The Pennsylvania State University

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# DEVELOPMENT OF STABLE ANODE AND CATHODE MATERIALS FOR RECHARGEABLE BATTERIES

A Dissertation in

Material Science and Engineering

by

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## ABSTRACT

Batteries have been employed in a variety of applications, such as portable electronics, electric vehicles (EVs), and stationary energy storage to preserve energy from other renewable sources (like wind or solar energy). The ultimate goal is to develop high energy density, long life span, better safety, and low cost of the batteries. However, current commercialized batteries (like lead-acid, zinc-alkaline, lithium-ion batteries (LIBs)) could not fulfill all the demands of diversified applications. LIBs predominate the market because of their high energy density. To achieve a higher capacity of the cell, high-nickel layered (Ni > 90%) cathode materials are promising candidates since they compose high specific capacity and discharge voltage.

In chapter 1, an introduction to cell energy density and the development of high-nickel layered cathode materials along with associated obstacles of poor cycling stability and thermal stability have been discussed. Associated works like doping or surface coating have also been mentioned in this section.

In chapter 2, Al doping in high-nickel layered cathode materials to enhance the structural and thermal stability was introduced. Uniform incorporation of Al doping is achieved by mechanical fusion and calcination processes. The Al doping not only decreased the Li/Ni mixing ratio but also enhance the thermal resistance to oxygen evolution because of strong Al-O bonding, which leads to elevated electrochemical and thermal stability.

In chapter 3, TiN is implemented as a Ti dopant for high-nickel layered cathode materials to improve the electrochemical performance in the LIBs. The Ti not only diffused within the bulk structure but also formed segregation on the surface, which improved the structural stability and led to better cycling performance. Although LIBs deliver high energy density, safety concerns of flammable organic electrolytes have not been resolved yet. Therefore, the aqueous rechargeable zinc-ion batteries (ZIB) have been praised for their safe, low-cost, eco-friendly stationary energy storage, which is considered as a complementary system to LIBs.

In chapter 4, the mechanism, advantages, and challenges of ZIBs would be given and the strategies for solving the zinc metal anode issues have been discussed in this section.

In chapter 5, a polymer coating method was reported to facilitate Zn deposition/ stripping by coordination with Zn<sup>2+</sup> and prevented direct contact with aqueous electrolyte to block corrosion side-reactions. With this coating, a boost in a lifetime (up to 400 hours) and lower polarization under extremely high current conditions (10 mA cm<sup>-2</sup>) have been achieved in repeated Zn deposition/ stripping cycling.

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# Chapter 1

# **Development of High-Nickel Layered Cathode Materials**

#### 1.1 Introduction of high-nickel layered cathode

Lithium-ion batteries (LIBs) have been widely used in the market for portable devices or EVs. To further boost the energy density of the LIBs, high-nickel layered cathodes like  $LiNi_xCo_yMn_{1-x-y}O_2$  (NCM) and  $LiNi_xCo_yAl_{1-x-y}O_2$  (NCA) (x> 0.8) have been extensively investigated in recent years because of their high specific capacity and high operating voltage<sup>1-5</sup>. Compared to commercialized LiFePO<sub>4</sub> (170 mAhg<sup>-1</sup>) and LiCoO<sub>2</sub> (165 mAhg<sup>-1</sup>, due to limited utilization), high-nickel cathode materials compose a high specific capacity over 200 mAhg<sup>-1</sup> with high operation voltage (3.8V) (**Fig 1.1**)<sup>6-9</sup>. Hence, high-nickel layered cathode materials are the promising cathode material candidates for the next generation of LIBs.



Fig 1.1 Comparison of thermal stability, capacity retention, and discharge capacity with different Ni content in NCM cathode materials<sup>9</sup>.

For battery evaluations, the amount of electrical energy storage is the core parameter to be considered. The energy density defines the total energy stored in a battery per unit mass/volume. It is calculated based on voltage (V) and capacity ( $mAhg^{-1}$ ). The voltage is the operating voltage of the battery during charge and discharge processes. The capacity of individual material is determined by Faraday's law (**Eq 1.1**)

$$Q = \frac{nF}{3.6 M}$$
 (Eq 1. 1)

Where,

 $Q(C) = Specific capacity (mAhg^{-1})$ 

*n* = *electrons transfer number* 

 $F = Faraday \ constant$ 

M = molecular mass of material (gmol<sup>-1</sup>)

Subsequently, the specific capacity of electrode materials ( $C_E$ ) is calculated based on the specific capacity of the cathode ( $C_C$ ) and anode ( $C_A$ ) materials in **Eq 1.2** 

$$\frac{1}{C_{\rm E}} = \frac{1}{C_{\rm C}} + \frac{1}{C_{\rm A}}$$
 (Eq 1. 2)

Therefore, the overall energy density of the battery could be determined by Eq 1.3 from the specific capacity of the electrode ( $C_E$ ), the voltage difference between anode and cathode (V), and the weight ratio of the electrode in the battery (W).

Energy density = 
$$C_E * V * W$$
 (Eq 1. 3)

To enhance the energy density of the batteries, efforts have to be paid to improve the specific capacity of the electrodes, enhance the working voltage of the cell and increase the weight ratio of the electrodes.

#### 1.2 Structure and reaction mechanism

Layered NCM cathode materials undergo Li<sup>+</sup> insertion and desertion during discharge and charge processes. During electrochemical processes under 4.3V, the Ni component undergoes major redox reactions. Therefore, layered NCM cathode materials with higher Ni content could deliver higher capacity under the standard operating voltage window. High nickel layered NCM cathode materials experience similar charge and discharge processes with multiple phase transitions<sup>10-12</sup>. During the charging process, the NCM undergoes hexagonal (H1)  $\rightarrow$  Monoclinic (M)  $\rightarrow$  Hexagonal (H2)  $\rightarrow$  Hexagonal (H3) phase transitions and reveres in the discharge process (**Fig 1.2**). H1 $\rightarrow$ M  $\rightarrow$ H2 phase transitions are stable while H2 to H3 phase transition leads to contraction of c-axis and shrinkage of the crystal structure. Hence, the repeated H2 to H3 transition in high-nickel layered cathode results in structural degradation and other problems, which causes capacity fading and impedance increase.



Fig 1.2 Typical dQ d $V^{-1}$  curve for Li/NCM811 cells (differential capacity vs voltage)<sup>10</sup>.

#### 1.3 Challenges of high-nickel layered cathode materials

Although high nickel layered cathode materials compose high capacity and high working voltage, there are two main issues associated with the materials. One is fast capacity fading due to structural degradation and another is safety concerns of a potential thermal runaway (flammable electrolytes) at high temperature because of poor thermal stability. The reasons for the capacity loss include residual lithium compounds, Li/Ni cation mixing, microcracks, oxygen evolution, and layer to a rock-salt phase transition, etc<sup>2, 3, 13</sup>.

#### 1.4 Failure mechanisms for high-nickel layered Cathode materials

## 1.4.1 Residual lithium components

Residual lithium components are inevitable during the synthesis and storage of high-nickel layered cathode materials. It results from the excess amount of LiOH during the calcination process to compensate for the lithium loss and suppress Li/Ni mixing. Additionally, the active cathode materials react with water and CO<sub>2</sub> in the air to form LiOH and Li<sub>2</sub>CO<sub>3</sub> during storage. Hence, the residual lithium components usually contain LiO<sub>2</sub>, LiOH, and Li<sub>2</sub>CO<sub>3</sub><sup>13-17</sup>(**Fig 1.3**). The residual lithium compounds could initiate gelation of the PVDF binder in the preparation of cathode slurry. Moreover, Li<sub>2</sub>CO<sub>3</sub> is oxidized during the electrochemical process to form oxygen gas and triggers battery swelling<sup>17, 18</sup>.



Fig 1.3 Schematic illustration of residual lithium formation (a) during calcination<sup>13</sup>, (b) during storage<sup>17</sup>.

## 1.4.2 Li/Ni cation mixing

In high-nickel layered cathode materials, Ni<sup>2+</sup> has a strong tendency to migrate from transition metal slab to lithium slab since Ni<sup>2+</sup> (0.69 Å) has a similar radius with Li<sup>+</sup> (0.69 Å). After Li/Ni mixing, the Ni<sup>2+</sup> occupies the Li<sup>+</sup> site, which decreases the mobility of Li<sup>+</sup> and the capacity of the cathode material. As a result of thermodynamic instability of high-nickel layered cathode, the Li/Ni mixing increases with higher Ni content, deeper state of charge, and enhanced temperature. In addition to the capacity loss, a phase transition occurs at the surface where layered structure transforms to spinel and finally rock-salt phase (**Fig 1.4**) <sup>19-23</sup>. The Li/Ni mixing initiates from the calcination process of cathode synthesis and consecutively deteriorates throughout the cycling process.



Fig 1.4 STEM image of the (a) surface of  $LiNi_{0.7}Co_{0.15}Mn_{0.15}O_2$  (b) high-resolution STEM image of the marked region of (a)<sup>23</sup> indicates the cation mixed phase and layered structure.

#### 1.4.3 Oxygen evolution reaction (OER)

OER occurs at the deep charged state (delithiated state) of NCM cathode materials. Especially in high nickel layered cathode materials, the OER onset potential decreases with the increase of Ni content. For example, the OER onset potential for NCM111 initiates at 4.6 V while the potential reduces to 4.2 V for the NCM811 cathode material<sup>12</sup>. **Fig 1.5** illustrates the correlation of gas evolution with potential, state of charge (SOC), and phase transitions in the high-nickel NCA cathode<sup>24</sup>. It shows that the gas evolution initiates at 75% SOC where H2 to H3 transition also occurs from 4.1 V. It is suggested that the OER results from thermodynamic unstable H2 to H3 phase transition process in the high-nickel layered cathode material. Based on various mechanism studies of OER, it is believed that the gas evolution is caused by the oxidation of lattice oxygen in the unstable H3 phase. The active oxygen intermediates react with electrolyte to generate gas like CO or CO<sub>2</sub> in the batteries, which leads to oxygen loss in the crystal structure and structure transformation upon cycling<sup>25</sup>. The OER damages the structure integrity and results in potential thermal runaway.



Fig 1.5 Correlation of gas evolution with SOC, cell potential, specific capacity, and phase transition in NCA cathode<sup>24</sup>.

#### **1.4.4 Phase transition**

Because of the Li/Ni mixing and OER in the high-nickel layered cathode materials, the cation migration and oxygen loss trigger the inevitable layered-spinel-rocksalt phase transition<sup>12, 16, 17</sup>. The transition becomes severe with high nickel content, deep SOC, and enhanced temperature. The mechanism proposed in **Fig 1.6** shows that the layered structure transforms to spinel and rock-salt structures due to Ni<sup>2+</sup> migration and OER in the crystal structure<sup>26</sup>. The transition initiates on the surface and further propagates into the bulk structure upon cycling. These processes proceed throughout cycling with electrolyte oxidation and gas evolution, which form NiO rock-salt surface with low conductivity and high impedance. Furthermore, the phase transition reduces the discharge working potential and larger polarization, which leads to capacity loss of the high-nickel layered cathode material.



Fig 1.6 Schematic illustration of phase transition from layered  $(R\bar{3}m)$  to rock-salt  $(Fm\bar{3}m)^{26}$ .

#### **1.4.5 Microcracks development**

During charge/discharge processes, the high-nickel layered cathode materials suffer from anisotropic volume change, where the mechanical strain of the process leads microcracks along the grain boundary of the primary particles<sup>27</sup>. The volume change is triggered by the unstable H2 to H3 phase transition, where the c axis and cell volume of the crystal structure experience expansion and contraction during the charge/discharge process<sup>28-30</sup>. The cross-sectional view of NCA (Ni =0.89) in **Fig 1.7** indicates obvious pulverization and microcracks formation from the center to the surface at charged state  $(4.3V)^{31}$ . Because of the consecutive volume change of the crystal structure, the cathode particles would pulverize and expose the fresh surface area to the electrolyte. The electrolyte penetrates inside the secondary particles and reacts with the exposed surface to generate

new cathode electrolyte interfaces (CEI), which results in impedance enhancement of the LIBs and electrolyte consumption within the batteries.



Fig 1.7 Bright-field STEM image of NCA (cross-sectional view) at charged state (4.3V)<sup>31</sup>.

#### 1.4.6 Safety hazard

A safety hazard is attributed to the thermodynamic unstable H3 phase in the high-nickel layered cathode material. In the unstable H3 phase, the generated oxygen intermediates would either react with electrolytes or generate oxygen gas itself, which causes gas evolution during the process. Furthermore, the intermediates could migrate to the anode side and react with lithiated graphite, which causes potential thermal runaway without an internal short-circuit.

#### 1.5 Strategies for high-nickel layered cathode materials

## 1.5.1 Doping

Doping is one of the most promising methods to improve structural and thermal stability due to its low cost and high efficiency. Foreign element doping alters the structural environment and changes the structural stability. Hence, various dopants like Al, B, Mg, Ti, Mo, Nb<sup>32-48</sup> have been reported in high-nickel layered cathode materials to improve their poor electrochemical and thermal stabilities. The doping elements could stabilize the crystal structure upon cycling because the inactive dopants constrain the migration of Ni<sup>2+</sup> to the lithium site, which suppresses the oxygen loss and structure evolution from layered to rock-salt. Additionally, some dopants could stabilize and enlarge the lithium slab to improve the Li<sup>+</sup> diffusion during cycling, which elevates the electrochemical stability and rate performance of the LIBs. Among various dopants, Al is one of the most effective dopants for high-nickel layered cathode materials. Zhao et al. applied Al doping in LiNi<sub>0.76</sub>Co<sub>0.1</sub>Mn<sub>0.14</sub>O<sub>2</sub> (NCM)<sup>49</sup>. The Al-doped NCM delivered better rate performance (**Fig 1.8a**) in different current densities and maintained a capacity retention of 79.2% after 500 cycles (**Fig 1.8b**). In the meanwhile, the bare NCM shows lower capacity at a high current rate and suffers from severe capacity fading especially after 300 cycles. The Al occupies the nickel site in the transition metal slab and blocks the migration path of Ni<sup>2+</sup> to the lithium site during cycling. These features contributed to stabilized layered structure and reduced layered to a rock-salt phase transition, which improves the overall cycling stability and rate performance of the cathode material.



Fig 1.8 (a) Rate performance and (b) cycling performance of NCM and Al-doped NCM<sup>49</sup>.

In addition to Al doping, Mg<sup>2+</sup> is also widely used as a dopant in high-nickel layered cathode materials. Xie et al<sup>50</sup>. implemented Mg doping in LiNi<sub>0.94</sub>CO<sub>0.06</sub>O<sub>2</sub> (NC) cathode and the electrochemical stability got improved. From the result of the electrochemical performance of the Mg-doped NC cathode (**Fig 1.9**), the Mg-doped NC cathode shows higher capacity retention after 150 cycles and higher CE throughout the cycling (**Fig 1.9a-b**). Moreover, the NC cathode sustains fast working voltage decline while the Mg-doped NC cathode presents a stable working voltage plateau (**Fig 1.9c-d**). It is proposed that the Mg<sup>2+</sup> would occupy the Li site rather than the TM site in the crystal structure, where the Mg acts as a pillar to support and stabilize the lithium slab and results in better cycling stability. Additionally, due to the charge compensation theory, the Mg<sup>2+</sup> doping would lead to a valence increase of Ni<sup>2+</sup> to Ni<sup>3+</sup>, which reduces the Li/Ni mixing in the structure.



Fig 1.9 Electrochemical performance of NC and Mg-doped NC. (a) cycling performance (b) Coulombic efficiency (c) voltage profiles of NC cathode (d) voltage profiles of Mg-doped NC cathode<sup>50</sup>.

#### 1.5.2 Concentration gradient structure

Due to the poor structural and thermal stability of the high-nickel layered cathode materials, core-shell structured cathode materials have been designed to enhance the electrochemical performance and thermochemical stability<sup>51-54</sup>, where high nickel cathode acts as core and low nickel cathode as the shell. Sun et al<sup>55</sup> proposed a multi-compositional cathode structure with LiNi<sub>0.94</sub>CO<sub>0.038</sub>Mn<sub>0.022</sub>O<sub>2</sub> as core and LiNi<sub>0.84</sub>CO<sub>0.077</sub>Mn<sub>0.08</sub>O<sub>2</sub> as the shell. The inner core contributes to the high capacity and the outer shell provides stability and safety of the cathode material. The cycling performance of the concentration gradient NCM cathode (CSG90) shows better capacity retention after 100 cycles compares to conventional chemical compositional NCM cathode (CC90) (**Fig 1.10**). This concentration gradient structure lags the H2 to H3 phase transition during charge/discharge and the outer shell could partially eliminate the microcrack nucleation in the core.



Fig 1.10 Schematic illustration of concentration gradient structure (left); stable cycling performance is achieved in CSG90 cathode material<sup>55</sup>.

#### 1.5.3 Surface coating

Surface coating on the particle surfaces protects high-nickel layered cathode materials from attack by HF, electrolyte, or other species. Oxides (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>, MgO, etc)<sup>56-60</sup>, artificial CEI layers<sup>61, 62</sup>, and phosphates<sup>63-65</sup> are common coating materials for cathodes. Oxides like Al<sub>2</sub>O<sub>3</sub> and

ZnO could act as a scavenger to eliminate HF attack from the electrolyte. Min et al<sup>66</sup>. coated highnickel cathode LiNi<sub>0.91</sub>Co<sub>0.06</sub>Mn<sub>0.03</sub>O<sub>2</sub> surface with spinel NCM (Li(NiCoMn)<sub>2</sub>O<sub>4</sub>) to minimize the microcracks formation upon cycling (**Fig 1.11**). The coating spinel phase with outstanding mechanical strength could limit the excessive volume change during lithiation/delithiation. As a result, the spinel-coated high-nickel layered cathode generated fewer cracks or voids than the bare NCM cathode material and achieved over 90% capacity retention after 50 cycles.



Fig 1.11 Cross-sectional SEM images of microcracks generation in NCM and spinel coated NCM cathode materials after 100 cycles<sup>66</sup>.

In summary, although high-nickel layered cathode materials compose high energy density, they suffer from poor structural and thermal stability. The H2 to H3 phase transition during cycling leads to shrinkage and microcrack formation. Phase transition also causes capacity loss and impedance increase. Various strategies (like doping, surface coating, concentration gradient) have been employed to solve the issues associated with high-nickel layered cathode materials.

## Chapter 2

# Enhanced Structural Stability of High-Nickel Layered Cathode Materials by Al doping for Lithium-ion Batteries

#### **2.1 Introduction**

lithium-ion batteries (LIBs) have been wildly implemented in various applications from portable devices to advanced fields such as electric vehicles (EVs). Nonetheless, these drastic extensions require high-energy-density and high safety LIBs, where cathode materials are key components limiting the boost of LIBs<sup>67, 68</sup>. Current cathode materials are expected to compose high specific capacity and low content of expensive cobalt metal <sup>4, 69, 70</sup>. LiNiO<sub>2</sub> was firstly considered as potential cathode material since it possesses a high theoretical capacity (270 mAh·g<sup>-</sup>) as well as low cost and toxicity<sup>71-73</sup>. Nonetheless, fast capacity fading and poor cycling performance of LiNiO<sub>2</sub> caused by the formation of unstable phases suppress the practical applications.<sup>74, 75</sup> Hence, substituting Ni with other elements like Co or Mn (Ni > 90 %, Co < 10 %) as high nickel layered cathodes is an alternative strategy to replace LiNiO<sub>2</sub> because they involve high capacity <sup>72</sup> and high stability.<sup>76-80</sup>

However, high nickel layered cathodes sustain poor electrochemical performance and thermal stability since the lattice structures are unstable during charge/discharge processes and side-reactions occur at the interface that damages the active materials. During cycling, Ni<sup>2+</sup> would potentially migrate from the transition metal layer (TM layer) to the lithium layer (Li layer) because they compose similar cationic sizes. The migration would result in Li/Ni mixing and block Li<sup>+</sup> diffusion and trigger irreversible phase transition (layer to spinel or even rock salt).<sup>81-83</sup> Moreover, lattice structure at a highly delithiated stage would lead to an oxygen evolution reaction and oxygen

loss from the lattice, which could give rise to the thermal runaway and capacity fading.<sup>12, 84, 85</sup> Consequently, it is critical to stabilizing the lattice structure and interface of the high nickel layered cathode during cycling.

To solve these issues associated with the high nickel layered cathode materials, structural modifications, surface coatings, electrolyte optimizations, and doping methods have been extensively implemented. For example, designing a concentration gradient cathode structure with high nickel at the interior core and low nickel at the outer surface could efficiently lower the interfacial reactivities, which extends cycle life and delivers better capacity retention.<sup>86</sup> Moreover, surface coating strategies like metal oxide, phosphate, fluoride, or other conductive material coatings can prevent direct contact with electrolyte at the interface and lead to better stability.<sup>87-95</sup> Besides, electrolyte optimizations are also employed to establish a stable interface on the cathode, which efficiently elevates cell performance.<sup>96-98</sup> However, among all these strategies, cation doping is one of the most practical and scalable solutions. <sup>50, 99-108</sup> Especially of Al<sup>3+</sup>, which has been comprehensively studied since it can promote structural stability to achieve better cycling performance and thermal stability. The Al dopant can restrain Ni<sup>2+</sup> migration and possesses stronger Al-O bonding in TM layer <sup>109-112</sup>. A tiny amount (<5%) of Al can fulfill the optimization of the cathode material since Al is inert during the charge and discharge processes.<sup>113, 114</sup> Within diverse coating methods on the precursors, the dry coating is one of the most practical methods for industry synthesis since it avoids additional steps to dispose of the waste solution from wet coating approach.

In this work, we implemented nano-sized Aluminum oxide and hydroxide to dope high nickel layered low cobalt cathode materials (**Fig 2.1**). Dry coating methods (ball milling, mechanical fusion) were carried out to achieve a uniform layer on the precursors' surface. Compared with dry coating methods, wet coating suffers from low yield, complicated steps, and extra waste management. Thus, dry coating strategies prove more scalable and low-cost manufacture for practical productions. After careful analysis and characterization of Al-doped high

nickel layered cathode materials, detailed Al distributions and functions have been carefully investigated in this chapter. The Al-doped NCM cathode materials demonstrate significant improvement in cycling stability, rate performance, and thermal stability at increased temperatures. Such advancement contributed from the stabilized bulk structure by Al doping.



Fig 2.1 Schematic illustration of the synthesis of Al-doped high Ni layer cathode materials by the dry coating process.

#### 2.2 Experimental section

#### 2.2.1 Material Synthesis

LiNi<sub>0.92</sub>Co<sub>0.055</sub>Mn<sub>0.025</sub> (NCM) is synthesized through calcination where LiOH·H<sub>2</sub>O (Sigma-Aldrich) and Ni<sub>0.92</sub>Co<sub>0.055</sub>Mn<sub>0.025</sub> (molar ratio 1.05:1) undergoes a two-step annealing process at 480 °C for 5 hours and 715 °C for another 15 hours under an oxygen atmosphere. For Al-doped NCM by dry coating processes (NCM\_Al), Ni<sub>0.92</sub>Co<sub>0.055</sub>Mn<sub>0.025</sub> precursor, and nano-size Al(OH)<sub>3</sub> (98.5%:1.5%) were mixing thoroughly by ball milling or mechanical fusion machine (Wuxi Taixian Powder Science and Technology Co., Ltd) with proper time and speed. The mixtures subsequently experience the same calcination condition with LiOH·H<sub>2</sub>O as NCM.

#### 2.2.2 Material Characterization

The specific area of cathode precursors was evaluated by Brunauer-Emmett-Teller (BET) Micromeritics ASAP 2000 BET apparatus equipped with liquid nitrogen. Chemical composition analysis of the cathode material was measured by Inductively Coupled Plasma Emission Spectrometry (ICP-AES) Thermo iCAP 7400. Morphologies of cathode materials were conducted via scanning electron microscope (NanoSEM 630). Elemental mapping of the Al-doped samples was carried out by energy-disperse X-ray spectroscopy (EDS) with SEM. Cross-sectional images of cathode samples were prepared by the Leica Ion milling machine. X-ray powder diffraction (XRD) Rigaku Miniflex II spectrometer with Cu K<sub> $\alpha$ </sub> radiation was employed to collect the structure information from  $10^{\circ}$  to  $80^{\circ}$  with  $0.02^{\circ}$  scan step. GSAS program was used for Rietveld refinement to obtain detailed crystal parameters. The HAADF-STEM imaging and EDS mapping were performed on the aberration-corrected JEOL JEM-ARM200CF in PNNL. The thermal stability test was taken by differential scanning calorimeter with TA Instruments Q2000 with Refrigerated Cooling System (RCS90) (DSC). The cathode electrodes for DSC were charged to 4.3 V with CC-CV mode. Subsequently, the electrodes were disassembled and washed with DMC in the Argonfilled glovebox. Then, the electrodes were scratched off the current collector then dried under vacuum to remove the solvent. DSC was measured under a heating rate of 5 °C ·min<sup>-1</sup> from 25 °C to 350 °C in a sealed aluminum pan.

#### 2.2.3 Electrode fabrications and Electrochemical Tests

Cathode electrodes were fabricated by mixing the active material, super C, and polyvinylidene fluoride (PVDF) (Sigma-Aldrich) in an 8: 1: 1 ratio in *N*-methyl-2-pyrrolidone (NMP) (Sigma-Aldrich) solvent. The slurry then was cast on aluminum foil through the doctor

blade to achieve a similar loading amount of about 3 mgcm<sup>-2</sup> and subsequently put into a vacuum oven over 12 hours to obtain thoroughly dry electrodes. CR2016 coin cell type was implemented for half-cell and assembled inside Argon-filled glovebox (H<sub>2</sub>O< 0.1 ppm, O<sub>2</sub>< 0.1 ppm). LP71 electrolyte (Gotion Company) composed of 1M LiPF<sub>6</sub> in a mixture of ethylene carbonate (EC): diethyl carbonate (DEC): dimethyl carbonate (DMC) [1:1:1 w/w] was used in the half cells. The cycling performance of the half cells was measured between 2.7-4.3 V under 1C (0.2 A/g) with three activation cycles at 0.1C. Rate performance was tested in the same voltage window with various current densities (0.1, 0.2, 0.5, 2, 5C). Galvanostatic intermittent titration technique (GITT) was carried on Landt system with a pulse of 0.1 C for 10 mins followed by one hour's rest. The processes would finish when the cells reach cut-off voltage (4.3 V). Electrochemical impedance spectroscopy (EIS) measurements were tested from frequency 1M Hz to 10 Hz with 5 mV potential perturbation.

#### 2.3 Results and Discussions

#### 2.3.1 Ball milling coating method

Although Al doping could improve the structural stability of the NCM cathode, too much Al would sacrifice the capacity of the materials. To figure out optimized Al doping for the high nickel layered NCM cathode, two Al dopant precursors (Al<sub>2</sub>O<sub>3</sub> and Al(OH)<sub>3</sub>) with different concentrations were mixed with NCM precursor to undergo ball milling processes. A speed of 250 RPM has been chosen for the ball milling process because higher speed might damage the integrity of NCM precursors and low speed could not proceed with homogenous mixing.

Concentrations of  $Al_2O_3(0, 0.5, 1, 2 \text{ wt\%})$  were selected to undergo doping processes with high nickel NCM precursors to synthesize corresponding cathode materials. The obtained materials

were subsequently made into electrodes and paired with Li metal anode as half cells to examine electrochemical performance at room temperature shown in Fig 2.2. The voltage profiles of the half cells with different Al-doped cathode materials are shown in Fig 2.2a. Bare NCM (BM\_NCM\_bare) delivers the highest discharge specific capacity with 217 mAhg<sup>-1</sup>, while the capacity drops with an increasing amount of  $Al_2O_3$  doping. This is caused by the Al doping is inactive and would not participate in electrochemical processes during cycling. Although Al doping decreases the initial discharge capacity, the cycling stability of the cells has been optimized significantly (Fig 2.2b). Fast capacity fading occurs in the cell with Bare NCM cathode due to the unstable structure, where the capacity retention drops to only 70% after 200 cycles. Among various Al-doped NCM cathodes, 0.5% Al<sub>2</sub>O<sub>3</sub> doped NCM cathode demonstrates better capacity retention but discharge capacity is lower than bare samples after 200 cycles. 2% Al<sub>2</sub>O<sub>3</sub> doped NCM shows the most improved capacity retention (86.7%) but too much Al<sub>2</sub>O<sub>3</sub> doping results in a lower specific capacity. Therefore, 1% Al<sub>2</sub>O<sub>3</sub> doped NCM cathode illustrates both high specific capacity after 200 cycles and good capacity retention (84.8%), which is the optimized concentration for Al<sub>2</sub>O<sub>3</sub> doping. Overall, although Al<sub>2</sub>O<sub>3</sub> doping would sacrifice some specific capacity of cathode materials, the cycling stability could be greatly boosted due to stabilized bulk structures.



Fig 2.2 Electrochemical performance of  $Al_2O_3$  doped NCM in different concentrations (a) Initial charge and discharge voltage profile at 2.7 - 4.3 V. (b) Cycling performance and coulombic efficiency at 1C.

Crystal structure information is collected by X-Ray Diffraction (XRD). The patterns suggest all the NCM and Al<sub>2</sub>O<sub>3</sub> doped NCM compose the same rhombohedral  $\alpha$ -NaFeO<sub>2</sub> structure ( $R\bar{3}m$  space group) without impurity peak (**Fig 2.3**). During the calcination process, Ni<sup>2+</sup> would migrate to the Li<sup>+</sup> layer due to a similar radius to cause Li/Ni mixing. The ratio between (003) and (104) peak intensity is an important parameter to evaluate the level of Li/Ni mixing. The higher ratio in the Al-doped NCM layered cathode material indicates a lower degree of Li/Ni mixing in the material, where fewer Li sites are occupied by Ni<sup>2+</sup> and more active Li<sup>+</sup> could transfer in the layer structures. Additionally, the Rietveld refinement results in the reasonable fitting of the simulated and experimental XRD patterns of bare NCM and BM\_NCM\_1%Al<sub>2</sub>O<sub>3</sub> (**Fig 2.3**). The a-axis and c-axis changes result from Al doping and reduced Li/Ni mixing ratio matches with the higher (003)/(104) ratio of the sample. These evolutions further suggest that Al<sub>2</sub>O<sub>3</sub> has diffused within the bulk crystal structures and limited Ni<sup>2+</sup> migration to achieve a lower Li/Ni mixing ratio.



Fig 2.3 XRD patterns of NCM and Al-doped NCM cathode materials (upper). Rietveld refinement results of XRD for  $BM_NCM_bare$  and  $BM_NCM_1\%$   $Al_2O_3$ .

In addition to Al<sub>2</sub>O<sub>3</sub> as a dopant precursor, nano-sized Al(OH)<sub>3</sub> particles have also been implemented to dope high nickel layered NCM cathode since Al(OH)<sub>3</sub> is more closed to NCM precursor hydroxide (Ni<sub>0.92</sub>Co<sub>0.055</sub>Mn<sub>0.025</sub>(OH)<sub>3</sub>) structure. To maintain the same molar Al concentration with Al<sub>2</sub>O<sub>3</sub> doping, concentrations 0, 0.75, 1.5, 3 wt% of Al(OH)<sub>3</sub> have been selected to dope NCM cathode materials. The Voltage profiles of half cells with various Al(OH)<sub>3</sub> doped NCM cathode electrodes have shown in **Fig 2.4a**. Similarly, with increasing concentration of Al(OH)<sub>3</sub>, the discharge specific capacity has decreased due to inactive Al components in the cathode materials. However, the cycling performance of the cells with Al(OH)<sub>3</sub> doped NCM cathode demonstrates improved cycling stability in **Fig 2.4b**. Especially, NCM with 1.5% Al(OH)<sub>3</sub> delivers better cycling stability without too much capacity loss in the initial cycle.



Fig 2.4 Electrochemical performance of  $Al(OH)_3$  doped NCM in different concentrations (a) Initial charge and discharge voltage profile at 2.7 - 4.3 V. (b) Cycling performance and coulombic efficiency at 1C.

Therefore, 1% Al<sub>2</sub>O<sub>3</sub> and 1.5% Al(OH)<sub>3</sub> are selected to be the optimized concentration for Al<sub>2</sub>O<sub>3</sub> and Al(OH)<sub>3</sub> doping in NCM cathode materials. When compares to each other, Al(OH)<sub>3</sub> doping delivers a higher initial specific capacity than Al<sub>2</sub>O<sub>3</sub> (**Fig 2.5a**). Additionally, although both Al(OH)<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> doping improve the overall cycling stability, Al(OH)<sub>3</sub> doped NCM cathode could provide higher capacity in the initial cycles (**Fig 2.5b**). Thus, Al(OH)<sub>3</sub> is considered as a more suitable Al dopant for high Ni layered NCM cathode and applied for further experiments in this chapter.



Fig 2.5 Electrochemical performance of bare, 1.5% Al(OH)<sub>3</sub> doped, 1% Al<sub>2</sub>O<sub>3</sub> doped NCM (a) Initial charge and discharge voltage profile at 2.7 - 4.3 V. (b) Cycling performance and coulombic efficiency at 1C.

The morphology of cathode materials with and without Al doping has been observed through SEM (**Fig 2.6**). The secondary particles of bare NCM (BM\_NCM\_bare) (**Fig 2.6a**) and Al-doped NCM (BM\_NCM\_Al) (**Fig 2.6b**) compose similar particle sizes around 5~7 µm. To understand the Al doping distribution within the NCM cathode materials, the secondary particle of BM\_NCM\_Al was cut by a focused ion beam (FIB) to obtain Al mapping inside the NCM cathode material (**Fig 2.6c-f**). With the EDS mapping of Co, Ni, Al, it is confirmed that the Al has penetrated the bulk lattice during calcination.



Fig 2.6 SEM images of (a) BM\_NCM\_bare and (b) BM\_NCM\_1.5 % Al(OH)<sub>3</sub> (c) SEM cross-sectional image of BM\_NCM\_1.5% Al(OH)<sub>3</sub> particle. (d-f) SEM EDS elemental mapping of the particle in (c)

Rate performance represents the capability of cathode materials to undergo fast charge/discharge processes, which is shown in **Fig 2.7a**. With increasing current density from 0.1 C to 5 C, the BM\_NCM\_bare cathode material sustains serve capacity fading while the capacity retention drops to only 72% at 5C. However, the BM\_NCM\_Al cathode material delivers sluggish fading and maintains 88% capacity retention under 5C. The impedance is one of the key factors influencing the rate capability. Hence, impedance spectra by EIS have also been investigated to reveal the impedance evolution of the cells with different cycles (**Fig 2.7b-c**). The impedance data is collected at the 1<sup>st</sup>, 10<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup> cycle (activation cycles are excluded). In the BM\_NCM\_bare cathode, the initial resistance is high and increases dramatically after cycling because the structure undergoes degradation which would hinder electron transfer and increase the polarization. Moreover, microcracks generate fresh surfaces and induce CEI formation. Nonetheless, in the BM\_NCM\_AI cathode, the impedance experiences limited growth during cycling since AI doping stabilizes the bulk crystal structure during cycling. Thus, the AI doping stabilizes the bulk structure and leads to lower impedance during cycling, which attributes to improved rate capability.



Fig 2.7 (a) rate performance comparison from 0.1 C to 5 C. EIS evolution from  $1^{st}$  to  $100^{th}$  cycle. (b)BM\_NCM\_Bare (c) BM\_NCM\_A1.

In general, through the ball milling dry coating method, Al(OH)<sub>3</sub> nano-sized particles could diffuse within high Ni layered NCM cathode to lower the Li/Ni mixing ratio and stabilize the crystal structure. These benefits contribute to better cycling stability, rate performance, and lower impedance upon cycling.
## 2.3.2 Mechanical fusion method

Although the ball milling method could achieve Al doping in the high nickel layered NCM materials, it would also damage the integrity of NCM secondary particles since collision breaks spherical particles into small portions and generate the fresh surface of the cathode material (**Table 2.1**). The freshly generated surface would consume extra electrolytes to form the CEI and lead to polarization enhancement, which results in poor electrochemical performance (**Fig 2.8a**). Therefore, we implement another mechanical fusion dry coating method to achieve Al doping into high nickel layered NCM cathode (MF\_NCM\_Al). During the process, Al(OH)<sub>3</sub> nano-particles could disperse by shear force and adhere to NCM precursor's surface by mechanical friction rather than collision as shown in **Fig 2.8b-d**.

Samples	BET Surface Area (m <sup>2</sup> / g)		
NCM_Al_(Mechanical Fusion)	9.4003		
NCM_Al_(Ball Milling)	15.3599		

Table 2.1. BET surface area analysis of coating Al(OH)<sub>3</sub> with mechanical fusion and ball milling methods



Fig 2.8 (a) SEM images of high nickel layered cathode precursor after ball milling. The integrity of spherical particles has been damaged (b) SEM images of high nickel layered cathode precursor after mechanical fusion. The spherical morphology is well maintained. (c-d) EDS elemental mapping of the particle in (b).

Learned from the experience from the ball milling method, 1.5 wt% nano-sized Al(OH)<sub>3</sub> is selected as Al dopant concentration to undergo mechanical fusion with NCM precursor and generate Al-doped high nickel layered cathode material (NCM\_Al). The elemental compositions of cathode materials were measured by ICP-AES (**Table 2.2**). The ICP results indicate that high Ni layered NCM contains 92% nickel (91.8%/5.6%/2.6% Ni/Co/Mn) while the NCM\_Al cathode material contains 1.9% Al (90.1%/5.5%/2.5%/1.9% Ni/Co/Mn/Al).

Samples	Ni (%)	Co (%)	Mn (%)	Al (%)
NCM	91.83	5.63	2.54	
NCM_Al	90.13	5.5	2.5	1.87

Table 2.2. ICP results of the high nickel layered NCM and NCM\_Al.

The morphology of high nickel layered material NCM and NCM\_Al observed from SEM is demonstrated in **Fig 2.9**. Both cathode materials consist of nano-sized primary particles and compose spherical secondary particles with a diameter of around 3~4 µm (**Fig 2.9a-b**). The cross-sectional view of the secondary particles shows that both materials contain packed interior morphology without large voids or crack in the pristine materials (**Fig 2.9c-d**). To further investigate Al doping distribution in high nickel layered NCM cathode, high-angle annular dark-field imaging in scanning transmission electron microscope (HAADF-STEM) has been applied to verify the allocation of Al element (**Fig 2.10**). EDS mapping reveals that the Al dopant forms a solid solution and uniformly penetrates within the bulk structure of NCM\_Al during the calcination process.



Fig 2.9 SEM of particles and corresponding cross-section images (a,c) NCM (b,d) NCM\_Al.



Fig 2.10 HAADF-STEM elemental distribution of NCM\_Al pristine particle.

XRD patterns (**Fig 2.11**) indicate both the NCM, NCM\_Al cathode materials have the same rhombohedral  $\alpha$ -NaFeO<sub>2</sub> structure ( $R\bar{3}m$  space group) without impurity peak. The splitting of (006)/(012) and (018)/(110) represents the level of the ordered layered structure where both cathode materials compose a highly ordered layered structure (**Fig 2.11a**).<sup>99, 109</sup> The Rietveld refinement results show the rational fitting of the simulated and experimental XRD patterns for NCM and

NCM\_Al cathode materials (**Fig 2.11b-c, Table 2.3**). The ratio of (003)/(104) suggests the Li/Ni mixing, where the higher ratio infers less Li/Ni mixing and better electrochemical performance. The ratio has been increased in the NCM\_Al sample, which indicates that the Li/Ni mixing has been decreased after Al doping and the calculated result of the Li/Ni mixing ratio in **Table 2.3** supports this conclusion. These evolutions infer that Al has diffused within the high Ni layered crystal structure.<sup>70</sup> The decline of lattice parameters in the NCM\_Al samples is caused by the Al<sup>3+</sup> (0.535 Å) substitution of the transition metal ions.



Fig 2.11 (a) XRD patterns of pristine NCM and NCM\_Al cathode materials. (b-c) Rietveld refinement results of XRD for NCM and NCM\_Al.

	a-axis (Å)	b-axis (Å)	c-axis (Å)	c/a	vol (Å <sup>3</sup> )	Li/Ni mixing
NCM	2.8841	2.8841	14.2325	4.935	118.39	6.19%
NCM_Al	2.8780	2.8780	14.2293	4.944	117.86	5.16%

Table 2.3. Lattice parameters and Li/Ni mixing for NCM and NCM\_Al.

The initial charge and discharge curves (0.1 C) (Fig 2.12a) suggest the NCM cathode material delivers a higher discharge specific capacity (218 mAhg<sup>-1</sup>) than the NCM Al cathode (213.8 mAhg<sup>-1</sup>) <sup>1</sup>) but the coulombic efficiency (CE) of NCM\_Al increases to 89.4%. This is because the inactive Al substitutes Ni in NCM\_Al and leads to specific capacity decline. Cycling performance and CE during cycling (1C rate) are presented in Fig 2.12b. Although NCM Al delivers a lower specific capacity (191 vs 197 mAhg<sup>-1</sup>), the capacity retention and specific capacity after 200 cycles show a significant distinction compared with NCM cathode material. The capacity retention of NCM-Al remains 86% compared to only 70.7 of NCM cathode. The specific capacity reserves over 164 mAhg<sup>-1</sup> while the NCM cathode only delivers below 140 mAhg<sup>-1</sup>. Rate performance (Fig 2.12c) is carried out from the current rate of 0.1 C to 5 C between 2.7 V and 4.3V. NCM and NCM Al cathode materials deliver similar specific retention at initial 0.1 C, but NCM cathode suffers from serious capacity fading with an increase of current density while NCM\_Al cathode maintains rational 81.0% capacity retention under 5C. These results suggest Al doping in NCM\_Al could enhance the cycling stability as well as the rate performance, which results from the stabilized crystal structure by mechanical fusion Al doping. The average charge and discharge voltage over 200 cycles are shown in Fig 2.12d. The NCM cathode experiences an evolution from 0.257 V to 0.788 V after 200 cycles while the NCM Al cathode only increases from 0.227 V to 0.472 V. Both materials deliver similar charge and discharge curves in the initial cycle. However, upon cycling, polarization increases dramatically within the NCM cathode while the NCM\_Al cathode undergoes a modest polarization enlargement. These results suggest fast decay and polarization enlargement of NCM cathode, which may result from the structural deterioration and enhancement of impedance upon cycling while NCM Al shows better structural stability due to Al doping.



Fig 2.12 Electrochemical performance of NCM and NCM\_Al (a) Initial charge and discharge voltage profile at 2.7 - 4.3 V. (b) Cycling performance and coulombic efficiency at 1C (c) rate performance comparison from 0.1 C to 5 C. (d) evolution of the average charge/discharge voltage over 200 cycles.

To explore the mechanism of the enhanced performance by Al doping in high nickel layered cathode,  $dQ \cdot dV^{-1}$  curve of cathode materials illustrates the electrochemical processes during charge and discharge, which has been shown in **Figure 2.13(a)**. Both cathode materials undergo similar steps of phase transitions (hexagonal (H1)  $\rightarrow$  Monoclinic (M)  $\rightarrow$  Hexagonal (H2)  $\rightarrow$  Hexagonal (H3)) during the charging process and reverse back after the discharge process.<sup>115</sup> The redox peaks corresponding to the H2  $\rightarrow$  H3 transition during the charging process, which is extremely important since structural deterioration and safety hazards (gas generation) may occur due to the poor stability of H3 phase.<sup>29, 30, 112, 116</sup> After Al doping by mechanical fusion, the H2 to H3 redox peaks in NCM\_Al cathode migrates to a higher voltage and intensity shows an obvious decline, which indicates the postponement and decreased intensity of detrimental H2  $\rightarrow$  H3 transition during cycling. This explains that the NCM\_Al cathode materials possess stabilized cycling performance in long-term cycling.



Fig 2.13 dQ·dV<sup>-1</sup> curves of (a) the first charge and discharge curves of NCM and NCM\_Al (b) magnification of selected region represented H2 to H3 phase transition from (a).

To investigate how Al doping influences the crystal structure and improves the overall cycling performance, it is significant to investigate the distribution of Al since it associates closely with structural stability. With HAADF-STEM, it is found that the Al not only diffuses within the bulk crystal structure but also generates an Al concentrated layer at the surface (Figure 2.14a,b) after cycling. This rearrangement of Al is caused by the nickel migration upon cycling<sup>117</sup>. A line scan from bulk to the surface indicates a concentrated Al layer with a thickness of 2 nm has been generated on the surface. The EDS mapping of NCM\_Al after cycling (Figure 2.15) confirms the Al has uniformly distributed within the bulk structure. Once in a while, the Al accumulates and forms a continuous layer near the surface. It infers the NCM\_Al would generate a core-shell structure with low Al in the core and Al concentrated layer as a shell.<sup>117, 118</sup> Additionally, it also shows a phosphate enriched cathode electrolyte interphase layer at the surface with a thickness around 4 nm. For NCM cathode (Figure 2.16), although phosphorus signal has been detected, there is only a scattered and discrete signal on the surface which indicates non-uniform CEI formation. XPS has been employed to detect chemical compositions on the cycled electrode (Figure. 2.17). The F 1s spectra suggest the LiF component is higher in the NCM Al than the NCM cathode materials after 120 cycles. The higher content of LiF comes from the decomposition of LiPF<sub>6</sub> salt,

which corresponds to the phosphate enriched CEI layer.<sup>119</sup> Although electrolytes would decompose at the interface, it would form a stable protection layer which is beneficial to the Li<sup>+</sup> transport at the interface and results in smaller polarization and stable interface, which leads to improved and stabilized cycling performance.



Fig 2.14 STEM-HAADF image of (a) NCM\_Al after 120 cycles. (b) Atomic compositional profile of Ni, Co, Mn, and Al along the arrow in (a).



Fig 2.15 HAADF-STEM image of NCM\_Al after 120 cycles and corresponding EDS mapping of NCM\_Al after 120 cycles.



Fig 2.16 HAADF-STEM image of NCM after 120 cycles and corresponding EDS mapping of NCM after 120 cycles.



Fig 2.17 XPS spectra (a) C 1s, (b) F 1s, and of NCM and NCM\_Al after 120 cycles.

The reconstruction layer evolutions on the surface are measured by HAADF-STEM (**Figure 2.18**). At pristine state, similar nm level reconstruction layers have been observed on the surface of primary particles of both cathode materials (**Fig 2.1c-d**). This layer is reported to block

Li-ion diffusion and results in an impedance increase. NCM\_Al contains a thinner reconstruction layer within 2 nm. After cycling, there is a thicker reconstruction layer about 13 nm covered on the NCM surface while the NCM\_Al only shows a thin layer (3 nm) which is similar to the pristine layer thickness. These results suggest that the Al doping would suppress reconstruction layer growth since Al would occupy the site in the transition metal layer and limit the Ni migration to form an irreversible rock-salt layer (reconstruction layer). Moreover, the construction layer is Al concentrated at the outer surface which protects the cathode material upon cycling.



Fig 2.18 HAADF-STEM images of pristine (a) NCM, (b) NCM\_Al, cycled (c) NCM, (d) NCM\_Al. The regions between the red and orange line represent the reconstruction layer on the primary grain's surface.

Cross-section SEM images have shown the inner structure deformation of cathode materials after 200 cycles (**Figure 2.19**). NCM cathode material (**Figure 2.19a**) after 200 cycles generates cavities and intergranular cracks from the center of secondary particles which is distinguishing from its pristine close-packed morphology (**Figure 2.9c**). This variation is caused by the anisotropic lattice change during long-term cycling.<sup>30, 120</sup> However, in the NCM\_Al (**Figure** 

**2.19b**), there are no obvious cracks or cavities in the secondary particles and show smooth morphology. This morphology difference refers to that the NCM\_Al has better intrinsic mechanical strength against anisotropic lattice distortion which results in fewer intergranular cracks.



Fig 2.19 Cross-section SEM images of (e) NCM, (f) NCM\_Al after 200 cycle.

Impedance is also an important factor to influence polarization and rate performance during cycling. Therefore, EIS is implemented to detect impedance evolution upon cycling. The impedance data is collected at the 1<sup>st</sup>, 10<sup>th</sup>, 50<sup>th</sup>, and 100<sup>th</sup> cycles (formation cycles are excluded). The data consists of two semicircles. The first one in high-medium frequency corresponds to the surface film resistance ( $R_{sf}$ ) and the second semicircle indicates the charge transfer ( $R_{cf}$ ) on the cathode.<sup>80</sup> NCM cathode experiences fast impedance growth due to rapid reconstruction layer growth at the surface and structural degradation within bulk crystal structure (Fig 2.20a). However, NCM Al cathode only experiences a small raise of impedance (Fig 2.20b). This evidence supports the Al doping can limit the reconstruction layer growth and generate a stable CEI layer on the surface, which further protects the interface and leads to stable long-term cycling performance.<sup>86,</sup> The chemical Li<sup>+</sup> diffusivities of both cathode materials are investigated by galvanostatic 116 intermittent titration technique (GITT)<sup>15</sup> in Fig 2.20c. The results suggest the Li<sup>+</sup> diffusivity gets improved after Al doping by mechanical fusion. The boosted diffusivity may due to the stable CEI formation and thinner reconstruction layer formation on the surface which leads to better rate capacity.



Fig 2.20 EIS evolution from  $1^{st}$  to  $100^{th}$  cycle of (a) NCM (b) NCM\_Al. (c) Measured diffusivities  $D_{Li}^+$  during charge process for NCM and NCM.

**Thermal Stability**: Differential scanning calorimeter (DSC) profiles have been implemented to evaluate the thermal stability of cathode materials at charged state (4.3 V) because safety is one of the significant concerns in practical LIBs. **Figure 2.21** shows the exothermic peak temperatures for both cathode materials. For high nickel content cathode (Ni > 0.9), phase transitions (from layered to spinel and then to rock salt structure) accompanied by oxygen evolution would occur at a raised temperature. Transition metal ions would migrate to the Li layer through adjacent tetrahedral sites and oxygen evolution reaction would also take place simultaneously. The charged NCM exhibits an exothermic peak at 202.5 °C which is 10 °C below NCM\_Al cathode material. The improved resistance to phase transition and oxygen evolution reaction in NCM\_Al suggests that the Al doping can alleviate cationic migration and oxygen generation due to stronger Al-O bonding after doping.<sup>121-123</sup> All these data infers the Al doping results in enhanced thermal stability at elevated temperature.



Fig 2.21 DSC profile of NCM and NCM\_ Al at charged state (4.3 V).

# **2.4 Conclusion**

In this work, Al-doped high nickel low cobalt layered cathodes by a dry coating method (ball milling and mechanical fusion) has been systematically investigated and compared with NCM cathode material. The electrochemical performance and thermal stability have been significantly boosted since Al doping decreases the Li/Ni mixing ratio and stabilizes the crystal structure upon cycling. Additionally, Al doping limits the reconstruction layer growth and generates a concentrated layer on the surface to protect active material. Remarkably, NCM\_Al delivered enhanced capacity retention 86.0 % over 200 cycles and the exothermic peak is 212.4 °C (10 °C higher than NCM). Overall, the Al-doping through dry coating provides a cost-efficient and scaleable path to improve the electrochemical and thermal stability for high nickel layered cathode materials.

# Chapter 3

# Titanium Doping of High-Nickel Cathode for Enhanced Structural Stability of Lithium-Ion Batteries

# 3.1 Introduction

In recent decades, lithium-ion batteries (LIBs) have been developed to become the main source for advanced electric vehicles (EVs) because of their high energy density and long cycle life<sup>1-5</sup>. Therefore, high-nickel layered NCM cathodes (LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>1-x-y</sub>O2, X >0.9) are considered as promising cathode materials for next-generation LIBs due to their high capacity and low cost<sup>6-9</sup>.

However, high-nickel layered NCM cathodes sustain rapid capacity fading and poor cycling stability<sup>72, 73</sup>. This instability is mainly caused by structural degradation and undesired side reactions. During cycling, the cathode materials undergo reversible H2 to H3 phase transition around 4.2 V, which would trigger contraction and expansion of the materials<sup>10-12</sup>. This volume change contributes to internal microcracks and electrolyte infiltration upon cycling<sup>10</sup>. These mentioned obstacles hinder the practical applications of high-nickel layered NCM cathode materials in LIBs.

Previous studies suggest several strategies to solve these challenges, where doping is one of the most efficient and scalable methods<sup>32-48</sup>. The doping method is suitable for scale-up production and stabilizes the crystal structure of the cathode material<sup>49</sup>. Some competent dopants like Al<sup>3+</sup>, Zr<sup>4+</sup>, Mg<sup>2+</sup>, have been reported to enhance structural stability, which elevates the electrochemical performance of the cathode materials. Among various doping selections, Titanium (Ti) doping in NCM could also improve the electrochemical performance but the mechanism in Ti-doped NCM is still unclear<sup>124-129</sup>.

Hence, we applied nano-sized TiN as a precursor to achieving Ti doping in the high-nickel layered cathode material (NCM\_Ti). TiN is uniformly dispersed and adhered to the surface of the NCM precursor by mechanical fusion dry coating. During calcination, the TiN precursor transforms into two types of  $TiO_2$  with different crystal structures, which achieves distinct Ti distribution within NCM. Moreover, Ti doping by TiN in NCM refines the primary particle growth and decreases their sizes. Because of this, comprehensive structural and electrochemical analyses have been implemented to reveal the effects of Ti doping in the high-nickel layered cathode.

## **3.2 Experimental section**

# **3.2.1 Material Synthesis**

The LiNi<sub>0.92</sub>Co<sub>0.055</sub>Mn<sub>0.025</sub>O<sub>2</sub> (NCM) and LiNi<sub>0.906</sub>Co<sub>0.054</sub>Mn<sub>0.025</sub>Ti<sub>0.015</sub>O<sub>2</sub> (NCM\_Ti) cathode were synthesized via co-precipitation and calcination processes. Precursor  $[Ni_{0.92}Co_{0.055}Mn_{0.025}](OH)_2$  was synthesized by the co-precipitation process. NiSO4, CoSO4, and MnSO4 were dissolved in de-ionized water to achieve proper concentration. Subsequently, mixed metal-containing solution (Ni: Co: Mn = 92: 5.5: 2.5 in molar ratio), NaOH, and NH<sub>4</sub>OH solutions were filled in a tank reactor with deionized water inside. Nitrogen gas flow was continuously pumped into the reactor to remove O<sub>2</sub> and keep the inert atmosphere inside. After co-precipitation, the precursor experienced washing, filtering, and vacuum drying processes to get the final product.

To obtain NCM cathode material, the precursor  $[Ni_{0.92}Co_{0.055}Mn_{0.025}](OH)_2$  was mixed with LiOH·H<sub>2</sub>O (Sigma-Aldrich). Then, the mixture was calcinated at 480 °C for 5 hours and 715 °C for 15 hours under an oxygen atmosphere. To obtain NCM\_Ti cathode material, TiN was mixed with NCM precursor by mechanical fusion machine. Subsequently, the modified NCM precursor with LiOH·H<sub>2</sub>O was calcinated under the same process as NCM.

#### 3.2.2 Material Characterization

The chemical composition of cathode materials is analyzed by Inductively Coupled Plasma Emission Spectrometry (ICP-AES) Thermo iCAP 7400. The morphology and cross-sectional images of cathode materials are conducted by SEM. Elemental mapping of Ti-doped NCM is taken by energy-disperse X-ray spectroscopy (EDS) with SEM. To observe the cross-section of secondary particles of cathode materials, the prepared electrode was cut by the Leica Ion milling machine. Crystal structure information is collected by X-ray powder diffraction (XRD) Rigaku Miniflex II spectrometer with Cu K<sub>a</sub> radiation from 10-80 degree with a 0.02° scan step. Rietveld refinement is implemented via the General Structure Analysis System (GSAS) program to obtain lattice parameters and Li/Ni mixing of the cathode materials. High-angle annular dark-field imaging in scanning transmission electron microscope (HAADF-STEM) and corresponding EDS images are observed through the aberration-corrected JEOL JEM-ARM200CF.

## **3.2.3 Electrochemical Test**

The cathode electrode is fabricated with the active material, super C45 carbon black, and poly(vinylidene) fluoride (PVDF) at an 8: 1: 1 ratio in *N*-methyl-2-pyrrolidone (NMP) solvent to generate a slurry. Subsequently, the slurry was cast on aluminum foil by a doctor blade with a mass loading of about 3 mgcm<sup>-2</sup>. The electrode was dried in a vacuum oven for over 12 hours. The cathode electrode was assembled with a lithium metal anode to form a half cell in the Argon-filled glovebox (H<sub>2</sub>O <0.1 ppm O<sub>2</sub> < 0.1 ppm). LP57 electrolyte (Gotion Company) with 1M LiPF<sub>6</sub> in ethylene carbonate (EC): ethyl methyl carbonate (EMC) [3:7 w/w] was implemented as the electrolyte. The half cells were cycled between 2.7 V and 4.3 V under current rate 1C (1C = 200 mAg<sup>-1</sup>) with three activation cycles at 0.1C. Electrochemical impedance spectroscopy (EIS)

measurements were carried out between frequency 1M Hz to 10 Hz with 5 mV potential perturbation.

#### **3.3 Results and Discussions**

# 3.3.1 Ti doping optimization by the ball milling process

The ball milling method is implemented to determine the optimized Ti doping ratio in highnickel cathode material (NCM) because the required sample amount of ball milling is limited. The mechanical fusion method needs large quantities of NCM precursors, therefore the ball milling method is selected to optimize the Ti doping concentration for NCM cathode before using mechanical fusion dry coating.

Nano-sized Titanium nitride (TiN) with different concentrations (0, 0.5, 1, 2 wt%) was mixed with NCM precursor and LiOH through the ball milling process. Then the mixtures were calcinated and made into cathode electrodes to test the electrochemical performance in the half cell (**Fig 3.1**). TiN doped NCM cathodes through the ball milling process (BM\_NCM\_TiN) show similar specific charge capacity and polarization in the initial cycle (**Fig 3.1a**). However, because of the substitution of Ni<sup>2+</sup> by Ti<sup>4+</sup>, where Ti<sup>4+</sup> is inert during cycling, the specific discharge capacity of BM\_NCM\_TiN decreases with an increase of Ti doping amount. The cycling performance of the BM\_NCM and the BM\_NCM\_TiN cathodes (**Fig 3.1b**) demonstrates distinct cycling stability in the half cells. The BM-NCM cathode suffers from rapid capacity fading due to structural degradation. However, the BM\_NCM\_TiN cathodes with 0.5% and 1% doping deliver improved capacity retention and high capacity after 200 cycles. The 2% TiN doping might be excess for NCM cathode, although it shows better capacity retention. Rate performance is implemented from 0.1C to 5C (1C = 200 mAhg<sup>-1</sup>) at room temperature (**Fig 3.1c**). The BM\_NCM\_TiN cathodes with 0.5% and 1% doping demonstrate better capacity retentions than the BM\_NCM cathode at an elevated current rate (5C). Moreover, both cathodes can recover to 100% capacity when the rate reduces back to 0.1C, which indicates good structural stability after Ti doping. Based on the electrochemical performance of the BM\_NCM\_TiN, 1% TiN doping is selected as the optimized concentration for the following experiments.



Fig 3.1 Electrochemical performance of NCM and TiN doped NCM with different ratios (a) Initial charge and discharge voltage profile at 2.7 - 4.3 V. (b) Cycling performance and coulombic efficiency at 1C. (c) rate performance comparison from 0.1 C to 5 C.

TiN reacts with oxygen to generate TiO<sub>2</sub> that acts as a Ti dopant to diffuse within NCM cathode material during calcination. To compare the effects between TiN and TiO<sub>2</sub> doping precursor, the electrochemical performance of NCM cathodes doped by TiN (BM\_NCM\_TiN) and TiO<sub>2</sub> (BM\_NCM\_TiO<sub>2</sub>) has been shown in **Fig 3.2**. Both TiN and TiO<sub>2</sub> doped NCM cathodes show analogous decreased specific discharge capacity due to inactive Ti<sup>4+</sup> incorporation (**Fig 3.2a**). However, BM\_NCM\_TiO<sub>2</sub> sustains from the huge capacity drop and low specific capacity at 1C current rate. The BM\_NCM\_TiN cathode displays a higher specific capacity under 1C that is similar to BM\_NCM and better cycling stability after 100 cycles, which suggests a stabilized structure within the BM\_NCM\_TiN cathode.



Fig 3.2 Electrochemical performance of NCM, TiN doped NCM, and  $TiO_2$  doped NCM cathodes. (a) Initial charge and discharge voltage profile at 2.7 - 4.3 V. (b) Cycling performance and coulombic efficiency at 1C.

To understand the mechanism for the electrochemical difference between BM\_NCM\_TiN and BM\_NCM\_TiO<sub>2</sub>, the crystal structure of TiO<sub>2</sub> and products generated by TiN have been investigated by XRD (**Fig 3.3**). To mimic the calcination process, TiN and TiO<sub>2</sub> nano-particles were placed into a tube furnace under 480 degree for 5 hours in an oxygen atmosphere. The XRD pattern of the generated product from TiN (**Fig 3.3a**) shows that the TiN would turn into two types of TiO<sub>2</sub> mixture. One is the rutile type of TiO<sub>2</sub> (TiO<sub>2</sub>\_R) and another is the anatase type of TiO<sub>2</sub> (TiO<sub>2</sub>\_A). However, TiO<sub>2</sub> stays as TiO<sub>2</sub>\_A type at elevated temperature.



Fig 3.3 XRD patterns of (a) TiN under 480 degree for 5 hours, (b)  $TiO_2$  under 480 degree for 5 hours, in an oxygen atmosphere.

The different types of TiO<sub>2</sub> generated by TiN and TiO<sub>2</sub> affect the diffusion processes of Ti doping during the calcination. Hence, the distribution of Ti in the cathode material after calcination is explored by HAADF-STEM (**Fig 3.4**). In BM\_NCM\_TiN cathode (**Fig 3.4a**), it shows that the

Ti not only penetrates the bulk structure of the NCM but also forms evident Ti segregation on the surface of primary particles. This phenomenon is caused by the different diffusion paths of the two types of TiO<sub>2</sub>. In the BM\_NCM\_TiO<sub>2</sub> cathode (**Fig 3.4b**), it indicates similar Ti diffusion within the NCM structure but no segregation situation was observed on the primary particle surface.



Fig 3.4 HAADF-STEM images and corresponding EDS mapping of (a) BM\_NCM\_TiN, (b) BM\_NCM\_TiO<sub>2</sub> cathodes.

The Ti distribution in the NCM materials explains the reason why TiN is a better Ti dopant precursor for Ti doping in the high-nickel layered cathode material. After optimization by the ball milling process, the mechanical fusion dry coating method is implemented for the Ti doping with 1% TiN as the dopant.

# 3.3.2 Ti doping by mechanical fusion

The elemental compositions of cathode materials were measured by ICP-AES. The ICP results (**Table 3.1**) indicate that high Ni layered NCM contains 92% nickel (91.7%/5.7%/2.6%

Ni/Co/Mn) while the Ti-doped NCM (NCM\_Ti) cathode material contains 1% Ti component within the NCM cathode material (91%/ 5.5%/ 2.5%/1% Ni/Co/Mn/Ti)

Samples	Ni (%)	Co (%)	Mn (%)	Al (%)
NCM	91.7	5.7	2.6	
NCM_Ti	91	5.5	2.5	1

Table 3.1. ICP results of the high nickel layered NCM and NCM\_Ti.

The morphology of the secondary particle of cathode materials is shown in **Fig 3.5**. NCM (**Fig 3.5a**) and NCM\_Ti (**Fig 3.5b**) cathodes compose spherical secondary particles with nanometer-sized primary particles. The diameter of the secondary particles is similar to around 2 to 3 µm. The cross-sectional images show different primary particle morphology within the cathode materials. The primary particle size in the NCM (**Fig 3.5c**) is larger than the size in the NCM\_Ti cathode (**Fig 3.5d**). This result indicates that the Ti doping in the NCM constrains the growth of primary particles and accomplishes a finer particle distribution within the cathode materials. The smaller and finer size of the primary particles is beneficial to Li<sup>+</sup> transportation and deters internal microcrack formation.

The distribution of Ti within the NCM cathode has been confirmed by HAADF-STEM (**Fig 3.6**). EDS mapping of the NCM\_Ti cathode suggests the penetration of Ti within the NCM cathode while Ti would also generate segregation at the surface of the primary particles (**Fig 3.4a**).



Fig 3.5 SEM of secondary particles and corresponding cross-section images (a,c) NCM (b,d) NCM\_Ti.



Fig 3.6 HAADF-STEM images and corresponding EDS mapping of NCM\_Ti cathode.

XRD patterns (**Fig 3.7**) suggest that both NCM and NCM\_Ti cathode materials involve rhombohedral  $\alpha$ -NaFeO<sub>2</sub> structure ( $R\overline{3}m$  space group) without an additional peak. The (003)/(104) ratio indicates that NCM\_Ti cathode material contains a higher Li/Ni mixing ratio. This is because of charge compensation in the material. As the Ti<sup>4+</sup> doping amount increase, Ni<sup>3+</sup> is converted to Ni<sup>2+</sup> due to charge compensation. Hence, there will be a higher possibility for Ni<sup>2+</sup> migration, which leads to higher Li/Ni mixing and lower (003)/(104 ratios. However,  $Ti^{4+}$  would occupy the Li<sup>+</sup> site and act as a pillar to prevent the Li layer from the collapse that results in better cycling stability.



Fig 3.7 XRD patterns of pristine NCM and NCM\_Ti cathode materials.

The electrochemical performance of NCM and NCM\_Ti cathode materials is shown in **Fig 3.8**. The initial voltage profile (**Fig 3.8a**) indicates that the NCM\_Ti cathode delivers higher charge capacity but lower discharge capacity due to the inactive Ti component in the NCM cathode. Nonetheless, the cycling performance of the NCM\_Ti shows a huge improvement in cycling stability (**Fig 3.8b**). The NCM\_Ti cathode remains 93.8% capacity retention with a specific capacity of 170.6 mAhg<sup>-1</sup> after 200 cycles. The NCM cathode suffers from fast severe capacity fading under 1C current with only 67.2% capacity retention. The enhanced cycling performance is attributed to the Ti doping within the NCM material, where Ti acts as a pillar in the Li slab to prevent the Li interlayer from collapse during cycling. The rate performance (**Fig 3.8c**) indicates that the NCM\_Ti cathode could maintain over 160 mAhg<sup>-1</sup> even under 5C current. This is because Ti doping reinforces the stability of the Li slab and enlarges the interlayer spacing of the Li slab, which results in better rate capability under high current. The average charge and discharge voltage during cycling demonstrate the polarization evolution of the cathode materials (**Fig 3.8d**). The NCM cathode undergoes an evolution of voltage difference from 0.144 V to 0.384 while the NCM\_Ti cathode only changes from 0.134 V to 0.239 V. Impedance increase in the NCM cathode

that is caused by structural degradation results in this larger polarization. The stabilized structure achieved by Ti doping constrains impedance growth and leads to small polarization evolution.



Fig 3.8 Electrochemical performance of NCM and NCM\_Ti (a) Initial charge and discharge voltage profile at 2.7 - 4.3 V. (b) Cycling performance at 1C (c) rate performance comparison from 0.1 C to 5 C. (d) evolution of the average charge/discharge voltage over 200 cycles.

Impedance is a key parameter associated with the electrochemical performance of the cathode materials upon cycling. Therefore, EIS is applied to measure the impedance after the 1<sup>st</sup>, 10<sup>th</sup>, 50<sup>th</sup>, 100<sup>th</sup>, and 200<sup>th</sup> cycles, which represents the impedance revolution during cycling (**Fig 3.9**). Compared to the NCM cathode (**Fig 3.9a**), the NCM\_Ti cathode (**Fig 3.9b**) only shows a small rise of impedance upon cycling, which results in stable cycling performance and better rate performance. The stable impedance is achieved through stabilized structure of the NCM\_Ti cathode.



Fig 3.9 EIS evolution from 1<sup>st</sup> to 200<sup>th</sup> cycle of (a) NCM (b) NCM\_Ti cathode material.

To further explore the mechanism of Ti doping effects in NCM cathode material, cyclic voltammetry (CV) curves of cathode materials are measured to investigate the electrochemical processes in the first three cycles (**Fig 3.10**). NCM and NCM\_Ti cathode experience similar phase transitions from hexagonal (H1)  $\rightarrow$  Monoclinic (M)  $\rightarrow$  Hexagonal (H2)  $\rightarrow$  Hexagonal (H3). Especially in H2 to H3 transition, c-axis contracts and results in shrinkage of the crystal structure. The consecutive contraction and expansion of volume change lead to structural degradation and microcracks formation after long-term cycling. Compared to the NCM cathode, the peak corresponded to H2 to H3 transition (dash line) shifts to a higher voltage, which indicates a lag of detrimental H2 to H3 transition.



Fig 3.10 CV curves of the first three cycles of NCM and NCM\_Al.

Because of the H2 to H3 transition and volume change, micro-cracks and structural deformation would occur after long-term cycling. Hence, cross-sectional SEM images of the secondary particles are shown to compare the structural stability of the cathode materials (**Fig 3.11**). After 200 cycles, the NCM cathode generated a lot of cavities and microcracks, which led to serious capacity loss and electrolyte infiltration (**Fig 3.11 a,b**). The secondary particle tends to pulverize and the crystal structure has been severely damaged by the anisotropic lattice change upon cycling. On the contrary, the NCM\_Ti cathode remained packed morphology without huge cracks and cavities, although minor crevices formed at the boundary of the primary particles (**Fig 3.11 c,d**). This result further confirms that the Ti doping in NCM cathode can alleviate the effect of volume change.



Fig 3.11 Cross-section SEM images of (a,b) NCM, (c,d) NCM\_Ti after 200 cycle.

# **3.4 Conclusion**

In this chapter, TiN is selected to dope high-nickel layered cathode material (NCM\_Ti). The NCM\_Ti cathode has been systematically analyzed and compared with the NCM cathode. The doped Ti occupies the Li site and stabilizes the Li slab in the crystal structure, which results in improved cycling stability and rate performance. Additionally, Ti doping improves the structural stability that avoids micro-crack formation upon long-term cycling. Remarkably, the NCM\_Ti cathode maintains 93.8% capacity after 200 cycles, which contributes to a practical strategy to enhance the electrochemical performance of high-nickel layered cathode materials.

# Chapter 4

# **Development of rechargeable zinc ion batteries (ZIB)**

# **4.1 Introduction**

With climate change and pollution concerns, renewable energy storages especially rechargeable batteries have been intensified compared to traditional fossils. Compared to traditional internal combustion engine vehicles, electric vehicles (EVs) can efficiently suppress the emission of greenhouse gas and decrease dependence on fuels<sup>130-133</sup>. In recent decades, battery technologies have been rapidly developed to satisfy the growing demands of various applications, such as EVs<sup>134</sup>. The ideal batteries should contain features like eco-friendly, high safety, high energy density, low cost. Currently, there is no commercialized available battery that could meet all these requirements at the same time. Therefore, different battery systems have been designed for the corresponding applications<sup>135-140</sup>.

Lithium-ion batteries (LIBs) are current mainstream technologies in EVs<sup>141-143</sup> due to their high energy density. Typically, LIBs compose graphite as anode and lithium iron phosphate (LFP) or lithium nickel cobalt manganese oxide (NCM) material as cathode<sup>6, 144, 145</sup>. Although LIBs contain high energy densities and extended cycle life, the safety issues of flammable organic electrolytes and the high cost of limited metal resources confine LIBs in some specific applications<sup>146, 147</sup>. Hence, developments of alternative battery technologies complementary to LIBs become urgent and necessary<sup>148, 149</sup>. Among various battery systems, zinc-ion batteries (ZIBs) could potentially solve most of the concerns, especially with non-flammable aqueous electrolyte<sup>139, 150</sup>. Unlike lithium metal, zinc metal is compatible with aqueous electrolytes and possesses a high volumetric capacity (5854 AhL<sup>-1</sup>) and a high specific capacity (820 mAhg<sup>-1</sup>). Additionally, Zn is more abundant than Li in the Earth's crust and cheaper in the material aspect<sup>151</sup>.

Primary zinc batteries in alkaline electrolytes have been widely used in the market over decades. However, these zinc batteries fail to recharge due to the formation of irreversible compounds on the surface of both anodes (ZnO, Zn(OH)<sub>2</sub>) and the cathode (Mn(OH)<sub>2</sub>) sides<sup>139, 152</sup>. These batteries could not implement in large-scale storage, where demands rechargeable batteries. Therefore, rechargeable zinc-ion batteries (ZIBs) are considered promising candidates for these specific applications<sup>153</sup>.

## 4.2 Mechanism of zinc-ion batteries

For a typical rechargeable zinc-ion battery, it is composed of four parts. Anode and cathode function as a host for reversible electrochemical  $Zn^{2+}$  (de)insertion<sup>154</sup>; aqueous electrolyte contains zinc salt and conducts zinc ions; separator isolates electrodes and prevents internal short-circuit. (**Fig 4. 1**)<sup>139</sup>. During discharging process, zinc metal would lose electrons and then transform to  $Zn^{2+}$  and dissolve in the aqueous electrolyte. Subsequently,  $Zn^{2+}$  ions migrate and intercalate into cathode sides (e.g.  $MnO_2$ )<sup>154</sup>. In the meanwhile, the electrons would also transfer to the cathode side through the external circuit. Upon charging process,  $Zn^{2+}$  ions and electrons transfer in the opposite direction<sup>139</sup>.



Fig 4.12 Schematic illustration of rechargeable zinc-ion batteries. Negative electrode: zinc metal, positive electrodes: MnO2, electrolyte: mild acidic aqueous electrolyte<sup>139</sup>.

# 4.3 Zinc metal anode

# 4.3.1 Challenges of zinc metal anode

In the ZIBs, zinc metal is usually used as an anode. Although zinc metal anode composes high volumetric capacity and is compatible with aqueous electrolytes, several obstacles hinder the practical applications of zinc metal anode in ZIBs. On the one hand, uneven deposition of Zn<sup>2+</sup> results in dendrite formation on the zinc metal anode surface. The dendrites cause low coulombic efficiency (CE) and the larger one could even penetrate through the separator to result in short-circuiting of the batteries<sup>155, 156</sup>. Moreover, the dendrite with low adhesion would easily peel off from the zinc metal anode surface, which generates "dead zinc" and leads to capacity loss<sup>135, 149, 157-160</sup>. On the other hand, hydrogen evolution reaction (HER) occurs at the surface of zinc metal anode, which usually follows by metal corrosion<sup>161</sup>. The HER consumes electrolyte and corrodes the zinc

metal surface with gas evolution. The generated gas would also increase the inner pressure of the battery, which results in swelling and leakage of the cell<sup>162, 163</sup>. These issues seriously influence the performance of zinc metal anode in ZIBs.

# 4.3.2 Strategies for zinc metal anode

To resolve the obstacles of the zinc metal, strategies have been focused on crystal, nanostructure, framework, interfacial engineering to tune the  $Zn^{2+}$  deposition process. Moreover, the electrolyte modifications allow stable long-term cycling in the ZIBs.

# 4.3.2.1 Crystal Engineering

During electrodeposition, zinc tends to deposit as hexagonal platelets and plates randomly in different orientations<sup>164-166</sup>. In the vertical direction to the substrate, the plated Zn would form dendrites and spur through the separator, which causes failure of the battery. Hence, Zhang et al<sup>167</sup>. reported reversible epitaxial electrodeposition of zinc metal on graphene to achieve flat Zn deposition that is paralleled to the substrate (**Fig 4.2**). Graphene is employed as the substrate because it contains a low lattice mismatch with zinc metal and makes the interface energy favorable for paralleled Zn deposition. Epitaxial regulation forms a thin plate paralleled to the graphene sheet and accomplishes high CE over thousands of cycles, which boosted the reversibility of the zinc metal anode for ZIBs.



Fig 4.13. Schematic illustration of Zn deposition on stainless steel and epitaxial regulated Zn deposition on graphene (left figure); Atomic arrangements of Zn and graphene, the low misfit ( $\sim$ 7%) indicates a semicoherent interface that is energy favorable for Zn deposition (right figure)<sup>167</sup>.

## 4.3.2.2 Nanostruc2ture Engineering

Novel nanostructure design of Zn anode is also a competent strategy to eliminate dendrite growth in ZIBs since extra surface area could reduce the local current during Zn<sup>2+</sup> plating<sup>168, 169</sup>. Hence, the 3D Zn structure is extensively investigated since the porous structures enlarge the surface area of the zinc metal anode that could decrease the overpotential during Zn deposition and facilitate more uniform Zn deposition<sup>170, 171</sup>. Parker et al<sup>135</sup>. proposed a 3D zinc sponge structure to enhance the utilization of Zn and charge capacity (**Fig 4.3**). The sponge structure efficiently increases the surface area of zinc anode decrease local current during deposition and stripping processes, which suppresses the dendrite formation. As a result, over 90% depth of discharge in primary cells could be used and over the tens of thousands of powering cycles could be completed.



Fig 4.14. Schematic illustration of conventional zinc powder anode (left) and 3D Zn sponge anode. The sponge Zn anode can effectively avoid dendrite formation<sup>135</sup>.

## 4.3.2.3 Framework Engineering

To lower the overpotential of Zn deposition, several frameworks of different materials have been developed to act as hosts, which reduces the local current and facilitates uniform Zn deposition<sup>172-174</sup>. Because of the high conductivity, low cost, and good affinity to Zn metal, copper (Cu) is considered as the host material for Zn metal in the ZIBs. Xu et al<sup>174</sup>. fabricated a 3D porous Cu skeleton host for Zn metal through the ammonia etching process (**Fig 4.4**). Because of the high surface area of the Cu skeleton, the local current density has been decreased during charging/discharging, which leads to reduced polarization and high CE during cycling.



Fig 4.15 Schematic illustration of preparation and Zn deposition process of 3D porous Cu skeleton<sup>174</sup>.

## 4.3.2.4 Interfacial Engineering

Inorganic layers that compose high mechanical strength, act as buffer layers and suppress the dendrite penetration through the layer, which efficiently avoids short-circuit in the ZIBs<sup>155, 175- $^{177}$ . Kang et al. developed nano-CaCO<sub>3</sub> protective layers on the zinc foils to suppress dendrite and enable uniform deposition (**Fig 4.5**)  $^{155}$ . Due to the uneven distribution of ion flux, dendrite, and rough surface morphology generated on the bare Zn anode surface after repeated cycling. With the CaCO<sub>3</sub> coating, the aqueous electrolyte could thoroughly infiltrate the coating layer, which results in uniform electrolyte flux and plating rate. Additionally, the coating layer can operate as a buffer layer to inhibit dendrite penetration.</sup>



Fig 4.16 Schematic illustration of morphology evolutions in the bare Zn foil and Nano-CaCO<sub>3</sub> coated Zn foil during Zn plating and stripping<sup>155</sup>.

The polymer coating is another material for zinc metal protection with the advantages of high flexibility and low cost. The polymer coating layer tunes the interfacial condition between zinc metal and aqueous electrolyte, which prompts the electrochemical performance and stability of zinc metal anode<sup>157, 178-182</sup>. For example, Cui et al<sup>157</sup>. proposed the polyamide (PA) coating on the zinc anode, which effectively influences the Zn deposition behavior (**Fig 4.6**). With the hydrogen-bonding and strong coordination with  $Zn^{2+}$ , the PA coating can homogenize  $Zn^{2+}$  flux with uniform nucleation. Additionally, the PA polymer coating can inhibit the corrosion side

reactions caused by water and dissolved oxygen. Different from the dendrite formation and corrosion on the bare zinc surface, the PA coating limits the  $Zn^{2+}$  migration during deposition through hydrogen-bonding of the amide group, which generates constrained 2D diffusion and uniform deposition without Zn dendrites. As a result, uniform Zn deposition can be accomplished even under a high areal capacity of 10 mAhcm<sup>-2</sup>.



Fig 4.17 Schematic illustration of Zn deposition in bare Zn anode and PA coated Zn anode (upper figure), Chronoamperograms of bare and PA coated Zn anode, inset: rampant 2D diffusion in bare Zn compares to constrained 2D diffusion in PA coated Zn<sup>157</sup>.

In addition to inorganic and organic coating material, the metallic coating could also serve

as a protection layer on zinc metal anode to form uniform Zn deposition and eliminate large dendrite

growth<sup>183, 184</sup>. Kang et al<sup>183</sup>. prepared Au nanoparticle coated Zn metal anode via the sputtering method (**Fig 4.7**). Sputtered Au nanoparticles act as seeds on the surface for Zn nucleation. During the deposition, the Au seeds induced Zn-flake array morphology on the zinc metal anode and led to uniform Zn plating. Moreover, the Au nanoparticle layer suppressed the formation of large protrusion or dendrite growth, which is beneficial to stable plating/stripping processes.



Fig 4.18 Schematic illustration of Zn deposition on bare Zn and Au nanoparticle coated Zn<sup>183</sup>.

# **4.3.3 Electrolyte Engineering**

Aqueous electrolyte contained zinc salt acts as a  $Zn^{2+}$  carrier during the plating/stripping process in ZIBs. Hence, electrolyte optimization is another significant strategy to tune the  $Zn^{2+}$ deposition/dissolution behavior on the zinc metal anode. Several methods including zinc salt selection, electrolyte additive, solvent adjustment, and zinc salt concentration optimization have been employed in the aqueous electrolyte to modify interfacial  $Zn^{2+}$  deposition<sup>136, 185-189</sup>.

Zinc sulfate (ZnSO<sub>4</sub>) is commonly used as salt in mid-acidic electrolytes due to its high abundance and low cost. However, due to its limited solubility in the aqueous electrolyte and side
reaction on the electrode, CE of Zn plating/stripping is confined. Therefore, various zinc salts have been implemented in the electrolyte to improve the CE of the zinc metal anode<sup>185</sup>. Zhang et al<sup>189</sup>. reported a novel electrolyte containing  $Zn(CF_3SO_3)_2$  with additive  $Mn(CF_3SO_3)_2$  to replace conventional ZnSO<sub>4</sub> solution (**Fig 4.8**). The larger anion group (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) reduces the water molecules in the Zn<sup>2+</sup> solvated shield, which decreases the solvation effect and boost Zn<sup>2+</sup> transportation and charge transfer in the electrolyte. Moreover, the  $Mn(CF_3SO_3)_2$  additive was added to suppress the dissolution of  $Mn^{2+}$  on the cathode side, which improves the overall cycling performance of ZIBs.



Fig 4.19 Schematic illustration of the rechargeable ZIB with  $Zn(CF_3SO_3)_2$  and  $Mn(CF_3SO_3)_2$  as electrolyte (left); Cycling performance of Zn-MnO<sub>2</sub> batteries with different electrolyte of KOH, ZnSO<sub>4</sub>, Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> and Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> + Mn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub><sup>189</sup>.

In an aqueous electrolyte, HER occurs at the interface between zinc metal and electrolyte, which generates by-products of gas and  $Zn(OH)_2$ . The HER decreases the CE of Zn deposition/dissolution and affects the electrochemical performance of ZIBs. Thus, the highly concentrated electrolyte has been proposed to reduce the HER on the zinc anode<sup>136, 190-192</sup>. In high concentration electrolytes, water molecules surrounding  $Zn^{2+}$  are replaced with other non-aqueous anion components, which decreases the corrosion and dendrite formation on the zinc metal anode. Wang et al<sup>136</sup>. designed a high concentration "water in salt" electrolyte with 1M Zn(TFSI)<sub>2</sub> and 20M LiFSI (**Fig 4.9**). In this electrolyte, the solvated sheath of  $Zn^{2+}$  is filled up with TFSI<sup>-</sup> anions rather than water molecules. As a result, the morphology of zinc metal is well maintained after plating/stripping without by-products formation on the zinc surface. Additionally, the cycling performance of ZIBs with this high concentration electrolyte shows stable cycling performance over 4000 cycles.



Fig 4.20 SEM images and XRD patterns (inset) of Zn metal anode after cycling (left); Stable cycling performance and high CE of ZIB with high concentration electrolyte<sup>136</sup>.

# 4.4 Cathode materials for Zinc-ion batteries

To meet the requirements of large-scale storage applications, the cathode materials for ZIBs are expected to contain a high reversible capacity and remain stable during long-term cycling. Additionally, these cathode materials should be affordable and environmentally -friendly for stationary energy storage.

# 4.4.1 Manganese oxide (MnO<sub>2</sub>)

Manganese oxide (MnO<sub>2</sub>) has been widely implemented in Zn-MnO<sub>2</sub> primary cells and is concerned a promising cathode material for ZIBs since it is eco-friendly, cheap, and composing a high theoretical capacity of 308 mAh/g <sup>193-196</sup>. The fundamental building block of manganese oxide is MnO<sub>6</sub> octahedral and connects via corner or edge-sharing to construct various polymorphs (**Fig 4.10**)<sup>149</sup>. These configurations can be classified into three categories. (i) tunnel structures (**Fig 4.10 a-f**), (ii) layered structures (**Fig 4.10g**), (iii) spinel structures (**Fig 4.10h**). Tunnel structures predominate in the MnO<sub>2</sub> polymorph and differ in tunnel sizes. For example,  $\alpha$ -MnO<sub>2</sub> contains 2\*2 tunnels,  $\beta$ -MnO<sub>2</sub> contains 1\*1 tunnel, todorokite-type MnO<sub>2</sub> contains 2\*3 and 3\*3 tunnels, which influence the diffusion of cations. Hence, due to the larger tunnel size, todorokite-type MnO<sub>2</sub> could accommodate water molecules and cations while  $\beta$ -MnO<sub>2</sub> with 1\*1 channels shows poor cation diffusion properties. Layered MnO<sub>2</sub> ( $\delta$ -MnO<sub>2</sub>) structures are generated through edge-sharing. The interlayer spacing could store water molecules and cations during intercalation. Spinel ( $\lambda$ -MnO<sub>2</sub>) structures compose Mn<sup>2+</sup> in the tetrahedral sites and Mn<sup>3+</sup> in the octahedral sites and are often expressed as AMn<sub>2</sub>O<sub>4</sub> like ZnMn<sub>2</sub>O<sub>4</sub>.



Fig 4.21 Polyhedral representations of MnO<sub>2</sub> crystal structures. (a)  $\beta$ -MnO<sub>2</sub> (pyrolusite-type); b) *R*-MnO<sub>2</sub> (ramsdellite-type); c)  $\gamma$ -MnO<sub>2</sub> (nsutite-type); d)  $\alpha$ -MnO<sub>2</sub> (hollandite-type); e) romanechite-type MnO<sub>2</sub>; f) todorokite-type MnO<sub>2</sub>; g)  $\delta$ -MnO<sub>2</sub> (birnessite-type); h)  $\lambda$ -MnO<sub>2</sub> (spinel-type)<sup>149</sup>.

### 4.4.2 Vanadium-based cathode

Compared with Mn-based cathode materials, vanadium(V)-based cathode materials in ZIBs show better cycling stability. V coordinated polyhedral could be constructed by corner/edgesharing, which allows reversible  $Zn^{2+}(de)$  insertion during cycling<sup>197</sup>. Kundu et al<sup>198</sup>. synthesized  $Zn_{0.25}V_2O_5 \cdot nH_2O$  as cathode material for ZIBs, which completed high stability and extended cycle life. After cell assembling, water molecules spontaneously insert into layered V<sub>2</sub>O<sub>5</sub> structure when the cathode material immerses into the aqueous electrolyte. During charging/discharging,  $Zn^{2+}$ intercalates into the layered structure while the water molecules evacuate from the cathode to the electrolyte. The reverse process occurs in the  $Zn^{2+}$  deintercalation. As a result, the electrochemical performance with this vanadium-based cathode shows outstanding stability and high capacity. The capacity retention of 81% remained at a high current density of 8C, which results from the special water molecules in the crystal structure of vanadium oxide.



Fig 4.22 Schematic illustration of reversible water insertion into  $Zn_{0.25}V_2O_5 \cdot nH_2O$  when cathode immerses into the electrolyte and the water (de)intercalation process with  $Zn^{2+}$  (de)intercalation during charging/discharging<sup>198</sup>.

In summary, practical applications of rechargeable ZIBs require the optimization of the anode, cathode material, and electrolyte. Uniform deposition/dissolution on the zinc metal anode, solvation effects, and stability of cathode material need to be solved for the actual implementation of ZIBs.

# Chapter 5

# A Polymer Layer Coating on Zinc Metal Anode for Rechargeable Zinc-ion Batteries

# **5.1 Introduction**

With climate challenges by releasing green-house gas, renewable technologies have been developed rapidly to eliminate environmental and economic concerns. High energy density, high safety, eco-friendly and low cost are the key parameters for practical applications like portable devices, large stationary storage, and electric vehicles (EVs)<sup>130-133</sup>. Although lithium-ion batteries (LIBs) currently predominate the battery market because they compose high energy density and extended cycle life; however, LIBs suffer from safety issues (flammable organic electrolyte), environmental concerns, and limited metal resources (Li, Co). These deficiencies motivate people to discover alternative batteries to solve mentioned challenges<sup>146, 147</sup>.

Among various metal batteries, zinc metal shows great potential to solve these issues since it is compatible with aqueous electrolytes (no flammable problem), eco-friendly, and abundant in the Earth's crust<sup>23</sup>. Alkaline zinc-manganese (Zn||MnO<sub>2</sub>) batteries have been widely supplied in the market since they are safe and affordable. Nonetheless, these batteries could be barely recharged because the irreversible by-products would generate on the surface of the anode (ZnO, Zn(OH)<sub>2</sub>) and the cathode (Mn(OH)<sub>2</sub>, MnOOH) during cycle<sup>139, 152</sup>.

Therefore, rechargeable zinc-ion batteries (ZIBs) are considered as a promising candidate to complement  $Zn||MnO_2$  batteries, especially with mild acidic aqueous electrolyte (eg.  $ZnSO_4$  solution PH ~4)<sup>10</sup>. Additionally, ZIBs can deliver high energy density since zinc metal has a high theoretical specific capacity (820 mAhg<sup>-1</sup>) and volumetric capacity (5851 mAh/L)<sup>23</sup> and

successfully paired with cathode like metal oxide (eg.  $MnO_2^{149}$  or  $V_2O_5^{198}$ ) layered sulfides, Prussian blue<sup>199</sup> analogues, and even organic compounds<sup>200, 201</sup>.

However, some obstacles associated with ZIBs at the electrolyte-Zn interface hinder the practical applications. The inhomogeneous  $Zn^{2+}$  deposition/stripping processes result in zinc dendrite formation or shape change (**Fig 5.1a**). Dendrites would penetrate through the separator and cause an internal short circuit<sup>155, 156</sup>. In the meanwhile, shape change of zinc metal leads to "dead zinc" and gives rise to poor Coulombic efficiency (CE) <sup>135, 149, 157-160</sup>. Another issue is the zinc corrosion by the aqueous electrolyte which contributes to hydrogen evolution and affects the electrochemical process<sup>161-163</sup>.

To mitigate these challenges, extensive efforts have focused on either electrolyte<sup>136, 185-189</sup>, or material aspects<sup>155, 175-177</sup>. Electrolyte modifications have been investigated to suppress the dendrite formation. For example, zinc trifluoromethanesulfonate ( $Zn(CF_3SO_3)_2$ ) salt with Mn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> as an additive is found to be efficient for the elimination of zinc dendrite and additive could suppress the dissolution of Mn<sup>2+</sup> in the cathode side<sup>189</sup>. Besides, the super-concentrated "water in salt" electrolyte (WiSE) could exclude water molecules from the  $Zn^{2+}$  solvation sheath<sup>136</sup>, thus it shows outstanding ability in hindering zinc dendrite growth and hydrogen evolution. However, the highly concentrated salt is too expensive to be widely used in practical ZIBs. Noval Zn structures or hosts have also been designed to relieve Zn dendrite<sup>172-174</sup>. Porous copper skeletons and carbon nanotubes are treated as zinc anode hosts since they compose high surface area and easier for uniform  $Zn^{2+}$  deposition/stripping. But these structures require complicated synthesis steps which are difficult to scale up. Moreover, surface modifications of zinc metal anode have been applied to tune the interfacial environments to block electrolyte corrosions and optimize the electrochemical processes<sup>157, 178-182</sup>. Zhang. etl implemented a polyamide coating layer to effectively impede zinc dendrite growth and extend the ZIB life span<sup>157</sup>.

Hence, we developed a polymer coating on zinc metal anode for ZIBs with cyclized polyacrylonitrile (CPAN) and Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> salt shown in **Fig 5.1b**. The CPAN provides functional groups to coordinate with  $Zn^{2+}$  which slows down the local ion flux and facilitates  $Zn^{2+}$  transportation during the deposition/stripping process. It would achieve homogeneous Zn deposition to avoid dendrite formation and increase CE. Additionally, CPAN coating could confine Zn dendrite and block direct contact with aqueous electrolyte to prevent corrosion. The zinc salt (Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>) has been implemented to increase Zn<sup>2+</sup> conductivity. With these features, the zinc metal anode with CPAN coating (CPAN-Zn) delivered better stability in the deposition/stripping processes (up to 300 hours at 0.5C in symmetrical cells) and no dendrite penetrated through the polymer coating. When paired with MnO<sub>2</sub> cathode, the cells perform better specific capacity retention (200 mAhg<sup>-1</sup> after 100 cycles). This low-cost, easy-approach polymer coating provides a potential solution for Zn metal anode in ZIBs.



Fig 5.1 Schematic diagrams of Zn deposition in zinc and CPAN-Zn. (a) Zn electrodes suffer from dendrite formation and electrolyte corrosion. (b) CPAN coating layer leads to homogenous  $Zn^{2+}$  deposition, confinement of zinc dendrite, and blocks direct contact with electrolyte to avoid corrosion reactions.

#### **5.2 Experimental Section**

### **5.2.1 Material Synthesis**

#### 5.2.1.1 C-PAN-Zn anode synthesis

PAN (Mw 150000), Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>, and DMF were purchased from Sigma-Aldrich chemical cooperation. The chemicals were used as received. PAN was put into DMF solution to get different concentrations: 2.5%, 5%, 6.67 wt%. The concentration of Zn(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub> is 1 wt% for all materials. The solutions were stirred for 3 hours to make sure PAN was fully dissolved and cast on the zinc foil and dried in air. The polymer-coated zinc was then annealed at 300 degrees to undergo thermal cyclization of the PAN. The annealing process is operated inside the glovebox under the Argon atmosphere.

# 5.2.1.2 Synthesis of layered $\delta$ -MnO<sub>2</sub> cathode

The cathode material is synthesized through the thermal decomposition reaction of KMnO<sub>4</sub>. KMnO<sub>4</sub> was placed in a muffle furnace and heated at 350 degree for 5 hours (heating rate 5 °C min<sup>-1</sup>). Subsequently, the mixture was cooled down naturally and washed with deionized water three times to remove the impurity. The final product was gained by drying at 80 degree under vacuum.

# **5.2.2 Material Characterization**

X-ray diffraction (XRD) spectra were measured through a Rigaku Miniflex II spectrometer with Cu K<sub> $\alpha$ </sub> radiation. Morphologies of the electrodes were observed by scanning electron microscope (SEM) (Nova NanoSEM 630 instrument). X-ray photoelectron spectroscopy (XPS) was operated on a PHI VersaProble II Scanning XPS microprobe. Fourier-transform infrared spectroscopy (FTIR) spectra were measured through a Bruker Vertex V70 spectrometer in the range of 4000-400 cm<sup>-1</sup>.

#### **5.2.3 Electrochemical measurement**

Electrochemical tests were operated using CR2032 coin-type cells. MnO<sub>2</sub> cathodes composed of MnO<sub>2</sub>, acetylene black, and polyvinylidene fluoride (PVDF) in a 7: 2: 1 ratio were dissolved in *N*-methyl pyrrolidone (NMP) solvent and cast on stainless steel (SS) with average mass loading around 2 mg cm<sup>-2</sup>. The  $\delta$ -MnO<sub>2</sub> electrodes were employed as the cathode, glass fiber as the separator, and zinc foil as the anode. The electrolyte consists of 2M ZnSO<sub>4</sub> + 0.1M MnSO<sub>4</sub> in aqueous solution. Symmetrical cells were fabricated using Zn or CPAN-Zn on both sides with 2M ZnSO<sub>4</sub> + 0.1M MnSO<sub>4</sub> as the electrolyte. The processes of Zn<sup>2+</sup> plating/stripping were measured with a two-electrode configuration, where Zn metals act as counter electrodes and CPAN coated Stainless steel (bare stainless steel) were used as working electrodes. The CE was calculated from the amount of Zn stripped from the substrate to that deposited amount in the same cycle. Cyclic Voltammetry (CV) and electrochemical spectroscopy tests were carried out on a Nuvant Ezstat Pro instrument. Zn-MnO<sub>2</sub> full cells were cycled from 0.8-1.8 V at room temperature using a BTS-5V1mA Neware battery test system.

# 5.3 Results and Discussions

The CPAN-Zn is achieved by facile slurry coating and annealing processes shown in **Fig 5.2**. PAN polymer powder with  $Zn(CF_3SO_3)_2$  was dissolved in DMF to generate a uniform slurry. After casting on the Zn foil, it would be transferred into the glovebox to undergo annealing at 300 degrees.



Fig 5.2 Schematic illustration of the synthesis of CPAN-Zn and the thermal cyclization of PAN polymer.

The CPAN coating is generated by converting PAN into functional polymeric coating through cyclization process<sup>202</sup>. This process is triggered by thermal annealing under an inert atmosphere. X-ray photoelectron spectroscopy (XPS) of the N 1s in **Fig. 5.3** reveals the chemical structure evolution in the polymer coating through the cyclization process. XPS spectrum on the left-hand side shows the nitrile group (C=N, at 397.6 eV) in the pristine PAN. After cyclization, new N species N2 (N coordinated with three Carbon) and new pyridinic N3 (C-N=C, at 397.2 eV) show up, which indicates the structural transformation during the process<sup>202-204</sup>. This polymer coating could coordinate with Zn<sup>2+</sup> during deposition/stripping to achieve uniform deposition<sup>205, 206</sup>. FTIR also confirms the chemical structure evolution of the functional group after cyclization. The peak at 2245 cm<sup>-1</sup> identifies the nitrile functional group in the pristine PAN polymer while the red line indicates the signal peaks of N2 and N3 after cyclization. The signature peak of the nitrile group (2245 cm<sup>-1</sup>) in the pristine PAN disappeared while new C=N and C-N species are generated<sup>207, 208</sup>. These facts demonstrate the nitrile functional group would be transformed to C=N and C-N after cyclization.



Fig 5.3 XPS analysis of CPAN conducting film generation. The pristine nitrile group (N1) turns into the pyridinic group (N2) and N3 group after cyclization.



Fig 5.4 FTIR spectrum of pristine PAN (before cyclization) and CPAN (after cyclization). The nitrile groups (2245 cm<sup>-1</sup>) transform to C-N and C=N groups after cyclization.

To optimize the thickness of the CPAN coating layer, various concentrations of PAN polymer in DMF were prepared to adjust the layer thickness (1.5 wt%, 2.5 wt%, 6.7 wt%). After cyclization, CPAN-Zn with three different interlayer thicknesses has been assembled with  $\delta$ -MnO<sub>2</sub> cathode as full cells to test the electrochemical performances (**Fig 5.5**). From the cycling performance of these three thicknesses, it is found that the 1.5 wt% and 6.7 wt% deliver poor capacity retention after 120 cycles while 2.5 wt% PAN demonstrates better cycling performance

than the others. Hence, PAN (2.5 wt%) in DMF has been implemented for the following experiments.



Fig 5.5 Cycling performance of CPAN paired with  $\delta$ -MnO<sub>2</sub> cathode as a full cell at C/3. CPAN with PAN (2.5 wt%) shows better capacity retention after cycling.

The Zn deposition/stripping processes of the Zn and CPAN-Zn anodes are tested in symmetrical cells with the construction of (CPAN)Zn|ZnSO<sub>4</sub> + MnSO<sub>4</sub>|(CPAN)Zn (**Fig 5.6**). Zinc anode (black lines) and CPAN-Zn (red line) undergo  $Zn^{2+}$  deposition/stripping at current density of 0.25 mA cm<sup>-2</sup> for 1 hour. Zn metal anode sustains from high overpotential even in the initial cycle and gradually increases with cycling. This results from uneven  $Zn^{2+}$  deposition during deposition and the morphology change of zinc surface with extended cycle time worsens the deposition process. However, with the CPAN coating, the initial overpotential is lower than the bare-Zn (26 mV vs 45 mV) and only has limited enlargement (50 mV) after 300 hours of cycling due to the facility of functional groups. The functional groups coordinate with  $Zn^{2+}$  during the deposition/stripping processes and lower the local  $Zn^{2+}$  ionic flux while the Zn salt also increases the ionic conductivity to achieve lower overpotential<sup>209</sup>. Moreover, uneven deposition within the bare-Zn anodes results in dendrite formation and it would spur through the separator to generate a short circuit of the cells. At cycle time around 125 hours, the sudden overpotential drop indicates a short circuit within the cell due to dendrite penetration. While with the CPAN coating, the cell

delivers a stable deposition/stripping process over 400 hours because the CPAN coating initiates uniform deposition of zinc to avoid dendrite formation and even if the dendrite generates on the zinc surface, the polymer layer can confine the dendrite underneath the polymer.



Fig 5.6 Galvanostatic cycling of symmetrical cells with bare-Zn and CPAN-Zn anodes at a current density of 0.25 mA cm<sup>-2</sup> and deposition amount is 0.25 mAh cm<sup>-2</sup>. Inset (left) is the initial cycle voltage profiles of the CPAN-Zn and bare-Zn and inset (right) is the voltage profile of CPAN-Zn after 300 hours of cycling. CPAN-Zn demonstrates a stable and extended cycling span with a lower overpotential.

We also measured the CPAN-Zn anode without zinc salt (**Fig 5.7a**). Without zinc salt, the overpotential has a sightly increase since the zinc salt improves the Zn<sup>2+</sup> conductivity. To further investigate the capability of CPAN coating, zinc deposition/stripping processes with the higher current rate (4 mA cm<sup>-2</sup>) and higher deposition amount (4mAh cm<sup>-2</sup>) are also measured (**Fig 5.7b**). The bare-Zn suffers deteriorative cycling stability under a higher current and deposition amount. Within 10 hours of cycling, the overpotential starts fluctuating, and the cell experiences a short circuit after 12 hours since higher current and deposition amount stimulates dendrite formation with uneven deposition. However, the CPAN-Zn delivers stable and extended cycling performance at elevated current and deposition amounts. All these results illustrate the C-PAN coating would be beneficial for Zn deposition/stripping process through coordination with zinc ion and elimination of zinc dendrite.



Fig 5.7 Galvanostatic cycling of (a) CPAN-Zn symmetrical cells with and without zinc salt. (b) bare-Zn and CPAN-Zn symmetrical cells at a current density of 4 mA cm<sup>-2</sup> and a deposition amount are 4 mAh cm<sup>-2</sup>.

The coulombic efficiency (CE) can be used to describe the reversibility of the zinc deposition/stripping process, which is significant for long-term Zn anode cycling. Due to dendrite Zn or "dead" Zn formation during cycling, deposited Zn can not fully reversible strip back and make Zn anodes suffer from low CE. Hence, we used zinc metal as a counter electrode and stainless steel (SS) current collector with (without) CPAN coating as the working electrode. The  $Zn^{2+}$  would dissolve from the Zn metal and deposit on SS during the deposition process. It would strip back to Zn metal after the stripping process (**Fig 5.8a**). The CE is calculated based on the amount of stripping back to deposition. The Zn||SS delivers lower CE throughout the deposition/stripping processes, but SS coated with CPAN coating demonstrates stable and higher CE which results from the functional group could coordinate with  $Zn^{2+}$  to accomplish uniform Zn deposition and confine the Zn deposition underneath polymer to avoid Zn deposition or growth within the separator. To figure out the reason why CE slip in the Zn||SS, the cell was disassembled and the separators have

been observed via SEM (**Fig 5.8b**). It was found a certain amount of residual Zn was trapped in the separator while the separator is clear and porous in the Zn||CPAN-SS cell. These results support the CPAN coating layer could confine deposited Zn within the polymer and prevent ZIBs from short circuit by residual Zn within the separator.



Fig 5.8 (a)CE of Zn||(CPAN-)SS cells with 1 mAhcm<sup>-1</sup> at 1 mAcm<sup>-1</sup>. (b) SEM images of Zn||SS separator(upper) after cycles and Zn||CPAN-Zn after cycles. Zn residual was trapped in glass fibers and led to poor CE of the Zn||SS cell.

The morphology evolutions of bare-Zn and CPAN-Zn are measured by SEM (Fig 3.11). The pristine Zn (**Fig 5.9a**) composes a flat and smooth surface before cycling. After 175 hours of cycling (current: 1mAcm<sup>-1</sup>, amount: 1mAhcm<sup>-1</sup>), the uneven deposition of Zn<sup>2+</sup>, micro-size protrusions, and flake-like pieces already covered the surface (**Fig5.9b**). Irregular and heterogenous Zn observed from a cross-sectional view (**Fig 5.9c**). These protrusions and flake-like Zn results in higher polarization and low CE during cycling. With the CPAN coating (**Fig 5.9d**), the surface remains flat and well covered by a dense polymer layer. The inset figure illustrates the cross-sectional view of CPAN coating with a thickness of around 1  $\mu$ m. After 175 hours of cycling, the CPAN layer still shows a flat and intact surface without dendrite or protrusions penetrated through (**Fig 5.9e**). The cross-sectional view (**Fig 5.9f**) confirmed the Zn deposition occurred beneath the coating layer. These results attest the CPAN coating could facilitate Zn<sup>2+</sup> deposition and confine the deposited Zn within the polymer to avoid short circuits.



Fig 5.9 SEM images of bare-Zn electrode (a-c) and CPAN-Zn electrode (d-f). (a,d) pristine bare-Zn and CPAN-Zn electrode. (b,e) after 175 hours plating/ striping cycles. (c, f) cross-sectional image of bare-Zn and CPAN-Zn after 175 hours cycles.

To prove that the CPAN coating layer could not only confine deposited Zn within the polymer layer but also benefits the Zn<sup>2+</sup> deposition process to avoid dendrite or protrusions growth, the polymer coating was removed to observe the morphology beneath them (**Fig 5.10**). Higher current and deposition amounts (4, 10 mAcm<sup>-2</sup>; 4, 10 mAhcm<sup>-2</sup>) were carried out to distinguish the morphology differences after the cycle. **Fig 5.10a** demonstrates dendrite and protrusions growth under 4mAhcm<sup>-2</sup> and even more, dendrites generate on the surface when the deposition amount increases to 10 mAhcm<sup>-2</sup> (**Fig 5.10c**). However, the Zn anodes with CPAN coating show distinct morphologies (removal of CPAN layer). With 4 mAhcm<sup>-2</sup> depositions, the Zn anode shows a clean and flat surface (**Fig 5.10b**). Even with 10 mAhcm<sup>-2</sup> depositions (**Fig 5.10d**), the morphology remains flat without dendrites or protrusions, which proves the CPAN coating could assist Zn<sup>2+</sup>transportation to achieve uniform morphology.



Fig 5.10 SEM images of bare-Zn electrodes with (a) 4 mAhcm<sup>-2</sup> (c) 10mAhcm<sup>-2</sup> deposition after cycles. SEM images of CPAN-Zn electrodes (CPAN polymer layers have been removed) with (a) 4 mAhcm<sup>-2</sup> (c) 10mAhcm<sup>-2</sup> deposition after cycles.

Apart from the uneven deposition of  $Zn^{2+}$ , corrosion caused by aqueous electrolytes would also affect the electrochemical reactions of ZIBs (H<sub>2</sub> evolution or passivation). Hence, the CPAN coating layer would act as a physical barrier to prevent direct contact between electrolyte zinc metal. To verify the anti-corrosion feature, the Tafel curve has been applied to determine the corrosion potential and current (**Fig 5.11a**). The junction represents the corrosion potential and its corresponding current. With CPAN coating, the corrosion potential enhanced from -1.016 V to -1.009 V and the corrosion current decreased as well, which infers to reduced corrosion reactions. Another test is carried out in the symmetrical cells with a limited amount of electrolyte ( $60\mu$ L for the 2032 coin cells). Corrosion reaction would consume electrolytes and generate hydrogen gas or passivated Zn surface, which results in polarization expansion, especially in a limited electrolyte. The symmetrical cells with limited electrolyte underwent deposition/stripping process (current:0.5 mAcm<sup>-2</sup>; amount 0.5 mAhcm<sup>-2</sup>) after 48 hours standing. The bare-Zn experiences a huge overpotential increase of over 300 mV while CPAN-Zn still delivers stable and lower overpotential (**Fig 5.11b**). These results suggest the CPAN coating could efficiently diminish corrosion reaction by preventing direct contact between Zn metal and electrolyte.



Fig 5.11 Anti-corrosion tests to the aqueous electrolyte. (a) Tafel curve of bare-Zn and CPAN-Zn electrode. (b) Galvanostatic cycling of symmetrical cells with bare-Zn and CPAN-Zn at limited electrolyte condition ( $60 \mu$ L) with 48 hours standing.

CPAN-Zn is further paired with layered MnO<sub>2</sub> cathode as a full cell to evaluate its electrochemical performance in real ZIBs. (CPAN-)Zn|ZnSO<sub>4</sub> + MnSO<sub>4</sub>|MnO<sub>2</sub> configuration is employed in coin cells. CV (**Fig 5.12a**) demonstrates the electrochemical process with/without CPAN coating. Similar redox reactions have been observed in **Fig 5.12a**, therefore, the coating would not affect the processes in the ZIBs. Two cathodic peaks at 1.36V and 1.16V are attributed to the reduction of Mn<sup>4+</sup> to Mn<sup>3+</sup> and subsequent to Mn<sup>2+</sup>. The anodic peak around 1.6 V corresponds to the oxidation processes. These redox peak positions are consistent with the plateau in the voltage profile of CPAN-Zn||MnO<sub>2</sub> (**Fig 5.12b**). Long-term cycling performance is shown in **Fig 5.12c** (with current density = C/3, 0.1 A/g). The battery with CPAN-Zn anode demonstrates a higher initial specific capacity and better cycling stability after activation cycles. The initial specific capacity is 187.3 mAhg<sup>-1</sup> and gradually enhances to 220 mAhg<sup>-1</sup> while the battery with bare-Zn anode only delivers 175.1 mAhg<sup>-1</sup> in the first cycle and stable at 130 mAhg<sup>-1</sup> after activation. After 40 cycles, the battery with bare-Zn anode starts fading while the CPAN-Zn battery shows stable cycling performance. The morphology of the bare-Zn anode after 100 cycles (**Fig 5.12d**) shows protrusions and flake-like shapes while the Zn anode protected by the CPAN layer remains smooth

and flat after cycling (Fig 3.12e). These electrochemical performances of full cells support the results in symmetrical cells and indicate CPAN-Zn anodes would be practical in ZIBs.



Fig 5.12 (CPAN-)Zn||MnO<sub>2</sub> full cell electrochemical performance. (a) Cyclic voltammetry curves. (b) Discharge-charge voltage profile of CPAN-Zn electrode-MnO<sub>2</sub> in the first and second cycle. (c) Cycling performance of full cells at C/3.

# **5.4 Conclusion**

In summary, the CPAN coating was coated on Zn metal anode to elevate the stability during deposition/stripping processes. The CPAN coating facilitates  $Zn^{2+}$  transportation via coordination with  $Zn^{2+}$  by functional groups. Additionally, the coating layer confines Zn plating underneath the polymer and blocks direct contact with an aqueous electrolyte. These features avoid the formation

of large dendrites or protrusions and decrease corrosion side reactions. When paired with  $MnO_2$  cathode in the full cells, the CPAN-Zn anodes demonstrated enhanced cycling stability, suggesting it could be practical in ZIBs.

# Chapter 6 Conclusions and Future Work

# 6.1 Conclusion

This thesis has discussed the development of zinc metal anode in ZIBs and high-nickel layered cathode materials in LIBs. To solve the issues of zinc metal anode, the CPAN polymer was coated on zinc foil to improve the cycling stability of the anode. The interface facilitates the  $Zn^{2+}$  transport by coordination through the functional group in the polymer. The coordination can reduce the local current density, which leads to uniform deposition of zinc metal. Moreover, the interface confines the zinc plating within the polymer to avoid short-circuit and blocks direct contact with aqueous electrolytes to reduce corrosion.

To improve the electrochemical and thermal stability of high-nickel layered cathode materials, Al and Ti doping methods have been implemented in cathode materials. The doping of Al and Ti elements improves the structural stability and reduces the formation of microcracks after cycling, which results in enhanced electrochemical performance. Additionally, the stronger Al-O bonding in the crystal structure elevates the thermal stability of the high-nickel layered cathode material at high temperatures.

#### 6.2 Future work

For aqueous ZIBs, since the cost of the cathode and anode materials are relatively low for battery fabrication, there is huge potential for ZIBs to be implemented in practical applications like stationary storages. Suffered from uneven deposition on the anode side and low efficiency on the cathode side, stable zinc anode, and efficient cathode could be paired to complete stable long-term cycling. In addition to materials, cheap and stable zinc salts in the electrolyte are worth investigating for the ZIBs.

To realize the practical application of high-nickel layered cathode materials in LIBs, the detailed mechanism behind the failure of cathode materials should be thoroughly understood. With present strategies in the cathode materials, the electrochemical performance could be adjusted via doping, surface coating, etc. Additionally, safety hazard still impedes the use of high-energy cathode. To solve the issues, multi-step protection should be implemented in high-nickel layered cathode materials to achieve stable long-term cycling in the real application

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# VITA

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