The Pennsylvania State University

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SOL-GEL DERIVED POLYMER COMPOSITES FOR ENERGY STORAGE AND CONVERSION

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by

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ABSTRACT

Sol-gel process is a simple chemistry to convert the small precursor molecules into an inorganic polymer, which could be applied to synthesize inorganic materials, modify the interface of materials, bridge the organic and inorganic materials, etc. In this dissertation, novel sol-gel derived composites have been developed for high dielectric breakdown capacitors, low high frequency loss capacitors and flexible piezoelectrics.

Numerous efforts have been made in the past decades to improve the energy storage capability of composite materials by incorporating nanometer scale ceramic addictives with high dielectric permittivity into dielectric polymers with high breakdown strength. However, most composites suffer from the low breakdown strength and make the potential gain in energy density small. Here, a new chemical strategy is proposed that, through sol-gel reactions between ceramic precursors and functional groups at the end of the functionalized Poly(vinylidene fluoride -co-chlorotrifluoroethylene) chains, amorphous low permittivity ceramics was in-situ generated in the polymer matrix and cross-linked the polymer chains simultaneously. By carefully tuning precursors, the polymer/precursors feeding ratios, a series of nanocomposites were systematically designed. All the samples are comprehensively characterized and the structure-property correlations are well investigated. The optimal samples exhibit higher breakdown strength than the pristine polymer. The enhanced breakdown strength ascribed to low contrast in permittivity, great dispersion and improved electrical and mechanical properties. This newly developed approach has shown great promise for new composite capacitors.

The percolative polymer composites have recently exhibited great potential in energy storage due to their high dielectric permittivities at the neighborhood of the percolation threshold. Yet high energy dissipation and poor voltage endurance of the percolative composites resulted from electrical conduction are still open issues to be addressed before full potential can be realized. Herein we report the percolative composites based on ferroelectric poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) as the matrix and sol-gel derived SiO₂ coated reduced graphene oxide

nanosheets as the filler. By capitalizing on the SiO₂ surface layers which have high electrical resistivity and breakdown strength, the composites exhibit superior dielectric performance as compared to the respective composites containing bare reduced graphene oxide nanosheet fillers. In addition to greatly reduced dielectric loss, little change in dielectric loss has been observed within medium frequency range (ie. 300 KHz - 3 MHz) in the prepared composites even with a filler concentration beyond the percolation threshold, indicating significantly suppressed energy dissipation and the feasibility of using the conductor-insulator composites beyond the percolation threshold. Moreover, remarkable breakdown strength of 80 MV/m at the percolation threshold has been achieved in the composite, which far exceeds those of conventional percolative composites (lower than 0.1 MV/m in most cases) and thus enables the applications of the percolative composites exhibiting high permittivity, reduced loss and excellent breakdown strength for electrical energy storage applications.

Flexible piezoelectric materials have attracted extensive attention because they can provide a practical way to scavenge energy from the environment and motions. It also provides the possibility to fabricate wearable and self-powered energy generator for powering small electronic devices. In the dissertation a new composite including BTO 3D structure and PDMS has been successfully fabricated using the sol-gel process. The structure, flexibility, dielectric and piezoelectric properties have been well studied. The new material shows a high g₃₃ value of more than 400 mV m/N. Moreover, the durability of this composite has been confirmed by cycle tests even though the BTO structure falls apart into small pieces in the PDMS matrix. The unique morphology of the composite allows the broken piece to connect with each other to generate power under stress. This work also opens a new route toward flexible piezoelectric composites.

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Chapter 1

Introduction

1.1 Capacitors

1.1.1 Capacitor Fundamentals

Current energy storage devices include batteries, fuel cells, capacitors, and supercapacitors. Each of these technologies has a different combination of power density and energy density. Among these technologies, capacitors possess the advantage of high power density due to the fast electrical energy storage and discharge capability. Capacitors are applied extensively in a broad range of electrical and electronic devices, where they are used to conserve energy by correcting the power factor of a circuit or perform specific functions, such as timing, filtering, and decoupling.

Capacitors are simple electronic devices typically consisting of two, noncontacting metal electrodes separated by an insulating material. By applying a voltage bias to the electrodes, an electrical field is applied across the insulating material. Charge accumulates on the metal electrodes until the voltage across the gap balances the applied bias. The capacitance of a capacitor is defined as

$$C = \frac{q}{V}$$
 1.1

where C is the capacitance, q is the total charge, and V is the voltage. In the absence of a dielectric material with a vacuum between the electrodes, the capacitance of a capacitor with parallel electrodes is

$$C = \varepsilon_0 \frac{A}{d}$$
 1.2

where ε_0 is the permittivity of free space, A is the area of the electrodes, and d is the distance between the electrodes. If an insulating dielectric material is placed between the electrodes, an increase in capacitance is observed over an empty capacitor under the same voltage bias and is represented by

$$C = \varepsilon_0 \varepsilon \frac{A}{d}$$
 1.3

where ε is the permittivity of the dielectric material. Figure 1-1 illustrates the difference between an empty and filled capacitor. The higher capacitance stems from an increase in charge, q, on the electrodes that originates with the dielectric material. Under a bias, the dielectric experiences a polarization that attempts to decrease the applied electric field passing through the material by setting up an opposing one. To compensate for the polarization, more charge accumulates on the electrodes until the circuit is balanced. The polarization vector has the opposite sign convention for electric field that emerges from negative charges and terminates on positive ones. The polarization is defined by

$$P = \varepsilon_0 E(\varepsilon - 1) \tag{1.4}$$

where P is the polarization and E is the electric field.¹ Equation 4 can be rearranged to create a new term called the electric displacement

$$D = \varepsilon_0 E + P \tag{1.5}$$

where D is the electric displacement. The electric displacement is simply the sum of the polarization obtained from an empty capacitor plus the dielectric material and represents the total charge on the electrodes.



Figure 1-1: Increase in capacitance upon filling a capacitor with a dielectric.¹

The origins of the polarization responses vary between materials. There are five polarization responses: electronic, ionic, dipolar, ferroelectric, and interfacial.^{2, 3} Electronic polarization is present in all materials and originates from the relative displacement of the electron cloud and nucleus on the atomic level. Under an applied electric field, the electron cloud and nucleus are displaced from their equilibrium position creating the polarization. Ionic polarization is present in ionic materials like salts and ceramics. This polarization mechanism originates from the displacement of positive and negative ions from their equilibrium positions under bias. Dipolar polarization originates from the rotation of permanent dipoles usually present in organic materials under electrical bias. Ferroelectric polarization is unique to ferroelectric materials which have crystals with permanent dipoles. Under bias, polarization can originate from either ferroelectric domain wall motion in the crystals or rotation of the crystals themselves depending on the material. Finally, interfacial polarization originates from the long range motion of charged species that accumulate at interfaces in the materials such as crystalline-amorphous, grain, and phase boundaries. These individual contributions are all addictive to the permittivity and can be represented by

$$\varepsilon = 1 + \frac{P}{\varepsilon_0 E} = 1 + \chi \tag{1.6}$$

where χ is the dielectric susceptibility. The dielectric susceptibility contains all of the contributing polarization mechanisms which can be separated through appropriate experimentation.

The permittivity of a material is a function of frequency of the applied electric field and the electric field strength. Each polarization mechanism has its own individual frequency response that is additive to the overall permittivity. As the frequency of the field is increased, each polarization mechanism drops out as the frequency passes the response time of that mechanism. Eventually at high enough frequencies, all of the polarization mechanisms drop out and have no contribution to the permittivity with the capacitor behaving as though it was empty. Under alternating current (AC) conditions, the complex permittivity is defined as

$$\varepsilon_c = \varepsilon' - i\varepsilon'' \qquad 1.7$$

where ε_c is the complex permittivity, ε' is the real part of the complex permittivity, and ε'' imaginary part of the complex permittivity. The real part, or ε' , is what is traditionally referred to as the dielectric constant and has been defined as the permittivity

(ϵ) so far and will continue to be referred to as such. The dielectric constant is defined by the real part of the permittivity measured at low frequency and electric field where this quantity has little variation. The imaginary part of the permittivity, ϵ ", is related to the loss in the dielectric and will be discussed later. In a perfect capacitor where the displacement responds in phase to the applied electric field, the current density can be defined as

$$J = \frac{dP}{dt} = -i\omega\varepsilon_0\varepsilon E_0 e^{-i\omega t}$$
 1.8

where the applied field is $E = E_0 e^{-i\omega t}$, J is the current density, ω is the frequency, ε is the material permittivity, and t is time. Dividing the current density by the electric field produces the equation

$$\frac{J}{E} = -i\omega\varepsilon_0\varepsilon \tag{1.9}$$

which defines the conductivity of the capacitor. For a perfect capacitor, there is no power loss in the dielectric since the integration of the product J and E over one period is always zero. This is due to fact that the current and electric field are always $\pi/2$ out of phase from each other.

In a real dielectric, the current and electric field are almost never $\pi/2$ out of phase resulting in a power loss in the dielectric. In this case, the current density of the capacitor is

$$J = \frac{dP}{dt} = -i\omega\varepsilon_0 \varepsilon E_0 e^{-i\omega (t-\delta)}$$
 1.10

where the applied field is $E = E_0 e^{-i\omega t}$ and δ is a time delay.⁴ The delay in the current response originates from the response times for the individual polarization mechanisms. Interfacial and dipolar polarization both usually have long response times. For interfacial polarization the long times are usually due to the size of the charged species and the large distances they move. The long times for dipolar polarization are due to the slow orientation of large dipoles. Response times for interfacial and dipolar polarization in general can extend to the hertz and megahertz range respectively. Ionic and electronic polarization mechanisms both have smaller response times due to the small ions, electrons, and atomic nuclei being displaced and their small displacements. Response times for ionic and electronics polarization mechanisms approximately extend to 10^{12} Hz and 10^{16} Hz respectively.

When complex permittivity is drawn as a simple vector diagram, the real and imaginary components are $\pi/2$ out of phase as shown in Figure 1-2. The loss in capacitor is usually reported as the loss tangent defined as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$
 1.11



Figure 1-2: Loss tangent vector diagram.

Figure 1-3 illustrates the frequency response of the various polarization mechanisms for both ε' and ε'' . The electronic and ionic polarizations fall within the category of instantaneous polarization because they occur so rapidly as to follow up with the frequency of external field above 10^{10} Hz. The dipolar and spontaneous polarization involve the rotational process and therefore happen within relatively low frequency range (below 10^8 Hz). Induced by migration of charge carriers, interfacial polarization can only be found in low or quasi-DC frequency range. Besides, the loss of each type of polarization usually reaches a local maximum near the maximum response times of the polarization mechanisms. The loss of a capacitor plays a tremendous role is judging a dielectric's worthiness. A dielectric with a high loss leads to a large conductivity which is not desirable.

Along with the loss, the energy stored in a capacitor is another important metric for performance and is defined as

$$du = V dq 1.12$$

where u is the energy stored in the dielectric.⁶ For a linear dielectric material, or a material whose permittivity is constant at all electric field strengths, the energy in a capacitor is

$$u = \frac{1}{2}CV^2 \tag{1.13}$$

which is a function of both the capacitance and the voltage.



Figure 1-3: Frequency response of the various polarization mechanisms.

The energy stored per unit volume can be calculated through Equation 14. The stored energy can be increased by increasing capacitance through a higher permittivity material. Energy can also be increased by applying a higher voltage giving each individual charge the ability to do more work.

$$u = \frac{1}{2}CV^2 \times \frac{1}{Ad} = \frac{1}{2}\varepsilon E^2$$
 1.14

1.1.2 Dielectric Polymers

Polymers offer an attractive alternative to traditional ceramics as dielectric materials for capacitors, owing to their great processability, low cost, and light weight. In addition, dielectric polymers enjoy inherent advantages of self healing mechanism and high breakdown strength, leading to compact and flexible capacitors with great reliability and high charge storage capability. The flexibility of molecular design and synthesis and hierarch assembly at multiple

length scales also make it feasible to fine-tune the physical properties of organic polymers to meet the application requirements.

Polymer capacitors are all based on thin films of polymer dielectrics usually less than 10 microns thick. Films are created from extrusion, solution casting, or evaporation deposition.⁵ The most common polymers used in capacitor applications are listed in Table 1.⁶⁻⁸ Polymer capacitors are constructed in a parallel plate configuration with metal electrodes in contact with the dielectric. Evaporated aluminum is often the metal of choice, though metal foils or other evaporated or sputtered metals are also used. Occasionally, a double metalized polymer is used an electrode where the polymer in not active in the actual capacitor which is shown in Figure 1-4. The application of the capacitor usually dictates the type of electrode. Since polymers are very flexible, they are typically rolled into cylinder configurations in actual devices. The rolled, metalized polymer films are inserted in cylindrical containers which are occasionally backfilled with insulating oils to reduce electrical discharge and improve heat dissipation.¹

Polarization in polymers typically results from electronic and dipolar mechanisms. Ferroelectric polarization is also possible for some polymers which can increase permittivity an order of magnitude. Outside of the ferroelectric polymers, the frequency responses of the dielectrics usually extend to the gigahertz range with low losses. Ferroelectric polymers have higher losses and only have frequency responses into the megahertz region. Permittivity and losses can be stable with temperature as long as no thermal transitions are approached. This is not the case for ferroelectric polymers which experience fluctuations around the Curie transition. The operating temperature range of polymers in fairly low compared to some ceramics due to low temperature thermal transitions. The maximum operating temperatures are often around 100 °C with specialty polymers going to 200 °C.⁹

						_
Polymer Films	3	Maximum Operating Temperature (°C)	Voltage Breakdown (V/µm)	Dissipation Factor (%) @ 1 kHz	Energy Density (J/cc)	-
Polypropylene (PP)	2.2	105	640	< 0.02	1-1.2	-
Polyester (PET)	3.3	105	570	< 0.50	1-1.5	
Polycarbonate (PC)	2.8	125	528	< 0.15	0.5-1	
Poly(vinylidene fluoride) (PVDF)	12.0	105	590	< 1.80	2.4	
Polyethylene-naphalte (PEN)	3.2	125	550	< 0.15	1-1.5	
polyphenylene sulfide (PPS)	3.0	140	550	< 0.03	1-1.5	

Table 1-1: Characteristics of polymer films utilized in energy storage capacitors.



Figure 1-4. Double metalized polymer layer structure.

One unique feature of metalized polymer films is the self-healing phenomenon, which makes polymer film capacitors very reliable for applications under high electric fields.¹⁰⁻¹² In other capacitors electrical breakdown usually results in a short, or the creation of a conducting path between the electrodes, in the capacitor rendering the device useless. The self-healing process is schematically illustrated in Figure 1-5. The self-healing mechanism during electrical breakdown causes a portion of the metalized film to evaporate around the failure point from the heat generated during breakdown. While a short may exist across the dielectric, it doesn't affect the rest of the device since it is isolated electrically. Many different factors affect self-healing such as polymer chemistry, applied voltage, electrode thickness, and pressure.⁸ Self-healing provides a mechanism for monitoring the lifetime of the capacitor through the capacitance decay with every event. Self-healing also reduces the need for extremely high quality films since defects are automatically.¹³



Figure 1-5: Schematic illustration of the process of self-healing in polymer dielectrics.¹²

The application of the polymer capacitor dictates the choice of the dielectric. Polyester is used in applications where high capacitance densities are needed and loss drift with temperature and frequency is not an issue. Polycarbonate is used for higher temperature applications where higher losses are tolerable. Polypropylene, the most popular polymer due to excellent properties and low cost, has a reasonable upper temperature limit of 90 °C and flat permittivity and loss with varying temperature and frequency. Specialty polymer dielectrics include polystyrene for its low loss and poly(phenylene sulfide), polyimide, and polytetrafluoroethylene for their high operating temperatures. Polymer capacitors find much use in pulse power applications since large capacitors can be fabricated with ease and the self-healing mechanism give long lifetimes.

1.1.3 Ferroelectric Poly(vinylidene fluoride)

The current state of polymer dielectrics calls for improvements in electrical energy density through increases in electrical breakdown strength and/or dielectric constant while maintaining energy losses at a minimum. Increases in the electrical energy density enable a reduction in capacitor size, which is desirable for applications such as in hybrid electric vehicles, electrical power systems, and implantable defibrillators just to name a few. BOPP is the material currently utilized in commercial capacitors. As described in previous section, high levels of molecular orientation induced by stretching aid in increasing electric breakdown strength and energy density in BOPP. Additionally, BOPP has very low dielectric losses (dissipation factor <0.02% at 1 kHz) due to the nonpolar nature of the molecules. BOPP capacitors have an energy density of 1-2 J/cm³ which is limited by its low dielectric constant.

Over the past decade, ferroelectric polymers represented by poly(vinylidene fluoride) (PVDF) have emerged as a promising alternative to BOPP in polymer film capacitors.¹³⁻¹⁵ The polar nature of the vinylidene fluoride group (net dipole moment ~ 2 Debye) results in a high dielectric constant (K ~12) in the polymer, much higher than typical nonpolar polymers (K < 2), leading to higher polarization levels and higher energy densities. PVDF is a typical semicrystalline polymer of approximately 50% crystallinity and possesses most of the same characteristics of other semicrystalline polymers that make them so desirable for a wide array of applications. It is usually synthesized via free radical polymerization and has a chemical structure of $(-CH_2-CF_2-)$ repeat units, providing not only large chain flexibility but also some constraints on atomic arrangement due to the high repulsive forces of the fluorine atoms. The highly electronegative fluorine atoms are also responsible for the C-F bonds existing as dipole moments giving the monomer a total dipole moment of about 2 Debye. The polarity of the PVDF molecules depends on the arrangement of these dipoles with respect to the molecular conformation. Since the 1960's there has been an abundance of research investigating the crystalline forms of PVDF and it is now known to crystallize into at different crystal phases with varied molecular conformations and lattice parameters as outlined in Figure 10.¹⁶⁻²²



Figure 1-6: Molecular conformations and unit cells of the three common polymorphs of PVDF.²³

The most common, thermodynamically stable, and easily obtainable phase is the α -phase, which has a *trans-gauche* (TGTG') conformation and does not show a net lattice polarization due to its antiparallel chain arrangement, i.e., the dipoles oppose each other. This form takes on a tetragonal unit cell with lattice parameters of a = 4.96 Å, b = 9.64 Å, c = 4.96 Å (along the backbone axis). The β -phase crystallizes with the molecules being configured in an all-*trans* (TTTT) zig-zag conformation, giving this phase polarity due to the parallel packing of polymer chains, i.e., the C-F dipoles are all aligned in the same direction. In this configuration the chains pack into an orthorhombic unit cell of lattice parameters a = 8.58 Å, b = 4.91 Å, and c = 2.56 Å (along the chain axis). This gives the β -phase crystals a spontaneous lattice polarization which is necessary to observe ferroelectricity in PVDF. The γ -phase is intermediate between the α and β -phases, consisting of a (T3GT3G') conformation and a monoclinic unit cell and lattice parameters a = 4.96 Å, b = 9.58 Å, c = 9.23 Å (along the chain axis). The nonorthogonal angle of the unit cell is 92.9°. A fourth polymorph of PVDF is the δ -phase, which is a polar version of the α -phase, with essentially the same unit cell parameters but a varying symmetry. Two or more of these PVDF crystal structures can often coexist over a wide range of compositions.^{23, 24}



Figure 1-7: Diagram of processing methods-crystalline structure relationships of PVDF.²⁵

There are many common processing methods that have been found to alter the crystalline structure of PVDF such as mechanical stretching, thermal treatments, poling with high electric fields, melt extruding, and solution casting;²⁵ detailed by Lovinger's diagram in Figure 1-7. When PVDF is solidified from the melt state it almost always crystallizes in the α -phase since this is the lowest energy state. In order to obtain the β -phase crystals there must be some external energy introduced to overcome the energy barrier. The most common method of converting the PVDF crystallites from the non-polar α -phase to the polar β -phase so that the material can be utilized as a piezoelectric is with mechanical stretching. Several groups have performed detailed studies of this transformation and demonstrated that it is highly dependent on the stretching temperature and stretch ratio.²⁶⁻²⁸ Although it is less effective than stretching, annealing at high temperatures can also be used to create crystalline phase transformations as Lovinger observed by transforming α -phase to γ -phase by annealing at temperatures greater than 154°C.²⁹ Moreover, other researchers have showed that by quenching the polymer from the melt before annealing they were able to crystallize the β -phase.³⁰ Electrical poling at high fields is another common method for

transforming the α -phase crystals to a more polar state, whether it be the δ , γ , or β -phase.^{31, 32} Essentially when the material is exposed to high fields for significant times and preferably high temperatures, the dipoles of the α -phase crystals are able to align with the direction of the applied field to a degree that results in a conversion of the nonpolar unit cell to a more polar structure. If the temperature is then cooled below the crystallization point while the field is still applied, the polymer can crystallize in the polar phase. In recent years, engineers have been looking to scale up technologies based on the piezoelectric properties of PVDF and are studying the effects of large scale processing such as film extrusion on the structure.^{33, 34} Melt processing methods such as extrusion and injection molding can induce large amounts of polymer chain orientation which can largely affect the crystallization of the polymer.

Additionally, the different polymer phases could be achieved by tuning the composition of polymer chain. PVDF based copolymer and terpolymer were synthesized and investigated to improve the properties of capacitors. Lando and Doll found that adding trifluoroethylene (TrFE) as a comonomer in the polymerization would facilitate the formation of β -phase since defects are introduced into the crystalline structure and cause the TTTT conformation to become a lower energy state than the TGTG' conformation.²⁰ In the early 1980's, Yagi *et al.* found out the incorporation of TrFE units into the PVDF induces the appearance of a ferroelectric-to-paraelectric transition below the melting temperature of the polymer crystals.³⁵

However, the major problem of PVDF copolymer as a capacitor material is that the polarity of the polymer also results in a high dissipation factor compared to the other non-polar polymers, causing high energy losses, which mitigates the discharged energy. In 1998, Zhang *et al.* treated P(VDF-TrFE) copolymer with electron irradiation and induced a polymorphic transformation of the ferroelectric phase into a phase that is structurally equivalent to the paraelectric phase. The state of crystalline region after irradiation is not a simple paraelectric but rather a phase containing nanopolar regions (nanometer-size, all-*trans* chains interrupted by trans and gauche bonds) that transform the material into a relaxor ferroelectric. These relaxor ferroelectric P(VDF-

TrFE)-based polymers posses little hysteresis in the charging-discharging cycle and significantly decrease the loss.¹⁴

Lu *et al.* introduced chlorotrifluoroethylene (CTFE) into the copolymer system and developed a systematic study of the structure-property correlations of P(VDF- CTFE-TrFE) terpolymer with different composition. As shown in Scheme 1-1, the terpolymers were prepared over a wide composition range by a two-step approach consisting of copolymerization of VDF and CTFE and a subsequent reductive dechlorination reaction. Due to the similar reactive ratios between VDF and CTFE and quantitative dechlorination yields, the chemical structures and compositions of the resulting terpolymers can be precisely controlled. It has been demonstrate that the crystalline conformations and the dielectric properties of the terpolymers could also be tuned between a normal ferroelectric and ferroelectric relaxor state by controlling the chemical compositions, with the particular state dependent on the CTFE contents. A three-dimensional plot of the room temperature dielectric constants for the terpolymers is shown in Figure 1-8. The terpolymer of 78.8 mol % of VDF, 7.2 mol % of TrFE, and 14 mol % of CTFE exhibits the highest room temperature dielectric constant of 50 and a low dielectric loss (tan $\delta < 0.05$) measured at 1 kHz. The ability to tailor these polymers provides unprecedented insight into the factors governing the dielectric responses in organic electroactive materials.³⁶⁻³⁸



Scheme 1-1: Synthesis of ferroelectric P(VDF-CTFE-TrFE) terpolymers.³⁶



Figure 1-8: A three-dimensional plot of room temperature dielectric constants at 1 kHz for the P(VDF-CTFE-TrFE) terpolymers.³⁶



Figure 1-9: D-E loops for P(VDF-TrFE) 75/25 mol% (dotted line) and P(VDF-TrFE-CFE) 58.3/34.2/7.5 mol% (solid line) measured at 10 Hz.¹³

For a capacitor, high energy density would help to reduce the volume, weight, and cost of the electric power system, which is one reason why the higher energy density is always a pursuit. In general, the energy density of a dielectric material is equal to the integral $Ue = \int E dD$, where E is the electric field and D is the electric displacement. In addition to a high E, a high D value is another key factor in achieving a high energy density. The dischargeable electric energy density

in typical PVDF and P(VDF-TrFE) is actually less than 5 J/cm³ due to their early electric displacement saturation at low electric field and large remnant polarization. Presented in Figure 1-9 is a typical electric displacement-electric field (D-E) loop for a P(VDF-TrFE) copolymer. When D saturates, the charge density cannot be further increased with E, which limits the energy it stores. Even worse, the electric energy density that can be effectively discharged from P(VDF-TrFE) and PVDF is further reduced by the large remnant polarization ($>0.08 \text{ J/cm}^3$) as illustrated by the shaded area in Figure 1-10. To completely discharge (utilize) the stored energy, a reverse electric field must be applied to switch the dipoles. From the molecular point of view, in the normal ferroelectric phase of PVDF and P(VDF-TrFE), the polymer chains are already in the alltrans conformation and an applied field along the original electric displacement D direction can only induce small changes in D (the curve section in Figure 1-9 from the point A to point B) and consequently low energy density. The hysteresis loop of ferroelectric terpolymer P(VDF-TrFE-CFE) (58.3/34.2/7.5 mol%, CFE: chlorofluoroethylene) is presented in Figure 1-10. Apparently, a much higher electric energy density of higher than 9 J/cm³ under 400 MV/m field can be obtained. In the terpolymer, CFE units that expand the interchain lattice spacing may lower the energy of the TGTG' conformation and achieve a reversible switch in conformations between the nonpolar and polar phases, which may avoid the early D-saturation.¹³

Incorporation of CTFE into the polymer was also found to greatly reduce remnant polarization by the defect modification. The bulkier size of CTFE in random P(VDF-CTFE) copolymers may also expand the interchain space and distort the crystalline ordering, which keeps the CTFE stabilized in the TGTG' conformation and α phase. The energy density exhibited more than 17 J/cm³ under a field of 575 MW/m due to the much smaller remnant polarization compared with that of PVDF, as shown in Figure 1-10.¹³ Hexafluoropropylene (HFP) was also selected as a comonomer to modify the PVDF and the copolymer displayed the similar effect as CTFE. From the structural point of view, bulky comonomers HFP and CTFE act as defects in the crystal structure of PVDF, just like the role of CFE in the P(VDF-TrFE-CFE) terpolymer. A fast

discharged speed of P(VDF-CTFE) capacitor films are monitored and the discharge time is less than 1µs, which is highly desirable for the pulsed power capacitor applications.³⁹



Figure 1-10: a) D-E loop and b) measured energy density for P(VDF-CTFE) 91/9 mol % at 10 Hz. 13

In addition to the displacement saturation, the electrical breakdown also plays an important role in determining the energy density. Claude *et al.* investigated the electrical breakdown mechanisms of P(VDF-CTFE) as a function of molecular weight and temperature. Energy density and breakdown strength were found to increase as molecular weight was increased and temperature was decreased.⁴⁰ The electromechanical breakdown mechanism was identified to be responsible for dielectric failure at 25 °C, which is a function of the yield strength of the polymers. Electrochemical breakdown occurs when the stresses induced by the applied field exceeds the yield stress of the polymers causing a rapid collapse of the electrodes inward and electric discharge. The thermal breakdown mechanism appears to contribute to the breakdown process at -35 °C which was below the glass transition of the material. Impulse thermal breakdown occurs when the electrical breakdown temperature. At -15 °C, a combination of the two mechanisms was found to operate in the copolymers. The operative electromechanical breakdown mechanism in the ferroelectric polymers was also verified in the P(VDF-CTFE-TrFE) terpolymers, where the breakdown strength depends positively on polymer crystallinity and storage modulus. Energy density and electrical breakdown

strength increased with increasing amounts of TrFE, as illustrated in Figure 1-11.¹ As also supported by theoretical calculations, the electromechanical stress is dominated by the Maxwell stress for the ferroelectric polymers with low crystallinity. For a ferroelectric relaxor, the electromechanical stress has contributions from both the Maxwell and electrostrictive effects.⁴¹ The results are in sharp contrast to polyethylene based dielectric polymers where the dielectric strength increases with the decrease of crystallinity as a consequence of the electron avalanche breakdown mechanism.



Figure 1-11: Energy density, and experimental and measured breakdown strengths for the P(VDF-TrFE-CTFE) containing 73.6 mol% VDF.¹

In summary, PVDF, a semicrystalline polymer has attracted great interest for use as electrical energy storage capacitors due mostly to its larger dielectric constant and higher energy density compared with other non-polar dielectric polymers. The big issue to prevent large scale commercialization is the high energy loss. To overcome the drawbacks of PVDF, processing and chemical defect modification have been developed to turn the normal ferroelectrics into relaxor ferroelectrics. These relaxor polymers are able to achieve high electric displacement arising from high levels of electric field induced phase transitions. In addition to the high dielectric constant, the advantage of the relaxor ferroelectric polymers is that there is very little hysteresis in the charging-discharging cycle, which significantly reduces the dielectric loss and render the polymers ultra-high energy densities.

1.2 Piezoelectric Materials

1.2.1 Piezoelectricity

In the year 1880 Pierre Curie and Jacques Curie discovered that some crystals when compressed in particular directions show positive and negative charges on certain positions of their surfaces.^{42.44} The amount of charges produced is proportional to the pressure applied and these charges were diminished when the pressure is withdrawn. They observed this phenomenon in the following crystals: zinc blende, sodium chlorate, boracites, tourmaline, quartz, calamine, topaz, tartaric acid, cane sugar, and Rochelle salt. Hankel proposed the name "piezoelectricity". "Piezo" is a Greek word which means "pressure". Piezoelectricity is an energy conversion manner by which electrical and mechanical energies can be reversibly converted to one another. When mechanical energy is the input, electrical charges are built up on a piezoelectric crystalline, undergoing a "direct effect"; when the voltage is applied on a piezoelectric crystalline, its shape is deformed, which is called "converse or indirect effect" in Figure 1-12.



Figure 1-12: A diagram of the (a) direct and (b) converse piezoelectric effects.

The physical mechanism of piezoelectric behavior entails good understanding of its crystallography and domain and other microstructures. And the mathematical representation can be expressed in the constitutive equations:
$$\begin{cases} S_{ij} = s_{ijkl}^E T_{kl} + d_{kij} E_k \\ D_i = d_{ikl} T_{kl} + \varepsilon_{ik}^T E_k \end{cases}$$
1.15

where S and D are mechanical strain and electric displacement, respectively; T and E the mechanical stress and electric field; s and ε the elastic compliance and dielectric (permittivity) constants; and d is the piezoelectric constant. The subscripts i, j and

k = 1,2,3, and p = 1,2,3,4,5,6, denote the space coordinates. The superscripts E and T mean at constant electric field or stress, respectively.

The d, also called piezoelectric charge constant, carries the unit of meter/volt or, equivalently, coulomb/newton, and is the polarization generated per unit of mechanical stress (T) applied to a piezoelectric material or, alternatively, is the mechanical strain (S) experienced by a piezoelectric material per unit of electric field applied. Because the strain induced in a piezoelectric material under an applied electric field is the product of the value for the electric field and the value for d, d is one of the most important material property indicators of its suitability for strain-dependent (actuator) applications.

One of the alternative forms of the above constitutive equations is

$$\begin{cases} S_{ij} = s_{ijkl}^D T_{kl} + g_{kij} D_k \\ E_i = -g_{ikl} T_{kl} + \beta_{ik}^T D_k \end{cases}$$
1.16

where β is the impermittivity constant (inversely related to ϵ), and g is another piezoelectric constant which relates with d by:

$$d_{ip} = \varepsilon_{ik}^T g_{kp} \tag{1.17}$$

where p is a compressed notation equivalent to ij.⁴⁵ The g, also called piezoelectric voltage constant is the electric field generated by a piezoelectric material per unit of mechanical stress applied or, alternatively, the mechanical strain experienced by a piezoelectric material per unit of electric displacement applied. The first subscript to g indicates the direction of the electric field generated in the material, or the direction of the applied electric displacement. The second subscript is the direction of the applied stress or the induced strain, respectively. Because the

strength of the induced electric field produced by a piezoelectric material in response to an applied physical stress is the product of the value for the applied stress and the value for g, g is important for assessing a material's suitability for sensing (sensor). In this case, a high dielectric constant is not desired, given the same piezoelectric charge constant d.

1.2.2 Piezoelectric Materials

There are several types of piezoelectric materials. In terms of the material type, they could be classified into single crystalline, ceramics, polymer and composites. Most of them require poling treatment to align the dipoles before use since the piezoelectric effect is directly related to the degree of polarization achieved. The piezoelectric ceramics are highly brittle and they have better electromechanical properties when compared to the piezoelectric polymers.

Quartz, lithium nibonate (LiNbO₃), and lithium tantalite (LiTaO₃) are some of the most popular single crystal materials which are anisotropic in general and have different properties depending on the cut of the materials and direction of bulk or surface wave propagation. These materials are essential used for frequency stabilized oscillators and surface acoustic devices applications.⁴⁶

Piezoelectric ceramics are widely used at present for a large number of applications. Most of the piezoelectric ceramics have perovskite structure which is made of mixed oxides containing corner-sharing octahedral of O²⁻ ions with a general formula ABO₃. This ideal structure consists of a simple cubic cell that has a large cation "A" at the corner, a smaller cation "B" in the body center, and oxygen O in the centers of the faces, as shown in Figure 1-13. In this class of materials, A could be Na, K, Rb, Ca, Sr, Ba, Pb, etc while B could be Ti, Sn, Zr, Nb, Ta, etc.



Figure 1-13: Crystalline structure of a Barium Titanate (Perovskite structure) (a) below and (b) above Curie temperature.⁴⁷

Barium titanate exhibits normal ferroelectricity below the Curie temperature, where the center of positive charge is displaced relative to the O^{2-} ions, giving rise to the formation of electric dipoles. After poling, the piezoelectric coefficient of barium titanate is high: d_{33} = 190 pC/N. Lead zirconate titanate (PZT) is a solid solution of lead zirconate and lead titanate where Zr^{4+} and Ti^{4+} ions occupy the B site of the ABO₃ randomly. The existence of monoclinic phase results in easy rotation of the polarization between tetragonal and rhombohedral phases. As a result of the large number of polarization orientations, this material shows efficient poling and large enhancement in the piezoelectric properties at this composition due to domain wall motion. The comparison of piezoelectric properties of several major ceramics is given in Table 1-2.

Materials	Quartz	PZT4	PZT 5H	BaTiO ₃	PVDF	LF4T
d ₃₃ (pC/N)	2.3	289	593	190	20	410
g ₃₃ (mV m/N)	57.8	26.1	19.7	12.6	200	20.2

Table 1-2: Comparison of piezoelectricity of typical piezoelectric materials.^{46,48}

The polymers like polypropylene, polystyrene, poly (methyl methacrylate), vinyl acetate, and odd number nylons are known to possess piezoelectric properties. However, strong piezoelectric effects have been observed only in polyvinylidene fluoride (PVDF) and PVDF copolymers. As discussed in the previous part, the β phase PVDF consists of all-trans conformation of CF₂-CH₂ unit with high net dipole moment. The permanent dipole polarization of PVDF could be obtained through a technological process that involves stretching and poling of extruded thin sheets of polymer. These piezoelectric polymers are mostly used for directional microphones and ultrasonic hydrophones applications.⁴⁶

Piezo-composites comprised piezoelectric ceramics and polymers are promising materials because of excellent tailored properties. These materials have many advantages including high coupling factors, low acoustic impedance, mechanical flexibility, a broad bandwidth in combination with low mechanical quality factor. More piezoelectric composites will be further discussed in Chapter 4.

1.2.3 Applications of Piezoelectric Materials

Piezoelectric materials can have wide range of properties, depending on their composition, processing and microstructures. According to the converse and direct effects, a piezoelectric material can act as a transducer to convert mechanical to electrical or electrical to mechanical energy. When piezoelectric transducer converts the electrical energy to mechanical energy it is called as piezo-motor/actuator, and when it converts the mechanical energy to electrical energy it is called as piezo-generator/sensor. The sensing and the actuation capabilities of the piezoelectric materials depend mostly on the coupling coefficient, the direction of the polarization, and on the piezoelectric coefficients. The main uses of piezoelectric materials are in the detection of mechanical vibrations, generation of charge at high voltages, control of frequency and generation of acoustic and ultrasonic vibrations. Bulk ceramics such barium titanate, lead zirconate titanate, with specific shapes are commonly employed for ultrasonic imaging, underwater hydrophones, thermal imaging, pollutant sensors and microphones.³

In addition, piezoelectric materials could be fabricated in the micro-electrical-mechanicalsystems (MEMS) to accomplish the task involving the conversion between electrical and mechanical energy.⁴⁹ Another modern use for piezoelectric materials is in ultrasonic medical applications since it's safer than x-ray imaging and able to distinguish soft tissues and organs with excellent resolution.⁵⁰ Moreover, the piezoelectric materials have been extensively used in the aerospace devices, structural health monitoring, vibration control, and energy harvesting applications. In the aircraft structures application the piezoelectric materials are used in the jet tailfins, helicopter rotor blades, morphing wings and telecommunication satellites.⁴⁴ In the recent years, a booming development of multi-billion dollar piezoelectric market at an annual growth rate of 9% has been visualized.⁵¹

1.3 Sol-Gel Process

Sol-gel process, known as the "inorganic polymerization", is a general method for preparing oxides by the 'wet route' (i.e. in solution), which was discovered in 1846 by Ebelmann.^{52, 53} In the sol-gel process, the precursors (starting compounds) for preparation of a colloid consist of a metal or metalloid element surrounded by various ligands. An alkoxide is the class of precursors most widely utilized in sol-gel approach, which contains only carbon and hydrogen linked exclusively by single bonds. Metal alkoxides are members of the family of metal organic compounds, which have an organic ligand attached to a metal or metalloid atom. Metal alkoxides are popular precursors because they react readily with water. The reaction is called hydrolysis as shown below, because a hydroxyl ion becomes attached to metal atom.

$$M(OR)_{x} + H2O \longrightarrow HO-M(OR)_{x-1} + ROH$$
 1.18

The R and M represent a proton or other ligand and metal, respectively, and ROH is an alcohol: the bar (-) is used to indicate a chemical bond. Depending on the amount of water and

catalyst present, the precursors could be completely hydrolyzed. Two hydrolyzed molecules can link with each other in a condensation reaction as below:

$$(RO)_{x-1}M-OH + HO-M(OR)_{x-1} - RO)_{x-1}M-O-Si(OR)_{x-1} + H_2O$$
 1.19

$$(RO)_{x-1} M-OR + HO-M(OR)_{x-1} \longrightarrow (RO)_{x-1} M-O-Si(OR)_{x-1} + ROH$$
 1.20

By definition, condensation liberates a small molecule, such as water or alcohol. This type of reaction can continue to build larger and larger silicon-containing molecules by the process of polymerization from small sol colloids. Herein, a huge molecule is formed from hundreds or thousands of monomers that have at least 2 functional groups as illustrated in Figure 1-14. If the macromolecule extends throughout the solution, the substance is called gel which could be thought of continuous solid and fluid phases of colloidal dimensions.⁵⁴ Bond formation does not stop at the gel point. In the first place, the network is initially compliant, so segments of the gel network can still move close enough together to allow further condensation. Moreover, there is still a sol within the gel network and those smaller polymers or particles continue to attach themselves to the network. Aging may change structure and properties after gelation and cause spontaneous shrinkage during drying. Most gels are amorphous even after drying. If the objective of the processing is to produce a pore-free ceramics, it's necessary to heat the gel to a high enough temperature to cause sintering, which may further favor the removal of pores and crystallization. Therefore, high temperature sintering is always required for the preparation of densified ceramics via sol-gel process.



Figure 1-14. Scheme of the different stages and routes of the sol-gel process.⁵⁵

As shown in Figure 1-14, the sol could be either deposited on a substrate to cast on a substrate or into a suitable container with the desired shape, or used to synthesize powders. The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. The unique structures, microstructures, and compositions that can be made by sol-gel methods open many possibilities for practical applications. The direct usage is for ceramics processing and manufacturing as a means of producing very thin films of metal oxides for various purposes. It could also be expanded to combine with organic chemistry to modify the properties of materials or create new organic-inorganic hybrid materials. Nowadays, Sol-gel derived materials have diverse applications in optics, electronics, energy, space, sensors, medicine, reactive material and separation technology.

Chapter 2

Novel Ferroelectric Polymer Nanocomposite Prepared by *In-Situ* Sol-gel Reaction Exhibiting Enhanced Breakdown Strength

2.1 Introduction

2.1.1 Polymer Nanocomposite Capacitors

The energy density of the capacitors strongly relies on both the dielectric constant and the breakdown strength. Polymers usually have high breakdown strength but relatively smaller permittivity, which apparently limits the energy storage of the polymer capacitors. To enhance the electrical energy density of the capacitors, numerous efforts have been made in the past few years to combine the dielectric polymers of high breakdown strength with nanometer scale addictives, such as ceramic particles and conductive fillers. Figure 2-1 shows a diagram of the dielectric nanocomposite. Compared to the micro scale fillers, there are large interfacial areas in a nanocomposite, which could promote the interfacial exchange coupling through a dipolar interface layer and lead to enhanced polarization and polarizability in polymer matrix near the interface.^{56, 57} Besides, the nanoscale particles also make it possible to reduce the thickness of polymer matrix film to nanoscale, and thus enhance its already high breakdown strength even further by avoiding avalanche effects.⁵⁸ Therefore, nanocomposites are beneficial to enhance the energy density of polymer-based capacitors.



Figure 2-1: Schematic diagram of a dielectric nanocomposite consisting of polymer matrix, nanoparticles, and interface.

One straightforward strategy is to improve the dielectric constant of a polymer is the addition of inorganic fillers with high dielectric constants. Normally, ferroelectric ceramics, such as BaTiO₃, Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) or other ferroelectrics or relaxor ferroelectrics, possess a very large dielectric constant.⁵⁹⁻⁶³ A wide variety of nano fillers have been used to enhance the permittivity. As expected, the introduction of high k fillers is able to increase the effective permittivity of composites, which is contributed by an increase in the average field in the polymer matrix with little of the energy being stored in the high permittivity fillers.⁶⁴ Figure 2-2 shows in both BaTiO₃/P(VDF-CTFE) and BaTiO₃/P(VDF-TrFE-CTFE) nanocomposites, the effective permittivity of composites increases with the filler content increasing.



Figure 2-2: Dielectric constant and loss tangent of the P(VDF-TrFE-CTFE)- BaTiO₃ (star) and P(VDF-CTFE)-BaTiO₃ (square) nanocomposites measured at 1 kHz and room temperature. Open circles and squares are the calculated effective permittivity from the Lichtenecker law for the P(VDF-TrFE- CTFE) and P(VDF-CTFE) based composites, respectively.⁵⁹

Meanwhile, as the nano fillers are incorporated into the polymer matrix, large area of interface has been created which plays a critical role not only in defining the permittivity and dielectric loss, but also in determining the dielectric breakdown strength. Tanaka *et al.* have proposed a multi-core model that describes charge behavior and interfacial structure arising in nanocomposites.⁶⁵ The model is based on the hypothesis of creation of interaction zone between polymer and nano fillers. A number of critical parameters may change at interface, such as polymer chain mobility, polymer chain conformation, crystallinity of polymer, degree of stiochiometry of polymer and filler, charge distribution, *etc.* All these parameters directly influence both electrical and mechanical properties of nanocomposites, which control the breakdown strength. ⁶⁶

2.1.2 Breakdown Strength of Nanocomposites

In most cases, the effective dielectric constants of the composites increase significantly while the addition of inorganic filler tends to decrease the breakdown field strength to values considerably less than those of the bulk polymers.

According to the energy density equation, the energy density is proportional to the permittivity but has an exponential relationship with the breakdown strength, giving rise to marked drop in the energy density. There are several reasons that account for the decrease in the dielectric breakdown strength.

One is the contrast in permittivity between the polymer matrix and fillers, that generates inhomogeneous local electric fields. The large incompatibility between the organophilic polymer matrix and metal oxide could enhance the distortion of local electric field and further fail composites at low electric field. Ma *et al.* observed that the modified titanium dioxide with a polar silane coupling agent increased the breakdown strength and decreased the mobility of charge carriers in their nanocomposite.⁶⁷ In contrast to introduction of low permittivity fillers

 $(SiO_2 \text{ and } Al_2O_3)$, incorporation of high permittivity particles like BaTiO_3, TiO_2 and ZnO in low permittivity polymer matrix is found to reduce the breakdown strength.⁶⁸ The reduction in breakdown strength with incorporation of high permittivity filler is believed to be due to the buildup of high local field at the junction of particle and matrix, arising due to large electric contrast in permittivity and conductivity of filler and polymer matrix.

Secondly, the dispersion of fillers in the polymer matrix is also critical. Due to the high surface energy of the particles without surface modification, fillers tend to aggregate and form a percolative pathway along which the charges transport to breakdown the composites. Therefore, the breakdown strength usually falls off as the content of the fillers increases, as observed in barium titanate/polymer composites in Figure 2-3.



Figure 2-3: the breakdown strengths at each volume fraction of barium titanate nanoparticles.⁶⁹

Along with the aggregation always comes the poor interfacial interaction. Therefore, how to address the issues of interaction between the organic phase and inorganic phase becomes a key to enhance the breakdown strength of nanocomposites. In order to overcome the limitations of composites and enhance the breakdown strength of nanocomposites, various effective physical and chemical modifications of fillers and polymers have been made in an attempt to improve the interfacial compatibility and dispersion of fillers.^{60, 63, 67, 70} For example, Kim et. al. reduced the aggregation of barium titanate nanoparticles in the polymer matrix by modifying the particle

surface with pentafluorobenzyl phosphonic acid:⁶³ Li et. al. utilized the reaction between the reactive terminal groups of the functionalized polymers and surface of the zirconia particles to stabilize the particles as shown in Figure 2-4;⁶⁰ Guo et al. functionalized the surface of nanoparticles and directly polymerized the olefin monomers on the inorganic particles.⁴ Although the interface and the breakdown of those composites have been greatly improved, the breakdown strength of most composites still exhibits lower value than that of pristine polymer. It's because surface modification of the filler particles may introduce another component that can have unintended consequences, including higher ionic conductivity and dielectric loss. Therefore, the modification of the interface has been of tremendous importance to the development of dielectric nanocomposite with high breakdown and energy density.



Figure 2-4: TEM images of the nanocomposites with 12 wt% ZrO_2 : a) covalent-bonded P(VDF-CTFE) nanocomposite and b) pristine P(VDF-CTFE) nanocomposite. c) Molecular structure of P(VDF-CTFE) polymers with phosphonic acid end-groups. d) Stored energy density of the polymer matrix and the nanocomposites versus the applied electric field for covalent-bonded P(VDF-CTFE) nanocomposites with various filler content.⁶⁰

In this chapter we report a completely novel approach for the preparation of ferroelectric polymer-based composites, which includes the synthesis of the ferroelectric poly(vinyldinene fluoride -co- chlorotrifluoro ethylene) (P(VDF-CTFE)) terminated with hydroxyl groups, subsequent in-situ sol-gel reaction of different precursors in the polymer matrix and directly coupling the produced tantalum oxide with reactive end-groups of the polymer to yield the covalent-bonded cross-linked composites. The designed strategy consists of several ideal features. First of All, the functional end groups of P(VDF-CTFE) are able to facilitate the distribution of inorganic phase and greatly enhance the interface via covalent bonds. Second, by controlling the polymerization time, the molecular weight of the prepared P(VDF-CTFE) is relatively low, leading to the increase in the concentration of the functional end groups in the composite and remarkable decrease in the size of the inorganic phase. Third, the in-situ prepared oxide has relatively lower permittivity than those of typical ferroelectric ceramics which reduce the contrast in the permittivity. Finally, the cross-linked network favors for the better electrical and mechanical properties. The results demonstrate that the inorganic-organic cross-linked composites not only lead to highly dispersed fillers without additional surface modification but also offer great stability and enhanced dielectric breakdown strength.

2.2 Ta₂O₅/P(VDF-CTFE) Nanocomposites Prepared by In-Situ Sol-Gel Process

2.2.1 Experimental Details

2.2.1.1 Materials

All reagents were purchased from Aldrich and used without further purification unless otherwise noted. All the solvents used for the synthesis were HPLC grade. Vinylidene fluoride (VDF) and chlorotrifluoroethylene (CTFE) were purchased from SynQuest Laboratory Inc. and purified by the freeze-thaw process prior to use. All manipulations of gas-condense transfer were carried out with rigorous exclusion of oxygen and moisture on a dual-manifold Schlenk line with 10⁻⁶ Torr high vacuum. Commercial P(VDF-CTFE) (including 15 wt% of CTFE) was supplied by Solvay (Solef 31508).

2.2.1.2 Synthesis of the 4-[(tetrahydropyran-2-yloxy) methyl] Benzoic Peroxide

The synthesis of the functional initiator followed the reference 23, as shown in the Scheme 2-1. To a stirred solution of methyl 4-(hydroxymethyl) benzoate (2.66 g) in anhydrous dichloromethane (120 mL) was added dihydropyran (2.0 g) and pyridinium p-toluenesulfonate (0.40 g). After 18 hours, the reaction mixture was diluted with ether (80 mL) and washed by brine three times. The aqueous phase was extracted with Et2O three times. The combined organic phases were dried over MgSO₄ and concentrated in vacuo. Purification by column chromatography (SiO₂, 1:5 ethyl acetate: hexane) gave methyl 4-[(tetrahydropyran-2-yloxy) methyl] benzoate as a colorless oil. After the saponification of resulting benzoate (2.5 g) with potassium hydroxide (1.1 g) in aqueous methanol (80 mL, 1:3 water: methanol), the pH value of the solution was adjusted to 6 with diluted hydrochloride acid. The collected white precipitate was recrystallized in diethyl ether to give [(tetrahydropyran-2-yloxy) methyl] benzoic acid as a white solid.

To a mixture of DCC dichloromethane solution (2.1 mL, 1M) and H_2O_2 aqueous solution (1.3 mL, 30%) [(tetrahydropyran-2-yloxy) methyl] benzoic acid (470 mg, 2 mmol) in dichloromethane (8 mL) was added at 0 °C under the stirring for 15 hours. The reaction mixture was diluted by addition of cold dichloromethane (20 mL), and the precipitate was removed via filtration five times. The organic phase was evaporated and the residue was recrystallized in the mixture of carbon tetrachloride and methanol (1:3). Then the 4-[(tetrahydropyran-2-yloxy) methyl] benzoic peroxide was obtained as a white solid. The ¹H-NMR spectrum in Figure 2-5 confirmed the chemical structure of functional initiator.



Scheme 2-1: Synthesis of functional initiator 4-[(tetrahydropyran-2-yloxy) methyl] benzoic peroxide.



Figure 2-5: ¹H NMR spectrum of the prepared 4-[(tetrahydropyran-2-yloxy) methyl] benzoic peroxide.

2.2.1.3 Preparation of Poly(vinylidene fluoride-co-chlorotrifluoroethylene) with Hydroxyl

Terminal Groups

Poly(vinylidene fluoride-co- chlorotrifluoroethylene) (P(VDF-CTFE)) with hydroxyl terminal groups was prepared via free radical polymerization following the Scheme 2-2 as reported in literature⁵. Initiated by 4-[(tetrahydropyran-2-yloxy) methyl] benzoic peroxide (300 mg), vinylidene fluoride (27 mL) and chlorotrifluoroethylene (2mL) in anhydrous acetonitrile (30 mL) were polymerized in the Parr reactor under stirring at 90 °C. After 6 hours, the reactor was cooled down, the residual gases were discharged and the solution was collected. The polymer was

precipitated by removal of the solvent, washed with the methanol three times, and dried in vacuo at 60 °C to yield 2.8 g white solid. To a mixture of tetrahydropyran ether terminated P(VDF-CTFE) (150 mg) in THF (100 mL) was added 3M HCl (5 mL) and acetic acid (20 mL). The mixture was stirred at 60 oC for 3 hours, and then was condensed in vacuo and poured into methanol (50 mL) to precipitate polymer. The polymer was collected by filtration, washed by methanol three times and dried in vacuo at 60 °C. The number molecular weight of the prepared copolymer is 45000 Dalton which is calculated according to the integrals of the characteristic peaks in ¹H NMR spectra in Figure 2-6 and further verified by gel permeation chromatography (GPC).

The chemical composition of the prepared polymers is determined according to the integrals of the characteristic peaks of VDF and CTFE in ¹⁹F NMR spectrum in Figure 2-7 by the following equation:

$$\frac{mol \% VDF}{mol \% CTFE} = \frac{I_1 + I_2 + 3I_3 - I_4}{I_5 + I_6 + 2(I_4 - I_3)^2}$$
2.1

where I_1 is the integral intensity of the resonance area of -92 to -97 ppm (peak a, b and c), I_2) -106 to -113.5 ppm (peak d, e and f), I_3) -114.3 ppm (peak g), I_4) -116.6 ppm (peak h), I_5) -118 to -123.3 ppm (peak i and j), and I_6) -129.4 to -137.2 ppm (peak k and l).⁶ The molar ratio of VDF and CTFE in the prepared P(VDF-CTFE) was 9:1.



Scheme 2-2: Synthesis of the Poly(vinylidene fluoride-co- chlorotrifluoroethylene) capped by hydroxyl groups.



Figure 2-6: ¹H NMR spectrum of the prepared P(VDF-CTFE).



Figure 2-7: ¹⁹F NMR spectrum of the prepared P(VDF-CTFE).

2.2.1.4 Preparation of Composites



Figure 2-8: A photo of the prepared composite film 5Ta.



Scheme 2-3: Preparation route of P(VDF-CTFE)-based composite.

Hydroxyl group capped P(VDF-CTFE) (POH) was dissolved in anhydrous dimethylformamide (DMF) while tantalum ethoxide was dissolved in anhydrous ethanol. Under stirring, the ethanol solution of tantalum ethoxide and 0.05mL of distilled water was slowly added to the DMF solution of the functionalized polymer at room temperature. Stirred for 24 hours, the transparent mixture was casted on the octadecyltrichlorosilane (OTS) treated glass substrates and dried at 64 °C overnight. The prepared light brown film was then further died in vacuo and heated to 150 °C stepwise by 10 °C/1hr. After heated at 150 °C for 72hrs, the films were hot pressed at 200 °C under 1500 psi to remove the voids and residual solvent and further proceed sol-gel reaction. Then the P(VDF-CTFE) chains in the composites should be cross-linked and formed a network as illustrated in Scheme 2-3. In this work, 5 flexible composite films with the precursor loadings of 4.76 %, 9.09 %, 13.04 %, 16.67 % and 23.08% (wt%) were prepared with the thickness of 11-20 µm. The rolled 5Ta film was as shown in Figure 2-8. The films of commercial P(VDF-CTFE) and POH with the thickness of 12 µm were hot pressed at 100 °C under 1500 psi

after solution casting as control samples. For the FTIR test, two composite films PTa-a and PTa-b of the precursor loading of 50% (wt%) were prepared. PTa-a was solution-casted without further heating while PTa-b was fabricated following the above procedures.

2.2.1.5 Characterization

1H and 19F NMR spectra were recorded on Bruker AM-300 spectrometer instrument at room temperature using tetramethylsilane (TMS) as internal reference. Molecular weight and polydispersity of the synthesized polymer were determined in a THF mobile phase at a flow rate of 1.0 mL/min using a Viscotek Model 302 triple detection gel permeation chromatography (GPC) system equipped with refractive index, right angle light scattering and viscometer detectors. The thermal analysis data were obtained by a TA Instrument Q100 differential scanning calorimeter (DSC) at a heating and cooling rate of 10 oC/min and TA Q50 thermogravimetric analyzer at the heating rate of 10 oC/min. Crystal analysis was studied by use of PANalytical xpert pro mpd theta-theta diffractometer. All data were analyzed using Jade software with a Gaussian-Lorentz superposition fitting functions. The cross-sectional morphology was explored using JEOL 6700 field emission scanning electron microscope (FE-SEM). FTIR spectra were obtained in the attenuated total reflectance (ATR) mode using diamond crystal as a contact to the samples on Bruker Vertex V70 spectrometer at room temperature. Dielectric constant and loss were acquired using an Agilent LCR meter (E4980A). Dielectric spectra were acquired over a broad frequency $(10 - 10^{6} \text{ Hz})$ and temperature $(-100 - 100 \text{ }^{\circ}\text{C})$ using a Hewlett Packard 4284A LCR meter in conjunction with a Delta Design oven model 2300. The Displacement-electric field (D-E) loops were recorded using a modified Sawyer-Tower circuit. The electrical energy density of the films was calculated from the unipolar D-E loops. The dielectric breakdown field was determined by applying a linear ramp voltage at a rate of 500 V/s on the polymer film in accordance with ASTM D149 standard. Resistivity and conductivity were obtained under a electric field provided by a Hewlett Packard 4140B pA meter/voltage source and KEPCO BOP 1000M amplifier in a Delta

Design 2300 oven. Thermally stimulated discharge current (TSDC) was also measured using Hewlett Packard 4140B pA meter with Kepco BOP 1000M as a high voltage source and performed in a Delta Design 2300 oven. Gold electrodes of 2.6 µm diameter and typical thickness of 60 nm were sputtered on both sides of the samples for the electrical measurements. Tensile tests were conducted at the pulling rate of 25 cm/min on the TA Instruments RSA-G2 Dynamic Mechanical Analyzer.

2.2.2 Results and Discussion

2.2.2.1 Structural Characterization





Figure 2-9: TGA curves of the POH and composite films at the heating rate of 10 °C/min in air.

Thermogravimetric analysis (TGA) curves of the pristine film and the prepared composite films at a heating rate of 10 °C/min in air are presented in Figure 2-9. Below 250 °C, there is light weight loss, indicating that most solvent and small molecules are removed in the film making. Compared to the great weight loss of POH film at above 400 °C, composite films are observed to degrade at around 250 °C. For the composite, the incorporation of addictives, such as the tantalum oxide and tantalum ethoxide, could lower the thermal activation energy and decrease the decomposition temperature of the polymer backbone in composites.^{71, 72} Besides, the incomplete

hydrolysis and condensation of the precursors in the filmmaking may also make the contribution to weight loss at high temperature. Although the sol-gel reaction of the precursors and the end groups of the copolymer is conducted at up to 200 °C, the temperature is not high enough to make the precursors completely hydrolyzed and condensed. Above 250 °C, the unreacted ethoxy groups in the precursors would be eliminated and uncondensed tantalum hydroxide would continue the condensation until all the precursors turn to tantalum oxide (Ta_2O_5) thoroughly. Therefore, great weight loss is found above 250 °C. The residues of the composites at 800 °C are believed to be Ta_2O_5 and the weight percentages of tantalum element in the composite films are calculated and shown in Table 1.

Name	Ta(OEt) ₅ loading weight percentage	Weight percentage of Ta ₂ O ₅ in composites determined by TGA	Weight percentage of Ta in composites determined by TGA
РОН	0	0	0
5Ta	4.76 %	3.21 %	2.63 %
10Ta	9.09 %	5.89 %	4.82 %
15Ta	13.04 %	8.09 %	6.63 %
20Та	16.67 %	10.65 %	8.89 %
30Ta	23.08 %	15.19 %	12.44 %

Table 2-1: Names and compositions of samples

Fourier Transform Infrared Spectroscopy



Figure 2-10: Fourier transform infrared spectra of the pristine P(VDF-CTFE) and all composites.

Frontier transformation infrared spectroscopy is applied to investigate the chemical nature of the composites and study the in-situ sol-gel reaction in the polymer matrix. As shown in Figure 2-10, the observed peaks at 532, 614 and 763 cm⁻¹ are the characteristic of non-polar TTTG conformation of CF_2 in the polymer backbone. The shoulder peak at 600 cm⁻¹ corresponds to Ta-O-Ta stretching. Moreover, as the concentration of the tantalum oxide increases, the intensity of the peak increases, confirming the *in-situ* sol-gel process.⁷³⁻⁷⁵ In the right graph of Figure 2-10, spectra of 20Ta and 30Ta have apparent bump peaks shown from 3200 to 3600 cm⁻¹, which could be assigned to the vibration of OH groups from the hydrolyzed precursors. It's postulated that the sol-gel reaction consumes most hydrolyzed tantalum hydroxide for the composites of low content (from 5Ta to 15Ta) while there are additional free unreacted hydroxyl groups left in the composites of high composition such 20Ta and 30Ta. The presence of the additional free OH groups may result in the enhance of To further study the reaction, composite samples PTa with the high precursor loading of 50 wt% are prepared in the same procedures to investigate the insitu sol-gel reaction in the film. Figure 2-11 presents the curves of commercial P(VDF-CTFE), PTa-a and PTa-b composites. The spectra of PTa-a and PTa-b both shows a wide absorption band from 400 to 1000 cm⁻¹ which could be assigned to Ta-O stretching vibration of tantalum ethoxide

and tantalum oxide. The significant peak at 600 cm⁻¹ is found in both composite curves, confirming the formation of tantalum oxide. It is suggested that the condensation reaction is both conducted before and after the thermal treatment and the heating effectively boosts the condensation since the intensity at 600 cm⁻¹ is higher in PTa-b. Broad peaks from 1540 to 1650 cm^{-1} could be mainly attributed to several vibration modes of C=O groups from dimethylformamide, OH tantalum hydroxide Ta-coordinated groups from and dimethylformamide mode as the literature reported.⁷⁶ After the thermal curing, this broad peak becomes weaker owing to the condensation of tantalum hydroxide and the further evaporation of the DMF. Besides, the broad peak at the wavenumber from 3200 to 3600 cm⁻¹ displays in the composite film originated from the stretching of hydroxyl groups in Ta-OH.⁷⁷ Therefore, it's demonstrated that the *in-situ* sol-gel reaction proceeds incompletely in the filmmaking.

Although the reaction between the hydroxyl groups at the end of polymers and the tantalum oxide has been reported by the literatures,⁷⁸⁻⁸⁰ the linkage still could not be directly confirmed by FTIR in our composites since the produced CH_2 -O-Ta bond between two phases shows the same vibration as the CH_2 -O-Ta of the precursors, as discussed above. Furthermore, the concentration of the polymer ending groups is relatively too low to be identified by FTIR. Thereby, other characterizations and information are required to confirm the cross-linking structure of the composite.



Wavenumber (cm⁻¹) Figure 2-11: Fourier transform infrared spectra of commercial P(VDF-CTFE) (black line) and solution casted nanocomposite PTa (red line) before and after baking (blue line). Inset showed the spectra from 475 to 950 cm⁻¹.

Differential Scanning Calorimetry and X-ray Diffraction

Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) have been applied to study the crystallization of the commercial P(VDF-CTFE), precursor polymer POH and composites of different compositions. As revealed in the DSC profiles in Figure 2-12, the precursor polymer POH and all the composites show both lower melting and crystallization temperature than commercial P(VDF-CTFE) probably due to the lower molecular weight of POH and different concentration of CTFE. Hence, the study of crystallization and melting temperatures is mainly conducted on the POH and the composites. In the cooling scan the crystallization temperature of the composites shifts by around 15 °C from 83.0 °C for the POH to 67.4 °C for composite 15Ta. The decreasing of crystallization temperature can be attributed to the incorporation of the defects, such as inorganic compounds and the cross-linking which restrains the motion of polymer chains. However, with the further increment of precursors loading, the crystallization temperature increased by 6 °C for the composite 20Ta and 7.4 °C for 30Ta, which may result from the promotion of heterogeneous nucleation. The agglomeration due to the large amount of inorganic compounds possibly facilitates the nucleation of the PVDF chain and led to the favored crystallization.⁸¹ The melting point of each sample is collected from the heating scan of the DSC thermographs as illustrated in Figure 2-12 and summarized in Table 2-2. The melting temperatures of composite samples were lower than that of POH, which is associated with the smaller crystallite size.^{82, 83} And the most depressed melting point is found in the composite 15Ta with the smallest crystal size. The degree of crystallinity by DSC was evaluated by: $\chi_c = \Delta H_m / (\Delta H_m^0 \cdot \omega)$, where $\Delta H_m^0 = 104.7$ J/g is the melting enthalpy of 100% crystalline PVDF. ω is the weight percent of PVDF, which is 0.85 for commercial P(VDF-CTFE). The crystallinity of each sample is calculated based on fusion enthalpy of melting peaks in the heating cycle of DSC, as shown in Table 2. Crystallinity obtained from XRD was computed by the software Jade after the peak fitting. It shows a good agreement with the result from DSC. In the

work, influenced by both the defect effect from the tantalum oxide and cross-linking, the crystallinity falls straight from 34 % for the POH and the commercial P(VDF-CTFE) to 22.7 % for the composite 30Ta. Additionally, the minor peak of commercial P(VDF-CTFE) at lower temperatures associated with the ferroelectric to paraelectric phase change of the Curie transition is not observed in POH and all composites.



Figure 2-12: DSC thermographs of cooling scan on the left and heating on the right. These DSC traces were collected with a heating/cooling rate of 10 °C/min.

The X-ray diffraction patterns of pristine polymer and composites with 20 from 10° to 40° are shown in Figure 2-13. All the patterns show obvious characteristics of PVDF α -phase other than β -phase since the (110/200) β peak is negligible. Moreover, the typical sharp intense peaks of tantalum oxide crystals are not observed in the patterns of composites, indicating that the sol-gel processing only produces amorphous tantalum oxide in the filmmaking condition. Amorphous metal oxides are believed to have lower leakage current and enhance the breakdown strength, which is favorable for high breakdown materials for capacitors.⁸⁴⁻⁸⁶ The size of the crystalline domain was calculated by use of Scherrer's formula, t= λ /B cos θ , where t is the crystallite size, λ is the wavelength, B is the normalized full width at half maximum (fwhm) diffraction peak, and θ is the diffraction angle. The crystallite sizes of all samples from the (020) α peak are listed in Table 2. As discussed earlier, the inclusion of inorganic compounds and the cross-linking significantly reduces the crystallite size from 31.2 nm for the POH and commercial P(VDF-CTFE) to about 25 nm for the composites. Since the cross-linking junction cannot be incorporated in crystal lattice, the formation of ordered phase presumably prefer to take place in shorter chain sections. However, the lattice spacing (d) doesn't change much suggesting that the lattice structure was not affected by the tantalum oxide and cross-linking.



Figure 2-13: XRD patterns of commercial P(VDF-CTFE) and 5 composites.

	P(VDF- CTFE)	РОН	5Ta	10Ta	15Ta	20Та	30Та
Heat of fusion (J/g)	30.5	29.3	25.4	20.4	19.8	17.9	16.7
Crystallinity (%) by DSC	34.3	33.8	30.2	25.0	24.5	23.1	22.7
Crystallinity (%) by XRD	35.4	34.2	31.7	26.7	26.3	25.1	21.5
Spacing d (Å) (from 020 peak)	4.80	4.81	4.84	4.85	4.83	4.86	4.85
Crystal Size (nm) (from 020 peak)	30.5	31.2	28.9	27.6	23.5	25.5	26.8
Melting Temperature (°C)	177.5	113.6	113.0	109.5	106.7	110.8	111.5
Crystallization Temperature (°C)	144.1	83.0	78.7	74.5	67.4	73.4	74.8

Table 2-2: Crystallization parameters of commercial P(VDF-CTFE), POH and 5 composites.

Thermostability

-



Figure 2-14: Photos of a) pristine POH film and b) the composite 15Ta film after 24 hr baking at 150 °C.

As shown in Figure 2-14, the pristine polymer film is partially melted after baking for 24 hours at 150 °C, which is higher than the melting point at 113 °C as revealed in DSC. Nevertheless, the brown flexible composite 15Ta film still remains in good shape. Even after the hotpressing at 200 °C, the composite films do not deform much. The excellent thermostability of the composites results from the formation of the cross-linking network in which the polymer chains and *in-situ* prepared tantalum oxide build the covalent linkage.

Scanning Electron Microscopy



Figure 2-15: Cross-sectional field emission scanning electron microscopy (FESEM) image of the composite 15Ta.

Figure 2-15 shows a cross-sectional field emission scanning electron microscopic (FESEM) image of composite 15Ta. The image displays smooth homogeneous cross-section with no identical particles or agglomeration observed, suggesting that the amorphous tantalum oxide were *in-situ* prepared and well dispersed in the polymer matrix. The good dispersion may ascribe to the improved interfacial interaction caused by the coupling between inorganic and organic phases.

Transmission Electron Microscopy



Figure 2-16. Transmission electron Microscope images of a) pure polymer POH, b) the composite 15Ta and c) 30Ta. The scale bar is 10 nm.

Transmission electron microscope was applied to observe the morphology of the polymer and composite films. In Figure 2-16b, tiny dark spots with the size less than 2 nm were well dispersed in the composite 15Ta, which is the tantalum element. Tantalum has the z number of 73 which is far greater than 6 of carbon so it looks darker in the transmission electron microscope. The excellent dispersion also implies the in-situ prepared tantalum oxides were homogeneously spread in the polymer matrix. However, at the high filler content, the aggregation appears. As shown in Figure 2-16c, formation of larger dark region demonstrates the agglomeration of the inorganic phase in the sample 30Ta, which probably limits the performance of the capacitor.

The sol-gel process in this system is so complicated that there may be couples of conformations of prepared amorphous tantalum oxide. For example, the tantalum oxide could linearly connect with one another. It's more likely that several tantalum hydroxide molecules formed a small cluster and condensed into amorphous tantalum oxide. No matter what structures they were, the numbers of tantalum oxide molecules could be roughly assessed according to the size of dark spots in TEM image. For a dark spot with the diameter of 1 nm, there may be approximately 3 tantalum oxide laying in a row since tantalum-oxygen bond is typically 2.05-2.06 Å long.⁸⁷ Theoretically, the molar ratio of hydroxyl groups at the end of P(VDF-CTFE) and

tantalum atoms is 1:8 for 15Ta. Therefore, the dark spots with the diameter of about 2 nm consists of 30 tantalum atoms, linking to 4 P(VDF-CTFE) chains.

2.2.2.2 Dielectric Properties

Breakdown Strength

Figure 2-17 compares the characteristic breakdown fields of the commercial P(VDF-CTFE) and the composite samples at room temperatures, whereas the breakdown results were analyzed using a two parameter Weibull distribution function,

$$P = 1 - \exp(-(E/\alpha)^{\beta})$$
 2.2

where P is the cumulative probability of electric failure, E is the measured breakdown field, α is the characteristic breakdown strength which corresponds to a ~63.2 % probability of failure, and β is the slope parameter that evaluates the scatter of data.⁸⁸ At least 15 measurements have been made for each Weibull fitting. The Weibull parameters of all the samples are listed in Table 2-3. Compared to the breakdown strength of 360 MV/m with a β of 7.45 for commercial P(VDF-CTFE), all the composites display improved breakdown strengths. For instance, the optimized composite 15Ta exhibits the breakdown strength of 504.8 MV/m, which is 40.2 % higher than the P(VDF-CTFE). Besides, with the tantalum loading increases, the α value is found to increase, reach the maximum, 504.8 MV/m for the 15Ta and then level off gradually, as illustrated in Figure 2-18. At higher loading concentration, the depression of the breakdown strength is probably relative to the agglomeration of tantalum oxide. Moreover, the sample 15Ta also possesses the higher β value of 15.29 than other samples, indicating the better dispersion of tantalum oxide in the polymer matrix.



Electric Field (MV/m) Figure 2-17: The Weibull distribution of breakdown fields of commerical P(VDF-CTFE) and 5 composites.

Table 2-3: Weibull	parameters of the	for the P(VD	DF-CTFE)	and 5 comp	posites.
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	P(VDF-CTFE)	2Ta	5Ta	10Ta	20Та	30Та
α (MV/m)	360.0	372.0	454.9	504.8	382.9	361.9
β	7.45	13.11	14.48	15.29	11.24	12.32



Figure 2-18: The dependence of Weibull breakdown strength on the tantalum weight percentage.

Weak-field dielectric measurement



Figure 2-19: The permittivity and dielectric loss (tan δ) as a function of frequency at 25°C for the commercial P(VDF-CTFE), POH and 5 composites.

The weak-field dielectric properties of all samples have been characterized as the function of frequency as shown in Figure 2-19. The synthesized POH shows almost the same dielectric properties as the commercial P(VDF-CTFE). As shown in Figure 2-20, the permittivity of the prepared composites is similar to that of POH and commercial P(VDF-CTFE) since the permittivity of amorphous tantalum oxide is 12-20 at the frequency from 100 to 100 kHz, just slightly higher that of P(VDF-CTFE).^{85, 89} As localized non-uniform field is a important factor to lower the dielectric breakdown strength, the little contrast in permittivity between the polymer and amorphous tantalum oxide could give rise to relatively homogeneous electric field and high breakdown strength.⁹⁰ However, the composites exhibited relatively lower permittivity than that of the pristine P(VDF-CTFE), associated to the cross-linking structure which could confine the chain motion and reduce the dipole orientation. For the dielectric loss plotted in Figure 2-19, the composites showed lower loss than the neat polymer, especially at low frequency. It suggests that the cross-linked composite greatly reduces the quantity of the space charge and limits the charge transportation. As illustrated in Figure 2-21, the loss tangent of the 20Ta and 30Ta levels up resulting from the aggregation of the inorganic phase at high composition.



Figure 2-20: The dependence of permittivity on the tantalum weight percentage.



Figure 2-21: The dependence of loss $(tan \delta)$ on the tantalum weight percentage.





Figure 2-22: Dielectric spectra of a) POH, b) 5Ta, c) 10Ta, d) 15Ta, e) 20Ta and f) 30Ta.

The temperature dependence of permittivity and loss of all samples at different frequency is measured as shown in Figure 2-22. Typically, the permittivity is low but not zero at low temperature, suggesting that not all the dipoles are quenched. As the polymer passes through the glass transition temperature, frozen dipoles start to actively response to the applied field and contribute to the permittivity. Meanwhile, the presence of a peak represents the α relaxation in the amorphous phase of polymer.



Figure 2-23: The dependence of permittivity on the temperature at a heating rate of 10 °C/min.

The temperature dependence of dielectric permittivity of all samples at the frequency of 1 kHz is illustrated in Figure 2-23. The dielectric permittivity of all the samples levels off as the precursor loading increased, consistent with the weak-field data. Besides, a new peak at 24-26 °C could be ascribed to the dipolar glass freezing transition from the polymer chains surrounding the tantalum oxides. In accordance with the changes in crystalline size and the thermal transition temperatures discussed earlier, the cross-linking restricts the chain mobility and thus enhances activation energy of the transition.⁹¹ Moreover, at elevated temperature, the permittivity of all composite samples is found less variability since the introduction of cross-linking restricted the polymer chain movement. As the dielectric loss versus temperature relationship presented in Figure 2-24, the significant peak at 1 kHz around -25 °C is visualized in all the samples, corresponding to the amorphous relaxation of the polymer. The position and magnitude of loss of composites are similar to those of the POH and commercial P(VDF-CTFE). The additional interfacial relaxation is further confirmed in loss spectra as small peaks appear at 24-26 °C in the loss plot. The interfacial peak could only be observed at low frequency, supporting that the peak is corresponding to the restricted chain motion. Additionally the surge in both permittivity and loss at above 40 °C that is only found in the POH and commercial P(VDF-CTFE) is due to the conduction, implying the better stability and greater depression of the conduction. For 20Ta and 30Ta, the elevation of loss at high temperature indicates more conduction, relative to the 10Ta and 15Ta.





0.05

0.05

Figure 2-24: a)The full plot of dependence of loss on the temperature and b) the zoomed plot in the temperature range from 10 to 50 $^{\circ}$ C.



Figure 2-25: Dielectric loss data vs frequency for POH at a) T > Tg and c) T < Tg, and 15Ta at b) T > Tg and d) T < Tg, focusing on the relaxation peak for selected temperatures as indicated on the plot. The insets are the Arrhenius plot for POH and 15Ta at the temperature above glass transition.

The representative loss spectra of POH and the composite 15Ta at variant temperatures are given in Figure 2-25. The corresponding frequencies, fmax, versus the reciprocal temperature are plotted in the insets. By linear fitting the log(fmax), the dielectric activation energies below and above the glass transition temperature are calculated based on the Arrhenius equation and listed in the Table 2-4.⁹²⁻⁹⁴ Compared to the POH, all the composites exhibit higher activation energy. At the temperature above Tg, the increase in the energy barriers manifests lower mobility of polymer due to formation of cross-linking network which in turn confirms the improvement of interfacial interaction between polymer and tantalum oxide.⁹⁵ Additionally, as the content of the inorganic
phase increasing, the activation energy increases and then reaches a plateau, indicating the saturation of cross-linking. It's suggested that overfeeding of tantalum oxide would not further enhance the cross-linking between the functional polymer end and tantalum oxide. At the temperature below Tg, the dielectric activation energy of composites is found higher than that of POH. This could be ascribed to the formation of tightly bounded polymer phase. Because of the covalent linkage of the polymer ends and inorganic phase, the mobility of polymer chains is partially restricted and thus the sub-Tg mode required more thermal energy to be activated.⁹⁴ It in turn demonstrates a marked improvement of interfacial interaction between the organic and inorganic phases.

Samples	Activation energy (eV)	Activation energy (eV)
	T > Tg	T < Tg
РОН	0.76 ± 0.02	0.36 ± 0.02
5Ta	0.81 ± 0.02	0.38 ± 0.01
10Ta	0.85 ± 0.02	0.40 ± 0.02
15Ta	0.84 ± 0.01	0.41 ± 0.01
20Та	0.85 ± 0.01	0.42 ± 0.01
30Ta	0.86 ± 0.02	0.42 ± 0.02

Table 2-4: Activation energies for all composites derived from dielectric spectroscopy



D-E loop and Energy density



Figure 2-26: Displacements of a) P(VDF-CTFE) and b) 15Ta versus the electric field with a 10 Hz unipolar triangle signal at 25 °C.

Figure 2-27: D-E loop of the commercial P(VDF-CTFE) and the composite 15Ta at an electric field of 350 MV/m, respectively.

The high electric field displacement has been examined with a 10 Hz unipolar triangle signal at 25 °C. Figure 2-27 shows that the D-E loops of the commercial P(VDF-CTFE) and 15Ta, are almost the same in shapes, the maximum displacements. Among 5 composites, 15Ta performs the minimal energy loss at all electric fields, which is well consistent with the low field dielectric results. Moreover, in the comparison with the P(VDF-CTFE), the composite 15Ta possesses lower energy loss all across the electric field and less remnant polarization, illustrated in Figure 2-27. Basically, the calculated energy loss consists of ferroelectric loss and conduction loss. For the ferroelectric loss, the smaller crystalline size is believed to cause reduction in ferroelectric domain size which benign suffering due to the fact that larger domain lost more energy during polarization process.⁹⁶ Based on the XRD data, the sample 15Ta with the smaller crystal size would have less ferroelectric loss, which renders the 15Ta the slimmer loop and lower energy loss. Therefore, the composite 15Ta dissipates less heat during the charging-discharging cycle and in turn achieves the improved breakdown strength. Beneficial from the lower loss and higher breakdown strength, the 15Ta could store and release more energy than commercial P(VDF-CTFE) as plotted in Figure 2-28. The maximum stored and discharged energy density could reach 22.0 and 13.6 J/cm³, respectively.



Figure 2-28: Energy densities and loss of the pristine polymer and the composite 15Ta.





Figure 2-29: The dependence of stress on strain for all the samples at room temperature.

The mechanical properties of cross-linked composites and polymer are also tested using the tensile tester with the pulling rate of 25 cm/min. According to The Young's moduli are extracted from the slope of initial linear portion of stress-strain curves, as shown in Figure 2-29. The tensile strength is collected as the maximum stress during the pulling process. The yield stresses of samples are determined using a linear force ramp to generate a stress versus strain curve where the yield stress is calculated from the intersection of the elastic and inelastic tangent lines. All the results are summarized in Table 2-5.

	Young's Modulus (MPa)	Yield Stress (MPa)	Tensile Strength (MPa)
P(VDF-CTFE)	554.6	11.3	17.1
РОН	419.0	9.1	16.3
5Ta	477.2	10.1	17.6
10Ta	571.9	11.8	22.3
15Ta	689.2	13.6	26.8
20Ta	740.0	16.2	26.1
30Ta	827.2	17.1	28.1

Table 2-5: Mechanical properties of all the samples at room temperature.

Compared to the commercial P(VDF-CTFE), the synthesized POH shows smaller Young's modulus and tensile strength, as a result of the lower molecular weight. However, the Young's moduli and tensile strengths of composites build with the content of tantalum oxide increasing. As observed in the crossectional SEM image, there is no apparent particles grown in the polymer matrix, which rules out the possibility that the hard particles strengthened the mechanical properties. So the enhancement of mechanical properties for the composites is mainly caused by the cross-linking of the polymers. In addition, when the content of tantalum oxide exceeds 8.09 wt% for 15Ta, the increment of tensile strength slows down, implying that the degree of cross-linking approaches the saturation.

Mechanical properties also play an important role in influencing the electrical properties especially, electrical breakdown strength since the electromechanical breakdown mechanism is believed dominate for the relatively soft polymeric materials at high electric field.

Whenever a capacitor is charged, an attractive force is generated from the oppositely charged electrodes which create the electromechanical compressive stress on the dielectric. This

Coulumbic force works against the elastic response that dielectric generates and deforms the dielectric at the same time. At the electrical breakdown field, the electromechanical stress exceeds yield stress of the dielectric causing it to deform plastically, leading to collapse of the dielectric. Garton and Stark who first raised this electromechanical breakdown mechanism provide a model to correlate breakdown strength with the Young's modulus.⁹⁷ In their paper, they define their failure criterion from an instability that occurs when the thickness ratio of the film $d/d_0 = e^{-1/2} = 0.606$. This can be implied that there is no stable thickness smaller than 0.606 d_0 therefore the failure occurs due to mechanical collapse at this critical field.

$$E_b = 0.606 \left(\frac{Y}{\varepsilon_0 \varepsilon}\right)^{\frac{1}{2}}$$
 2.3

where E_b is the electrical breakdown filed, Y is Young's modulus for the dielectric, ε_0 is the permittivity of free space and ε is the relative permittivity of the dielectric.

Besides, Claude et. al. also proposed a modified model to interpret the electromechanical breakdown process at the room temperature.⁴⁰ At the breakdown field, the compressive stress induced by the applied field exceeds the yield stress of the films giving rise to a rapid collapse and discharge between the electrodes. Therefore, the modified model replaces term of Young's modulus with yield stress to represent the failure point more accurately,

$$E_b' = \left(\frac{2\sigma_y}{\varepsilon_0\varepsilon}\right)^{\frac{1}{2}}$$
 2.4

where σ_y is the yield stress.

To further explore the effect of mechanical property on the electrical breakdown strength, the electrical breakdown strengths of all samples are calculated according to two electromechanical breakdown models and listed in Table 2-6. Since the permittivities of composites and polymers don't vary much, the calculated breakdown strengths follow the trend of mechanical properties as a function of filler content. In other words, the improved calculated breakdown strength for composites of high content is ascribed to the enhancement of the stiffness due to the cross-linking

in the electromechanical mechanism. However, the calculated results from the two models do not match the experimental data perfectly. In particular the calculated breakdown strengths from Gorton and Stark's model are far higher than the experimental ones, which is also observed for other polymers in the literature,⁹⁸ while the Claude's modified model fit the measured data better. Moreover, for the composites of low content and polymers, the measured breakdown strength increased with the stiffness increasing, displaying a good agreement with the trend of calculated values. But for 20Ta and 30Ta, excellent mechanical properties don't give rise to the high breakdown strength. It suggests that the electrical breakdown strength of these composites could not be satisfactorily explained only by the electromechanical mechanism, especially for the samples of high tantalum oxide content. This is to say that there should be other mechanisms cooperating with electromechanical breakdown mechanism to explain the failure of these composites.

	Young's Modulus (Y) (MPa)	Yield Stress (σ _y) (MPa)	Permittivity (ε)	Calculated from Young's Modulus (Eb) (MV/m)	Calculated from Yield Stress (Eb') (MV/m)	Experimental Breakdown (MV/m)
P(VDF-	554.6	11.3	10.5	1480.5	493.2	360.0
CTFE)						
РОН	419.0	9.1	10.3	1299.2	446.8	301.1
5Ta	477.2	10.1	10.1	1400.2	475.4	372.0
10Ta	571.9	11.8	10.0	1540.5	516.4	454.9
15Ta	689.2	13.6	10.0	1691.3	554.4	504.8
20Та	740.0	16.2	9.9	1761.1	608.1	382.9
30Ta	827.2	17.1	9.7	1881.1	631.2	361.9

Table 2-6: Calculated and experimental electrical breakdown strengths of all samples.

DC Conductivity



Time (s) Figure 2-30: The dependence of DC current density on the time under the electric field of 10 MV/m at 25 $^{\circ}$ C.



Figure 2-31: The dependence of DC equilibrium conductivity on the tantalum weight percentage under the electric field of 10 MV/m at 25 $^{\circ}$ C.

In order to study the conduction loss, the current density of all samples with a variation of time under a field of 10 MV/m at 25 °C is tested in Figure 2-30. Following the charging current decay region, the curves of current turn into a relatively steady region. As the equilibrium current density shown in Figure 2-31, the composite samples all perform lower equilibrium current density than the neat P(VDF-CTFE) and the 15Ta is found with the minimum conductivity which is more than one order of magnitude lower than that of the neat P(VDF-CTFE), as displayed in Figure 2-31. The current density versus electric field correlation shown in Figure 2-32 and the resistivity versus tantalum concentration in Figure 2-33 also demonstrates that the composites are

less conductive and the 15Ta is the most optimized composition. For the composites 5Ta, 10Ta and 15Ta, well-dispersed amorphous tantalum oxide and polymer forms cross-linking network via the covalent bonds, which give rise to the reduced mobility of charge carriers in the composites.⁶⁷ As the feeding of precursors increases, the probability of cross-linking and breakdown strength increases simultaneously. However, for 20Ta and 30Ta, increment in the current density is caused by the agglomeration of inorganic phase as verified in the TEM images. The aggregates could overlap the local conductive regions, leading to the enhancement of conduction and the decline of dielectric strength.^{67, 70} Besides, the presence of excess unreacted hydroxyl groups may also give rise to the enhancement of conduction since hydroxyl groups are likely to be ionized under high field and provide more charge carriers to move in the composites. Therefore, the 15Ta exhibits the most optimal ability to prohibit the charge transportation and the highest breakdown strength.



Figure 2-32: The dependence of DC current density on the electric field at 25 °C.



Figure 2-33: The dependence of resistivity on the tantalum weight percentage under the electric field of 80 MV/m at 25 $^{\circ}$ C.

Thermally Stimulated Discharge Current



Figure 2-34: TSDC curves for pristine P(VDF-CTFE) and composite 15Ta.

The discharge behavior of the composites has been measured to further probe the mechanism of the dielectric breakdown by thermally stimulated discharge current (TSDC) technique. Each sample is charged with a voltage of 10 MV/m at 50 °C for 30 mins and then rapidly cooled down to -100 °C with the electric field still applied. Afterwards the electric field is removed and the samples are short circuited and heated to 100 °C at the heating rate of 5 °C/min while the current is measured across the sample. The TSDC curves of the pristine P(VDF-CTFE) and the composite 15Ta are presented in Figure 29. The β a relaxation is corresponding to the amorphous relaxation of the glass transition. The βc peak is ascribed to molecular motions in the crystalline region, which is considered as a prefusion phase.^{99, 100} Finally, γ_L and γ_H are considered as low temperature charge trap and high temperature charge trap, respectively. In Figure 2-34, the peak locations of the 15Ta are observed significantly shifting to high temperature, compared to that of neat polymer. The shift of βa and βc peaks suggests that cross-linking constrained the motion of some chains in both amorphous and crystalline phase. The reason why relaxation peaks become broader is that both the cross-linked and uncross-linked polymer chain sections make the contribution. As we discussed above, the prepared composites are not highly cross-linked so it's reasonable to observe both the relaxation of both free and constrained polymer chains of both

amorphous and crystalline phases. The upwards shift of γ_L indicated the formation of deeper traps owing to the disordered structure and the polar Ta-O bonds. Moreover, a new trap peak γ_H is found at high temperature in the 15Ta. In the composites, due to the small size of the inorganic fillers, large inorganic-organic interface is created and acted as high temperature charge traps which is responsible for such peaks.¹⁰¹ As to the intensity of TSDC, from the pristine polymer to the 15Ta, the intensity of βc is lower and the βa became higher since the ratio of the crystalline to the amorphous volume decreased, which has been reported.^{100, 102}





Figure 2-35: The dependence of DC conductivity on the temperature under the electric field of 10 MV/m.



Tantalum (wt%) in composites Figure 2-36: The calculated activation energy on the tantalum percentage under the electric field of 10 MV/m at 25 $^{\circ}$ C.

DC conductivity as a function of temperature is measured to confirm the formation of high temperature traps which requires more energy to release the charges for transporting shown in Figure 2-35. According to Arrhenius equation, the calculated activation energy of the composite 15Ta was 1.3 eV, which was 0.41 eV higher than that of the commercial P(VDF-CTFE) in Figure 2-36. The presence of the deeper trap sites could depress space charge mobility, which is coherent with the conduction data and energy loss data in the dielectric measurement. The lower power dissipation in turn improves the breakdown strength of the composites in terms of the thermal and electrical breakdown mechanism.¹⁰³ Otherwise, the conduction would be facilitated due to the loosely bounded interface. For the composites of high content, relatively larger amount of charge carriers (i.e. protons from free hydroxyl groups) and lower conductivity lead to the lower activation energy. The apparent increase of activity energy for the composites also manifests that the covalent linkage of the organic and inorganic phase effectively enhances the interface. The decrease in activation energy for 20Ta and 30Ta also in turn demonstrates that interfacial interaction has been decreased as the aggregation forms and free OH groups appears at the interface.

2.2.3 Summary

In summary, we have demonstrated a unique route, using in-situ sol-gel reaction of tantalum ethoxide with the functionalized chain-end of the ferroelectric polymer, to prepare cross-linked composites. The optimal composite achieves the dielectric breakdown strengths of 504.8 MV/m, 40.2 % higher than that of the commercial P(VDF-CTFE). This result suggests an important improvement over what has been reported in the past with the conventional dielectric polymer composites. As demonstrated, the functional hydroxyl groups at the end of short ferroelectric polymer chains favor the molecular level dispersion of inorganic products and improvement of interfacial interaction. The in-situ prepared amorphous tantalum oxide possesses little contrast in the permittivity with the base polymer to lower the local field distortion. Additionally, the incorporation of the polar Ta-O groups creates deeper traps, which remarkably diminishes the conduction loss. Moreover, the cross-linked network effectively improves the mechanical

properties of composites. All of above improvements have been synergized and consequently enhance the dielectric breakdown strength. Therefore, this work opens a new route toward dielectric composites with high breakdown strength for electrical energy storage applications and provides a method to prepare inorganic-organic composites.

2.3 HfO₂/P(VDF-CTFE) Nanocomposites Prepared by In-Situ Sol-Gel Process

2.3.1 Experimental Details

2.3.1.1 Materials

All reagents were purchased from Aldrich and used without further purification unless otherwise noted. All manipulations of gas-condense transfer were carried out with rigorous exclusion of oxygen and moisture on a dual-manifold Schlenk line with 10⁻⁶ Torr high vacuum. Commercial P(VDF-CTFE) (including 15 wt% of CTFE) was supplied by Solvay (Solef 31508).

2.3.1.2 Preparation of Composites



Scheme 2-4: Preparation route of P(VDF-CTFE)-based composite.

Scheme 2-4 shows the preparation route of the composites. Hydroxyl group capped P(VDF-CTFE) (POH) was dissolved in anhydrous dimethylformamide (DMF) while hafnium isopropoxide was dissolved in anhydrous ethanol. Under stirring, the ethanol solution of hafnium isopropoxide and 0.05mL of distilled water was slowly added to the DMF solution of the functionalized polymer at room temperature. Stirred for 24 hours at 65 °C, the transparent mixture was casted on the octadecyltrichlorosilane (OTS) treated glass substrates and dried at 64 °C overnight. The prepared light brown film was then further died in vacuo and heated to 150 °C stepwise by 10 °C/1hr. After heated at 150 °C for 72hrs, the films were hot pressed at 200 °C under 1500 psi to remove the voids and residual solvent and further proceed sol-gel reaction. Then the P(VDF-CTFE) chains in the composites should be cross-linked and formed a network as illustrated in Scheme 1. In this work, 3 flexible composite films with the precursor loadings of 1.96 %, 4.76 % and 9.09 % (wt%) were prepared with the thickness of 11-20 μ m. The films of commercial P(VDF-CTFE) and POH with the thickness of 12 μ m were hot pressed at 100 °C under 1500 psi after solution casting as control samples.

2.3.1.3 Characterization

The thermal analysis data were obtained by a TA Instrument Q100 differential scanning calorimeter (DSC) at a heating and cooling rate of 10 oC/min and TA Q50 thermogravimetric analyzer at the heating rate of 10 oC/min. Crystal analysis was studied by use of PANalytical xpert pro mpd theta-theta diffractometer. All data were analyzed using Jade software with a Gaussian-Lorentz superposition fitting functions. The cross-sectional morphology was explored using JEOL 6700 field emission scanning electron microscope (FE-SEM). FTIR spectra were obtained in the attenuated total reflectance (ATR) mode using diamond crystal as a contact to the samples on Bruker Vertex V70 spectrometer at room temperature. Dielectric constant and loss were acquired using an Agilent LCR meter (E4980A). Dielectric spectra were acquired over a

broad frequency $(10 - 10^{6} \text{ Hz})$ and temperature (-100 - 100 °C) using a Hewlett Packard 4284A LCR meter in conjunction with a Delta Design oven model 2300. The Displacement-electric field (D-E) loops were recorded using a modified Sawyer–Tower circuit. The electrical energy density of the films was calculated from the unipolar D-E loops. The dielectric breakdown field was determined by applying a linear ramp voltage at a rate of 500 V/s on the polymer film in accordance with ASTM D149 standard. Resistivity and conductivity were obtained under a electric field provided by a Hewlett Packard 4140B pA meter/voltage source and KEPCO BOP 1000M amplifier in a Delta Design 2300 oven. Gold electrodes of 2.6 μ m diameter and typical thickness of 60 nm were sputtered on both sides of the samples for the electrical measurements. Tensile tests were conducted at the pulling rate of 25 cm/min on the TA Instruments RSA-G2 Dynamic Mechanical Analyzer.

2.3.2 Results and Discussion

2.3.2.1 Structural Characterization





Figure 2-37: TGA curves of the POH and composite films at the heating rate of 10 °C/min in air.

Name	Hf(OiPr) ₄ loading weight percentage	Weight percentage of HfO_2 in composites determined by TGA	Weight percentage of Hf in composites determined by TGA
P(VDF- CTFE)	0	0	0
2Hf	1.96 %	1.20 %	1.02 %
5Hf	4.76 %	2.70 %	2.29 %
10Hf	9.09 %	5.04 %	4.27 %

Table 2-7: Names and compositions of samples

Thermogravimetric analysis (TGA) curves of the pristine film and the prepared composite films at a heating rate of 10 °C/min in air are presented in Figure 2-37. Below 250 °C, there is light weight loss, indicating that most solvent and small molecules are removed in the film making. Compared to the great weight loss of POH film at above 400 °C, composite films are observed to degrade at around 250 °C. For the composite, the incorporation of addictives, such as the hafnium isopropoxide and hafnium oxide, could lower the thermal activation energy and decrease the decomposition temperature of the polymer backbone in composites. Besides, the incomplete hydrolysis and condensation of the precursors in the filmmaking may also make the contribution to weight loss at high temperature. Although the sol-gel reaction of the precursors and the end groups of the copolymer is conducted at up to 200 °C, the temperature is not high enough to make the precursors completely hydrolyzed and condensed. Above 250 °C, the unreacted propoxy groups in the precursors would be eliminated and uncondensed hafnium hydroxide would continue the condensation until all the precursors turn to hafnium oxide (HfO₂) thoroughly. Therefore, great weight loss is found above 250 °C. The residues of the composites at 800 °C are believed to be HfO₂ and the weight percentages of hafnium element in the composite films are calculated and shown in Table 2-7.

Fourier Transform Infrared Spectroscopy



Figure 2-38: Fourier transform infrared spectra of the pristine P(VDF-CTFE) and 10Hf.

Frontier transformation infrared spectroscopy is applied to investigate the chemical nature of the composites and study the in-situ sol-gel reaction in the polymer matrix. As shown in Figure 2-38, the observed peaks at 532, 614 and 763 cm⁻¹ are the characteristic of non-polar TTTG conformation of CF_2 in the polymer backbone. Now much change observed in these peaks for 10Hf implies that the configerations of PVDF are not altered by the introduction of the inorganic phase. The shoulder peak at 680 cm⁻¹ corresponds to Hf-O-Hf stretching,¹⁰⁴ confirming the successful formation of hafnium oxide in the polymer matrix.

Differential Scanning Calorimetry and X-ray Diffraction

Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) have been applied to study the crystallization of the commercial P(VDF-CTFE), functional polymer POH and composites of different compositions. As revealed in the DSC profiles in Figure 2-39, the precursor polymer POH and all composites show both relatively lower melting and crystallization temperature than the POH. In the cooling scan the crystallization temperature of the composites shifts by around 15 °C from 83.0 °C for the POH to 76.5 °C for composite 10Hf. The decreasing of crystallization temperature can be attributed to the incorporation of the defects, such as inorganic compounds and the cross-linking which restrains the motion of polymer chains. The

melting point of each sample is collected from the heating scan of the DSC thermographs as illustrated in Figure 2-39 and summarized in Table 2-8. The melting temperatures of composite samples were also lower than that of POH, which is associated with the smaller crystallite size. As the precursor loading increases, the melting temperature decreases. The crystallinity of each sample is calculated based on fusion enthalpy of melting peaks in the heating cycle of DSC, as shown in Table 2-8. Crystallinity obtained from XRD was computed by the software Jade after the peak fitting. It shows a good agreement with the result from DSC. In the work, influenced by both the defect effect from the tantalum oxide and cross-linking, the crystallinity falls straight from 34 % for the POH and the commercial P(VDF-CTFE) to 23.9 % for the composite 10Hf. Additionally, the minor peak of commercial P(VDF-CTFE) at lower temperatures associated with the ferroelectric to paraelectric phase change of the Curie transition is not observed in POH and all composites.



Figure 2-39: DSC thermographs of cooling scan on the left and heating on the right. These DSC traces were collected with a heating/cooling rate of 10 °C/min.

The X-ray diffraction patterns of pristine polymer and composites with 20 from 10° to 40° are shown in Figure 2-40. All the patterns show obvious characteristics of PVDF α -phase other than β -phase since the (110/200) β peak is negligible. Moreover, the typical sharp intense peaks of hafnium oxide crystals are not observed in the patterns of composites, indicating that the sol-gel process only produces amorphous hafnium oxide in the filmmaking condition. The size of the crystalline domain was calculated and listed in Table 2-8. As discussed earlier, the inclusion of inorganic compounds and the cross-linking significantly reduces the crystallite size from 31.2 nm for the POH to about 24.6 nm for 10Hf.



Figure 2-40. XRD patterns of commercial P(VDF-CTFE) and 3 composites.

	P(VDF-CTFE)	РОН	2Hf	5Hf	10Hf
Crystallinity (%) by DSC	34.3	33.8	32.8	26.5	23.9
Crystal Size (nm) (from 020 peak)	30.5	31.2	28.6	25.5	24.6
Melting Temperature (°C)	177.5	113.6	112.0	111.6	109.7
Crystallization Temperature (°C)	144.1	83.0	79.6	78.8	76.5

Table 2-8. Crystallization parameters of commercial P(VDF-CTFE), POH and 3 composites.

Scanning Electron Microscopy



Figure 2-41: Cross-sectional field emission scanning electron microscopy (FESEM) image of the composite 5Hf.

Figure 2-41 shows a cross-sectional field emission scanning electron microscopic (FESEM) image of composite 5Hf. The image displays homogeneous cross-section with no identical particles or agglomeration observed, suggesting that the amorphous hafnium oxide were *in-situ* prepared and well dispersed in the polymer matrix. The good dispersion may ascribe to the improved interfacial interaction caused by the coupling between inorganic and organic phases.

2.3.2.2 Dielectric Properties

Breakdown Strength



Figure 2-42: The Weibull distribution of breakdown fields of commerical P(VDF-CTFE) and 3 composites.

Figure 2-42 compares the characteristic breakdown fields of the commercial P(VDF-CTFE) and the composite samples at room temperatures. The Weibull parameters of all the samples are listed in Table 2-9. Compared to the breakdown strength of 360 MV/m with a β of 7.45 for commercial P(VDF-CTFE), all the composites display improved breakdown strengths. For instance, the optimized composite 5Hf exhibits the breakdown strength of 470.6 MV/m, which is 30.7 % higher than the P(VDF-CTFE). Besides, with the hafnium loading increases, the α value is found to increase, reach the maximum, 470.6 MV/m for the 5Hf and then level off gradually, as illustrated in Figure 2-43. At higher loading concentration, the depression of the breakdown strength is probably relative to the agglomeration of tantalum oxide. Moreover, the sample 5Hf also possesses the higher β value of 17.3 than other samples, indicating the better dispersion of hafnium oxide in the polymer matrix.

	P(VDF-CTFE)	2Hf	5Hf	10Hf
α (MV/m)	360.0	415.7	470.6	398.4
β	7.45	15.62	17.3	15.82

Table 2-9. Weibull parameters of the for the P(VDF-CTFE) and 3 composites.



Figure 2-43: The dependence of Weibull breakdown strength on the hafnium weight percentage.

Weak-field dielectric measurement



Figure 2-44: a) The permittivity and b) dielectric loss (tan δ) as a function of frequency at 25°C for the commercial P(VDF-CTFE) and 3 composites.

The weak-field dielectric properties of all samples have been characterized as the function of frequency as shown in Figure 2-44. The P(VDF-CTFE) shows almost the same dielectric properties as the commercial P(VDF-CTFE). The little contrast in permittivity between the polymer and amorphous tantalum oxide could give rise to relatively homogeneous electric field and high breakdown strength. However, the composites exhibited similar but slightly lower permittivity than that of the pristine P(VDF-CTFE), associated to cross-linking structure which could confine the chain motion and reduce the dipole orientation. For the dielectric loss plotted in Figure 2-44, the composites shows lower loss than the neat polymer, especially at low frequency. It suggests that the cross-linked composite greatly reduces the quantity of the space charge and limits the charge transportation.

The temperature dependence of permittivity and loss of all samples at different frequency is measured as shown in Figure 2-45. Typically, the permittivity is low but not zero at low temperature, suggesting that not all the dipoles are quenched. As the polymer passes through the glass transition temperature, frozen dipoles start to actively response to the applied field and contribute to the permittivity. Meanwhile, the presence of a peak represents the α relaxation in the amorphous phase of polymer.



Figure 2-45. The dependence of a) permittivity and b) loss on the temperature for all the samples at a heating rate of 10 °C/min.

The temperature dependence of dielectric permittivity of all samples at the frequency of 1 kHz is illustrated in Figure 2-45. The dielectric permittivities of all samples are similar, consistent with the weak-field data. At elevated temperature, the permittivity of all composite samples is found less variability since the introduction of cross-linking restricted the polymer chain movement. As the dielectric loss versus temperature relationship presented in Figure 2-45, the significant peak at 1 kHz around -25 °C is visualized in all the samples, corresponding to the amorphous relaxation of the polymer. The position and magnitude of loss of composites are similar to that of POH. Additionally the surge in both permittivity and loss at above 40 °C that is only found in the POH is due to the conduction, implying the better stability and greater depression of the conduction. For 10Hf, the elevation of loss at high temperature indicates more conduction, relative to the 5Hf.







Figure 2-46: Electric displacements of 5Hf versus the electric field with a 10 Hz unipolar triangle signal at 25 °C.

Figure 2-47: D-E loop of the commercial P(VDF-CTFE) and the composite 5Hf at an electric field 350 MV/m.

The high electric field displacement has been examined with a 10 Hz unipolar triangle signal at 25 °C. Figure 2-46 shows that the D-E loops of the composite 5Hf, which is almost the same in shapes, the maximum displacements. Among 3 composites, 5Hf performs the minimal energy loss at all electric fields, which is well consistent with the low field dielectric results. Moreover, in the comparison with the P(VDF-CTFE), the composite 5Hf possesses lower energy loss all across the electric field and less remnant polarization, illustrated in Figure 2-47. Basically, the calculated energy loss consists of ferroelectric loss and conduction loss. For the ferroelectric loss, the smaller crystalline size is believed to cause reduction in ferroelectric domain size which benign suffering due to the fact that larger domain lost more energy during polarization process. Based on the XRD data, the sample 5Hf with the smaller crystal size would have less ferroelectric loss, which renders it the slimmer loop and lower energy loss. Therefore, the composite 5Hf dissipates less heat during the charging–discharging cycle and in turn achieves the improved breakdown strength. Beneficial from the lower loss and higher breakdown strength, the 5Hf could store and release more energy than commercial P(VDF-CTFE) as plotted in Figure 2-48. The maximum stored and discharged energy density could reach 14.6 and 9.1 J/cm³, respectively.



Figure 2-48: Energy densities and loss of the composite 5Hf.

2.3.2.3 Electrical Properties



MV/m at 25 °C.



Figure 2-50: The dependence of DC equilibrium conductivity on the hafnium weight percentage under the electric field of 10 MV/m at 25 $^{\circ}$ C.

In order to study the conduction loss, the current density of all samples with a variation of time under a field of 10 MV/m at 25 °C is tested in Figure 2-49. Following the charging current decay region, the curves of current density turn into a relatively steady region. As the equilibrium conductivity shown in Figure 2-50, the composite samples all perform lower equilibrium conductivity than the neat P(VDF-CTFE) and the 5Hf is found with the minimum conductivity which is more than one order of magnitude lower than that of the neat P(VDF-CTFE), as displayed in Figure 2-51. The current density versus electric field correlation shown in Figure 2-51 and the resistivity versus tantalum concentration in Figure 2-52 also demonstrate that the composites are less conductive and the 5Hf is the most optimized composition. For the composites 2Hf, 5Hf, well-dispersed amorphous tantalum oxide and polymer forms cross-linking network via the covalent bonds, which give rise to the reduced mobility of charge carriers in the composites. As the feeding of precursors increases, the probability of cross-linking and breakdown strength increases simultaneously. However, for 10Hf, increment in the current density may be caused by the agglomeration of inorganic phase which could overlap the local conductive regions, leading to the enhancement of conduction and the decline of dielectric strength. Therefore, the 5Hf exhibits the most optimal ability to prohibit the charge transportation and the highest breakdown strength.



Figure 2-51: The dependence of DC current density on the electric field at 25 °C.



field of 80 MV/m at 25 °C.

DC Activation Energy



Figure 2-53: The dependence of DC conductivity on the temperature under the electric field of 10 MV/m.



of 10 MV/m at 25 °C.

DC conductivity as a function of temperature is measured to confirm the formation of high temperature traps which requires more energy to release the charges for transporting shown in Figure 2-54. According to Arrhenius equation, the calculated activation energy of the composite 5Hf was 1.1 eV, which was 0.21 eV higher than that of the commercial P(VDF-CTFE). It suggests that composites could depress space charge movement, which is coherent with the conduction data and energy loss data in the dielectric measurement. The lower power dissipation in turn improves the breakdown strength of the composites in terms of the thermal and electrical breakdown mechanism. In addition, the apparent increase of activity energy for the composites also manifests that the covalent linkage of the organic and inorganic phase effectively enhances the interface. Otherwise, the conduction would be facilitated due to the loosely bounded interface.

2.3.3 Summary

Using *in-situ* sol-gel reaction of hafnium isopropoxide with the functionalized chain-end of the ferroelectric polymer, cross-linked composites are prepared. Similar as the previous part of this chapter, the optimal composite achieves the dielectric breakdown strengths of 470.6 MV/m, 30.7 % higher than that of the commercial P(VDF-CTFE). This result demonstrates that this strategy could be applied in more cases for the fabrication of high breakdown dielectric composites.

2.4 SiO₂/P(VDF-CTFE) Nanocomposites Prepared by In-Situ Sol-Gel Process

2.4.1 Experimental Details

2.4.1.1 Materials

All reagents were purchased from Aldrich and used without further purification unless otherwise noted. All manipulations of gas-condense transfer were carried out with rigorous exclusion of oxygen and moisture on a dual-manifold Schlenk line with 10⁻⁶ Torr high vacuum. Commercial P(VDF-CTFE) (including 15 wt% of CTFE) was supplied by Solvay (Solef 31508).

2.4.1.2 Preparation of Poly(vinylidene fluoride-co-chlorotrifluoroethylene) with

Triethoxysilane Terminal Groups

Poly(vinylidene fluoride-co- chlorotrifluoroethylene) (P(VDF-CTFE)) with hydroxyl terminal groups was employed as prepared in the previous work. The characterizations of hydroxyl groups capped P(VDF-CTFE) has been fully characterized in previous part. The modification of the end groups follows the Scheme 2-5. Poly(vinylidene fluoride-cochlorotrifluoroethylene) (P(VDF-CTFE)) with hydroxyl terminal groups and isocyanatopropyltriethoxysilane were both dissolved in THF under stirring, After the reaction at 70 °C for 12 hours under the protection of dry nitrogen gas, the clear solution was poured into hexane for the precipitation of polymers. The final polymer was purified by dissolving in THF and precipitating in hexane three times and dried in vacuo at 50 °C. ¹H NMR spectrum shows that the end groups of P(VDF-CTFE) have been successfully modified to triethoxysilane groups and the integrals of characteristic peaks in the end groups agree well with ratio of protons at the end groups, as shown in Figure 2-55.



Scheme 2-5. Synthesis of the Poly(vinylidene fluoride-co- chlorotrifluoroethylene) capped by triethoxysilane groups.



Figure 2-55: ¹H NMR spectrum of the prepared functional P(VDF-CTFE).

2.4.1.3 Preparation of Composites

Scheme 2-6 shows the preparation route of the composites. Triethoxysilane group capped P(VDF-CTFE) (PSi) was dissolved in anhydrous dimethylformamide (DMF) while tetraethoxysilane (TEOS) was dissolved in anhydrous ethanol. Under stirring, the ethanol solution of tetraethoxysilane, 0.05mL of distilled water and 0.05mL of hydrogen chloride was slowly added to the DMF solution of the functionalized polymer at room temperature. Stirred for 24 hours, the transparent mixture was casted on the octadecyltrichlorosilane (OTS) treated glass substrates and dried at 64 °C overnight. The prepared clear film was then further died in vacuo and heated to 150 °C stepwise by 10 °C/1hr. After heated at 150 °C for 72 hours, the films were hot pressed at 200 °C under 1500 psi to remove the voids and residual solvent and further proceed sol-gel reaction. Then the P(VDF-CTFE) chains in the composites should be cross-linked and formed a network as illustrated in Scheme 3. In this work, 4 flexible composite films with the precursor loadings of 0 wt%, 0.5 wt%, 0.99 wt% and 1.96 wt% were prepared with the thickness

of 11-20 μ m. The films of commercial P(VDF-CTFE) and POH with the thickness of 12 μ m were hot pressed at 100 °C under 1500 psi after solution casting as control samples.



Scheme 2-6: Preparation route of P(VDF-CTFE)-based composite.

2.4.1.4 Characterization

1H NMR spectra were recorded on Bruker AM-300 spectrometer instrument at room temperature using tetramethylsilane (TMS) as internal reference. The thermal analysis data were obtained by a TA Instrument Q100 differential scanning calorimeter (DSC) at a heating and cooling rate of 10 °C/min and TA Q50 thermogravimetric analyzer at the heating rate of 10 °C/min. Crystal analysis was studied by use of PANalytical xpert pro mpd theta-theta diffractometer. All data were analyzed using Jade software with a Gaussian-Lorentz superposition fitting functions. The cross-sectional morphology was explored using JEOL 6700 field emission

scanning electron microscope (FE-SEM). FTIR spectra were obtained in the attenuated total reflectance (ATR) mode using diamond crystal as a contact to the samples on Bruker Vertex V70 spectrometer at room temperature. Dielectric constant and loss were acquired using an Agilent LCR meter (E4980A). Dielectric spectra were acquired over a broad frequency $(10 - 10^6 \text{ Hz})$ and temperature (-100 – 100 °C) using a Hewlett Packard 4284A LCR meter in conjunction with a Delta Design oven model 2300. The Displacement-electric field (D-E) loops were recorded using a modified Sawyer-Tower circuit. The electrical energy density of the films was calculated from the unipolar D-E loops. The dielectric breakdown field was determined by applying a linear ramp voltage at a rate of 500 V/s on the polymer film in accordance with ASTM D149 standard. Resistivity and conductivity were obtained under a electric field provided by a Hewlett Packard 4140B pA meter/voltage source and KEPCO BOP 1000M amplifier in a Delta Design 2300 oven. Thermally stimulated discharge current (TSDC) was also measured using Hewlett Packard 4140B pA meter with Kepco BOP 1000M as a high voltage source and performed in a Delta Design 2300 oven. Gold electrodes of 2.6 µm diameters and typical thickness of 60 nm were sputtered on both sides of the samples for the electrical measurements. Tensile tests were conducted at the pulling rate of 25 cm/min on the TA Instruments RSA-G2 Dynamic Mechanical Analyzer.

2.4.2 Results and Discussion

2.4.2.1 Structural Characterization

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) curves of the pristine film and the prepared composite films at a heating rate of 10 °C/min in air are presented in Figure 2-56. The PSi polymer and composites shows similar thermal behavior as the pristine POH. It implies that the functionalization of the end groups and the addition of small amount of precursors do not significantly change the thermostability of polymer chains, giving rise to similar TGA curves. As

discussed in the previous part, the fillers lower the activation energy for the decomposition. Herein, the composites show lower decomposition temperatures due to the introduction of fillers and incomplete hydrolysis and condensation in the sol-gel process. Moreover, as the inset in Figure 1 illustrates, with the precursor loading increasing, the weight residual increases, which could be ascribed to the increment of prepared silicon dioxide after heating up to 800 °C. The residues of each samples are read out from the TGA and listed in Table 2-10 which also consists of the calculated weight percentage of Si.



Figure 2-56: TGA curves of the POH and composite films at the heating rate of 10 °C/min in air.

Name	Si(OEt) ₄ loading weight percentage	Weight percentage of SiO_2 in composites determined by TGA	Weight percentage of Si in composites determined by TGA
РОН	0	0	0
PSi	0	0.21 %	0.06 %
PSi1	0.99 %	0.45 %	0.14 %
PSi2	1.96 %	0.7 %	0.21 %
PSi4	3.85 %	1.3 %	0.4 %

Table 2-10: Names and compositions of samples

Fourier Transform Infrared Spectroscopy



Figure 2-57: Fourier transform infrared spectra of the pristine P(VDF-CTFE) and all composites.

Frontier transformation infrared spectroscopy is applied to investigate the chemical nature of the composites and study the in-situ sol-gel reaction in the polymer matrix. As shown in Figure 2-57, the additional peaks at 800 and 1050 cm-1 are found in the composite PSi1 and PSi2, which correspond to Si-O-Si bending and asymmetric stretching, respectively.¹⁰⁵⁻¹⁰⁷ Moreover, as the concentration of the silicon oxide increases, the intensity of the peak increases, confirming the insitu sol-gel process. Absence of apparent peaks at 950 cm-1 suggests that the appearance of Si-OH is negligible and most of the Si-OEt groups are hydrolyzed and condensed.¹⁰⁸

Differential Scanning Calorimetry and X-ray Diffraction

Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) have been applied to study the crystallization of the precursor polymer POH and PSi and composites of different compositions. As revealed in the DSC profiles in Figure 2-58, in the cooling scan the crystallization temperature of the composites shifts up by around 7 °C from 83.0 °C for the POH to 90 °C for PSi and its composites. The increasing of crystallization temperature can be attributed to favored heterogeneous nucleation for crystallization. The in-situ prepared silicon oxide could serve as the heteronuclei to facilitate PVDF chain folding in order. The melting point of each sample is collected from the heating scan of the DSC thermographs as illustrated in

Figure 3 and summarized in Table 2-11. The melting temperatures of composite samples are similar that of POH, which is associated with the lamellar thickness. The crystallinity of each sample is calculated based on fusion enthalpy of melting peaks in the heating cycle of DSC as described in the previous part and shown in Table 2-11. Crystallinity obtained from XRD was computed by the software Jade after the peak fitting. It shows a good agreement with the result from DSC. In the work, influenced by both the defect effect from the silicon oxide and cross-linking, the crystallinity exhibits lower value for the PSi composites, relative to that of P(VDF-CTFE).



Figure 2-58. DSC thermographs of cooling scan on the left and heating on the right. These DSC traces were collected with a heating/cooling rate of 10 $^{\circ}$ C/min.

The X-ray diffraction patterns of pristine polymer and composites with 20 from 10° to 40° are shown in Figure 2-59. All the patterns show obvious characteristics of PVDF α -phase other than β -phase since the (110/200) β peak is negligible. Moreover, the typical sharp intense peaks of silicon oxide crystals are not observed in the patterns of composites, indicating that the sol-gel processing only produces amorphous silicon oxide in the filmmaking condition. The size of the crystalline domain was calculated and listed in Table 2-11. As discussed earlier, the inclusion of inorganic compounds and the cross-linking significantly reduces the crystallite size from 31.2 nm for the POH and commercial P(VDF-CTFE) to about 16 nm for the PSi composites. Therefore, the incorporation of silicon oxide reduces the crystallinity and crystallite size of PVDF, although it facilitates the nucleation of crystallization.

	P(VDF- CTFE)	РОН	PSi	PSi1	PSi2	PSi4
Crystallinity (%) by DSC	34.3	33.8	24.4	23.5	21.9	22.0
Crystallinity (%) by XRD	35.4	34.2	26.7	24.7	21.3	22.1
Crystal Size (nm) (from 020 peak)	30.5	31.2	15.6	16.6	15.8	17.7
Melting Temperature (°C)	177.5	113.6	114.4	114.2	113.9	114.4
Crystallization Temperature (°C)	144.1	83.0	90.4	90.4	91.0	90.4

Table 2-11: Crystallization parameters of commercial P(VDF-CTFE), POH, PSi and 3 composites.



Figure 2-59: XRD patterns of commercial P(VDF-CTFE), PSi and 3 composites.

Scanning Electron Microscopy



Figure 2-60. Cross-sectional field emission scanning electron microscopy (FESEM) image of the composite PSi2.

Figure 2-60 shows a cross-sectional field emission scanning electron microscopic (FESEM) image of composite PSi2. Since the amount of silicon oxide has been well controlled at a low level, the image displays smooth homogeneous cross-section with no identical particles or agglomeration observed. In addition, the good dispersion could be ascribed to the improved interfacial interaction caused by the coupling between inorganic and organic phases.

2.4.2.2 Dielectric Properties

Breakdown Strength

Figure 2-61 compares the Weibull breakdown fields of the commercial P(VDF-CTFE) and the composite samples at room temperatures. The Weibull parameters of all the samples are listed in Table 2-12. Compared to the breakdown strength of 360 MV/m with a β of 7.45 for commercial P(VDF-CTFE), all the PSi composites display improved breakdown strengths. For instance, the optimized composite PSi2 exhibits the breakdown strength of 512.1 MV/m, which is 42.3 % higher than the P(VDF-CTFE). Besides, with the silicon loading increases, the α value is found to increase, reach the maximum, 512.1 MV/m for the PSi1 and then level off for PSi4. At higher loading concentration, the depression of the breakdown strength is probably relative to the agglomeration of silicon oxide. Moreover, the pure PSi and the composites all possess the higher
β value of around 12 than commercial P(VDF-CTFE), indicating the better dispersion of silicon oxide in the polymer matrix.



Figure 2-61: The Weibull distribution of breakdown fields of commercial P(VDF-CTFE), PSi and 3 composites.

	P(VDF-CTFE)	РОН	PSi	PSi1	PSi2	PSi4
α (MV/m)	360.0	301.1	478.5	489.9	512.1	442.4
β	7.45	12.03	12.04	11.19	13.83	12.95

Table 2-12: Weibull parameters of the for the P(VDF-CTFE), POH, PSi and 3 composites.

Weak-field dielectric measurement



Figure 2-62: The permittivity and dielectric loss (tan δ) as a function of frequency at 25°C for the commercial P(VDF-CTFE), PSi and 3 composites.



Figure 2-63: The dependence of loss on the precursor loading for all samples.

The weak-field dielectric properties of all samples have been characterized as the function of frequency as shown in Figure 2-62. The permittivity of the prepared composites is slightly lower than that of commercial P(VDF-CTFE) due to the cross-linking that constrict the chain motion and dipole orientation. Although the permittivity of prepared silicon oxide is low (~3), small amount of inorganic phase should not remarkably change the effective permittivity of composites. As localized non-uniform field is a important factor to lower the dielectric breakdown strength, the little contrast in permittivity between the polymer and silicon oxide could give rise to relatively homogeneous electric field and high breakdown strength. For the dielectric loss plotted in Figure 2-62, the composites show lower loss than the neat polymer, especially at low frequency. It suggests that the in-situ prepared silicon oxide act as insulating components, greatly reducing the space charge transportation. As illustrated in Figure 2-63, the loss tangent of the PSi4 levels up resulting from the aggregation of the inorganic phase at high composition.





Figure 2-64: The dependence of permittivity on the temperature for all samples.

Figure 2-65: The dependence of dielectric loss on the temperature for all samples.

The temperature dependence of dielectric permittivity of all samples at the frequency of 1 kHz is illustrated in Figure 2-64. The dielectric permittivity of PSi and composite samples shows similar value as that of P(VDF-CTFE), consistent with the weak-field data. Besides, a new peak at 24-26 °C could be ascribed to the dipolar glass freezing transition from the polymer chains surrounding the silicon oxides. In accordance with the changes in crystalline size and the thermal transition temperatures discussed earlier, the cross-linking restricts the chain mobility and thus enhances activation energy of the transition. Moreover, at elevated temperature, the permittivity of all composite samples is found less variability since the introduction of cross-linking restricted the polymer chain movement. As the dielectric loss versus temperature relationship presented in Figure 2-65, the significant peak at 1 kHz around -25 °C is visualized in all the samples, corresponding to the amorphous relaxation of the polymer. The loss peaks of the PSi composites are 2 °C higher than that of the commercial P(VDF-CTFE) as a result of cross-linking. The additional interfacial relaxation is further confirmed in loss spectra as small peaks appear at 24-26 °C in the loss plot. The interfacial peak could only be observed at low frequency, supporting that the peak is corresponding to the restricted chain motion. Additionally the surge in both permittivity and loss at above 40 °C that is only found in the commercial P(VDF-CTFE) is due to

the conduction, revealing the better stability and greater depression of the conduction. For PSi4, the elevation of loss at high temperature indicates more conduction, relative to the PSi1 and PSi2.



D-E loop and Energy density

Figure 2-66: Hysteresis Loop of PSi2 with a 10 Hz unipolar triangle signal at 25 °C.



Figure 2-67: D-E loop of the commercial P(VDF-CTFE) and the composite PSi2 at an electric field of 350 MV/m, respectively.

The high electric field displacement has been examined with a 10 Hz unipolar triangle signal at 25 °C. Among 5 composites, PSi2 performs the minimal energy loss at all electric fields, which is well consistent with the low field dielectric results. Moreover, in the comparison with the P(VDF-CTFE), the composite PSi2 possesses lower energy loss all across the electric field and less remnant polarization, illustrated in Figure 2-67. Basically, the calculated energy loss consists of ferroelectric loss and conduction loss. For the ferroelectric loss, the smaller crystalline size is

believed to cause reduction in ferroelectric domain size which benign suffering due to the fact that larger domain lost more energy during polarization process. Based on the XRD data, all the composites shows the smaller crystal size which renders them less ferroelectric loss and slimmer loop. Therefore, the optimized composite PSi2 dissipates less heat during the charging–discharging cycle and in turn achieves the improved breakdown strength. Beneficial from the lower loss and higher breakdown strength, the PSi2 could store and release more energy than commercial P(VDF-CTFE) as plotted in Figure 2-68. The maximum stored and discharged energy density could reach 18.3 and 11.7 J/cm³, respectively.



Figure 2-68: Energy densities and loss of the pristine P(VDF-CTFE) and the composite PSi2.

2.4.2.3 Mechanical Properties



Figure 2-69: The dependence of stress on strain for all samples at room temperature.

The mechanical properties of cross-linked composites and polymer are also tested using the tensile tester with the pulling rate of 25 cm/min. According to The Young's moduli are extracted from the slope of initial linear portion of stress-strain curves, as shown in Figure 2-69. The tensile strength is collected as the maximum stress during the pulling process. The yield stresses of samples are determined using a linear force ramp to generate a stress versus strain curve where the yield stress is calculated from the intersection of the elastic and inelastic tangent lines. All the results are summarized in Table 2-13.

	Young's Modulus (MPa)	Yield Stress (MPa)	Tensile Strength (MPa)
P(VDF-CTFE)	554.6	11.3	17.1
РОН	419.0	9.1	16.3
PSi	693.2	13.7	26.8
PSi1	760.3	16.5	26.2
PSi2	842.3	17.1	28.1
PSi4	865.6	17.5	31.5

Table 2-13: Mechanical properties of all the samples at room temperature.

Compared to the commercial P(VDF-CTFE), the synthesized POH shows smaller Young's modulus and tensile strength, as a result of the lower molecular weight. However, the Young's moduli and tensile strengths of composites build with the content of silicon oxide increasing. As observed in the cross-sectional SEM image, there is no apparent particles grown in the polymer matrix, which rules out the possibility that the hard particles strengthened the mechanical properties. So the enhancement of mechanical properties for the composites is mainly caused by the cross-linking of the polymers. In addition, when the content of silicon oxide exceeds 0.7 wt%

for PSi2, the increment of tensile strength slows down, implying that the degree of cross-linking approaches the saturation.

	Young's	Yield	Permittivity	Calculated	Calculated	Experimental
	Modulus	Stress	(3)	from	from Yield	Breakdown
	(Y)	(σ_y)		Young's	Stress (E _b ')	(MV/m)
	(MPa)	(MPa)		Modulus	(MV/m)	
				(E_b)		
				(MV/m)		
P(VDF-	5516	11.2	10.5	1490 5	402.1	260.0
CTFE)	554.6 FE)	11.5	10.5	1400.3	495.1	300.0
РОН	419.0	9.1	10.3	1299.2	446.8	301.1
PSi	693.2	13.7	10.5	1655.1	543.0	478.5
PSi1	760.3	16.5	10.3	1750.1	601.7	489.9
PSi2	842.3	17.1	10.5	1824.5	606.7	512.1
PSi4	865.6	17.5	10.1	1885.8	625.8	442.4

Table 2-14: Calculated and experimental electrical breakdown strengths of all samples.

To further explore the effect of mechanical property on the electrical breakdown strength, the electrical breakdown strengths of all samples are calculated according to two electromechanical breakdown models and listed in Table 2-14. Since the permittivities of composites and polymers don't vary much, the calculated breakdown strengths follow the trend of mechanical properties as a function of filler content. In other words, the improved calculated breakdown strength for composites of high content is ascribed to the enhancement of the stiffness due to the cross-linking in the electromechanical mechanism. However, the calculated results from the two models do not match the experimental data perfectly. In particular the calculated breakdown strengths from Gorton and Stark's model are far higher than the experimental ones, which is also observed for

other polymers in the literature, while the Claude's modified model fit the measured data better. Moreover, for the composites of low content and polymers, the measured breakdown strength increased with the stiffness increasing, displaying a good agreement with the trend of calculated values. But for PSi4, excellent mechanical properties don't give rise to the high breakdown strength. It suggests that the electrical breakdown strength of these composites could not be satisfactorily explained only by the electromechanical mechanism, especially for the samples of high tantalum oxide content. This is to say that there should be other mechanisms cooperating with electromechanical breakdown mechanism to explain the failure of these composites.

2.4.2.4 Electrical Properties





Time (s) Figure 2-70: The dependence of DC current density on the time under the electric field of 10 MV/m at 25 $^{\circ}$ C.



Figure 2-71: The dependence of DC equilibrium conductivity on the precursor loading under the electric field of 10 MV/m at 25 $^{\circ}$ C.

In order to study the conduction loss, the current density of all samples with a variation of time under a field of 10 MV/m at 25 °C is tested in Figure 2-70. For the equilibrium conductivity shown in Figure 2-71, the composite samples all perform lower values than the neat P(VDF-CTFE) and the PSi2 is found with the minimum conductivity which is more than one order of magnitude lower than that of the neat P(VDF-CTFE). The current density versus electric field correlation shown in Figure 2-72 and the resistivity as a function of precursor loading in Figure 2-73 also demonstrates that the composites are less conductive and the PSi2 is the most optimized composition. For the composites PSi, PSi1 and PSi2, well-dispersed silicon oxide and polymer forms cross-linking network via the covalent bonds, which give rise to the reduced mobility of charge carriers in the composites.⁶⁷ As the feeding of precursors increases, the probability of cross-linking and breakdown strength increases simultaneously. However, for PSi4, increment in the current density is caused by the agglomeration of inorganic phase. The aggregates could overlap the local conductive regions, leading to the enhancement of conduction and the decline of dielectric strength.^{67, 70}. Therefore, the PSi2 exhibits the most optimal ability to prohibit the charge transportation and the highest breakdown strength.



Figure 2-72: The dependence of DC current density on the electric field at 25 °C.



Figure 2-73: The dependence of resistivity on the tantalum weight percentage under the electric field of 80 MV/m at 25 $^{\circ}$ C.



Figure 2-74: Current density vs square of electric field for the fitting of conduction model.

In the dielectric polymer materials, there are many types of conduction mechanisms to classify different conduction behaviors. For each case, the current density behaves differently as a function of applied voltage, temperature and time. Some are controlled by the interface such as Schottky emission $(J \sim exp[\frac{a\sqrt{E}}{T} - \phi_B/(kT)])$. Some are bulk conduction processes including Poole-Frenkel emission $(J \sim exp[\frac{2a\sqrt{E}}{T} - \phi_B/(kT)])$, space charge limited current $(J \sim V^2)$ or hopping conduction $(J \sim exp[\frac{bE}{T}) - U/(kT)])$, where a and b are constants, ϕ_B is the barrier height, U is the activation energy, V is the applied voltage, K is the Boltzmann constant.^{109, 110} As shown in Figure 2-74, all the samples exhibit linear dependence of current density on the square

of electric field, implying that space charge limited current is the dominant in this system. The space charge limited conduction is highly associated with the distribution and depth of charge traps in the materials.

Most polymers can be thought of as a mixture of crystalline and amorphous regions. Traps could be generated by several sources such as the boundary of the amorphous and crystalline region, surface states because of dangling bonds and impurities, structure disorder and extinct defects. These traps create different energy states at the surface of a material, at the interface between two materials, or in the bulk of a materials, which are going to impose impacts on the conduction process.^{110, 111} For example, it has been observed that surface states create different shallow and deep traps at the interface between the metal electrodes and a semiconductor or a polymer. These traps modify the interface properties so that the energy barrier at the interface is completely determined by the traps. In the PSi composites, silicon oxide could be in-situ formed as the defect to the P(VDF-CTFE) and lower the crystallite size of P(VDF-CTFE) crystals. It's reasonable to postulate that more interface between P(VDF-CTFE) crystalline and amorphous phase, resulting in the more traps to lower the conduction.

Thermally Stimulated Discharge Current



Figure 2-75: TSDC curves for pristine P(VDF-CTFE) and composite PSi2.

The discharge behavior of the composites has been measured to further probe the mechanism of the dielectric breakdown by thermally stimulated discharge current (TSDC) technique. Each

sample is charged with a voltage of 10 MV/m at 50 °C for 30 mins and then rapidly cooled down to -100 °C with the electric field still applied. Afterwards the electric field is removed and the samples are short circuited and heated to 100 °C at the heating rate of 5 °C/min while the current is measured across the sample. The TSDC curves of the pristine P(VDF-CTFE) and the composite PSi2 are presented in Figure 20. The β a relaxation is corresponding to the amorphous relaxation of the glass transition. The βc peak is ascribed to molecular motions in the crystalline region, which is considered as a prefusion phase.^{99, 100} Finally, γ and γ' are considered as charge traps for P(VDF-CTFE) and PSi2, respectively. In Figure 2-75, the peak locations of the PSi2 are observed significantly shifting to high temperature, compared to that of neat polymer. The shift of β a and β c peaks suggests that cross-linking constrained the motion of some chains in both amorphous and crystalline phase. The reason why relaxation peaks become broader is that both the cross-linked and uncross-linked polymer chain sections make the contribution. As we discussed above, the prepared composites are not highly cross-linked so it's reasonable to observe both the relaxation of both free and constrained polymer chains of both amorphous and crystalline phases. For PSi2, the trap peak γ ' does not shift too much but intensity becomes stronger, indicating the formation of more traps in the complex cross-linked structure. As to the intensity of TSDC, from the pristine polymer to the PSi2, the intensity of βc is lower and the βa became higher since the ratio of the crystalline to the amorphous volume decreased, which has been reported.^{100, 102}

Additionally, the nonpolar silicon oxide would not offer polar moieties to the composites as the tantalum oxide and hafnium oxide do. It's reported to destabilize the charge traps, which may lead to that high content of silicon oxide enhances the conduction and lower the breakdown strength even although it could favor the expansion of the interface.() The silicon oxide itself could exhibit extremely high breakdown strength when it's made under high temperature and fine condition. The low process temperature may impair the quality of silicon oxide and possibility fails to grant the prepared silicon oxide with extremely high breakdown strength. This may be the other reason why the high concentration of silicon oxide decreases the dielectric strength.

DC Activation Energy



Figure 2-76: The dependence of DC conductivity on the temperature under the electric field of 10 MV/m.



Figure 2-77: The calculated activation energy on the tantalum percentage under the electric field of 10 MV/m at 25 $^{\circ}$ C.

DC conductivity as a function of temperature is measured to confirm the formation of more charge traps which requires more energy to release the charges for transporting shown in Figure 2-76. According to Arrhenius equation, the calculated activation energy of the composite PSi2 was 1.12 eV, which was 0.23 eV higher than that of the commercial P(VDF-CTFE) in Figure 2-77. The presence of the additional trap sites could depress space charge movement, which is coherent with the conduction data and energy loss data in the dielectric measurement. The lower

power dissipation in turn improves the breakdown strength of the composites in terms of the thermal and electrical breakdown mechanism.¹⁰³ In addition, the apparent increase of activity energy for the composites also manifests that the covalent linkage of the organic and inorganic phase effectively enhances the interface. Otherwise, the conduction would be facilitated due to the loosely bounded interface.

2.4.3 Summary

In summary, we have demonstrated a unique route, using in-situ sol-gel reaction of silicon ethoxide with the functionalized chain-end of the ferroelectric polymer, to prepare cross-linked composites. The optimal composite achieves the dielectric breakdown strengths of 512.1 MV/m, 42.3 % higher than that of the commercial P(VDF-CTFE). This result suggests an important improvement over what has been reported in the past with the conventional dielectric polymer composites. As demonstrated, the functional hydroxyl groups at the end of short ferroelectric polymer chains favor the molecular level dispersion of inorganic products and improvement of interfacial interaction. The in-situ prepared silicon oxide possesses little contrast in the permittivity with the base polymer to lower the local field distortion. Additionally, the incorporation of the tiny silicon oxide creates deeper traps, which remarkably diminishes the conduction loss. Moreover, the cross-linked network effectively improves the mechanical properties of composites. All of above improvements have been synergized and consequently enhance the dielectric breakdown strength.

2.5 Conclusion

One series of inorganic materials with relatively low permittivity are in-situ prepared into the functionalized P(VDF-CTFE) matrix. Due to the small contrast in permittivity and conductivity, the distorted local electric field is depressed. By forming covalent bonding between the organic and inorganic phase, the interfacial interaction and dispersion have been markedly improved. At

the same time, the direct linkage cross-links the polymer chains, which effectively enhance the mechanical properties. In addition, the proper content of fillers can reduce the electrical conduction. For the Ta_2O_5 fillers, polar Ta-O bonds are able to service as deep traps to increase the activation energy of charge transport while in the presence of SiO₂ could increase the interfacial area and numbers of traps although Si-O is less polar. All these are synergized to enhance the breakdown strength and energy density of composites as observed. However as the content of fillers exceed the optimized concentration, the conductivity is further promoted as the percolative pathways have been formed, which in turn mitigates the breakdown strength again. In all, this work opens a new route toward dielectric composites with high breakdown strength for electrical energy storage applications and provides a method to prepare inorganic-organic composites.

Chapter 3

Suppression of Energy Dissipation and Enhancement of Breakdown Strength in

Ferroelectric Polymer-Graphene Percolative Composites

3.1 Introduction

3.1.1 Percolative Composites for Capacitors



Figure 3-1. Schematic of nonlinear changes in the properties. The insets show the geometric phase transition of fillers in the composites' microstructure near percolation.¹¹²

Percolation theory was initially employed to analyze physical phenomena found above or below the onset of global connectivity in disordered systems. However, this theory then found its broadest application in materials research as a powerful tool to account for the physical properties of all heterogeneous multicomponents (or phases) of materials (1). The significance of the percolation transition lies in the fact that the particles of a minor phase (i.e., fillers) come into contact with each other, and a continuous cluster extends throughout the system, as the volume fraction f of this minor phase approaches a critical value fc, i.e., the percolation threshold. Meanwhile, as the volume fraction approach and exceed the percolation threshold, the properties of heterogeneous materials alter dramatically and follow a power law, as shown in Figure 3-1.¹¹²

In conductor-insulator composites, as discussed above, when the percolation threshold is approached from below, the dielectric constant ε of the composites diverges as follows:

$$\varepsilon_r \propto \varepsilon_m |f - f_c|^{-s}$$
 3.1

where ε is the dielectric constant of the insulator matrix and *s* is a critical exponent of approximately 1. The equation illustrates that a large dielectric constant can be achieved in composites as $f \rightarrow f_c$. Therefore, instead of incorporating large amount of high- ε_r ceramic powders.^{113,114} small concentration of conductive fillers may enhance the dielectric constant of percolative composites based on the percolation theory.¹¹⁵⁻¹²²



Figure 3-2. Variation of the relative dielectric constants ε_r of Ni/PVDF (poly(vinylidene fluoride)) and BaTiO₃/PVDF composites with the volume fraction *f* of particles.¹¹²

The physical reason for the critical behavior of the dielectric constant near percolation is the existence of microcapacitor networks.¹²³ Each microcapacitor is formed by the neighboring conductive filler particles and a very thin layer of dielectric in between and contributes an abnormally large capacitance.¹²⁴ The large capacitance contributed by each of these microcapacitors can then be correlated with a significant increase in the intensity of local electric field when the conductive fillers are very close to each other near *fc*. The significant increase in the intensity of the local electric field promotes the migration and accumulation of charge carriers at the interfaces between the fillers and the matrix. Due to different relaxation times of the two phases, the charges generated either by surface plasma resonance or by charge injection from the external electrodes are accumulated at the interfaces as a result of Coulomb blockade by the insulating matrix, until the adjacent conductive fillers approach each other and the charges are relaxed either by tunneling or by ohmic conduction. This interfacial polarization, also known as the Maxwell-Wagnar effect, is responsible for the enhancement of dielectric constant observed at low frequency.

In particular, graphene nanosheets,¹²⁵ known as perfect atomically-thin two dimensional nanostructures with remarkably high electrical conductivity and specific surface area,^{126, 127} have attracted tremendous research interest as the fillers in the percolative composites. Greatly improved ε_r values have been obtained at extremely low filler concentration (less than 5 vol.%) in the composites as a consequence of excellent geometry of graphenes to facilitate the microcapacitor formation.¹²⁸⁻¹³³

However, a general feature of the percolative composites is that sharp enhancement of the ε_r value at the perocolative threshold is accompanied by a rapid increase of tan δ owing to the electrical conduction of the fillers. The dielectric loss is mainly resulted from leakage current that happens near f_c . Because energy dissipation (P) is directly proportional to tan δ as shown by the equation below:

$$P \quad \mathcal{F}_{o}E^{2}f \operatorname{tank} \delta \qquad 3.2$$

where ε_0 is the permittivity of free space, E is the applied field strength and f is the frequency,¹³⁴ the increase of tan δ leads to considerable energy dissipation during the charge-discharge process of the capacitors. Also, as indicated by Equation above, energy dissipation becomes more pronounced at high frequency of the applied electric field since *P* is positively relative to *f*. It is worth noting that even a very small overloading of conductive filler beyond the threshold results in extremely high *tan* δ because of the creation of conduction pathway in the composites. Therefore, the concentration of conductive filler has to be precisely controlled in the percolative composites, which poses great difficulty in practical operation, especially for those systems with very low percolation thresholds. Besides, as conductive components are involved, the breakdown strength of the percolative composites is typically several orders of magnitude lower than that of polymer matrix, thus unable to meet demands of high-field applications.

In the chapter, we report the percolative dielectric composites consisting of ferroelectric poly(vinylidene fluoride-*co*-chlorotrifluoroethylene) (P(VDF-CTFE)) copolymer matrix and SiO₂ coated reduced graphene oxide (r-GO@SiO₂) nanosheets as the fillers. Due to the presence of SiO₂ as a coating layer on graphene nanosheets, the composites, denoted as r-GO@SiO₂/P(VDF-CTFE), exhibit significantly suppressed dielectric loss in comparison to the composites containing bare reduced graphene oxide (r-GO) nanosheets (referred to as r-GO/P(VDF-CTFE)). At a relatively high frequency, *i.e.* 1 MHz, *tanô* of r-GO@SiO₂/P(VDF-CTFE) even decreases to a level of as low as that of the polymer matrix. Meanwhile, the breakdown strength of r-GO@SiO₂/P(VDF-CTFE) is several orders of magnitude higher than those of the typical percolative composites. Moreover, unlike the previously reported graphene-based percolative composites, it is found that *tanô* of r-GO@SiO₂/P(VDF-CTFE) shows no evident increase even past the threshold as compared to that of the polymer matrix within the medium frequency range (ie. 300 KHz -3 MHz). This yields the percolative composites with a wide composition range to exhibit desirable dielectric performance for energy storage applications.

3.2 Experimental Details

3.2.1 Synthesis of Graphene Oxide (GO)

GO was prepared through a modified Hummers method.¹³⁵ Graphite flakes (2.5 g, NP302, Beijing Nanopowder Science & Technology Co., Ltd., China) and NaNO₃ (1.5 g) were added into concentrated H₂SO₄ (98%, 80 mL) in a flask in an ice-bath, to which 15 g of KMnO₄ was then slowly added while stirring vigorously and the temperature was kept below 20 °C. After that, the temperature was increased to 35 ± 3 °C, and the stirring was maintained for 3 h. Then the mixture was diluted with 150 mL deionized water, which was followed by slow addition of hydrogen peroxide solution (10 mL, 30 wt.%). Subsequently, the mixture was filtered through nylon membrane filters (0.22 µm pore size) and washed with 1:10 HCl solution for several times. The resulting solid was dispersed in deionized water under sonication (200 W, 40 KHz, 5 h) and centrifuged at 4000 rpm for 30 min. The obtained supernatant was vacuum-dried at 40 °C for 12 h. Finally, the solid was re-dispersed in deionized water (1 mg mL⁻¹) with the aid of sonication (200 W, 40 KHz, 2 h) and centrifuged at 8000 rpm for 20 min. to further remove aggregates. The supernatant was again vacuum-dried at 60 °C for 24 h to generate GO.

3.2.2 Synthesis of SiO₂ Coated Graphene Oxide (GO@SiO₂)

First, 50 mg of GO was dispersed in 200 mL ethanol with the aid of sonication (200 W, 40 KHz, 0.5 h) to form a homogeneous dispersion. Subsequently, aqueous ammonia (6 mL) in 40 mL distilled water was added to the dispersion under sonication (200 W, 40 KHz) before stirring in a 500 mL three-neck flask. Tetraethyl orthosilicate (150 mg) was dissolved in 80 mL ethanol and subjected to a 30-min sonication (200 W, 40 KHz), which was then added to the aforementioned flask and the mixture was stirred for 12 h at room temperature. The resultant mixture was centrifugated at 10,000 rpm for 30 min, and the precipitate was collected before redispersing in 100 mL ethanol for another round of centrifugation. This was repeated for three times to remove any impurities. Afterwards, the precipitate dispersed in 100 mL ethanol was

filtered through nylon filter membrane (0.45 μ m pore size) to remove individual SiO₂ particles. After drying at 70 °C in vacuum overnight, GO@SiO₂ was obtained.

3.2.3 Synthesis of r-GO@SiO₂

To restore the electronic conjugation in the basal plane of GO, 150 mg GO@SiO₂ was dispersed in 200 mL DMF with the aid of sonication (200 W, 40 KHz, 0.5 h) to obtain a homogeneous dispersion which along with 600 mg hydrazine was then added in a 500 mL three-neck flask for a 24 h-refluxing at 90 °C. The mixture was filtered through PTFE filter membrane (0.22 μ m pore size) and washed three times with DMF and twice with distilled water. Afterwards, the filter cake was vacuum dried at 70 °C for 24 h to yield r-GO@SiO₂.

3.2.4 Synthesis of r-GO

The control sample of r-GO was prepared by first dispersing 80 mg GO in 200 mL DMF with the aid of sonication (200 W, 40 KHz, 0.5 h), and then mixing with 600 mg hydrazine for a 24 h-refluxing at 90 °C. The mixture was filtered through PTFE filter membrane (0.22 μ m pore size) and washed three times with DMF and twice with distilled water, and finally vacuum dried at 70 °C for 24 h to generate r-GO.

3.2.5 Fabrication of Composite Films

The r-GO@SiO₂ (or r-GO) dispersion was prepared at concentration of 4 mg/mL in DMF by sonication (200 W, 40 KHz, 0.5 h). It was blended in the required ratio with P(VDF-CTFE), and the mixture was stirred vigorously overnight to give a homogeneous dispersion which was then drop cast on glass plates. The cast films were first dried at 60 °C for 6 h, and subsequently peeled off the glass plates for further drying in vacuum at 80 °C for 48 h. The solution-cast films were hot pressed at 180 °C and 3000 dpi for 1 h, and then cooled down to room temperature while maintaining the pressure.

3.2.6 Calculation of Volume Fraction of r-GO

The volume fraction of r-GO (f) in the composite can be determined by the following equation,

$$f = \frac{\frac{m_{r-GO}}{d_{r-GO}}}{\frac{m_{r-GO}}{d_{r-GO}} + \frac{m_{SiO2}}{d_{SiO2}} + \frac{m_{p}}{d_{p}}}$$
3.3

where m_{r-GO} , m_{SiO2} and m_p represent the weight of r-GO, SiO₂ and P(VDF-CTFE) in the composites, respectively; d_{r-GO} , d_{SiO2} and d_p are the density of r-GO (2.1 g/cm³), SiO₂ (2.65 g/cm³) and P(VDF-CTFE) (1.8 g/cm³). The volume fraction of r-GO in r-GO/P(VDF-CTFE) films can also be calculated by using Equation 2 with $m_{SiO2}=0$.

3.2.7 Characterization

IR measurements were carried out on a Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Nexus) using KBr pellets. UV-vis absorption spectrum was acquired on a diode array UV-vis spectrometer (UV-2550, SHIMADZU). X-ray photoelectron spectroscopy (XPS) experiments were performed using a KRATOS XSAM800 spectrometer, and Mg K α X-rays were used as the source (hv = 1253.6 eV). Transmission electron microscopy (TEM, Joel JEM-2001F coupled with an energy-dispersive X-ray analysis system) images were obtained by placing a few drops of the dispersion on a copper grid, and evaporating them at room temperature prior to observation. Scanning electron microscopy (SEM) measurements were performed with a Hitachi S-4800 field emission electron microscope. Atomic force microscopy (AFM) measurements were performed using a DI Nanoscope IV (Veeco, USA) equipped with a tapping probe, and the samples were prepared by drop-casting onto a freshly cleaved mica surface and kept at room temperature overnight to let the solvent evaporate. Thermogravimetric analysis (TGA) measurements were performed with a simultaneous thermal analyzer (Netzsch, STA 499C) under air flow. The differential scanning calorimetry (DSC) was conducted by using a TA Instrument Q100 differential scanning calorimeter at a heating and cooling rate of 10 °C/min. X-ray diffraction analysis was studied by use of PANalytical xpert pro mpd theta-theta diffractometer. All data were analyzed using Jade software with a Gaussian-Lorentz superposition fitting

functions. Gold electrodes of a typical thickness of 60 nm were sputtered on both sides of the polymer films for the electrical measurements. Dielectric constant and loss were measured using an Agilent LCR meter (E4980A). Alternating current (AC) conductivity was calculated based on the impedance data collected by Agilent LCR meter (E4980A). Dielectric breakdown strength measurements were performed on a TREK P0621P instrument using the electrostatic pull-down method under a DC voltage ramp of 500 V/s.

3.3 Results and Discussion

3.3.1 Structural Characterization

The fabrication of r-GO@SiO₂ involves in-situ growth of SiO₂ on the basal plane of GO nanosheets to yield the hybrid nanosheets of SiO_2 coated graphene oxides (GO@SiO₂), which are subsequently converted to r-GO@SiO₂ through chemical reduction. To our knowledge, the coating of SiO_2 on conductive fillers has not been employed in the preparation of the percolative dielectric composites prior to this report. The selection of SiO₂ as a functional layer is based on the following considerations. First, as a well-known dielectrics with remarkably high electrical resistivity (eg. 10^{14} - $10^{16} \Omega \cdot cm$ at 25 °C), ¹³⁶ SiO₂ can physically restrict the formation of conduction pathways by blocking direct contact of adjacent graphene nanosheets, and therefore, efficiently reduce the energy dissipation resulted from leakage current. Second, SiO₂ possesses high mechanical and breakdown strength (ie. 10⁷ V/cm).¹³⁶ Thirdly, surface modification using SiO₂ provides dispersibility of graphene nanosheets in polar solvents such as N, Ndimethylformamide (DMF) that can dissolve the PVDF based ferroelectric polymers and thus allows the preparation of the polymer composites with uniform filler distribution.^{59, 60} It is also expected that hydrogen bonding between the hydroxy groups on the surface of SiO₂ and fluorine atoms of the copolymers faciltates the homogeneous dispersion of the fillers in the ferroelectric polymer matrix.

The presence of SiO₂ on the surface of graphitic platelet has been verified spectroscopically.

As shown in Figure 3-3a, in comparison to that of the control sample (*ie.* r-GO), the FTIR spectrum of r-GO@SiO₂ displays pronounced additional absorbance at around 1089 cm⁻¹, which is attributed to Si-O-Si/C-O-Si stretching. UV-vis spectroscopy was utilized to monitor the reduction process of the hybrid nanosheet. As can be seen in Figure 1b, the absorption peak at 235 nm corresponding to π - π * transitions of aromatic C-C bonds redshifts to 275 nm after GO@SiO₂ has been converted to r-GO@SiO₂, while no visible peak could be detected within this region in the UV-vis curve of r-GO, suggesting the restoration of electronic conjugation in the basal plane of graphenes upon reduction.¹³⁷



Figure 3-3: (a) FTIR spectra of r-GO and r-GO@SiO₂, (b) UV-vis spectra recorded in aqueous solutions at 0.05 mg/mL of SiO₂, GO@SiO₂ and r-GO@SiO₂.





Figure 3-4: C1s XPS spectra of (a) $GO@SiO_2$ and (b) r-GO@SiO_2. (c) XPS spectra of r-GO@SiO_2.



Figure 3-5: SEM images of (a, b) GO and (c, d) r-GO@SiO₂. Scale bar: a) 1 μ m, b) 500 nm, c) 1 μ m, d) 300 nm.

The conversion from GO@SiO₂ to r-GO@SiO₂ has been further verified by XPS. Figures 3-4a and 4b are C1s core-level spectra in which the relative intensity of the signal at 286 eV related to the epoxide and hydroxyl groups decreases significantly after chemical reduction, indicating that GO sheets have been transformed to r-GO. Again, the existence of the signals of Si 2s and Si 2p in the XPS spectrum of r-GO@SiO₂ in Figure 3-4c, validates the coating of SiO₂ on graphene sheets, which is consistent with the FTIR results.



Figure 3-6: TEM images of (a, b) GO and (c, d) r-GO@SiO₂, and EDX analysis of (e) GO and (f) r-GO@SiO₂. Scale bar: a) 200 nm, b) 100 nm, c) 200 nm, d) 50 nm.

SEM and TEM were employed to reveal the morphology of r-GO@SiO₂ hybrid nanosheets. As a comparison, typical SEM and TEM images of GO are presented in Figures 3-5(a-b) and 3-6(a-b), respectively, showing transparent and wrinkled nanosheets with slim thickness and smooth surface. In sharp contrast, as illustrated in Figures 3-5(c-d) and 3-6(c-d), 2dimensional plates decorated uniformly with numerous SiO₂ clusters on the surface are clearly seen in the r-GO@SiO₂ hybrid nanosheets. Energy-dispersive X-ray (EDX) analysis was performed on the samples during the TEM measurements. The comparison of Figures 3-6(e-f) further confirms the successful coating of SiO₂ onto the graphene nanosheets, as evidenced by the presence of extra peaks attributed to Si in the spectrum of r-GO@SiO₂. This is again in accordance with the results of FTIR and XPS studies. The height profile of the coating layer has been obtained from AFM studies. Figure 3-7 are typical topographic images and height profiles of GO and r-GO@SiO₂. A thickness of 9.8 nm was identified in the hybrid planar flake of r-GO@SiO₂ in Figure 3-7b, which is markedly thicker than that of the GO nanoplate (i.e. ~1.2 nm) in Figure 3-8a. This denotes a ~4.3 nm thickness of the SiO₂ coating layer on each side of the graphene sheet in the hybrid nanoflakes.



Figure 3-7: Tapping mode AFM topographic images and corresponding height profiles of a single layer of (a) GO and (b) r-GO@SiO₂.

The weight fractions of the two constituent moieties (i.e. r-GO and SiO₂) in the hybrid nanosheets can be estimated from TGA analysis in Figure 3-8. It is found that r-GO is almost

fully decomposed as temperature increases to 800 °C (1.7 wt.% remaining) while only a 5.7 % weight loss has been found in SiO₂ up to the maximum temperature allowed in the instrument (ie. 800 °C). Given the 57.4 wt.% residual at 800 °C of the r-GO@SiO₂ hybrids heated at the identical experimental conditions, the weight percentage of r-GO in r-GO@SiO₂ is determined to be approximately 39.8%. The atomic ratio yielded from XPS measurements also allows the calculation of the weight fraction of SiO₂ in the hybrid nanosheets in Table 3-1. With the assumption that all of Si atoms in the materials under investigation are in the form of SiO₂, the content of SiO₂ is assessed to be approximately 59.3 wt.% in r-GO@SiO₂, which in turn suggests a 40.7 wt.% of r-GO in the hybrids, very close to the value obtained from TGA data.



Table 3-1: Atomic ratio of C, O, and Si elements in r-GO@SiO₂.

Element	С	0	Si
Atomic ratio (%)	48.0	36.7	15.3

	$T (^{0}C)$	T _c	Crystallinity	D ₍₁₁₀₎
	$I_{m}(C)$	(°C)	(%)	(nm)
P(VDF-CTFE)	168	130	16.4	17.1
1.49%r-GO@SiO ₂	168	133	16.8	17.9
3.19%r-GO@SiO ₂	168	134	17.1	19.7

Table 3-2: Melting temperature, crystallization temperature and crystallinity of the polymer and the composites.



Figure 3-9: DSC thermograph of cooling scan. These DSC traces were collected with a heating/cooling rate of 10 $^{\circ}$ C/min.



Figure 3-10: X-ray diffraction patterns of P(VDF-CTFE) and 2 r-GO@SiO₂ composites.

The influence of inorganic filler on the crystal structure of the polymer matrix in the composite has been examined by using DSC and XRD. As revealed in the DSC profile obtained in the cooling scan in Figure 3-9, the crystallization temperature (T_c) of the composites shifts by around 3 $^{\circ}$ C toward high temperatures. This could be attributed to the incorporation of the SiO₂ coated r-GO fillers, which promotes the heterogeneous nucleation and in turn increases the crystallization temperature.⁶⁰ Additionally, the crystallinity of the composites appears to be slightly higher that of the pristine polymer in Table 3-2 as calculated from the heat of fusion. Table 1 also summarizes the crystal size computed from XRD profiles in Figure 3-10, which increases systematically in the composites upon the filler content increasing, clearly manifesting that the introduction of fillers improves the crystallization of P(VDF-CTFE). Since unique dielectric responses of the ferroelectric polymers originate from the crystal domains in the polymer, an improved crystallinity would benefit the dielectric properties as shown in the following results and discussion. Typical SEM images of the fracture surface of the r-GO@SiO₂/P(VDF-CTFE) nanocomposite is shown in Figure 3-11. Obviously, the wrinkled r- $GO@SiO_2$ nanosheets are well dispersed throughout the polymeric matrix without any discernible aggregation.



Figure 3-11: SEM images of the fracture surface of the r-GO@SiO₂/P(VDF-CTFE) composite film. Scale bar: left: 200 nm, right: 100 nm.

3.3.2 Electrical Conductivity

Note that energy dissipation and breakdown strength are intimately related to leakage current in the percolative dielectric composites, the AC conductivity of the composites as a function of the filler content and frequency has been carefully studied. As plotted in Figure 3-12a, the conductivity of the r-GO@SiO₂/P(VDF-CTFE) composite increases slightly with the increase of the r-GO content and then experiences an apparent boost when the filler content reaches the percolation threshold (f_c). The effective conductivity of the composites near the transition is further analyzed by the power law according to the two-phase polymer composite percolation theory,¹³⁸

$$\sigma \propto (f_c - f)^{-s}$$
 for $f_c > f$

$$\sigma \propto (f - f_c)^t$$
 for $f > f_c$ 3.5

where σ represents the effective conductivity of the composites, f is the volume fraction of r-GO, f_c is the critical volume fraction at the percolation threshold, s is the critical exponent in the insulating region, and t is the conductivity exponent in the conduction region. As shown in the inset of Figure 3-12a, the best linear fitting of the experimental data to log-log plot for the power law in Equation above gives $f_c = 1.49$ vol.% and t = 1.25. The critical exponent in conducting region, t = 1.25 is in excellent agreement with the universal ones ($t_{un} = 1.1-1.3$) for dimensionality d = 2.¹¹² Comparatively, a much lower value of f_c , ie. 0.51 vol%, is attained in the r-GO/P(VDF-CTFE) composites.



Figure 3-12: (a) Dependence of electrical conductivity of r-GO@SiO₂/P(VDF-CTFE) on the content of the fillers at 1 KHz. The inset shows the fit of experimental data according to Equation 3.5. (b) Variation of $\log(\sigma)$ at 1 KHz on the $f^{-1/3}$ for r-GO@SiO₂/P(VDF-CTFE) composites. The inset shows the critical frequency ($\log(\omega_c)$) vs. reduced volume fraction ($\log(f - f_c)$).

Also, as illustrated in Figure 3-12a, the r-GO@SiO₂ containing P(VDF-CTFE) composites display a strong frequency dependent conductivity, which is characteristic of the conductorinsulator composites.¹³⁹⁻¹⁴² Under an AC field, the conductivity is determined by the highest barrier experienced as the carriers travel for one half period of the field. At low frequency, for the volume fraction above the percolation threshold, the carriers undertake random walks and are able to travel through the film along the available conductive network within the long time scale. The AC conductivity equals to the DC conductivity at low frequency. As frequency keeps increasing, the charge carriers can only scan the limited conductive network in one half period of AC field, leading to the decrease in the potential barrier that they cover and increase in the conductivity. Hereafter, the AC conductivity of the composites is higher than the DC conductivity and shows frequency dependent regions.^{139, 142} The critical frequency depends on the filler content and can be expressed as a scaling law,^{140, 143}

$$\omega_c \propto \left(f - f_c\right)^{\mathcal{V}\delta_{\mathrm{TW}}}$$
 3.6

where the exponent $v\delta_{rw}$ is a scaling exponent. In the r-GO@SiO₂/P(VDF-CTFE) percolative composites, an linear relationship is found between the angular critical frequency (log(ω_c)) and the reduced volume fraction (log($f - f_c$)) as shown in the inset of Figure 3-12b. This indicates that introduction of conductive r-GO@SiO₂ reduces the frequency dependence by shifting ω_c to higher frequency, which coincides well with the previously reported results.^{139, 140} However, the obtained exponent $v\delta_{rw}$ =1.25, is different from the value predicted by the traditional percolation theory in which $v\delta_{rw}$ = 3.7 for d = 2 and $v\delta_{rw} = 3.1$ for d = 3.^{140, 144} The discrepancy probably stems from partially biased random walk and the dimensionality of the system.¹³⁹



Figure 3-13: Frequency dependent electrical conductivity of (a) r-GO@SiO₂/P(VDF-CTFE) and (b) r-GO/P(VDF-CTFE) films with various filler contents.



 $\begin{array}{ccc} 10^3 & 10^4 & 10^5 & 10^6 \\ Frequency (Hz) & \\ Figure 3-14: Frequency dependent electrical conductivity of r-GO/P(VDF-CTFE) and r-GO@SiO_2/P(VDF-CTFE) films with various filler contents. \end{array}$

As can easily be seen in Figure 3-14, the conductivities of the r-GO@SiO₂ containing composites are significantly lower than those of r-GO/P(VDF-CTFE). For instance, at 1.49 vol.% (f_c) loading of r-GO@SiO₂, the conductivity of the composite at 1 KHz is 1.63×10^{-8} S/cm, two orders of magnitude lower than 1.7×10^{-6} S/cm of the r-GO/P(VDF-CTFE) composite at the threshold (ie. 0.51 vol.%). More interestingly, the conductivity of the r-GO@SiO₂ based composites remains little changed at high frequencies even when the filler content exceeds the percolation threshold. At 1 MHz, the composite with the filler content above the threshold, eg. $3.19 \text{ vol.\% r-GO@SiO}_2$, has the conductivity of 9.2×10^{-6} S/cm, which is nearly at the same level of the composite at the threshold and still markedly lower than the r-GO composite with a conductivity of 2.0×10^{-4} S/cm at 0.59 vol.% r-GO. The observed greatly depressed conductivity

of r-GO@SiO₂/P(VDF-CTFE) has been rationalized by the presence of insulating SiO₂ layer on the surface of conductive fillers, which prevents direct connections of the fillers from the formation of conductive channels. At high frequency, carriers can only scan the distance within the finite network and need to overcome potential barriers for the transport within the conductive network. The r-GO@SiO₂ based composites are thus believed to only allow charges to tunnel within the conductive clusters. On the other hand, charges are likely to travel through the interconnected conductive clusters in the r-GO based composites via Ohmic conduction.¹²⁰ Therefore, the electrical resistance in the r-GO based composites is lower than that of r-GO@SiO₂ composites even when $f > f_c$.

To further corroborate the tunneling mechanism in the r-GO@SiO₂/P(VDF-CTFE) composites, the dependence of DC conduction on the filler content has been analyzed. Assuming the fillers are randomly dispersed in the polymer matrix, the DC conductivity is proportional to $f^{-1/3}$,¹⁴⁵

$$Log(\sigma) \propto f^{-1/3}$$
 3.7

Since the composites with $f > f_c$ display frequency independent at low frequency in Figure 3-13a, the conductivity at 1 KHz can be considered as the DC conductivity and used to investigate the DC conduction mechanism. Figure 3-12b presents the variation of the DC conductivity on the volume fraction of the fillers, in which the linear fitting of the conductivity suggests the fluctuation induced tunneling conduction mechanism for the composites after the percolation threshold.¹⁴⁶ Therefore, it is likely that the electrical conductivity of the r-GO@SiO₂/P(VDF-CTFE) composites is governed by the tunneling between the conductive r-GO regions which are separated by the SiO₂ surface-functionalized layers.

3.3.3 Dielectric Properties

Energy dissipation depends completely on dielectric loss in the capacitive composites. A low loss value is especially important for high frequency usage because energy dissipation is directly proportional to frequency as afore-mentioned. Figure 3-15 and 3-16 compare the loss

tangent of the r-GO@SiO₂ and r-GO based P(VDF-CTFE) composites with different filler contents. As discussed above, the presence of SiO_2 layers breaks the connectivity of the fillers and lowers the Ohmic conduction. Therefore, the dielectric loss of the r-GO@SiO₂/P(VDF-CTFE) composites has been reduced significantly as compared to that of r-GO based composites. For instance, at the percolation threshold, the loss tangent of 1.49 vol.% r-GO@SiO₂ composite is 0.4, one order of magnitude smaller than that of 0.51 vol.% r-GO composite at 1 KHz. Remarkably, the dielectric loss of r-GO@SiO₂ based composites decreases to a level of as low as that of the pure polymer at relatively high frequency even past the percolation threshold. As evident in Figures 3-16 and 3-18, at 1 MHz, the loss tangent of 3.19 vol.% r-GO@SiO₂/P(VDF-CTFE) remains as low as 0.35, only barely higher than 0.23 of the pristine P(VDF-CTFE). On the other hand, the loss tangent of 0.59 vol.% r-GO/P(VDF-CTFE) is 3.06 at 1 MHz, a typical value of the percolative dielectric composites in Figure 3-15b.^{129, 147} Apparently, the considerably reduced energy loss, especially at high frequencies, of r-GO@SiO₂/P(VDF-CTFE) relative to those of the previously reported percolative composites is attributed to the presence of the SiO₂ layers that acts as potential barriers for the charge tunneling and gives rise to lower conduction. In contrast to the traditional percolative composites whose loss increases abruptly when the filler content surpasses the percolation threshold, the loss of r-GO@SiO₂/P(VDF-CTFE) varies little with the filler concentration even beyond the critical volume, consistent with the trends shown in the conductivity measurements. This result not only demonstrates the potential applications of the r-GO@SiO₂/P(VDF-CTFE) composites at high frequencies but also open a window for the use of conductor-insulator composites beyond the percolation threshold.¹⁴⁸





Figure 3-15: Frequency dependent loss tangent of (a) r-GO@SiO₂/P(VDF-CTFE) films and r-GO/P(VDF-CTFE) with different filler contents.

Figure 3-16: Frequency dependent loss tangent of r-GO@SiO₂/P(VDF-CTFE) films and r-GO/P(VDF-CTFE) with different filler contents.

Dielectric permittivity of the r-GO/P(VDF-CTFE) and r-GO@SiO₂/P(VDF-CTFE) composites as a function of frequency is plotted in Figure 3-17. As summarized in Figure 3-18, the permittivity increases dramatically as the filler content approaches to and exceeds the percolation threshold, following the percolating theory. The enhancement of the dielectric permittivity has been mainly ascribed to the formation of microcapacitor networks.¹¹² Each microcapacitor is established by the neighboring conductive r-GO nanoplates with insulating SiO_2 and P(VDF-CTFE) layers in between. When the fillers are very close to each other due to the increase of the filler content, the local electric field is elevated and promotes the migration and accumulation of charges at the interfaces, which is known as Maxwell-Wagnar-Sillars (MWS) interfacial polarization. Although the permittivity of the composites drops with the frequency as a result of the characteristic relaxation of MWS polarization, the composites maintain higher permittivity than the pristine polymer at high frequencies. For example, the permittivity of 3.19 vol.% r-GO@SiO₂ composites reaches to 26.8 at 1 MHz, four times higher than that of pristine P(VDF-CTFE) as shown in Figure 3-17b. Nevertheless, compared with the r-GO composites in Figure 3-17b, the permittivity is lower because the SiO_2 layers separate the conductive r-GOs, leading to the increase in the thickness of dielectric layers and decrease in the capacitance.


Figure 3-17: (a) Variation of dielectric permittivity of r-GO@SiO₂/P(VDF-CTFE) films and (b) r-GO/P(VDF-CTFE) films with different filler contents on the frequency.



Figure 3-18: Dependence of permittivity and loss tangent of r-GO@SiO₂/P(VDF-CTFE) films on the volume fraction of r-GO at 1 kHz and 1 MHz, respectively.

The breakdown strength is another critical parameter of dielectric materials, which denotes the highest electrical field that can be applied on the films without losing their insulating properties. The dielectric strength also determines the energy density (U_e) of a dielectric material that is equal to the integral,

$$U_e = \int E dD \tag{3.8}$$

where *E* is the electric field and *D* is the electric displacement (charge density). As depicted in Figure 3-19, the breakdown strength exhibits a classic feature of the dielectric polymer composites, which falls monotonically as the loading of filler increases. It is interesting to note that, at the critical 1.49 volume fraction, the r-GO@SiO₂/P(VDF-CTFE) composite film has a

breakdown strength of 80 MV/m which is way higher than 8 MV/m of r-GO/P(VDF-CTFE) at the percolation threshold. To the best of our knowledge, this is the highest breakdown strength that has been reported for the percolative dielectric composites.¹¹³ For instance, this value far exceeds that of r-GO based composites at the percolation threshold which is less than 0.1 MV/m. Again, the improvement of dielectric strength shall be attributed to the presence of SiO_2 layer on the surface of r-GO nanosheets, which leads to greatly suppressed leakage current within the composite as shown in the conductivity measurements. In addition, the high mechanical strength of SiO_2 layer shall contribute to the exceptionally high breakdown strength of the percolative composites since the SiO_2 layer can sustain high electric field without deforming pronouncedly and thus inhibits further increase of overlapped tunneling range of adjacent r-GO nanosheets that degrades field durability. For conventional percolative composites at the neighborhood of percolation threshold, the very thin interparticle layer of polymer between adjacent conductive fillers has strong tendency to deform and break down under high fields due to their low mechanical stiffness. The breakdown results shine a light to the application of the percolative dielectric composites for high field applications, which has been rarely reported before the present work. More notably, the observed high dielectric strength translates into the electrical energy densities, which are calculated from the leading edge of the polarization-electric field (P-E)loops, of 6.2 and 5.7 J/cm³ for the r-GO@SiO₂/P(VDF-CTFE) composite containing 0.34 and 0.68 vol% filler, respectively. These values are substantial among the energy densities reported in the literature for the percolative polymer composites.³



Figure 3-19: Dependence of breakdown strength of r-GO/P(VDF-CTFE) and r-GO@SiO₂/P(VDF-CTFE) films on the r-GO content.

3.4 Conclusion

In this work, a new class of graphene-based percolative dielectric composites has been successfully prepared by using ferroelectric P(VDF-CTFE) copolymer as matrix and SiO₂ coated reduced graphene oxide nanosheets as filler. It is found that the fluctuation induced tunneling conduction mechanism plays a dominate role in the composites. Due to the presence of the SiO₂ surface-functionalized layers on graphene nanosheets, the resultant composites have much lower conductivity in comparison to the corresponding composites containing bare reduced graphene oxide nanosheets. Consequently, the composites not only exhibit significantly suppressed dielectric loss, especially at a relatively high frequency, but also possess high breakdown strength even at the percolation threshold. Moreover, different from the typical percolative composites whose loss increases abruptly beyond the percolation of the filler concentration. These results enable the preparation of the percolative dielectric composites with a much wide window of the filler concentration to exhibit desirable dielectric performance and the applications of the percolative composites under high electric fields.

Chapter 4

Flexible Piezoelectric Composite Generator Containing 3D Barium Titanate Prepared by Sol-gel Precoss

4.1 Introduction

4.1.1 Flexible Piezoelectric Materials



Figure 4-1: The wearable human generators.¹⁴⁹

As electronic technology becomes increasingly compact and integrated into various aspects and people rely heavily on personal portable digital assistants or devices, the concept of harvesting the energy lost during everyday human activities has become more appealing.¹⁵⁰ In the recent few years, the wearable power generators as possible solution of building self-powered systems have drawn great attention due to the slow revolution of battery revolution, as shown in Figure 4-1.¹⁵¹ The idea of wearable piezoelectric devices is to scavenge the energy from various body movements including footsteps, heartbeats, breathes and muscle motions.¹⁵² Therefore, the piezoelectric materials require high flexibility to insure the comfort and also harness the mechanical energy from various types of stresses such as bending and compressing. However, the typical piezoelectric ceramic materials are not able to complete this task because they are not elastic and can crack under the stress. New flexible piezoelectric materials are highly required for the self-powered implantable devices to turn the kinetic energy into electricity.

Piezoelectric polymers are especially promising for devices with this type of functionality, because they combines structural flexibility, ease of processing and good chemical resistance, with large sensitive areas, simplicity in device design and associated potential for low cost implementation. Ferroelectric poly(vinylidenefluoride) (PVDF) and its copolymers have particularly attractive piezoelectric properties with a d₃₃ value of 20-30 pC/N.⁴⁸ Electrical poling is usually required to create maximum polarization and stabilize the aligned dipole in the direction orthogonal to the film plane.^{153, 154} Typically, their plastic behavior makes them suitable for high-throughput processing based on molding, casting, drawing and spinning.¹⁵⁵ Recently, researchers developed new methodology to electrospin PVDF piezoelectric nanofibers, in which the associated extensional forces and electric fields naturally cause local poling and, by consequence, enhanced properties. The resulting materials are mechanically robust and can be handled easily, with the capability to be bent or twisted without fracture. Under bending conditions, these fibres exhibit currents up to 40 nA and voltage about 1.5 V. Flexible pressure sensors built simply by establishing electrical contacts to the ends of the aligned fibres show excellent sensitivity in the low-pressure regime (0.1 Pa) and respond to both compressive and bending forces.¹⁵⁶

There are some biopolymers that possess remarkable piezoelectricity. For example, Teijin Limited and Kansai University have developed a flexible, transparent piezoelectric material that is made with a simple manufacturing process that alternately laminates two types of polylactic acid (PLA) films: poly-L-lactic acid (PLLA) and optical isomer poly-D-lactic acid (PDLA). Poly(lactic acid) (PLA) is a type of chiral polymer with two optical isomers: one is left-handed helical poly(L-lactic acid) (PLLA), and the other is right-handed helical poly(D-lactic acid) (PDLA). The PLLA fiber is reported a high shear piezoelectric constant of 10 pC/N without poling, which is comparable to that of PVDF after poling.^{157, 158} By alternating PLAA and PLDA, the world's first binary-blended PLA multilayer film is found with piezoelectric performance that surpasses that of lead zirconate titanate (PZT). The other biopolymer poly(α -benzyl g,L-glutamate) (PBLG) also exhibits high piezoelectricity because this polar helical polypeptide with stable rod-like structure with large dipole moment could be allowed to align the dipoles in one direction after poling or electrospinning. When blending with PMMA, the piezoelectric performance results of the composite film is revealed with a d33 piezoelectric coefficient of 20 pC/N (with only 20% orientation of electrical dipoles).

When the size of hard materials, such as ceramics or semiconductors, decreases to micro or nano scale, the flexibility could be improved. Dr. Zhonglin Wang's group has reported aligned nanowires in developing and improving flexible piezoelectric nanogenerator by growing nano mateirals on the flexible plastic substrates. They aligned numbers of zinc oxide nanowires vertically and laterally into arrays. A lateral integration is capable of producing a peak voltage of 1.26 V at a low strain of 0.19 % and a vertical integration of three layers of zinc oxide nanowire arrays produces a peak power density of 2.7 mW/cm³.¹⁵⁹ A flexible zinc oxide thin film with the thickness of around 87 nm was fabricated on a plastic substrate as well, as shown in Figure 4-2. The maximum output of voltage and current density are 0.66 V and 55.5 nA/cm², respectively, under the bending motion.¹⁶⁰ Similar architecture has also been fabricated to transfer lead



Figure 4-2: a) Schematic diagram of the all-solution-processed flexible thin film piezoelectric nanogenerator on a plastic substrate. b) Cross-sectional scanning electron microscopy image of ITO-ZnO-P3HT/PCBM-PEDOT:PSS stacks. c,d).Measured output voltage and current density of the flexible thin film piezoelectric nanogenerator from mechanical rolls.¹⁶⁰

A third flexible piezoelectric material is the composite which basically consists of polymers and piezoelectric ceramics such as lead zirconate titanate. The refined geometry could maintain both the flexibility of polymers and piezoelectricity of ceramics. Various nano materials with piezoelectricity have been selected as fillers.^{162, 163} For instant, the device consists of a NaNbO3 nanowire and poly(dimethylsiloxane) (PDMS) polymer composite were prepared with an output voltage of 3.2 V and output current of 72 nA (current density of 16 nA/cm²) under a compressive strain of 0.23%.¹⁶⁴ So far, the highest reported output voltage of 20V and an output current density value of about 1 mA/cm² are achieved in a composite of single-crystalline piezoelectric perovskite zinc stannate nanocubes and PDMS under rolling of a vehicle tire.¹⁶⁵ Although many results have been reported to demonstrate the success of binary composite geometry, the efficiency could also be enhanced by introduction additional conductive fillers. As Figure 4-3 illustrated, Lee's group reported a ternary flexible composite including barium titanate nanoparticles and graphitic carbons to address the issue of conduction pathways for the charge transport out of the composites. By adding the carbon materials, the output voltage of composites with carbon materials is almost 10 times higher than that of the one without carbon materials.¹⁶⁶ The importance of conduction channels are also discussed and approved by this reference.¹⁶⁷



Figure 4-3: (a) Schematics of the cross-sectional structure of NCG devices and the calculated piezopotential distributions for explaining the role of CNTs. The CNTs act as dispersing (ii) and stress reinforcing agents (v) which are well supported by the calculated piezopotential difference (iii and vi). (b) The output voltages generated from a device containing only BTO NPs and a NCG device. The good distribution of NPs and stress enhancement by CNTs lead to the superior output voltage.¹⁶⁶



Figure 4-4: The connectivity patterns for a diphasic solid.¹⁶⁸

Connectivity plays an important role to determine the properties in multiphase solids since physical properties can change by many orders of magnitude depending on the manner in which connections are made. Each phase in a composite may be in 0, 1, 2 or 3 dimensions. As summarized in the literature, there could be many different connectivites in the diphasic composite: 0-0, 1-0, 2-0, 3-0, 1-1, 2-1, 3-1, 2-2, 3-2 and 3-3, as illustrated in Figure 4-4.¹⁶⁸ As a matter of convention, the first and second numbers in the connectivity denote the continuity of piezoelectric and polymer phases, respectively. The important connectivity patterns are 0-3, 1-3, 3-3 and 2-2. For the piezoelectric composites, the most common 0-3 composites are made with a homogeneous distribution of piezoelectric ceramic particles within polymer matrix. The primary advantage of these composites is their ability to be formed into shapes while remaining piezoelectrically active. However, the main drawback is that the 0-3 composites cannot be

sufficiently poled because the ceramic phase is not self-connected in the poling direction. On the other hand, the soft polymer with low modulus may absorb most stress applied on the composite and allow the particle to suffer from the low stress, which in turn lowers the output. In composites with 3-3 connectivity, the piezoceramic and polymer phases are continuous in three dimensions in the form of two interlocking networks, favoring the stress and charge transfer.⁴⁶ Additionally, 2-2 piezoelectric composites in both series connection (in which layers are parallel to the electrodes) and parallel connection (in which layers are perpendicular to the electrodes) have been investigated. In the case of series connection, it has been demonstrated that low permittivity layer could lower the d coefficient but has little effect on the corresponding g coefficient. In the case of parallel connection, the g coefficient has been effectively amplified, which accounts for better sensitivity of transducers and ability for energy harvesting.^{168, 169}

In this chapter, a new flexible 3-3 piezoelectric composite is proposed, consisting of 3D barium titanate (BTO) and polydimethylsilane (PDMS) polymer matrix. The 3D BTO featuring open porous continuous network will be template synthesized via sol-gel process. The morphology and advantages of the structure will be comprehensively discussed. Eventually the piezoelectric performance of the device is investigated.

4.2 Experimental Details

4.2.1 Materials

All chemicals were purchased from Aldrich and used without further purification unless otherwise noted. The open-cell polyurethane foams (TX704) with 100 pores per inch were purchased from ITW Texwipe. Dow Corning Sylgard 184 Silicone Elastomer were selected as the flexible polymer matrix.

Synthesis of barium titanate 3D structures

Titanium (IV) isopropoxide (5.5 g) was first dissolved into the mixture of acetic acid (4.8mL) and ethanol (3.2 mL) while barium acetate (4.128 g) was dissolved in the distilled water. After the solution became clear, the aqueous solution of barium titanate was added into solution of titanium (IV) isopropoxide under stirring. The resultant mixtures were dropwise infiltrated into the polyurethane foams at room temperature. The foams were flipped several times for the uniform 3D structure until they were completely dried. The infiltration were conducted different times for different morphologies of prepared barium titanate 3D structures. The prepared foams were sintered to 600 °C for 2 hours to completely remove the organic compounds and further calcinated to 1200 °C for 3 hours to promote the crystallization of barium titanate which may further enhance the mechanical strength of the ceramics. After the slow cooling to room temperature, the white firm barium titanate (BTO) 3-dimensional structure has been obtained. The prepared foam always exhibit shrinkage relative to the polyurethane foam due to mass transfer of ceramics and loss of organic materials. The open-cell structure could be apparently observed under the optical microscope in Figure 4-5, which demonstrates the successful preparation of BTO 3D structures.



Figure 4-5: The microscope images of a BTO 3D structure (a) in the reflection mode and (b) transmission mode. The scale bar is $200 \,\mu$ m.

4.2.2 Preparation of Composites

The procedures of making composites is shown in Scheme 4-1.The foams with the thickness of 2 mm were put into petri dishes and mixture of PMDS and cross-linking agent of the weight of 10:1 were poured into the petri dishes so that the ceramic foam has been completely emerged into the polymers. Afterwards, the mixture was put into the vacuum oven to remove the air bubble and insure the complete filling of PDMS into the ceramic foams. PDMS was cross-linked at 80 °C for 12 hours. The PDMS on the surface were removed to make the ceramic foam exposed, which could highly increase the piezoelectric properties of the composite films.¹⁵⁹ Figure 4-6 shows that PDMS well preserves the 3D structure of BTO.



Scheme 4-1: Scheme of the processing route used for producing composites.



Figure 4-6: A microscopic image of a composite film in the transmission mode. The scale bar is $150 \ \mu m$.

4 samples were prepared including 3 composites of different composition and a PDMS as a control. The porosity and BTO concentration were calculated using the weight, volume and density data, and listed in Table 4-1. The densities of PMDS and BTO are 1.03 and 6.02 g/cm³, respectively.

	PDMS	C1	C2	C3
Porosity (%) of foam	0	91.2	87.4	73.1
BTO concentration (vol.%)	0	8.8	12.6	26.9
BTO concentration (wt.%)	0	36.1	46.0	68.2

Table 4-1: The porosity and weight percentage of BTO in the composites for all the samples.

4.2.4 Characterization

Crystal analysis was studied by use of PANalytical xpert pro mpd theta-theta diffractometer. All data were analyzed using Jade software with a Gaussian-Lorentz superposition fitting functions. The microscopic morphology was explored using Olympus BX51 microscope. Gold electrodes with typical thickness of 60 nm were sputtered on both sides of the samples for the electrical measurements. Dielectric constant was acquired using an Agilent LCR meter (E4980A). Before the piezoelectric test, the composite samples were poled at 10 MV/m at 100 °C for 3 hours. The d₃₃ value was collected by Piezo meter Model ZJ-2. The voltage and current data were obtained by LeCroy WwaveSurfer 24Xs-A oscilloscope accompanied with Keithley 6517A electrometer/high resistance meter. The Young's Moduli of samples were collected on the TA Instruments RSA-G2 Dynamic Mechanical Analyzer.

4.3 Results and Discussion

4.3.1 Structural Characterization

Flexibility

The composite films with the thickness of 1-1.5 mm show great flexibility, as shown in Figure 4-7. The ceramics are brittle so that under the large stain, the BTO skeleton may break. However, the broken part could be kept in their original position owing to the presence of PDMS. And when the stress on the composite film is released, the broken parts are able to keep the contact with one another, as illustrated in Figure 4-8. Especially when the stress is applied in the 3 direction, the broken parts could be pushed to be closely contacted, giving rise to the favored charge transfer outside the piezoelectric device.



Figure 4-7: Images of the flexible composite film C2.



Figure 4-8: A microscopic image of cracks in composite C2 after bending and compressing. The scale bar is 75 μ m.

X-ray diffraction

X-ray diffraction is utilized to confirm the structure of BTO in Figure 4-9. It's obvious that the perovskite BTO phase has been successfully prepared into 3D structure, which implies the possible piezoelectric properties of flexible films.^{170, 171}



Figure 4-9: The XRD pattern of the 3D barium titanate.

4.3.2 Dielectric Properties

The dielectric constant of all samples has been measured to quantify the g33 value. The permittivity of all samples as a function of frequency is plotted in Figure 4-10. As the content of BTO increases, the permittivity increases gradually. Aside of flexibility, the other reason why

PDMS is selected is that it possesses low permittivity of 2.6 so that the permittivity of composites could be lowered, which would in turn benefit g33. And all the permittivity data are listed in Table 4-2.



Figure 4-10: Dependence of permittivity on the frequency for all samples at the room temperature.

Table 4-2: The d_{33} value and g_{33} values of all samples.

	PDMS	C1	C2	C3
d ₃₃ (pC/N)	0	8	20	28
ε _r	2.6	3.5	5.1	6.4
g ₃₃ (mV m/N)	0	258	434	497

4.3.3 Piezoelectric Properties

The d_{33} value of a material reflects how much charge would be generated under the stress. However, the piezoelectric potential that will be transferred to the parallel electrodes and can be applied to an external circuit be directly related to g_{33} . The output voltage can be calculated as

$$V = \int g_{33} \,\varepsilon(l) E_p \,dl \tag{4.1}$$

where g_{33} is the piezoelectric voltage constant, which is proportional to the piezoelectric coupling coefficient (d_{33}), $\epsilon(l)$ is the strain, and Ep is the Young's modulus.¹⁶² And g_{33} could be calculated according to the following equation:

$$g_{33} = \frac{d_{33}}{\varepsilon_r \ \varepsilon_0}$$

$$4.2$$

where the d_{33} is the piezoelectric coefficient, ε_r is the permittivity of the material and ε_0 is the permittivity of space. As shown in Table 4-2, the g_{33} increases as the BTO content increases. Beneficial to low permittivity of all the composites, the g_{33} values of C2 and C3 are higher than those of typical piezoelectric materials. For instance, although the d_{33} of C2 and C3 is comparable to that of PVDF, the g_{33} is almost doubled of that of PVDF (200-300 mV m/N).⁴⁸ Moreover, at the thickness of 1-2 mm, the PVDF-based polymers become stiff and lose the flexibility. When compared to ceramic thin film, the g_{33} is low owing to the high dielectric constant. So the design of composites could effectively increase the piezoelectric voltage constant as a result of relatively low dielectric constant.

Device performance

The strain and Young's modulus of the composite were determined by the DMA compression test. As shown in Figure 4-11, the composite C2 shows one order of magnitude higher Young's modulus than pure cross-linked PDMS. It implies that the 3D BTO effectively enhances the mechanical properties of composites and confirms the advantages of the BTO continuous network.



Figure 4-11: Dependence of Young's modulus on frequency for PDMS and composite C2

The prepared interpenetrating network shows great piezoelectric performance. It implies that as deigned, the 3D structure effectively concentrate the stress on BTO and further generate voltage and current. Meanwhile PDMS of low Young's modulus as polymer matrix allow the BTO absorb more stress as possible so as to enhance the output. Although the 3D BTO fracture into small pieces, those pieces are still kept in their original position as discussed in previous part. When another compression is applied, they are pushed closely, facilitating both stress and charge transfer.



Figure 4-12: Dependence of output voltage on the strain of the composite C2.

The dependence of output voltage on the strain of composite is studied. As illustrated in Figure 4-12, the generated voltage is proportional to the applied strain for C2. Under the strain value of 9.1 %, the output voltage and current is 3.26 V and 0.31 μ A. When compared with the BTO nanoparticle/PDMS composite in the literature¹⁶⁶, the voltage and current of this 3D BTO/PDMS are more than 10 times higher. The voltage and current data under the strain of 9.1 % are plotted in Figure 4-13 and 4-14, respectively. As Figure 8b and 9b shown, the signals of voltage and current are symmetric, indicating the great reversibility of strain. Figure 4-15 shows that the test of voltage and current are conducted simultaneously. Then the power density of C2 is assessed to be 12.5 μ W/cm³ for a 1 cm *1 mm composite C2 film. When the strain decreases to 4.8 %, both output voltage and current drop as shown in Figure 4-16, resulting in a lower power density of 3.1 μ W/cm³. When a higher strain than 9.1 % is also applied on the

composite C2, the power output would not be stable because the strong stress would destroy the 3D BTO network permanently and make the device performance unrecoverable.



Figure 4-13. The measured output voltage of C2 under the strain of 9.1 %.



Figure 4-14: The measured output current of C2 under the strain of 9.1 %.



Figure 4-15: The measured output voltage and current of C2 under the strain of 9.1 %.



Figure 4-16: The measured output a) voltage and b) current of C2 under the strain of 4.8 %.



Figure 4-17: The stability and durability results of C2 under the strain of 9.1 %.

The stability of the BTO/PDMS composites is tested by continuously applying and releasing the compressive strain. As shown in Figure 4-17, continuous 75 cycles of staining have been repeated during almost 30 seconds. While there are some fluctuations, the output voltage is very stable, demonstrating that this fractured structure could provide stable output. The average output voltage for C2 is 3.26 V.

It's also worth mentioning that C3 could not withstand high strain due to high content of BTO. Although the g_{33} is higher for C3, large amount of fractured BTO pieces could not be preserved by PDMS. Therefore, C2 shows more stable energy generating performance.

4.4 Conclusion

In summary, we have fabricated a flexible piezoelectric 3-3 composite based on 3D barium titanate and PDMS. Although the 3D BTO shows fractured structure under the strain, applied stress is able to push the broken pieces to closely contact with each other, beneficial stress and charge transfer. The prepared composites exhibit a high g₃₃ coefficient of more than 400 mV m/N and an output voltage of more than 3 V. It provides a new method to fabricate flexible piezoelectric generator for the conversion of the mechanical deformation and even tiny biomechanical movements into electric energy. This result innovatively expands the feasibility of low cost self-powered energy systems for application in consumer electronics, sensor networks, and energy harvesting in indoor environments.

Chapter 5

Conclusions and Future Work

5.1 Conclusions

This dissertation explored applications of sol-gel process in the fabrication of the high dielectric breakdown composites for energy storage capacitors, low loss percolative composites for radio frequency capacitors and flexible piezoelectric composites for energy conversion.

Chapter 2 systematically investigates one series of functionalized P(VDF-CTFE) based composites including fillers of different in-situ prepared inorganic materials with relatively low permittivity. Due to the small contrast in permittivity and conductivity, the distorted local electric field is depressed. By forming covalent bonding between the organic and inorganic phase, the interfacial interaction and dispersion have been markedly improved. At the same time, the direct linkage cross-links the polymer chains, which effectively enhance the mechanical properties. In addition, the proper content of fillers can reduce the electrical conduction. For the Ta_2O_5 fillers, polar Ta-O bonds are able to service as deep traps to increase the activation energy of charge transport while in the presence of SiO₂ could increase the interfacial area and numbers of traps although Si-O is less polar. All these are synergized to enhance the breakdown strength and energy density of composites as observed. Moreover, HfO₂/P(VDF-CTFE) were also prepared to achieve the high breakdown strength, which demonstrates it's a universal approach to fabricate the high breakdown composites. However as the content of fillers exceed the optimized concentration, the conductivity is further promoted as the percolative pathways have been formed, which in turn mitigates the breakdown strength again. In all, this work opens a new route toward dielectric composites with high breakdown strength for electrical energy storage applications and provides a method to prepare inorganic-organic composites.

Chapter 3 studies a new class of SiO_2 coated graphene-based percolative dielectric composites. In the new composites, the fluctuation induced tunneling conduction mechanism plays a dominate role in the composites. Due to the presence of the SiO_2 surface-functionalized layers on graphene nanosheets, the resultant composites have much lower conductivity in comparison to the corresponding composites containing bare reduced graphene oxide nanosheets. Consequently, the composites not only exhibit significantly suppressed dielectric loss, especially at a relatively high frequency, but also possess exceptional breakdown strength even at the percolation threshold. Moreover, different from the typical percolative composites whose loss increases abruptly beyond the percolation threshold, the loss of the prepared composites remains little changed with the variation of the filler concentration. These results enable the preparation of the percolative dielectric performance and the applications of the percolative composites under high electric fields.

Chapter 4 provides a new approach to fabricate flexible lead-free piezoelectric 3-3 composites based on 3D barium titanate and PDMS. Although the 3D BTO shows fractured structure under the strain, applied stress is able to push the broken pieces to closely contact with each other, effectively improving stress and charge transfer. Therefore, the prepared flexible composites exhibit a g₃₃ value of more than 400 mV m/N and an output voltage of more than 3 V. It provides a new method to fabricate flexible piezoelectric generator for the conversion of the mechanical deformation and even tiny biomechanical movements into electric energy. This result innovatively expands the feasibility of low cost self-powered energy systems for application in consumer electronics, sensor networks, and energy harvesting in indoor environments.

5.2 Future Work

5.2.1 Nanocomposites Prepared by Sol-Gel Process

In Chapter 2, several different oxide have been *in-situ* prepared in the same P(VDF-CTFE) matrix. For the composites of high content, the excess functional groups could decrease interfacial interaction and increase the conduction. In the future, functional P(VDF-CTFE) with different molecular weight would be synthesized through the free radical polymerization following the same procedures in Chapter 2. By tuning the molecular weight, the concentration of functional end groups could be adjusted to address the issue of excess functional groups and investigate how the concentration of functional end groups affect optimal composition of inorganic phase and dielectric performance. Besides, by tuning molecular weight of polymers and concentration of precursors, the optimized composite would be fabricated for the best dielectric performance.

5.2.2 New 2-3 Composites for Capacitors

In Chapter 3, the effect of randomly dispersed functionalized r-GOs on the electrical and dielectric properties has been investigated. The morphology and dispersion are key factors to determine the dielectric performance. By different processing, the morphology of 2 dimensional fillers could be tailored. For instance, the layered silicate could be aligned in the polymer matrix by spraying deposition.¹⁷² One other future work could be fabrication of 2-3 composites including aligned r-GO/r-GO@SiO₂ to study how the morphology change affects the dielectric properties of the percolative composites.

Aside of graphene or r-GO, hexagonal boron nitride (h-BN), a 2 dimensional structure with boron and nitrogen atoms occupying the inequivalent A and B sublattices in the Bernal structure, is a wide bandgap ($\sim 6 \text{ eV}$) insulator with a dielectric strength of 800 MV/m.^{173, 174} The

breakdown voltage of h-BN can be further improved by decreasing the thickness of h-BN sheet down to few layers.¹⁷⁵ And thin boron nitride nanosheets could be exfoliated from bulk h-BN powders.^{176, 177} One other future work will focus on the investigation of new boron nitride nanosheet/polymer composites with high breakdown strength.

5.2.3 Flexible Piezoelectric Composites with High g₃₃

(1 - x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃ (PMN-PT) has been demonstrated with high is the new single crystal piezoelectric, which has a piezoelectric coupling coefficient (d₃₃) up to 2500 pm/V¹⁷⁸ and much higher than that of conventional ceramics. For example, the piezoelectric coupling coefficient (d₃₃) of single-crystal bulk PMN-PT is almost 30 times higher than that of BaTiO3, which is approximately 85.3 pm/V,¹⁷⁹ and almost 4 times higher than that of PZT bulk material. The piezoelectric coupling coefficient (d₃₃) of PMN-PT nanowires synthesized recently by our group was measured as 371 pm/V.¹⁸⁰ This is over 13 times higher than that of BaTiO₃ nanoparticles and 90 times higher than that of NaNbO₃ nanowires, which are approximately 28 and 4 pm/V, respectively.^{181, 182} And PMN-PT could also be made by sol-gel process as reported.¹⁸³⁻¹⁸⁵

As demonstrated in Chapter 4, the 3-D ceramic/PDMS composite could exhibit great flexibility and great piezoelectric effect. As the dielectric data shown, the high-k ceramics would not change the permittivity too much. However, d₃₃ value make been directly determined by ceramic structures. Therefore, when PMN-PT is selected to form the 3D foam structure, the g33 value would be further increased to enhance the voltage outage performance. The possible future work to fabricate PMN-PT foam/PDMS composite is to achieve a higher voltage output under the lower strain.

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