Next, they were reoxidized at 700\(^0\) C in air for three hours. These
samples, produced based on the conventional manufacturing technique [367], would be called ‘Conventional’.

The source of oxygen was the cylinders with 0.1% oxygen balanced with nitrogen. This gas was diluted with UHP (ultra-high purity) nitrogen to obtain the above oxygen flows. The BaTiO₃ powder was supplied courtesy of Ferro Corporation and was commercially known as X7R312N.

The electrical properties of the capacitors were measured by Keysight Technologies E4980AL LCR meter, and their temperature was controlled by Delta Design 9023 oven. The impedance spectroscopy test were executed by Solartron Module Lab XM in the frequency range of 0.01 Hz to 10⁶ Hz. The SEM (scanning electron microscope) micrographs and FIB (Focused Ion Beam) cross sections were obtained by FEI Helios NanoLab 660 FIB/SEM. The TEM (transmission electron microscope) samples were prepared by the same FIB system and the TEM analysis was done by FEI Titan G2. The TOF-SIMS analyses were done by PHI nano TOF II manufactured by Physical Electronics (Chanhassen, US).

9.3 The effect of Ni coated particles on MLCCs

The effect of three variables: sintering schedule, oxygen flow, and Li₂CO₃ coating, were all studied in the sintering of the MLCCs. The first step was to explore at what conditions (i.e. sintering schedule and oxygen flow) we were able to a functional MLCC prototype. If either sintering temperature or oxygen flow were too high, the Ni electrode would be completely oxidized and could not transfer electrons due to their high resistance. As a consequence, the capacitance would be on the order of Pico-farads. On the other hand, in the devices with no or partial Ni oxidation, the capacitance would be on the order of Nano-farads. Thus, simply
measuring the capacitance of MLCCs after manufacturing can offer a criteria to differentiate between the failed and the functional MLCCs.

Table 9.1 shows the capacitance and loss of MLCCs, produced at different conditions. The data were all measured at 1 V and 1 kHz. The box for the failed devices was left blank in Table 9.1. One can see that the maximum oxygen flow for manufacturing a functional MLCC decreases by increasing the maximum temperature in the sintering schedules. It indicates that the higher sintering temperatures increased the kinetic of NiO formation and caused the Ni electrodes to be oxidized in less oxygen flow. In addition, one can compare the influence of coating Ni particles at different conditions to its counterpart without coating. In all cases, the amount of capacitance increased and loss decreased by using coating Ni particles. As a reference, the capacitance and loss of the sample produced in the conventional manner is also given in Table 9.1 before and after the reoxidation process. It can be seen that the loss of all the samples with the coated Ni particles is lower than that of the conventional MLCC after the reoxidation. However, since the microstructure and the grain size of the conventional MLCC is not similar to the fast fired ones due to the different heat treatment history, the comparison of their property cannot be justified. However, presenting the results of the conventional MLCCs would provide a context for the results of the fast-fired MLCCs introduced in this study. More conclusions with the support of further characterization will be drawn later from Table 9.1.
A standard test to evaluate the performance of MLCC is temperature-dependent permittivity and dissipation factor tests. The results of these tests are shown in Figure 9.1 for the MLCCs, fast fired in different oxygen flow with the coated and uncoated Ni particles. DF is the ratio of resistivity (R) over reactance (X), and since both R and iX have the same unit, DF is a dimensionless parameter. Because of that, geometry factors do not contribute to DF, and it is a suitable parameter to compare the merit of different capacitors. As seen in Figure 9.1, DF is the same for the coated and uncoated samples in 10 and 40 ppm oxygen flow; however, it increased considerably by increasing oxygen flow to 80 and 120 ppm. As demonstrated in Supporting Information (Figure S1), the lowest DF is the optimum point between the lowest dielectric conductivity and the highest conductivity of electrodes. By increasing the oxygen flow during the sintering, the number of oxygen vacancies decrease and cause the dielectric conductivity
decrease. But due to the Ni oxidation, the electrode conductivity declines in the uncoated sample, and consequently the DF in these samples will increase. In the following, the Ni electrode oxidation will be studied.

Figure 9.1 permittivity and DF, measured at 1 V and 1 kHz versus temperature for the MLCC with the coated and uncoated Ni particles, which were sintered at 1330-3 at different partial pressure of oxygen.
The oxidation of Ni electrode as function of increasing the oxygen flow was systematically tracked by SEM (scanning electron microscope) imaging from the FIB (focused ion beam) cross section of electrodes of Uncoated MLCCs, sintered at 1330-3 and in different oxygen flow. The micrographs are shown in Figure 9.2.

As seen in Figure 9.2 (a), no oxidation was detected at 10 ppm around Ni electrode. 10 ppm is equivalent to $10^{-5}$ of partial pressure of oxygen, and based on the Ellingham diagram, it is high enough for the formation of NiO under equilibrium conditions. However, the fact that no NiO phase was detected in the electrode—at least in the magnification, shown in Figure 9.2 (a)—suggests that the fast sintering process kinetically prevent the NiO formation.

A thick layer of NiO was detected on the back of Ni electrode at 40 ppm, as shown in Figure 9.2 (b). This layer was formed due to the fact that the gas flowed directly toward the top of the sample and oxidized the top of the top electrode more than the other parts. The sample and the gas flow were shown schematically in Figure S3 in Supporting Information. However, the NiO layer was not between the electrode and the active layer (the dielectric between two electrodes is called active layer); it does not affect the electron transfer from the electrode to the dielectric.

These observations suggest that the fast firing alone is sufficient for the prevention of NiO formation at the interface of electrode-dielectric in 10 and 40 ppm oxygen flow. This is why the DF is similar for the Coated and Uncoated samples in Figure 9.1.

By increasing the amount of oxygen to 80 and 120 ppm, as shown in Figure 9.2 (c) and (d), the NiO phase spread all around the electrode, and since it has high resistivity, it will hinder the electron transfer between the electrode and the dielectric. It was demonstrated elsewhere [134,322] that the resistance of the coated Ni particles stays below 1 $\Omega$ at the oxygen flows
below 200 ppm, while the resistance of the uncoated particles increase to 140 kΩ. This is why the DF would increase in the Uncoated samples at 80 and 120 ppm in Figure 9.1, while it would remain low for the Coated counterparts. In addition, it should be noted that the minimum DF of 0.9% was detected for the Coated MLCC, sintered at the oxygen flow of 120 ppm, as presented in Table 9.1. The low DF is indicative of the fact that the optimum condition of lowest electrode resistivity and highest dielectric resistivity can be achieved by utilizing the coated Ni particles. The Coated sample would be compared to each other in the next section.

Figure 9.2 (e) shows the extreme oxidizing atmosphere of 200 ppm oxygen flow, in which all of the Ni electrode becomes entirely oxidized. Since NiO density is lower than the Ni density, the oxidized electrode would be expand by 52%, and the original 2.8 µm Ni electrode will expand to 4.2 µm NiO layer.

It should be noted that the heating rate of 100 °C/min, utilized in this study, provided a fast densification [134,297] for the Ni particles. So one can argue that the Ni particles densified in the early stage of sintering process (i.e. at 700 °C [134]) and then starts to be oxidized at the interface of Ni-BaTiO₃ at higher temperatures. So this is why the NiO phase would appear as a layer around the Ni electrodes and no NiO phase was detected inside the Ni electrodes.
Figure 9.2 SEM micrographs of the Ni electrodes, buried in BaTiO$_3$ dielectric, the sample are sintered at 1330-3 and in oxygen flow of (a) 10, (b) 40, (c) 80, (d) 120, and (e) 200 ppm.

It should be noted that the capacitance/permittivity of the Coated samples are larger than that of their Uncoated counterpart in every case, shown in Table 9.1 or Figure 9.1. Every processing parameter (i.e. sintering schedule, oxygen flow, and dielectric powders) was kept the same during the manufacturing of both Coated and Uncoated MLCCs except the electrodes, which could be made of the coated or the uncoated Ni particles. Thus, one can argue that their difference was due to the Li$_2$CO$_3$ coating.

Impedance spectroscopy can be extremely useful to separate the contributions of the different elements in MLCCs (i.e. grain, grain boundary, and electrode interface impedances) [82,214,229]. Thus, impedance spectroscopy analysis was applied to the samples at four different
temperatures of 220, 235, 250, and 265° C. Typical results of impedance spectroscopy tests are shown in Cole-Cole format in Figure 3 (a). The Cole-Cole plot can be interpreted by an equivalent circuit to find the contribution of every entity separately. The 3-RC model has been frequently used for MLCCs [215,229], based on the justification that the total impedance of MLCCs has three contributors: grains, grain boundaries, and electrode interfaces. Figure 3 (b) shows the equivalent circuit used in this study. It is recommended to consider a resistance and an inductor in series with the equivalent circuit to account for the inductance and the resistance of wires and contacts [227,228]. However, they do not make much difference in the large impedances at low frequencies.

The result of impedance fit to the 3-RC model and the associated electrode-interface contribution vs. temperature is shown in Figure 3 (c) and (d) for Uncoated and Coated samples, respectively. The resistance of all Uncoated samples is lower than that of their counterpart of the coated samples. This difference can be represented better by the activation energy required to pass the barriers at interface of the electrode-dielectric, which in Ni-BaTiO₃ is generally agreed to be a Schottky barrier [215,229]. The activation energies were calculated by using Eq.1 for all the samples and the results are presented in Table 9.2.

\[ R = R_0 \exp\left(\frac{E_A}{kT}\right) \]  

(1)

where \( R_0 \) is a constant, \( E_A \) activation energy, \( k \) the Boltzmann's constant, \( T \) absolute temperature in Kelvin.
Figure 9.3 (a) Typical Cole-Cole plot at different temperatures. (b) The equivalent circuit of 3RC model. The resistance of the electrode contribution vs temperature for the MLCC manufactured by c) uncoated and d) coated Ni particles.

Table 9.2 The activation energy (in eV) of electrode-dielectric interface*

<table>
<thead>
<tr>
<th>Oxygen</th>
<th>1300°C-3min</th>
<th>1330°C-3min</th>
<th>1360°C-4min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Coated</td>
<td>Uncoated</td>
<td>Coated</td>
</tr>
<tr>
<td>10 ppm</td>
<td>1.21</td>
<td>0.98</td>
<td>1.25</td>
</tr>
<tr>
<td>40 ppm</td>
<td>1.24</td>
<td>1.05</td>
<td>1.28</td>
</tr>
<tr>
<td>80 ppm</td>
<td>1.31</td>
<td>1.19</td>
<td>1.32</td>
</tr>
<tr>
<td>120 ppm</td>
<td>1.34</td>
<td>1.22</td>
<td>1.34</td>
</tr>
<tr>
<td>200 ppm</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>No Reoxid.</td>
<td>0.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conven.</td>
<td>1.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All data have the error margin of ±0.01 eV
One trend in Table 9.2 is that the activation energy is higher for all of the coated samples in comparison to their uncoated counterparts. As mentioned above, the only difference between these two samples is that the Li$_2$CO$_3$-coated Ni particles were used in the Coated samples. Li$_2$CO$_3$ can introduce carbon and lithium to the system. Carbon does not have a significant influence since it was already in both the coated and uncoated systems due to the organic materials used in the manufacturing process [133,347]. In addition, the Li$_2$CO$_3$ coating decomposed to Li$_2$O and CO$_2$ at 1086 °C, as shown in the previous work [134], so most of the carbon leaves the system in the form of gas. The map of carbon distribution is presented in Figure 9.4 (c). It indicates that the carbon concentration is low and there is no carbon accumulation at the electrode. Lithium is the only element that can be found in the Coated MLCCs, which is absent in the Uncoated MLCCs. So one can argue that the presence of Li is causing the difference in their activation energies.

A chemical map of Li ion distribution can help explain its effect in MLCCs. However, mapping Li can be challenging. The energy-dispersive spectrometry (EDS) detectors cannot detect the low energy of Li$_{K\alpha}$ X-rays (54 eV) [368]. Also, EELS is not a suitable technique because of the overlap of Li- K spectrum and Ti-M$_{2,3}$ spectrum. Among the characterization techniques that can provide mapping at the nanoscale, TOF-SIMS was chosen. The Li$^+$ ions have a strong and separated peak that can be readily used for mapping Li. The TOF-SIMS chemical maps, together with a line scan across the width of the maps, are shown in Figure 9.4. The Ti and Ni maps show the position of the dielectrics and the electrode, respectively. The amount of Ti is not zero in the electrode area since 3 wt% of BaTiO$_3$ were added to the Ni electrode to compensate their shrinkage mismatch during sintering. In addition, it is possible that the Ni and
BaTiO	extsubscript{3} particles intermixed during screen printing in the manufacturing process of green MLCCs. Li mainly stays at the interface of electrode and dielectric as illustrated by the Li map.

The quantitative representation of the ion distribution by a vertical summation of all the counts across the width of the maps is presented in Figure 9.4 (e) as a line scan. The dotted line shows the middle of the electrode, where the Ni counts are maximum. It appears that the Li ions were pushed back from the center of electrode toward the interface of electrode-dielectric. In the previous study [322], it was demonstrated that during the sintering of the coated particles, Li\textsubscript{2}CO\textsubscript{3} was melted and pushed out of the coarsening grains and eventually sat at grain boundaries. One can think of a similar scenario here, where the original Li\textsubscript{2}CO\textsubscript{3} was melted and pushed toward the dielectric in both sides. It is known that Li\textsuperscript{+} ions can diffuse into BaTiO\textsubscript{3} and be substituted onto the B-site with Ti\textsuperscript{4+} [369–371]. This substitution introduces a new negative species (\textit{Li}_{\textit{Ti}}\textsuperscript{II}) at the electrode interface, which can be consider as an acceptor doping in front of electrode.
One can though of two mechanisms, responsible of high activation energy in Coated MLCCs. First, Li$_2$CO$_3$ has been used as a sintering aid in many systems [372,373]. It can improve the bonding (i.e. the interdiffusion) between the electrode and dielectric at the interface and increase the activation energy at the electrode interface [202]. Second, the work function of the Ni electrode or the intermix layer between electrode and dielectric (i.e. the intermetallic layer of Ni, Ba, and Ti) [361] may increase due to incorporation of Li ions. Both mechanisms increase the height of Schottky barriers at the electrode-dielectric interfaces which eventually increase the
charge storage at these interfaces. This is why the capacitance is larger in the Coated samples than the Uncoated ones.

A second trend inferred from Table 9.2 is that by increasing the amount of oxygen flow, the activation energy increases in both Coated and Uncoated samples. As mentioned before, it was demonstrated elsewhere [134] that the resistance of the coated Ni particles remains below 1Ω in the sintering schedule of 1330-3, with the oxygen flow between 10 ppm to 200 ppm, while the resistance of the uncoated particles increased to 140 kΩ. In the Uncoated samples, this increase is mainly due to the fact that a nickel oxide layer forms and grows around the Ni electrode by increasing oxygen flow, as presented in Figure 9.2. The oxide layer hindered the charge transfer from the electrode to the dielectric, which increased the voltage drop and, consequently, the activation energy [202]. However, the resistance of the coated electrode does not significantly increase up to 200 ppm of oxygen flow in the coated electrode [134]. So one can argue that the dominant reason for the activation energy increase is not the increase of electrode resistance rather the decline of $V_0$ concentration by increasing the oxygen flow during sintering. The oxygen vacancies as positive charge can contribute to the formation of the tail of positive charges in the dielectric side (Figure S4), and the decline in the number of $V_0$ increases the width of Schottky barriers so that the activation energy for passing the Schottky barrier increases. This phenomena will be further studied later.

As a simple demonstration of the effect of oxygen vacancies on the activation energy of electrode interfaces, the activation energy of Conventional MLCCs before and after reoxidation annealing are given in Table 9.2. The activation energy increases from 0.37±0.01 eV to 1.25±0.01 eV by decreasing the number of oxygen vacancies. The interface of electrode and dielectric was examined by FIB cross sectioning, and no NiO was found at the interface (as
presented in Figure S5), so all the increase in activation energy is due to the decline of $V_0^-$ concentration. This correlation between oxygen vacancies and activation energy, which can be eventually related to the resistances degradation of MLCCs, has been observed in other studies as well [214,374].

### 3.2 Measuring the concentration of oxygen vacancies in the MLCCs

The correlation between the oxygen flow and the number of oxygen vacancies can be simply seen through the color change of samples. Figure S3 shows a photo of the samples sintered in atmospheres with $pO_2$ from $10^{-9}$ atm to $3 \times 10^{-4}$ atm (equivalent to 300 ppm of oxygen flow). The color changes from dark brown to bright yellow. Yoo et al. have observed the same correlation between the color of BaTiO$_3$ and the concentration of oxygen vacancies [375].

One can quantitatively measure the amount of oxygen vacancies in the dielectrics by EELS (electron energy loss spectroscopy) [367,375–378]. In this study, the concentration of Ti$^{3+}$ ions was first measured by EELS oxygen spectrum and then it is correlated to $V_0^-$ concentration.

Fujimori et al. [379] have shown the change of the EELS oxygen spectrum by increasing the amount of $x$ in La$_{1-x}$Sr$_x$TiO$_3$ crystals. Later, Sefat et al. [380] conducted a similar study on Nd$_{1-x}$TiO$_3$ crystals by systematically decreasing $x$ from 0.33 to 0 and making sure of single phase purity by X-ray powder diffraction. Both studies showed that the height of the first edge in the EELS oxygen spectrum decreased by increasing the percentage of Ti$^{3+}$, determined by the amount of $x$ based on the charge neutrality.

Two typical EELS spectra from the regions with high-concentrated and low-concentrated Ti$^{3+}$ ions are shown in Figure 9.5 (a). As can be seen the height of the first edge, labeled as (1), decreased in the region with high concentration of Ti$^{3+}$. This phenomenon can be explained by studying the electron excitations in the oxygen atoms during EELS. In the oxygen atoms,
electrons in O 2p orbital will be excited to Ti 3d orbitals. In the case of 0% Ti$^{3+}$, the 3d band is empty, and it causes the intensity of the first peak in the spectrum to be maximum. However, by increasing the amount of Ti$^{3+}$ ions, the 3d bands begin to be filled from the lowest available energy state, causing the intensity of the first peak start to decline.

The percentage of Ti$^{3+}$ would be only varied from 4% to 22% in the present study; because of that, the entire variation of the first peak has not been shown in Figure 9.5 (a). In order to see the variation of the peak height in the full range from 0% to 100% of Ti$^{3+}$, one can refer to Fujimori et al. [379] and Sefat et al. [380] papers.

Regarding Sefat et al. study [380], one can calculate the percentage of Ti$^{3+}$ from the ratio of the first peak over the second peak in oxygen spectra. Then, by the assumption that the positive charge of $V_O^-$ in the system will be compensated by Ti$^{4+}$ converting to Ti$^{3+}$, the chemical formula of barium titanate will be

$$ Ba(Ti_{1-x}^{4+}, Ti_{x}^{3+})O_{3-x/2} $$

Eq.9.1

where x is the fraction of Ti$^{3+}$. This formula is based on the principle of charge neutrality and the fact that Ba$^{2+}$ ions always preserve their oxidation state [381]. However, one should consider that there are other possibilities for maintaining charge neutrality in the BaTiO$_3$ system, such as charge balance with cation (Ti or Ba) vacancies and donors [233,382]. The presence of other charge neutralization mechanisms introduces an error in the estimation of $V_O^-$ concentrations. However, it is well known that the electro-neutrality condition in donor-doped BaTiO$_3$, sintered in high or intermediate partial pressure, is as follows [383,384]:

$$ n \approx 2[V_O^-] + [D^-] $$

Eq.9.2

214
Since the same BaTiO$_3$ powder was used in the manufacturing of the MLCCs, the donor concentration was the same in all samples. Thus, the donor contribution to the total number of free electrons is the same in all measurements; one can argue this technique is still valid for the comparison between different samples. Later, it will be shown that the $V_0^{−}$ concentrations calculated in this study are comparable to the data reported in the similar studies [215].

It is worth mentioning that one can compare the samples based on the concentration of Ti$^{3+}$, which is equivalent to the number of free electron (n) in the system, without the need of the extra calculation of oxygen vacancies. However, the other works reported the number of oxygen vacancies for MLCCs and to be able to have a comparison with their data, both $V_0^{−}$ and Ti$^{3+}$ concentration would be reported in this paper.

For collecting EELS spectra, the areas shown in Figure 9.5 (c) and (d) were mapped with short exposure time, and then the final spectra were formed through the integration of every sub-area, which roughly include 800 points. As explained in “EELS experiment” section at Supporting Information, this method can provide spectra, which are a better representative of samples and more reliable than the spectra obtained through point analyses.

Based on the above discussion, the molar percentage of both Ti$^{3+}$ and the number of $V_0^{−}$ vs distance are presented in Figure 9.5 (b). The number of $V_0^{−}$ is shown by oxygen deficiency ($\delta$ in BaTiO$_{3-\delta}$). In order to provide a better understanding of $\delta$, it is worth mentioning that $\delta$ was reported 0, 0.07, 0.14 for PME (precious metal electrode), BME (base metal electrode), and degraded BME BaTiO$_{3-\delta}$ capacitor [367]. The PME capacitors were sintered in air, while the BME capacitors were produced in the same manner as this study.

The result indicated that oxygen deficiency ($\delta$) in the Conventional sample is in average 0.02 higher than the uncoated sample. This result matches well with the color change due to
variation of oxygen vacancies in the samples, shown in Figure S 9-3. In addition, δ in both sample is high in front of electrode and decreases with distance from the electrode. This tail of oxygen vacancies inside the BaTiO$_3$ appears to be in concert with our understanding of accumulation of oxygen vacancies at the electrode Schottky barriers, which is schematically shown in Figure S 9-4. In addition, this observation confirms the Weiss work [364] in which he assumed that oxygen vacancies would be created at the interface of Ni and BaTiO$_3$ during their cofiring at 1300$^\circ$ C. The higher concentration of oxygen in front of electrode has been reported in other works [214,215,367]. δ is reported 0.07 for the conventional samples, which matches well for δ far from Ni electrode in Figure 9.5.

The same line scan is reported for the coated sample in Figure 9.5 (b). Due to the introduction of Li to the system and the formation of $Li'''_{7\text{Ti}}$ species with negative charge, both Eq.9.1 and Eq.9.2 are not valid anymore. This is due to the fact that the charge neutrality may be balanced between $V'O'$ and $Li'''_{7\text{Ti}}$ so that less Ti$^{3+}$ will be produced. Thus, measuring less Ti$^{3+}$ in front of electrode in the coated sample does not mean there are less oxygen vacancies in this region. However, 1.5 micrometer from the electrode, the concentration of Li is low, and the same relation as before exists between $V'O'$ and Ti$^{3+}$. The fact that the average of δ is the same in both Coated and Uncoated samples indicates they are only different at the electrodes, and their active layer are same.
Figure 9.5 (a) Two typical EELS oxygen spectra with low and high Ti$^{3+}$ concentration. (b) Oxygen vacancy concentration and Ti$^{3+}$ vs. distance (the electrode interface is at Distance=0). STEM (scanning transmission electron microscope) micrographs of the interface of Ni electrode and BaTiO$_3$ dielectrics of (c) the conventional (d) the coated sample, in which the ELLS map area is marked with boxes.

9.4 The effect of oxygen flow on Coated MLCCs

The samples with coated Ni particles, sintered at 1330-3 in different oxygen flow, were subjected to temperature-dependent electrical property tests and the results are presented in Figure 9.6. The data were measured at 1 V and 1 kHz. They suggest that both permittivity and DF decreased by increasing oxygen flow. As explained above, increasing oxygen flow during sintering decreased the number of oxygen vacancies, while the Li$_2$CO$_3$ coating was keeping the
electrode resistance low. As explained by the equivalent circuit in Figure S 9-1 in Supporting Information, the combination of both high dielectric resistance due to decline in $V_O^-$ concentration and the preservation of electrode conductivity cause DF decrease in the Coated samples, as shown in Figure 9.6 (a).

The permittivity also decreased by increasing oxygen flow, as illustrated in Figure 9.6 (b). It was demonstrated that the resistance of the coated Ni electrode stays below 1 Ω up to 200 ppm oxygen flow in the sintering profile, the same as the sintering profile in this study [134]. So regarding the fact that the electrode resistance does not increase in these MLCCs, one can argue that the permittivity decline can be due to the decrease in the number of oxygen vacancies. The formation of $V_O^-$ introduces two electrons to the conduction band of the dielectric [385], which can contribute to the total permittivity as a space charge.

This effect can be simply demonstrated by comparing the capacitance (which is directly related to permittivity) of conventional MLCCs before and after reoxidation annealing. These are respectively reported as 4.7 and 3.8 in Table 9.1. Since no trace of nickel oxide phase was found during reoxidation process (as confirmed by FIB cross section in Figure S 9-5), one can argue that the decline in capacitance is merely due to the decrease of oxygen vacancies and, consequently, decrease in the space charge contribution. In addition, the influence of the space charge in the permittivity can be demonstrated by the drop in permittivity by increasing frequency [386], since the space charges cannot keep up with the electric field variation in high frequencies and, consequently, will have less contribution in the total permittivity. As illustrated in Figure S 9-6 in Supporting Information, the permittivity of conventional MLCC decreased by 7.3% with increasing the frequency from 100 Hz to 100 kHz, while this difference dropped to 4.8% and 4.2 % in the coated MLCC, sintered at 10 and 120 ppm of oxygen flow. Furthermore,
as demonstrated in Table 9.2, the voltage offsets of electrode-dielectric interface would increase by increasing oxygen flow. As mentioned before, this observation can be justified by the fact that the number of $V_{o^-}$ in front of electrode decreased by increasing oxygen flow. Less $V_{o^-}$ caused an increase of the length of the depletion region in front of electrode, which manifested as an increase in the voltage offsets. The longer depletion region cause more separation between plus and negative charges at the interface and decrease the capacitance contribution of electrode interface to the total capacitance based on the 3RC model presented in Figure 9.3 (b) . Thus, the second reason of the capacitance decline in the Coted samples in Figure 9.6 (b) by increasing oxygen flow is the less capacitance contribution of the electrode interfaces.

As shown by many studies [214,215,374], oxygen vacancies can localize in front of cathode and increase the leakage current in MLCCs significantly. This phenomenon can be studied by DC degradation tests, in which the leakage current is monitored during the application of DC voltage in high temperatures. The DC degradation tests were executed on the coated and uncoated sample at 200 °C, and the results were shown in Figure 9.6 (c). Due to the field emission at Schottky barrier of electrode interfaces [83,202,204], it is expected that leakage current increases by electric field. However, the amount of leakage current increase was more in the uncoated sample than the coated ones, and also it decreased by increasing oxygen flow, so that the coated capacitor, sintered at 120 ppm, has the minimum increase in the leakage current vs electric field. This observation can be justified by considering the fact that oxygen vacancies decrease by increasing the oxygen flow and the effect of Li$^+$ at the electrode interface. Both parameters were discussed in the explanation of voltage offsets in Table 9.2.

At the end, it is worth noting that the fast-fired MLCCs do not need the reoxidation process as the Conventional samples do. Thus, one can eliminate the need for the reoxidation
processes by utilizing the manufacturing method in this study. Both the utilization of fast firing and the elimination of reoxidation processes can decrease the energy consumption of manufacturing process from 40 MJ to 1.3 MJ for every batch of samples, as measured by monitoring current and voltage of the furnace, used in this study.

Figure 9.6 (a) dissipation factor, (b) relative permittivity for the sample with the Ni particles with Li$_2$CO$_3$ coating. (c) Leakage current density vs electric field for the MLCCs, with and without coated particles at 200 °C; the samples were sintered at 1330-3 in different oxygen flow.
9.5 Conclusions

It has been shown that the coated Li$_2$CO$_3$, which was developed in the previous studies, can actually improve the electrical properties of MLCCs.

First, the coating provided the possibility of sintering the MLCCs in higher partial pressure of oxygen by preserving the electrical conductivity of the electrodes. Using higher pO$_2$ during sintering introduced less oxygen vacancies to the system, as was demonstrated by the color change in the samples and EELS analyses. The combination of low resistance at electrodes and high resistance at dielectrics result in a decrease in the dissipation factor of MLCCs.

Second, Li increases the activation energy of the electrode interface and decreases the leakage current of the MLCCs. The distribution of Li was mapped by TOF-SIMS, and it showed that Li accumulates at the interface of electrodes.

The decline in the number of oxygen vacancies and the accumulation of Li$^+$ at interface are the two main reasons for the improvement of the Coated MLCCs in comparison to the Conventional and Uncoated ones. An ideal capacitor should have high capacitance, low dissipation factor, and low leakage current at high electric fields. This paper demonstrated that all these parameters can be improved by utilizing the combination of the fast firing technique and the Li$_2$CO$_3$ coating on Ni particles.

9.6 Supporting information

As described in Introduction, the energy loss in MLCCs with the same dielectric materials have two contributors, the dielectric conductivity and the electrode resistance. This idea can be explained by the equivalent circuit in Figure S 9-1. The ‘electrode resistance’ can impose a large voltage drop to the capacitor, if they have high resistivity, and decrease the
amount of the stored charge in the capacitor. In addition, if the dielectric resistance is too low, the charge passes through the ‘dielectric resistance’ and the stored charged would drop significantly. An ideal MLCC is the one with low ‘Electrode resistance’ and high ‘dielectric resistance’. However the electrode resistance depends on Ni oxidation and dielectric resistance depends on the number of oxygen vacancies. In oxidizing atmosphere, the number of oxygen vacancies will decrease, but Ni oxidation will be severe. On the other hand, in the reducing atmosphere, the Ni oxidation will be prevented, but the number of oxygen vacancies increase significantly.

![Figure S 9-1 equivalent circuit of MLCCs](image1)

![Figure S 9-2 schematic of the multilayer ceramic capacitor and the gas lance of the furnace.](image2)
Because of the Fermi level difference between electrode and dielectrics, the electrons accumulate in the electrode side and cause a tail of positive carriers (i.e. depleted region) in the dielectric side due to the charge balance. This results in the barrier for electron transfer and is called Schottky barriers.

In an ideal Schottky barrier, in which there is no insulation gap between semiconductor and electrode and no interface states, the difference between metal work function ($\phi_m$) and semiconductor affinity ($\chi$) is the Schottky barrier height ($\phi_B$) \cite{202,203}, as shown in Figure S 9-4:

$$\phi_B = \phi_m - \chi$$
Figure S 9-4 The schematic of an ideal Schottky barrier and three conduction mechanisms

Figure S 9-5 SEM micrograph of FIB cross section of Ni electrode in the conventional sample after reoxidation.
Figure S 9-6 Normalized relative frequency vs temperature at different frequency for a) conventional MLCCs and the one sintered at b) 10 and c) 120 ppm of oxygen flow. The data suggest that by increasing the amount of oxygen vacancies in the sample, the permittivity drop will increase.

**EELS experiments**

Due to the nature of sintered materials, which have the possibility of a small inhomogeneity from one grain to another, and the fact that the amount of oxygen vacancies is higher at the grain boundaries than the center of grains [215], one should not expect to obtain smooth curves for $V_0^-$, as evident in other studies [367]. The other limitation is the TEM instrument itself. The other studies [215,367,379,380] used EELS point analyses, which add another uncertainty to the measured data since first, the spectrum was collected from a small area
(theoretically a point) and second, every point needs a long exposure time to obtain an acceptable signal-to-noise ratio. Long exposure times increase the chance of losing the detail of the EELS spectrum due to the electron source instability or specimen drift [387] and also increase the chance of beam damage [316]. Instead of using point analyses, the area marked with a box in Figure 9.5 (c) was mapped with the resolution of 1 point per every 10 nm with a short exposure time of 0.5 seconds and then, to provide an acceptable signal-to-noise ratio, the resultant spectra were integrated. The mapped area was divided into nine sub-boxes, included ~800 point analyses, and the integration of the spectra of these points would provide one point in the graph of Figure 9.5 (b).

Since the integrated spectrum was the summation of small contributions from the entire set of sub-boxes, the line scan obtained in this technique was a better representative of changes in the sample than its alternative, the point analysis, which was collected from a small area and with a long exposure time.
10 Conclusions and Future Works

10.1 General Remarks

In this document the effects of two coatings have been shown on the improvement of the performance of electroceramic devices, mostly MLCCs. It was illustrated that hydrogen and humidity can degrade the electrical resistance of BaTiO$_3$ MLCCs and ZnO varistors and then ALD coating was explored as a solution to prevent this degradation. Although the ALD coatings have very thin thickness (e.g. 20 nm), they can effectively prohibit the degradation process. Their encapsulation properties comes from the continuous and conformal nature of ALD coatings and the lower diffusion rate of hydrogen ions in the ALD coatings. The diffusion coefficient of protons was calculated three orders of magnitudes lower in the HfO$_2$ and Al$_2$O$_3$ ALD coatings than those in ZnO and BaTiO$_3$ substrates. So the combination of hermetic sealing and low diffusivity of ALD coatings resulted in very effective encapsulation power. For more details, readers are encouraged to consult with conclusion of chapter four and five.

Due to the unique features of ALD coatings, described above, they were potential candidates to be applied to Ni nanoparticles to prevent or hinder their oxidation during sintering in oxidizing atmospheres. If this idea works, one can use the coated particles to co-sinter BaTiO$_3$ and Ni in more oxidizing atmosphere and prevent the formation of oxygen vacancies.

In chapter six, this idea was examined by applying four ALD coatings (e.g. HfO$_2$, Al$_2$O$_3$, ZnO, SnO$_2$) on Ni foil substrates. The result showed that the ALD coating will be buried under the Ni substrate at 900°C and eventually dissolved into the NiO film, which had been formed on the Ni foil. Both electrical characterization and EELS analysis reveal that the ALD coatings cannot prevent oxidation above 900°C. However, they will dope the newly formed NiO film and
can decrease the resistance of the foil by increasing the ratio of Ni$^{3+}$/Ni$^{2+}$, which eventually result in the increase of the chance of electron hopping between those species.

Based on what was learned in chapter six, Li salts were recommended to be used for coating of Ni particles. In chapter seven, a novel and inexpensive coating method was invented to coat Ni particles with Li salts. Three compounds of LiF, LiOH, and Li$_2$CO$_3$ were used in the coating process and it was shown that the method is successful in depositing these salts around Ni particles. The electrical characterization suggested five orders of magnitude decrease in the resistance of the Ni particles after the oxidizing sintering due to the Li$_2$CO$_3$ coating. In chapter eight, the physical mechanisms, caused this decline in the resistance, were explored and documented. Two mechanisms of Li$_2$CO$_3$ decomposition and Li$^+$ doping were found being effective in this process.

In chapter nine, the Li$_2$CO$_3$ coated particles and fast firing were utilized to manufacture MLCCs. The electrical properties of these devices were compared with MLCCs without Li$_2$CO$_3$ coatings or conventional MLCCs. It was demonstrated that the coated MLCCs have both lower dissipation factor and higher relative permittivity than the uncoated MLCCs specifically in sintering atmospheres with high oxygen flow. The coated sample has a lower dissipation factor than the conventional one. The detail conclusion was provided in chapter nine. In short, EELS analysis and impedance spectroscopy showed that the number of oxygen vacancies can be declined and the voltage offset at electrode-semiconductor can be increased by this manufacturing technique. These two phenomena were responsible in the improvement of the electrical properties.

There was a concern about adding Li to the MLCCs due to their high diffusion coefficient in ceramics. They can deteriorate the insulation properties of MLCCs. In chapter ten,
the influence of Li doping in DC degradation of MLCCs was explored by using HALT tests and TSDC on three types of samples (i.e. coated, uncoated, and conventional samples). The result suggested that the oxygen vaccines are the most mobile species during degradation. The oxygen vacancy concentration determined the resilience against DC degradation. The conventional sample (it was demonstrated that they have more oxygen vacancies than the fast fired samples in chapter nine) showed the lowest resilience to DC degradation. The uncoated samples had the highest resilience due to the fact that Li$^+$ as acceptor species can slightly increase the number of oxygen vacancies.

**10.2 Future works**

In this work, it is successfully illustrated that the Ni particles can be coated with Li salts and the salts (specifically Li$_2$CO$_3$) can preserve the electrical conductivity of Ni electrodes and eventually improve the electrical properties of MLCCs. Since the sintering profile was manipulated and Li$^+$ ions were doped in the system in the new manufacturing technique, one should modify the other manufacturing parameters accordingly to obtain the maximum electrical properties. In addition, the coating technique itself can be modified or be used in other applications. In short, a coating method was invented and illustrated to work effectively for MLCCs; in the next step of this research, it should be modified to obtain the optimum electrical properties and developed to be used in other applications.

An ideal MLCC should have low dissipation factor, high relative permittivity, and high resilience to DC degradation (also known as insulation resistance). These properties can be further improve by making sure that the final microstructure of BT grains have the optimum grain size and chemical homogeneity as well as core-shell structures. These features depends on
the amount of diffusivity during sintering and the sintering profile, which both dramatically changed in the presents technique, when it compares to the conventional one. Thus, some techniques/arrangements should be considered to provide enough diffusivity. The particle size of additive powders may be further decreased to shorten the diffusion paths during sintering or increase the initial size of BT grains to obtain the same grain size to the BT grains in conventional methods.

In chapter seven, it was shown that the conductivity of Ni electrode can be preserved in the range of Li$_2$CO$_3$ concentration. This fact can provide the opportunity to study the influence of Li$_2$CO$_3$ concentration in MLCC electrical performance (e.g. dissipation factor, relative permittivity, and insulation properties). Regarding the influence of Li$^+$ addition in introducing more oxygen vacancies to the system, discussed in chapter ten, one can improve the lifetime of MLCCs by adding less Li ions to the system. Through a systematic study on Li concentration, one can find the optimum concentration of Li$^+$, in which the resistance of electrode is as low as possible and the lifetime of MLCCs would be as long as possible.

The influence of other salts such as LiF and LiOH in the electrical properties of MLCCs can be explored. This study would be particularly interesting because these salts do not produce carbon during their decomposition. However, no carbon accumulation was found at electrodes in TOF-SIMS chemical maps as presented in chapter nine. As pointed out in the chapter seven, LiOH is the second protective Li salts after the Li$_2$CO$_3$ but its decomposition temperature is lower than the Li$_2$CO$_3$ and the by-product of the decomposition process is water vapor (instead of CO$_2$ in Li$_2$CO$_3$). These differences make the LiOH coatings worthy of consideration for the preservation of Ni particle conductivity.
The coating technique can be used for other cofired systems to prevent aggressive metal powder oxidation. For example, in the Low-temperature cofired ceramic (LTCC) and ultra Low-temperature cofired ceramic (ULTCC), aluminum has been used for electrodes [409–411]. The aluminum particles can react aggressively with oxygen during sintering, particularly if they have small nano-size powders. One way to prevent this reaction can be coating the Al particles with Li salts through our coating process.
APPENDIX: Li$_2$CO$_3$ coated Ni particles for inner electrodes of multilayer ceramic capacitors: the preliminary evaluation of lifetime

A.1 Introduction

Oxygen vacancies are a major issue in dielectric devices because they introduce electrons to the conduction band and increase electrical conductivity in ceramics [383,385] and, consequently, increase the leakage current. In addition, there is a direct relationship between the resilience of the device toward DC degradation and the amount of oxygen vacancies. The oxygen vacancies can migrate and pile up at the cathode interface and considerably decrease the voltage offset of Schottky barrier. Since this phenomenon is usually observed by applying DC bias at high temperatures, it has been called DC degradation. It is also known as insulation resistance degradation [214,215].

MLCC’s with Ni electrodes are inexpensive devices with high capacitance and are found ubiquitously in applications in electronic industries [132,133,289–291]. The MLCCs with Ni are usually sintered under $10^{-10}$ atm of partial pressure oxygen to protect the Ni electrodes from oxidation. This reducing atmosphere introduces a large concentration of oxygen vacancies in the oxide dielectric. Researchers have tried to minimize the concentration of oxygen vacancies through many techniques, such as designing various reoxidation processes [364] and complex compositional formulations [385].

The present approach in decreasing oxygen vacancies is rather different from the previous studies. A new Ni electrode has been developed and is able to preserve its conductivity in oxidative atmospheres [104,134,322]. This coating, together with fast-firing, ultimately allowed one to sinter MLCCs in oxidizing atmospheres (e.g. pO$_2$ = $10^{-4}$). Thus, the formation of
oxygen vacancies could be avoided through minimizing the reduction reaction in the BaTiO$_3$ (i.e. during the sintering process).

An ideal capacitor should have the combination of high permittivity, low dissipation factor, and high insulation resistance. In the previous investigation [388], it was shown that the Li$_2$CO$_3$ coating, together with the fast firing, provides the possibility of sintering the MLCCs in the oxygen flow of 120 ppm. Without the coating, the oxygen flow should decrease to 40 ppm to prevent the rise of electrode resistivity. It demonstrated that Li increased the voltage offset of Schottky barriers and increased the dielectric constant by 30%. In addition, it was shown that the dissipation factor (also known as dielectric loss) of the coated MLCCs is lower than the sample sintered conventionally by 60%.

In this paper, the effect of the coating will be studied in regard to development of a high performance prototyped MLCC (i.e. high resilience against the degradation). One concern is that Li$^+$ ions have been used as a charge carrier in many applications [389–391] and could migrate and significantly degrade the insulation property of MLCCs. However, there are other species (i.e. oxygen vacancies) in the coated MLCCs and, as explained above, can be the sources of DC degradation. Thermally stimulated depolarization current (TSDC) is a powerful analytical method that can be used to differentiate different depolarization transient phenomena, including defect complex configuration, trap charge, and ionic space charge relaxation in the degradation of different samples [392]. Liu et al. utilized TSDC to study the energy depth of trap sites, and trap density in Fe-doped SrTiO$_3$ [212,213]. Yoon et al. studied both Mg-doped [393,394] and Mn-doped [395,396] BaTiO$_3$, also by TSDC. It was inferred that the oxygen vacancies can diffuse both in-grain (i.e. inside one grain) and inter-grain (i.e. between grains), and since the former has a lower activation energy than the latter, they measured two space charge peaks
related to an oxygen vacancy relaxation. All in all, there are important signatures in TSDC that will enable the detection of the degradation processes in MLCC capacitors.

A.2 Experimental sections

The sample preparation [388] and Li$_2$CO$_3$ coating process [134] were explained in detail elsewhere. The green MLCCs were produced through tape casting, screen printing with Ni uncoated particles or Ni Li$_2$CO$_3$-coated particles, and pressing [51]. Then the sample were sintered in two different schedules. The conventional samples were heated to 1300°C at the rate of 4°C/min and held for 2 hours in partial pressure of $10^{-9}$ atm, followed by a reoxidation annealing at 700°C for three hours in air. The fast fired samples were heated to 1330°C at the rate of 100°C/min and holding for three minutes in the oxygen flow of 10, 40, 80, and 120 ppm. The fast-fired samples with the coated and the uncoated Ni particles were prototyped in the same conditions. Those samples will be referred to as coated and uncoated for convenience in this paper.

The TSDC analyses were executed in a system described elsewhere [212]. The samples were poled at the electric field of 0.33 V/µm for 10 minutes at respective temperatures of 250, 275, 300, and 325°C, and then cooled down to 150°C under a bias. Note that this temperature is above the Curie temperature (120°C) and thereby avoids pyroelectric current contributions from the ferroelectric phase. In the relaxation section, the samples were shorted (i.e. the external bias=0) and heated up to 450 °C at heating rate of 4°C/min, while the leakage current was monitored with HP4140B PA meter (Hewlett Packard Santa-Clara, CA). The HALT in dry and humid atmospheres was executed by a home-made system [247] and Temperature Humidity Chamber (Blue M, Illinois, USA) [67], respectively. The TEM (transmission electron
microscope) samples were prepared by FEI Helios NanoLab 660 FIB/SEM and the TEM analysis was done by FEI Titan G2. The TOF-SIMS analyses were done by PHI nano TOF II manufactured by Physical Electronics (Chanhassen, US).

A.3 Thermally stimulated depolarization current analyses

The raw data of TSDC analyses for the coated MLCCs are presented in Figure A.1. As explained above, the bias voltage was zero in the relaxation part of TSDC. However, the leakage current kept growing by temperature for all the tests with different polarization temperatures. This type of leakage current increase is not abnormal in TSDC analyses. Yoon et al. have observed the same trend in MLCCs with fine grains (sub-micrometer) [394], which was absent for the same MLCCs but with larger grain size [393]. One may conclude that the increase of leakage current by temperature is due to the fact that the MLCCs become more conductive at high temperature. The sintered BaTiO₃ has back-to-back Schottky barriers at each of the grain boundaries [82]. These Schottky barriers are closer to each other in MLCCs with fine grain size, and the electron can pass over the barrier by thermionic emission controlled conductivity [83,202], which increases by temperature. Thus, the increase of leakage current with temperature had nothing to do with ionic species (e.g. Li ions or oxygen vacancies) migration, and it is only due to the electrical conductivity. This trend has been observed in all samples, coated, uncoated, and conventional ones.

In the BME (base metal electrode) capacitor, there is an excess of oxygen vacancies, which compensate electrically and, as a donor, give free electron to the conduction band. However, in the acceptor doped system, this phenomena may not be observed [397].
In order to validate the above conclusion, the TSDC test was conducted on the conventional sample with two opposite polarizing biases (i.e. +0.33 V/µm and -0.33 V/µm). The peaks related to diffusion conductivity should be flipped, because the polarization direction was reversed, but the peaks related to electron conductivity should not change. The results are shown in Figure A.2. One can spot one broad peak (later, it will be demonstrated there are actually two peaks) in the +0.33 V/µm curve, which will be flipped in the +0.33 V/µm curve. After this broad peak, related to the diffusion, the rise in the leakage current in both tests follows the same trend. Thus one may conclude that the leakage current in the TSDC in the present study is the result of superimposing the depolarization current due to oxygen vacancy diffusion and the background current due to increase in electron-based conductivity. The source of background current can be due the fact the bias is not completely zero in the relaxation section of the TSDC test. Even a small voltage bias can cause background current. As was to be expected, holding the sample at 450 °C for one hour did not cause the background current to disappear.

The other observation, which supports the idea of electron-based conductivity in base metal BaTiO$_3$ based dielectrics, is that the background current can be fitted with exponential function (compare the dotted line and the solid line in the plots of Figure A.1), and this can be indicative of thermionic conductivity. The fitted curve was calculated based on the small area before the peak, labeled as ‘used data’.
Figure A.1 Leakage current vs temperature for the coated MLCCs, poled at (a) 250, (b) 275, (c) 300, and (d) 325 °C at 10 V bias. The measured leakage currents (i.e. “actual data”) were fitted by using the data before the first peak, labeled as “Used data”.

(a) 
(b) 
(c) 
(d)
By deducting the background current from the leakage current, one can find the additional depolarization current, which is only due to the ionic space charge created via electro-migration. The depolarization currents are presented for different samples at different polarization temperatures in Figure A.3. Although the peaks, even without the background deduction, can be detected in the plots of Figure A.1, the background-eliminated plots in Figure A.3 illustrate a better presentation of the depolarization currents.

Two peaks can be differentiated for all three samples in Figure A.3 (a-c). In addition, both peaks shift to high temperature with polarization temperature. As Liu et al. [212] have demonstrated, this shift is indicative of Li ion or oxygen vacancy space charge relaxation. Since these peaks have been detected in all three types of samples, they should belong to oxygen vacancies. In addition, Yoon et al. [393,394,398,399] found the oxygen vacancy peak in the TSDC of BaTiO$_3$ MLCCs in the same temperature range to the one reported in this paper. Thus, the peaks, shown in Figure A.3 (b) for the coated MLCC were due to the oxygen vacancy...
relaxation. Regarding the fact that there are no other peaks that were associated to Li\textsuperscript{+} transfer, one may conclude that the oxygen vacancies have higher mobility than Li ions. This conclusion that oxygen vacancies have higher mobility than Li ions is in concert with their diffusion coefficient in BaTiO\textsubscript{3}, as reported respectively 8×10\textsuperscript{-5} [400] and 1.5×10\textsuperscript{-17} cm\textsuperscript{2}s\textsuperscript{-1} [401] at 800 °C.

The other trend that can be seen in the graphs of Figure A.3 is that the peak of the in-grain transfer appears at the lower polarization temperature and then, by increase in the polarization temperature, the peak of the inter-grain transfer both appears and grows. This observation indicates that 250°C and applied polarizing field (0.33 V/µm) are not strong enough to transfer \( V_{O}^{-} \) between grains. In other words, it cannot provide the activation energy necessary for \( V_{O}^{-} \) to pass the grain boundaries. However, the polarization temperatures of 300°C and above provide enough energy for the inter-grain transfer of \( V_{O}^{-} \).

Additional data can be provided from the depolarization curves in Figure A.3, such as the number of oxygen vacancies per unit volume and their mobility. For example, no peak was detected for the uncoated MLCCs at Tp=250°C, as shown in Figure A.3 (a). It indicates that the depolarization current due to the small number of oxygen vacancies was too weak to be detected with a pA Meter. To be able to compare the different samples, their depolarization currents vs temperature are presented in Figure A.3 (d) for Tp= 300°C. The following equation exists between the depolarization current (I) and depolarization (P):

\[
\frac{I}{A} = \varepsilon \frac{\delta E}{\delta t} + \frac{\delta P}{\delta t} \\
\text{Eq. A.1}
\]
Where \( \varepsilon \) is permittivity, \( E \) electric field, \( A \) area, and \( t \) time. Since \( E \) in the depolarization part of TSDC measurements is zero (or at least for sure \( \frac{\delta E}{\delta t} = 0 \)), the above equation is simplified to

\[
I = A \frac{\delta P}{\delta t}
\]

Eq. A.2

Since the geometry of the three types of samples are very similar, one can argue that the measured depolarization current is the representative of the depolarization rate in these three samples. Polarization is equal to the number of charge carriers (in the present discussion \( V_O^+ \)) per volume multiplied by their migration distance. In simple words, the depolarization would be larger if there was either larger number of oxygen vacancies or oxygen vacancies with higher mobility. In the previous work [388], it was demonstrated that the number of \( V_O^+ \) is 2% larger in the conventional MLCC than that of the fast fired ones. In addition, the grain size of the conventional sample is larger than the fast fired ones, as can be inferred from TEM micrographs of their microstructures in Figure A.4. The grain size was measured based on these micrographs and ASTM E112-96 as 477±33 nm and 685±84 nm. Thus, the larger grain size means less grain boundaries and makes the mobility of oxygen vacancies easier. This, together with a larger number of oxygen vacancies, causes the depolarization curve in Figure A.3 to be much larger for the conventional samples than the fast fired ones.

The depolarization current of the coated sample is slightly above that of the uncoated one. It indicates that the number of oxygen vacancies in the coated sample is larger. It can be due to the fact that Li ions are intermixed with BaTiO\(_3\) at the electrode-dielectric interface and forms
$Li_{Ti}^{'''}$ acceptors [388]. Due to the charge neutrality, the acceptor increases the concentration of oxygen vacancies.

The concentration and the mobility of $V_o^-$ are important in resilience to the DC degradation. On the other hand, both parameters have a direct effect on the amount of depolarization current. Thus, one can expect that the samples with higher depolarization currents have lower resistance to the DC degradation and vice versa. In order to investigate this hypothesis, the following HALT testing was conducted.

Figure A.3 Depolarization current vs temperature for (a) uncoated, (b) coated, and (c) conventional MLCCs poled at 10V bias and different temperature, (d) for different samples poled at 10V bias and 300 °C.
A.4 Highly accelerated lifetime tests

There is a long-standing concern about how the leakage current and dissipation factor would depreciate in the life time of MLCCs [402–405].

As shown in Table A.1, three types of samples (i.e. conventional, coated, and uncoated) were exposed to high temperatures and electric fields. During the tests, when the leakage current increased by 1000%, this was taken as the failure time. The life time of the devices was suitable to illustrate the effect of oxygen vacancies and Li$^+$ ions; the samples were ranked bases on their lifetime from shortest to longest.

The results suggest that the type of sample (i.e. conventional, coated, and uncoated) and oxygen flow during sintering determine the lifetime. The results can be well justified by considering the amount of oxygen vacancies in MLCCs. Based on the EELS analyses in the
previous study [388] and TSDC results in the previous sections, the concentration of oxygen vacancies is maximum in the conventional sample; it decreased in both coated and uncoated fast-fired samples. However, $V_0^-$ in the coated samples is higher than that of the uncoated ones, due to presence of Li as an acceptor. In addition, the increase of oxygen flow during sintering can decrease the number of oxygen vacancies. Thus, the uncoated sample sintered at 40 ppm shows the longest lifetime.

It should be further noted that all samples were placed in the HALT chamber at once, and conditions listed in Table A.1 were applied to each sample type. So an accumulative lifetime should be considered in the estimation.

In order to demonstrate, the repeatability of the trend in the HALT data in Table A.1 a similar HALT was executed and the results are presented in the Supporting Information. Although different estimation of lifetime have been obtained, the trend is similar to the one in Table A.1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Electric field (V/µm)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>conventional</td>
<td>130</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>coated_10ppm</td>
<td>130</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>coated_40ppm</td>
<td>130</td>
<td>30</td>
<td>12</td>
</tr>
<tr>
<td>coated_80ppm</td>
<td>130</td>
<td>30</td>
<td>47</td>
</tr>
<tr>
<td>coated_120ppm</td>
<td>150</td>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>Uncoated_10ppm</td>
<td>150</td>
<td>25</td>
<td>31</td>
</tr>
<tr>
<td>Uncoated_40ppm</td>
<td>150</td>
<td>30</td>
<td>10</td>
</tr>
</tbody>
</table>

Table A.1 HALT results together with estimated life time for working condition of 80°C and 15 V/µm for different samples
Adding humidity to the HALT experiments makes the testing condition more prone to degradation. Humidity can diffuse into the electroceramic devices in the form of hydroxide or protons and decrease the voltage offset of Schottky barrier at electrode interfaces and grain boundaries [51,67,82,83,407]. So one should expect failure in lower temperature and electric field in the presence of humidity.

The other concern is that water can dissolve both Li$_2$CO$_3$ and Li$_2$O and form an electrolytic flux at grain boundaries, which facilitates the Li diffusion and causes an early degradation. This phenomenon has been observed for MLCCs with Ag-Pd alloy electrodes where Ag$^+$ could electro-migrate through grain boundaries and causing early failures [231,408].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)/humidity (%)</th>
<th>electric field (V/µm)</th>
<th>time(hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>conventional</td>
<td>90/90</td>
<td>7.5</td>
<td>4</td>
</tr>
<tr>
<td>coated_40ppm</td>
<td>90/90</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>coated_120ppm</td>
<td>90/90</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>Uncoated_40ppm</td>
<td>90/90</td>
<td>12.5</td>
<td>40&gt;**</td>
</tr>
</tbody>
</table>

** The leakage current did not increase in the conditions, applied in this experiment.

The humidity HALT was conducted in quite extreme conditions, 90°C and 90% humidity in the electric interval of 2.5 V/µm to 12.5 V/µm with the increment of 2.5 V/µm; the samples were held for 40 hours at each electric field. Four samples (conventional, coated sintered at 40 and 120 ppm, and uncoated at 40 ppm) were tested. The conventional sample failed at 7.5 V/µm. Both coated samples failed at 10 V/µm, and the uncoated one did not fail during this measurement. The detailed results are presented in Table A.2. As can be seen, the failure will
occur in both temperatures and electric fields lower than the ones reported in Table A.1. As explained above, these declines were because of the 90% humidity during the HALT testing. Regardless of the general decline in reliability of the samples due to humidity, the samples would fail in the same order as presented in Table A.1. This is due to the fact that protons need oxygen vacancies to enter into BaTiO$_3$ based on the following equation [83,88]:

$$H_2O(g) + V_o^- + O_0^x \rightarrow 2[OH]_o^-$$

One can argue that the number of oxygen vacancies determines the reliability of the samples in both dried and humid environments, and the effective parameters (i.e. sintering schedule, Li doping, and oxygen flow during sintering) in the number of oxygen vacancies would determine the order of samples in both Table A.1 and Table A.2.

It appears that the Li ions did not migrate during the humidity HALT testing. In order to verify this conclusion, TOF-SIMS was executed on the coated-120ppm sample before and after the test, and the results are shown in Figure A.5. The overlay maps of Ni and Ti in Figure A.5 (a) shows the place of the two Ni electrodes, surrounded with BaTiO$_3$. The line scans were formed from the vertical integration of Ni, Ti, and Li intensity and are shown in Figure A.5 (b) and (c) for the coated-120ppm sample before and after its degradation. The line scans clearly suggest that the relative location Li ions to Ni atoms did not change during the entire of the HALT test. Thus, Li does not migrate during HALT tests even after the degradation. However, Li as an acceptor introduced oxygen vacancies to the sample. The number of oxygen vacancies are high enough to make the coated sample fail earlier than the uncoated ones. But the number of oxygen vacancies is still lower than the conventional samples.
Figure A.5 (a) SIMS map of Ni and Ti chemical distribution; the Li intensity is too low to be visible. Line scan on the coated MLCC, sintered at 1330-3 in 120 ppm oxygen flow; (b) before (c) after the HALT test (90°C, 90% humidity, 15 V/µm, 48 hours).

A.5 Conclusions

In this paper, the effect of the Li$_2$CO$_3$ coating on the insulation resistance and reliability of MLCCs was determined.

TSDC results suggested that the number of oxygen vacancies and their mobility decrease from the conventional samples to the coated and then to the uncoated ones. The same order could
be seen in both dry and humidity HALTs, where the conventional, coated, and uncoated sample have the lowest to highest resilience to the DC degradation. Regarding to the consistent order in all the experiments, and the fact that oxygen vacancies are the dominant species in determining the insulation properties, one can conclude the following remarks. The sintering schedule (fast-firing or conventional) is the most effective parameter to determine the insulation properties. The second effective parameter is the presence of Li ions, which can introduce oxygen vacancies to the system, but they do not have any role in the degradation process. The third effective parameter is oxygen flow during sintering.

A.6 Supporting Information

Table A.3 HALT results together with estimated life time for working condition of 80°C and 15 V/µm for different samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Failure conditions (T₁, V₁, t₁)</th>
<th>Estimated life time (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Electric field (V/µm)</td>
</tr>
<tr>
<td>conventional</td>
<td>130</td>
<td>24</td>
</tr>
<tr>
<td>coated_10ppm</td>
<td>130</td>
<td>24</td>
</tr>
<tr>
<td>coated_40ppm</td>
<td>130</td>
<td>28</td>
</tr>
<tr>
<td>coated_80ppm</td>
<td>150</td>
<td>24</td>
</tr>
<tr>
<td>coated_120ppm</td>
<td>150</td>
<td>28</td>
</tr>
<tr>
<td>Uncoated_10ppm</td>
<td>150</td>
<td>28</td>
</tr>
<tr>
<td>Uncoated_40ppm</td>
<td>170</td>
<td>24</td>
</tr>
</tbody>
</table>
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VITA

Damoon Sohrabi Baba Heidary was born on March 17th, 1985 in the providence of Isfahan, Iran. He participated in the national examination at 2003 and was accepted in Isfahan University of Technology at materials science and metallurgy program. In this program, he conducted a research on coating of low carbon steel by molybdenum carbides formed through a GTAW welding process. The work was successful and it was later published in Tribology Transactions. This early success made a foundation for his future works in materials science and mechanical engineering of MSc programs in University of Tehran at Tehran, Iran and The City College of New York at New York, USA respectively. During these studies, Damoon built two apparatus and one of them was later patented, and published six peer review papers.

Having MSc degrees in both materials science and mechanical engineering made Damoon a researcher, who can understand physics and math behind hypothesizes on papers and design experiments to evaluate their validity in practice. After his graduation from CCNY, Damoon was accepted to three PhD programs in US. Based on the ranking system, he should chose the mechanical department of the Georgia Institute of Technology. But knowing that the advisor is one of the most important factors in a successful PhD, he decided to meet his future advisors in these three universities. After his meeting with Dr. Clive Randall at the Pennsylvania State University, he was certain that he could excel in Dr. Randall’s group.

Clive was a true description of a mentor. He was the encyclopedia of electroceramics and put Damoon in the right track of thinking or challenged him to obtain a better understanding through fruitful discussions. He was fair and generous, Damoon learned a quite a bit about electroceramics and numerous characterization techniques under his supervision. Damoon’s PhD was concluded in less than three years by publishing eleven journal papers as the first author. This may be considered as a record (although it was never formally investigated to be proven) in the PhD program of MATSE department and as a testimony of successful collaboration between a great mentor and a curious student.