INVESTIGATION OF STRUCTURE-PROPERTY RELATIONS IN NANOCOMPOSITES FOR ENERGY STORAGE

By

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To my parents and wife
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LIST OF ABBREVIATIONS

κ  Dielectric permittivity

$E_b$  Breakdown strength of the materials

PZT  Lead zirconate titanate

PVDF  Polyvinylidene-fluoride

BST  Barium strontium titanate

NWs  Nanowires

NRs  Nanoparticles

SEM  Scanning Electron Microscopy

FTIR  Fourier-transform infrared

XRD  X-ray diffraction

LCR  Inductance-capacitance-resistance

BET  Brunauer, Emmet, Teller

V  Voltage

d  Distance

Q  Charge

A  Area

$\varepsilon_0$  Dielectric permittivity of the free space

$\varepsilon_r$  Dielectric constant of the dielectric materials

$\varepsilon'_r$  Complex permittivity

P  Polarization charge

$\sigma_s$  Charge density

D  Electric displacement

E  Electric field

U  Energy density
\[ \tan \delta \quad \text{Loss tangent} \]
\[ \text{DF} \quad \text{Dissipation factor} \]
\[ \text{W} \quad \text{Energy loss} \]
\[ f \quad \text{Frequency} \]
\[ \alpha_e \quad \text{Electronic polarization} \]
\[ \alpha_i \quad \text{Ionic polarization} \]
\[ \alpha_d \quad \text{Dipolar polarization} \]
\[ \alpha_s \quad \text{Space charge polarization} \]
\[ \Phi \quad \text{Volume fraction} \]
\[ BOPP \quad \text{Biaxial oriented polypropylene} \]
\[ \text{PP} \quad \text{Polypropylene} \]
\[ \text{PET} \quad \text{Polyester} \]
\[ \text{PC} \quad \text{Polycarbonate} \]
\[ \text{PEN} \quad \text{Polyethylene-naphate} \]
\[ \text{PPS} \quad \text{Polyphenylene-sulfide} \]
\[ P(\text{VDF-TrFE}) \quad \text{Poly(vinylidene fluoride-trifluoroethylene)} \]
\[ P(\text{VDF-HFP}) \quad \text{Poly(vinylidene fluoride-hexafluoropropylene)} \]
\[ P(\text{VDF-CTFE}) \quad \text{Poly(vinylidene fluoride-chlorotrifluoroethylene)} \]
\[ P(\text{VDF-TrFE-CFE}) \quad \text{Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene)} \]
\[ \varepsilon_1 \quad \text{Dielectric permittivity of filler} \]
\[ \varepsilon_2 \quad \text{Dielectric permittivity of matrix} \]
\[ \Phi_1 \quad \text{Dielectric permittivity of filler} \]
\[ \Phi_2 \quad \text{Dielectric permittivity of matrix} \]
\[ \text{CCTO} \quad \text{Calcium copper titanate} \]
\[ \text{ZTO} \quad \text{Zr}_x\text{Ti}_{1-x}\text{O}_2\cdot n\text{H}_2\text{O} \]
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<th>Definition</th>
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<td>DMF</td>
<td>Dimethylformamide</td>
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<tr>
<td>D-E</td>
<td>Electric displacement - electric field</td>
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<td>DUT</td>
<td>Device under test</td>
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<td>HOF</td>
<td>Herman’s orientation factor</td>
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<tr>
<td>FFT</td>
<td>Fast fourier transform</td>
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<tr>
<td>MMT</td>
<td>Organomontmorillonite</td>
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<tr>
<td>$d_{33}$</td>
<td>Piezoelectric strain coefficient</td>
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INVESTIGATION OF STRUCTURE-PROPERTY RELATIONS IN NANOCOMPOSITES FOR ENERGY STORAGE

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High energy density capacitors are critically important in advanced electronic devices and electric power systems that rely on pulsed-power, such as defibrillators, and high power microwaves. Nanocomposites have great potential as high energy capacitors, since they combine the high breakdown strength of polymers with the high dielectric permittivity of ceramics, to produce energy density greater than either in its pure form. Most of the current research has focused on improving the energy density of nanocomposites by choosing a high dielectric permittivity filler and high breakdown strength matrix. However, the improvement of dielectric permittivity comes at the expense of the breakdown strength thus limiting the ultimate performance of the capacitors.

This dissertation has investigated the relationship between filler’s structure (aspect ratio and orientation) and energy storage performance of nanocomposites. Initially, the effect of the filler’s aspect ratio on the nanocomposite’s energy density was studied. It is demonstrated that the nanocomposites with PZT nanowires (NWs) show 77.8% increase in energy density compared to samples with PZT nanorods at 50% volume fraction. Second, this work investigates the role of NW orientation towards the
improvement in the energy density of nanocomposites. It is demonstrated that the energy storage capacity of the nanocomposite can be enhanced by 51.6% through the alignment of PZT nanowires in the direction of the applied electric field as compared to the sample with randomly aligned nanowires at 20% volume fraction. Further research is performed to quantify the dielectric constant of nanocomposites as a function of both aspect ratio and orientation factor of the fillers. Based on these findings, two different types of nanocomposites with high energy density are fabricated. The nanocomposites with 7.5 vol.% Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs in PVDF are shown to have an ultra-high energy density of 14.86 J/cc at 450 MV/m with microsecond discharge time speed, which exceeds those reported in the literature for ceramic/polymer composites, and is 1138% greater than the reported commercial capacitor biaxial oriented polypropylene (1.2 J/cc at 640 MV/m). This dissertation will serve to disseminate a state-of-the-art method of preparing nanocomposites with high energy density and fast discharge for development of future pulsed-power capacitors.
CHAPTER 1
INTRODUCTION

Motivation

The motivation for this research lies in the development of high energy density nanocomposite capacitors with fast discharge speed. Over the past few decades, high energy density capacitors have gained significant attention for future advanced pulsed-power electronic devices and electric power systems, such as lasers, radar, pacemakers, electromagnetic armors, defibrillators and high power microwaves [1-8]. By releasing large amounts of electrical energy in a short duration, typically less than a microsecond, high energy density capacitors possess large power densities to meet the requirements of pulsed-power devices [1,6-8]. Theoretically, the energy density is linearly proportional to the dielectric constant and quadratically related to the breakdown strength of the capacitor [6,9,10]. Therefore, many efforts have been devoted to enhancement of the material’s permittivity and/or breakdown strength to improve the energy density. Currently, commercial monolithic materials are reaching a plateau in terms of energy density due to the trade-off between the dielectric permittivity and breakdown strength of the materials as shown in Figure 1-1 [11]. For example, ceramics have a high dielectric permittivity but low breakdown strength, while polymers have a high breakdown strength but low dielectric permittivity [2,5,12]. In addition, other energy storage technologies, for example, batteries and fuel cells, have greater energy density but have a very long discharge time compared to polymers and ceramics [11], which result in a low power density that is not suitable for pulsed-power applications. Therefore, it is important to develop a novel energy storage material having high energy density with fast discharge speed.
Nanocomposites combining a high breakdown strength polymer and high dielectric permittivity ceramic filler offer significant promise for future high energy density capacitors [9,13-16,16-18]. However, while current nanocomposites improve the dielectric permittivity of the capacitor, the gains come at the expense of the breakdown strength, which limits the ultimate performance of the capacitor [14-16,19-21]. This dissertation will present a new fabrication route by using high aspect ratio nanowires rather than equiaxial particles. The relationship between the structure (aspect ratio and orientation) and energy storage will be investigated. Based on the findings, a novel nanocomposite with higher energy density and higher power density than monolithic material will be fabricated to fill the green gap as shown in Figure 1-1. Furthermore, the advances made through the development of high energy density nanocomposite capacitors such as those here will pave the way for the development of future pulsed-power devices.

![Figure 1-1. Energy and power density of several energy storage technologies. (Reprinted with permission from Kōtz et al. [11])](image)

**Fundamentals of Capacitor**

A capacitor, also known as a condenser, is a simple electronic device that typically consists of two electrodes that are separated by a dielectric material as shown
in Figure 1-2 [22]. When there is a voltage across two electrodes, an electric field is formed across the dielectric material. Positive charge accumulates on one electrode until the induced electric field across the gap balances the applied field, while the negative charge is on the other electrode [22]. By this process, the energy is stored by an electrostatic field in the dielectric material. The performance of a capacitor can be characterized by the following parameters: capacitance, dielectric loss, breakdown strength, polarization-electric field response, energy density and power density, which will be discussed in detail below.

![Figure 1-2. Typical mode of the capacitor.](image)

**Capacitance, Dielectric Constant and Loss Tangent**

As shown in Figure 1-2, it is assumed that there is a voltage $V$ (volt, v) across a distance $d$ (meter, m) in a dielectric material (first assume vacuum). The positive charge $+Q$ (coulomb, c) is accumulated on the bottom electrode with an area $A$ (m$^2$), while the negative charge $-Q$ is on the other side. The capacitance $C$ (Farad, F) can be defined as the ratio of the charge to voltage between two electrodes [23]:

$$C = \frac{Q}{V} = \varepsilon_0 \frac{A}{d}$$

where $\varepsilon_0$ is the dielectric permittivity of vacuum with a value of $8.854 \times 10^{-12}$ F/m.
If a dielectric material is inserted between two electrodes, the charge is redistributed on the dielectric material and the electrodes in response to the applied field, resulting in inducing a polarization charge $P$ at the surface of the material. The resulting charge density ($\sigma_s$) of the capacitor consists of two parts: one part is from the vacuum charge, and the other part is $P$ ($\sigma_{pol}$) from the charge compensation on the surface of the dielectric in contact with the electrodes as shown in Figure 1-2 [23,24]. Therefore, the total charge density can be expressed by the following equation:

$$\sigma_s = D = \varepsilon_0 E + P = \varepsilon_r \varepsilon_0 E$$

$$C = \frac{Q}{V} = \frac{\sigma_s A}{V} = \varepsilon_r \varepsilon_0 \frac{A}{d}$$

where $D$ is the electric displacement (C/m$^2$), $E$ is the electric field (V/m), $\varepsilon_r$ is the dielectric constant of the material with respect to the $\varepsilon_0$ of vacuum. $\varepsilon_r$ is typically larger than one; therefore, by inserting a dielectric material, the energy storage capacity of the capacitor will be improved as compared to vacuum. The energy density $U$ (J/m$^3$) of the linear capacitor can be expressed [25]:

$$U = \frac{1}{2} DE = \frac{1}{2} \varepsilon_r \varepsilon_0 E^2$$

(1-1)

In reality, energy loss is always associated with dielectric materials. In order to understand the energy loss of a material, the complex permittivity ($\epsilon_r'$) is introduced:

$$\varepsilon = \frac{D}{E} = (\varepsilon_r - j \varepsilon_r') \varepsilon_0$$

where $\varepsilon$ is the dielectric permittivity and $\varepsilon_r$ is the real permittivity part of the material. The relative magnitude of the losses can be estimated by the loss tangent ($\tan \delta$), defined as the below equation [24]:

$$\tan \delta = \frac{\varepsilon_r'}{\varepsilon_r}$$
The loss tangent is a measurement of energy loss in the dielectric material during the AC operation, which is independent of the geometry of the capacitor. The energy loss, $W$, is linearly proportional to the loss tangent and can be determined by:

$$W \propto \pi \varepsilon_r E^2 f \tan \delta$$

where $f$ is the frequency of the electric field. Therefore, a dielectric material with low loss tangent can reduce the energy loss of the capacitor and improve the efficiency of energy storage.

**Polarization Mechanisms**

Material exhibits a unique dielectric property due to polarization in which the dipole is switched according to the application of an external electric field. Here, four different mechanisms of polarization are introduced as shown in Figure 1-3: electronic polarization, ionic polarization, orientation polarization and space charge polarization [24,26].

![Figure 1-3](image)

Figure 1-3. Four different polarization mechanisms: A) electronic polarization, B) ionic polarization, C) orientation polarization, D) space charge polarization.
Electronic polarization exists in all dielectrics because every material is composed of atoms [24,26,27]. The electronic polarization is formed by shifting the electronic cloud within each atom under an electric field as shown in Figure 1-3a. When an electric field is applied across the dielectric material, the positive charge distribution is shifted with respect to the negative charge distribution. As a result, a polarization vector develops in the dielectric material. The electronic polarization can respond to most frequencies up to $10^{17}$ Hz due to the small mass of atoms. Also, this mechanism is independent of temperature since the electronic structure is stable over a wide temperature range [24,26,27]. However, the electronic polarization is smaller compared to other polarization mechanisms due to the short arms of the dipoles [24,26,27].

Ionic polarization typically occurs in an ionic crystal, which is similar to electronic polarization [24,26,28]. As shown in Figure 1-3b, each pair of oppositely charged neighboring ions has a dipole moment in the ionic crystal. In the absence of an electric field, there is no net polarization since the dipole moments of equal magnitude are lined up head-to-head and tail-to-tail resulting in a zero net dipole moment. Under an electric field, both the anions and cations are shifted relative to their normal positions leading to the formation of net dipole moment across the dielectric material. Like electronic polarization, ionic polarization is independent of temperature, and responds to a high frequency of up to $10^{13}$ Hz.

As shown in Figure 1-3c, orientation polarization occurs in molecules with a permanent dipole moment such as ferroelectric materials [24,26,29]. In the absence of an electric field, there is no net polarization in the dielectric material because the thermal agitation causes a totally random molecule distribution resulting in a zero net
dipole moment. Under an applied electric field, the dipoles rotate and shift to align along the field leading to a net average dipole moment in the material. Orientation polarization is larger compared to other mechanisms and can response to frequency less than $10^{13}$ Hz and dependent on temperature. For example, the dielectric permittivity of the ferroelectric material changes sharply at Curie temperature [24,26,27].

Space charge polarization occurs whenever there is an accumulation of charge at an interface between two materials or between two regions within a material like grain boundaries and defects in the material [24,26,30]. As shown in Figure 1-3d, the absence of a field creates a zero net dipole in the material since there is no separation between all the positive charge carriers and all the negative ones. Under an electric field, the negative charge carriers migrate toward the positive electrode and accumulate there, while the positive ones move to the negative side. As a result, interfacial polarization arises within the dielectric material because of this separation. This mechanism commonly exists in grain or phase boundaries and free surfaces. Space charge is highly related to temperature, and it can only respond to low frequencies ($<10^3$ Hz).

The average induced dipole moment per molecule ($\alpha$) in the electrical material can be measured by the sum of all contributions: electronic polarization ($\alpha_e$), ionic polarization ($\alpha_i$), dipolar polarization ($\alpha_d$) and space charge polarization ($\alpha_s$)

$$\alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s$$

The frequency dependence of polarization in different mechanisms can be summarized in Figure 1-4. Electronic polarization and ionic polarization can respond at high frequency, while dipolar polarization and space charge polarization can only
respond at low frequency. A relaxation frequency is the reciprocal of the minimum reorientation time. A dipole will not make a contribution to the polarization when the frequency of the applied electric field is higher than the relaxation frequency and the dipole cannot shift orientation direction to keep up with the field [31]. Therefore, the polarizability decreases with an increase in frequency as shown in Figure 1-4. For ferroelectric materials, the space charge polarization reduces first with increasing frequency, and then the orientation polarization dominates the overall polarization.

![Figure 1-4](image)

**Figure 1-4.** The frequency dependence of the polarization in the presence of different polarization mechanism. (Reprinted with permission from Kingery et al. [26])

**Energy Density**

The energy density of a linear dielectric capacitor can be directly determined by the dielectric permittivity and the breakdown strength using Equation 1-1. However, for ferroelectric materials, the electric displacement of the material is not linearly dependent on the applied electric field. Even in the commercial linear capacitor biaxially-oriented polypropylene (BOPP), the electric displacement is not linear to the electric field because of electrical conduction at high electric field. Therefore, the energy density is not only dependent on the dielectric permittivity and breakdown strength but also related
to the polarization and applied electric field. Therefore, in order to calculate the energy density of the capacitor, it is important to utilize the Sawyer-Tower circuit to determine the electric displacement-electric field (D-E) relationship, especially at high electric field.

The true energy density of the capacitor is shown as the shaded area in Figure 1-5 [32,33], which is computed from the integration of the discharge curve in the D-E loop:

$$U = \int EdD$$

![Figure 1-5. Typical D-E loop used to calculate energy density of non-linear capacitor.](image)

There are four different types of D-E loops for a polarization electric field response: linear, relaxor ferroelectric, ferroelectric and anti-ferroelectric as shown in Figure 1-6 [32]. The linear dielectric has a linear relationship between the polarization and electric field as shown in Figure 1-6a, such as polypropylene. The linear dielectric has low loss; however, it does not have high dielectric permittivity and limits the energy density [34]. It should be mentioned that even the best linear dielectric can become non-linear above a certain electric field due to the increased conduction loss, such as BOPP. The relaxor ferroelectric and ferroelectric materials have a higher polarization compared to linear capacitor because of the heavy contribution from the orientation
polarization mechanism. However, the ferroelectric properties of these materials have polarization saturation and a hysteresis loop leading to a higher loss compared to linear capacitors as shown in Figure 1-6b and c. Another type of D-E loop is from the anti-ferroelectric materials (Figure 1-6d). Anti-ferroelectric material has low remnant polarization and relatively narrow D-E hysteresis loop, which implies higher energy storage ability [32,35,36]. With increasing the electric field, the antiferroelectric phase of the dielectric material is changed into ferroelectric phase resulting in a limited energy storage performance [37,38]. Currently, many researchers are trying to maintain the antiferroelectric phase at high electric field to yield higher energy density [39,40].

Figure 1-6. Four typical D-E loops: A) linear, B) relaxor ferroelectric, C) ferroelectric, D) antiferroelectric. (Reprinted with permission from Burn et al. [32])
Capacitor Technology

To date, several types of dielectric materials have been used to manufacture capacitors, such as ceramics, polymers, and glass ceramics so on. Here, a review of typical capacitors will be presented with a special focus on the recent progress of the nanocomposite capacitors for energy storage.

Ceramic

Ceramic capacitor is one of the most commercial and popular capacitors characterized by moderate energy density (~2 J/cc), high power density and small to midsize capacitance (pF to 100 uF) [12,41]. The ceramic capacitors can be classified into two different categories: one is low dielectric permittivity ceramics (15-500) and the other is high dielectric permittivity ceramics (2000-20000), as shown in Table 1-1 [42]. Ceramic capacitors are composed of two electrodes attached directly to the ceramic dielectrics as shown in Figure 1-7a [43]. In order to improve the capacitance density of the capacitors, two kinds of constructions are developed and employed: multilayer ceramic capacitor and hollow tubular ceramic capacitor as shown in Figure 1-7b and c, respectively [43]. The multilayer ceramic capacitors are widely produced in industry as they can include hundreds of dielectric layers to achieve the desired capacitance. The obvious disadvantage of the ceramic capacitors is the low breakdown strength (around 10 MV/m) leading to low energy density. For example, BaTiO$_3$ has a dielectric constant between 1800 and 4500 and a breakdown strength of approximately 6 MV/m, and the energy density can reach 2 J/cc [41,43]. Additionally, ceramics are very fragile, and hard to process to intricate configurations for electronic and electric devices [44]. In summary, ceramic capacitors are more suitable for low and medium voltage application due to their limited breakdown strength.
Table 1-1. The dielectric constant of typically used ceramics as capacitors. PMN-PT(65/35) is the abbreviation for 65% lead magnesium niobate and 35% lead titanate. (Reprinted with permission from Nalwa et al. [42])

<table>
<thead>
<tr>
<th>Composition</th>
<th>Dielectric constant</th>
<th>Composition</th>
<th>Dielectric constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ba, Sr)TiO₃</td>
<td>250-2,000</td>
<td>TiO₂</td>
<td>80</td>
</tr>
<tr>
<td>Pb(Zr, Ti)O₃</td>
<td>400-3,000</td>
<td>SiO₂</td>
<td>3.9</td>
</tr>
<tr>
<td>PMN-PT (65/35)</td>
<td>3,640</td>
<td>Al₂O₃</td>
<td>9</td>
</tr>
<tr>
<td>Pb(Mg, Nb)O₃</td>
<td>&gt;3,000</td>
<td>Ta₂O₅</td>
<td>22</td>
</tr>
<tr>
<td>CaCu₃Ti₄O₁₂</td>
<td>~60,000</td>
<td>ZrO₂</td>
<td>25</td>
</tr>
<tr>
<td>La₁.₈Sr₀.₂NiO₄</td>
<td>~100,000</td>
<td>SiN</td>
<td>7-9</td>
</tr>
</tbody>
</table>

Figure 1-7. Ceramic capacitors with different shapes: A) disk capacitor, B) tube capacitor, C) multilayer capacitor.

Polymer

Compared to ceramic capacitors, polymer capacitors feature a high breakdown strength (>300 MV/m), moderate energy density (~2 J/cc), light weight, longer operation life and grace failure because of its self-healing capability [45-47]. The common polymer based capacitors include polypropylene (PP) [48,49], polyster (PET) [50], polycarbonate (PC) [51], polyethylene-naphate (PEN) [52], polyphenylene-sulfide (PPS)
and polyvinylidene-fluoride (PVDF) [54-56]. The dielectric property and performance of various polymer capacitors are detailed in Table 1-2 [48]. Among them, BOPP is the most widely used commercial capacitor because of its high breakdown strength, low loss, low cost and the ease at which it can be manufactured. However, BOPP offers an energy density of only 1.2 J/cc at 640 MV/m due to its low dielectric permittivity (2.2) [48]. In order to improve the overall capacitance value, polymer capacitors are typically manufactured into a multilayer structure for use as commercial capacitors. Additionally, the frequency response of polymer capacitors can extend to the gigahertz range with low loss [57].

Table 1-2. Dielectric properties of the most commonly used polymers. (Reprinted with permission from Rabuffi et al. [48])

<table>
<thead>
<tr>
<th>Polymer Film</th>
<th>Dielectric Constant</th>
<th>Maximum Temperature (°C)</th>
<th>Breakdown Strength (MV/m)</th>
<th>Loss Tangent (% at 1 kHz)</th>
<th>Energy Density (J/cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>2.2</td>
<td>105</td>
<td>640</td>
<td>&lt;0.02</td>
<td>1-1.2</td>
</tr>
<tr>
<td>PET</td>
<td>3.2</td>
<td>125</td>
<td>570</td>
<td>&lt;0.5</td>
<td>1-1.5</td>
</tr>
<tr>
<td>PC</td>
<td>2.8</td>
<td>125</td>
<td>528</td>
<td>&lt;0.15</td>
<td>0.5-1</td>
</tr>
<tr>
<td>PEN</td>
<td>3.2</td>
<td>125</td>
<td>550</td>
<td>&lt;0.15</td>
<td>1-1.5</td>
</tr>
<tr>
<td>PPS</td>
<td>3.0</td>
<td>200</td>
<td>550</td>
<td>&lt;0.03</td>
<td>1-1.5</td>
</tr>
<tr>
<td>PVDF</td>
<td>12</td>
<td>125</td>
<td>&gt;600</td>
<td>&lt;1.8</td>
<td>2.4</td>
</tr>
</tbody>
</table>

In order to improve the energy density of polymers, many efforts have been devoted to improve their dielectric permittivity without sacrificing the breakdown strength. Recently, ferroelectric polymers PVDF [56], and copolymers such as poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) [16], poly(vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP)) [18] and poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE)) [16] as well as terpolymers such as
poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)) simultaneously exhibit high breakdown strength (>300 MV/m) and relatively high dielectric permittivity (approximately 50) [16,17]. Figure 1-8 shows the polarization response under a high field for PVDF copolymer and terpolymer [6]. It can be seen that PVDF terpolymers have higher energy density and storage efficiency than PVDF copolymers. This results due to the large chlorine atom in CFE and CTFE which acts as a defect in crystal lattice, and then break up the ferroelectric domains into local nanopolar regions [58,59]. It should be mentioned that the polarization property of P(VDF-TrFE-CFE) is dependent on their composition [58,59]. The disadvantage of the PVDF based polymers for energy storage comes from their ferroelectric properties, such as high loss and polarization saturation that limits the energy density.

Figure 1-8. The polarization response under high field for PVDF based copolymers and terpolymers. The shaded region indicates the energy density of the material. (Reprinted with permission from Chu et al. [6])

**Nanocomposite**

Nanocomposites represent a class of materials with multiple solid phases where at least one of the phases has nanoscale dimension range from one nanometer to hundreds of nanometers [2,14,16,17,60-63]. In this dissertation, the inorganic/polymer
nanocomposites will be discussed. As mentioned, a tradeoff between the dielectric permittivity and breakdown strength exists in nanocomposites and limits the design of high energy density capacitors [14,63-67]. Therefore, much research has been conducted to understand the physical phenomena governing a composite’s dielectric permittivity and breakdown strength in order to improve the energy storage properties.

**Dielectric Permittivity of Composite**

There are many theoretical models developed to predict the effective dielectric permittivity of a nanocomposite. The simplest model is the volume faction average to estimate the effective dielectric constant of the composite.

\[ \varepsilon = \Phi_1 \varepsilon_1 + \Phi_2 \varepsilon_2 \]

where \( \varepsilon \) is the effective dielectric permittivity of the composite, \( \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric permittivity of the ceramic filler and polymer matrix, respectively, \( \Phi_1 \) and \( \Phi_2 \) are the volume fraction of the ceramic and polymer, respectively. This simplest model cannot predict correctly the effective dielectric permittivity of the composites, since it predicts very high dielectric constant even at low volume fraction of the filler, which far diverges from the value obtained from experimental research [68,69]. Another more reasonable simple model is the Lichtenecker logarithmic rule [70], which is also based on the volume-fraction average.

\[ \log \varepsilon = \Phi_1 \log \varepsilon_1 + \Phi_2 \log \varepsilon_2 \]

Li et al. demonstrated that the experimental data agrees reasonably well with this model, except at volume fraction greater than 20% [16]. Lichtenecker logarithmic law over predicts the effective dielectric permittivity of the nanocomposite as compared to experimental research.
In order to accurately predict the effective dielectric permittivity of the binary composites, the Bruggeman model is developed. It is based on the mean field theory and treats spherical inclusion in the center of the matrix [70,71]. The effective dielectric permittivity of the binary composites can be obtained with the following equation:

\[
\varphi_1 \left( \frac{\varepsilon_1 - \varepsilon}{\varepsilon_1 + 2\varepsilon} \right) + \varphi_2 \left( \frac{\varepsilon_2 - \varepsilon}{\varepsilon_2 + 2\varepsilon} \right) = 0
\]

The Bruggeman model can predict the effective dielectric permittivity of the composites at low volume fraction, but the prediction increases sharply at filler’s volume fractions larger than 20% and it also over estimates the dielectric permittivity of the binary nanocomposite at high volume fraction.

Another model based on the mean field theory is Maxwell equation [71]:

\[
\varepsilon = \varepsilon_1 \frac{\varepsilon_2 + 2\varepsilon_1 - 2(1 - \varphi_1)(\varepsilon_1 - \varepsilon_2)}{\varepsilon_2 + 2\varepsilon_1 + (1 - \varphi_1)(\varepsilon_1 - \varepsilon_2)}
\]

However, the Maxwell equation is only reasonable for prediction at low volume fraction. The above mentioned models are summarized in Figure 1-9, which assumes the dielectric permittivity of filler (\(\varepsilon_1=1000\)) and polymer (\(\varepsilon_1=2.3\)).

![Figure 1-9](image.png)

Figure 1-9. The effective dielectric permittivity of composite is predicted by various model assumed the spherical filler (\(\varepsilon_1=1000\)) in polymer matrix (\(\varepsilon_2=2.3\)).
Many experiments have demonstrated that the dielectric constant of a composite is improved by using high dielectric permittivity fillers [14-16,19-21]. However, the experimental value is always lower than that predicted by models. In addition, the aforementioned theoretical models all treat the filler as spherical shape and assume they are homogenously dispersed in the polymer matrix. Therefore, the high aspect ratio filler are motivated to improve the dielectric permittivity of the composites [55,56,67,72-74]. The aspect ratio effect can be described by the Maxwell-Garnet model

$$\varepsilon = \varepsilon_2 + \varepsilon_2 \frac{\Phi_1}{3} \sum_{i=x,y,z} \frac{\varepsilon_{1-\varepsilon_2}}{\varepsilon_2 + N_i(\varepsilon_{1-\varepsilon_2})} \left(1 - \frac{\Phi_1}{3} \sum_{i=x,y,z} \frac{N_i(\varepsilon_{1-\varepsilon_2})}{\varepsilon_2 + N_i(\varepsilon_{1-\varepsilon_2})}\right)$$

where $N_i$ is the depolarization factor of ellipsoids in the $x$, $y$, $z$ direction. For needle shaped fillers, where the radii $a_x > a_y = a_z$, a simple expression of $N_i$ can be expressed as:

$$N_i = \left(\frac{\ln(1+e)}{1-e} - 2e\right)(1-e^2)/2e^3$$

$$e = \sqrt{1 - \frac{a_y^2}{a_x^2}}$$

The Maxwell-Garnet model demonstrates that the dielectric permittivity of composite is improved by high aspect ratio filler. Andrews et al. also developed micromechanics and finite element models to study the effect of aspect ratio, and show that the higher aspect ratio of the filler plays critical role in achieving high dielectric permittivity as shown in Figure 1-10 [67]. Guo et al. experimentally demonstrated that rod-shaped TiO$_2$/polypropylene has higher dielectric constant than the sample with sphere-shaped TiO$_2$ at the same volume fraction of filler. However, the authors did not test the D-E loop to indicate the effect of the filler aspect ratio on the energy density of...
the nanocomposites. They also did not show higher dielectric constant nanocomposites with high aspect ratio nanowires, since traditional inorganic materials are not available in high aspect ratio until recently.

Additionally, the orientation of the filler plays another important role in the dielectric constant and energy density of the composites. The detailed effect will be discussed in Chapter 3.

Figure 1-10. Predicted dielectric permittivity of the nanocomposites with different aspect ratio PZT-7A filler at different volume fraction; \( \alpha \) is the aspect ratio of the filler. (Reprinted with permission from Andrew et al. [67])

**Breakdown Strength of Composite**

Dielectric materials are widely used as insulating materials between two electrodes to avoid flashover or short circuit between two electrodes [24,75]. However, the applied electric field in the dielectric material cannot be increased without limit. Eventually, the threshold voltage is reached resulting in mechanical damage and electric conduction, which is called dielectric breakdown. The maximum electric field that the dielectric material can withstand is called breakdown strength. The breakdown strength of the capacitor is highly dependent on the defect density, where the samples are always broken at the weakest place. There are many mechanisms developed to
understand the dielectric breakdown of material. The most common type of breakdown mechanisms is electron avalanche breakdown [76-78]. With increasing electric field, a free electron acquires enough energy and then collides with a host atom of the material to knock out the other electrons. Both the primary and the released electrons can further cause ionization by colliding with other host atoms and thereby generate an electron avalanche, leading to conductivity and breakdown of the material. Electron avalanche breakdown is highly depended on the temperature. With increasing temperature, the possibility of the avalanche breakdown becomes much higher, since it is much easier for the electrons to migrate between two electrodes.

Another common mode of the breakdown of dielectric materials is thought to be caused by intrinsic, thermal and ionization mechanisms [24,75]. As the electric field in the dielectric material increases, the electric conduction and dielectric losses generate more heat leading to an increase in temperature. Consequently, certain parts of the material become hot spots inducing local melting and triggers physical and chemical erosion, resulting in breakdown. Therefore, thermal breakdown represents failure due to localization and non-uniform fields arising from conduction and dielectric losses.

Electromechanical breakdown and electro-fracture are another type of the materials’ breakdown mechanisms [79,80]. By increasing the electric field, two electrodes are pulled to each other because of the electrostatic field accumulated on the surfaces. The gap between two electrodes decreases and induces a mechanical stress in the sandwiched dielectric material. Eventually, the capacitor breaks down when the material cannot withstand this mechanical stress. Another cause for breakdown is the
initiation and growth of the internal cracks in the material because of the mechanical stress, which is called electro-fracture [79,80].

In conventional composites, the introduction of micro or even larger size fillers into the polymer usually reduces the breakdown strength of the composites [2,81-84]. The decreased breakdown strength is due to the aggregation of the fillers, which introduces defect center that distort and enhance the local electric field, leading to reduce the breakdown strength of the material [2,81-84]. The distortion of the electric field is primarily caused by the different dielectric permittivity between the filler and matrix. Additionally, the larger particle size, the higher probability of local field enhancement and the lower breakdown strength. Compared to conventional composites, nanocomposites with much smaller fillers improve the breakdown strength. In addition, the large interfacial areas of nanocomposites reduce the charge accumulation in the composite system, resulting in the improvement of breakdown strength [85]. Therefore, the breakdown strength in the nanocomposites is much higher than conventional composite. Roy et al. demonstrated that the nanocomposites with nanofillers have higher breakdown strength compared to the samples with microfillers [86]. They believed that the nanoparticles can disrupt the continuity of the path provided to the charge carriers resulting in higher breakdown strength [81].

Tanaka et al. proposed a famous model with multi-core construction to understand and describe the interfacial structure and charge behavior of spherical filler embedded in a polymer matrix [87]. As shown in Figure 1-11, the interface is composed of three layers. The first layer is a bonded layer which is equivalent to a transition layer tightly bonded to the polymer and particle filler by coupling agents such as silane. The
The second layer is an interfacial region including polymer chains interacting with the first layer. The thickness is around 2-9 nm depending on the strength of the polymer-particle interaction. The third layer is the loose layer containing free volume and the crystalline region of the polymer matrix. Due to the three different layers, a gradient of charge distribution is established between the particle and matrix. The charge distribution at the interfacial layers has a significant effect on the dielectric properties of the nanocomposite. Suitable alteration at the interface results in a change of charge carriers' mobility, free volume and trap sites. Better charge distribution at the interface can improve the breakdown strength. This can explain the phenomena of higher breakdown strength in the nanocomposites. For example, Ma et al. observed a decrease in the mobility of the charge carriers in the nanocomposite by incorporation of modified titanium dioxide with a polar silane coupling in the matrix [81]. The low concentration of the filler in the nanocomposites decrease the possibility of overlapping of the local conductive regions, leading to an improvement in the breakdown strength.

Figure 1-11. Muti-core model of interface in the nanocomposites. (Reprinted with permission from Tanaka et al. [87])
Based on the Tanaka’s model, the breakdown strength can be improved by filler’s surface functionalization to increase compatibility between filler and matrix and then help the filler’s dispersion in the matrix. Ma et al. reported an improvement in the breakdown strength by introduction of the polar silane modified TiO$_2$ nanoparticles into a polyethylene matrix [81]. The author found that the functionalization technique improved the electron scattering by the polar interfacial groups to decrease the possibility of the materials’ breakdown. Similar observations were made by Dou et al., who demonstrated that BaTiO$_3$/PVDF nanocomposites have increased breakdown strength after modifying the filler with iso-propyl alcohol [88]. Large enhancement of breakdown strength was observed at 7 vol.% of BaTiO$_3$ in PVDF. Without surface functionalization, the breakdown strength decreased with increasing filler concentration. In contrast, Perry et al. embedded phosphonic acid surfaced-modified BaTiO$_3$ into P(VDF-HFP) to fabricate high energy density nanocomposites (7-8 J/cc) [14]. Clearly, the surface functionalization can improve the dielectric property of nanocomposites; however, there is little agreement on how interfacial modification affects breakdown strength.

Based on the discussion about the mechanisms of dielectric permittivity and breakdown strength, nanocomposites offer significant promise for fabricating high energy density capacitor. The following sections will review the recent progress about nanocomposites for energy storage. They are classified into two different categories: nanocomposites with ferroelectric fillers and nanocomposites with non-ferroelectric fillers.
Nanocomposites with Ferroelectric Filler

Most of the current research has focused on nanocomposites with ferroelectric fillers for energy storage, since they typically have high dielectric constants, such as BaTiO$_3$, PZT, and PbTiO$_3$ so on [14,55,89-91]. Most ferroelectric ceramics have perovskite structure with the general composition of ABO$_3$, as shown in Figure 1-12.

![ABO$_3$ perovskite-type unit cell](image)

Figure 1-12. ABO$_3$ perovskite-type unit cell, with A$^{2+}$ ions shown in green and BO$_6$ corner-sharing octahedron.

Perovskites have high dielectric permittivity due to the spontaneous polarization, which is the net dipole moment within the unit cell as shown in Figure 1-13. The dipole moment results from the relative displacement of the O$^{2-}$, A$^{2+}$, and B$^{4+}$ ions from their symmetrical positions within the unit cell. The O$^{2-}$ ions are located near but slightly below the centers of each six faces, whereas the B$^{4+}$ ion is displaced upwards from the unit cell center [92]. Thus, a permanent dipole moment is associated with each unit cell as shown in Figure 1-13. This asymmetric structure gives rise to ferroelectric behavior with high dielectric permittivity ranging from 1000-6000. Therefore, researchers have tried to develop composites that utilize high dielectric permittivity from the perovskite fillers to produce high energy density.
BaTiO$_3$ is perhaps the most widely investigated ferroelectric filler for preparing high dielectric constant or high energy density nanocomposites. Wang et al. demonstrated the improvement of dielectric constant by dispersing surface-functionalized BaTiO$_3$ nanoparticles into two different ferroelectric polymer matrices: P(VDF-TrEE-CTFE) and P(VDF-CTFE) [16]. The authors showed that the surface functionalization of BaTiO$_3$ with ethylenediamine was important for the filler’s dispersion in the matrix and the nanocomposites based on P(VDF-TrFE-CTFE) had higher energy density due to its higher permittivity than that with P(VDF-CTFE). The incorporation of BaTiO$_3$ nanoparticles improved the polarization of the nanocomposites as shown in Figure 1-14. However, both nanocomposites showed the breakdown strength saturated around 150 MV/m. At 150 MV/m, the energy density of the nanocomposites with 30 vol% BaTiO$_3$ was 7.0 J/cc, which showed 120% improvement compared to neat P(VDF-TrFE-CTFE). This research generated a lot interest in the research community, since it was perhaps the first report of high energy density nanocomposites. This high energy density is based on the improved dielectric permittivity. Therefore, the incorporation of
high dielectric permittivity filler is an effective way to improve the dielectric permittivity of the overall composites. However, the reduced breakdown strength of the composite limits the improvement of the energy density at higher electric field.

Figure 1-14. The dependence of energy density of the nanocomposites on the volume fraction of BaTiO$_3$ in the P(VDF-TrFE-CTFE) and P(VDF-CTFE). A) energy density of nanocomposites with different concentration under electric field 100 and 150 MV/m. (B) D-E loops measured under different electric field for nanocomposites. (Reprinted with permission from Li et al. [16].)

Recently, Perry et al. embedded phosphonic acid surface-modified BaTiO$_3$ into P(VDF-HFP) with focus on fabricating high energy density capacitors with relatively high breakdown strength (>200 MV/m) as shown in Figure 1-15 [14,15]. The authors performed a very detailed study to demonstrate that the surface modification helped particles form uniform and high quality thin films. The research experimentally demonstrated that the nanocomposites with very high concentration fillers produced low energy density. Both dielectric constant and breakdown strength decreased at high volume fraction fillers (>50%) leading to a decrease of energy density as shown in Figures 1-15 and 1-16. The decreases were due to more defects and voids produced in the nanocomposites. The measured energy density was around 3.2 J/cc with 60 vol.% BaTiO$_3$, while the calculated maximum energy density was predicted as high as 7-8 J/cc.
as shown in Figure 1-16. The difference of energy density based two methods is because the calculated maximum energy density treated the nanocomposites as linear capacitors, which did not account the energy loss. This suggests that it is important to obtain actual energy density by calculation from D-E loop at high energy field.

Figure 1-15. Dielectric property of nanocomposites with BaTiO$_3$ in the P(VDF-HFP). A) Dielectric constant, B) loss tangent dependence on frequency. (Reprinted with permission from Philseok et al. [15]).

Figure 1-16. The breakdown strength and maximum energy density of nanocomposites with BaTiO$_3$ in the P(VDF-HFP). A) breakdown strength, B) maximum energy density of the nanocomposites with different concentration of filler in the P(VDF-HFP). (Reprinted with permission from Philseok et al. [15]).

One of the disadvantages of the nanocomposites with ferroelectric fillers is polarization saturation and high remnant polarization. Zhang et al. fabricated
nanocomposites by incorporation of functionalized BaTiO$_3$ particles into the ferroelectric polymer matrix P(VDF-CTFE) [19]. The incorporation of BaTiO$_3$ highly improved the dielectric permittivity and polarization of the nanocomposite. However, the D-E loop became large and polarization reached saturation at high electric fields as shown in Figure 1-17, which resulted in very low energy density. The large D-E loop came from the ferroelectric property of filler and matrix. Therefore, in order to fabricate high energy density capacitors, it is important to avoid ferroelectric properties from filler and matrix.

![Image](image_url)

Figure 1-17. D-E hysteresis of loops P(VDF-CTFE) 91/9 mol%/BaTiO$_3$ nanocomposite films with different concentration BaTiO$_3$ under unipolar electric field. (Reprinted with permission from Xia et al. [19])

**Nanocomposites with Non-ferroelectric Filler**

In order to capture high dielectric permittivity and simultaneously avoid ferroelectricity from fillers, a perovskite-like (ABO$_3$) body-centered cubic oxide, such as calcium copper titanate (CCTO) and Ba$_x$Sr$_{1-x}$TiO$_3$ ($x<0.7$), exhibits another promising solution for producing high energy density nanocomposites [93-97]. The crystal structure of CCTO is shown in Figure 1-18. This type of material exhibits giant dielectric constant and no curie temperature to affect the dielectric property because of the cubic
structure [98]. For example, CCTO exhibits giant dielectric constant ranging from approximately 10,000 for polycrystalline to 100,000 for single crystal along with no polarization saturation [99,100].

![Figure 1-18. The unit cell of CCTO crystal (green sphere represents Ca$^{2+}$, blue sphere represents Cu$^{2+}$ and octahedron represents TiO$_6$).](image)

Dang et al. incorporated CCTO particles in a polyimide matrix to prepare high dielectric permittivity composites [101]. The dielectric constant of the nanocomposites with 40 vol.% of CCTO (49) was 14 times larger than pure polyimide. In contrast, Prakas et al. created three phase composites with 25 vol.% of metallic aluminum powder into the CCTO/epoxy mixture [96]. The composites reached a dielectric constant as high as 700 compared to neat epoxy (4.81) [96]. However, most research did not report the breakdown strength to indicate the energy density of these composites. Tuncer et al. reported a similar composite with nano and sub-micron CCTO fillers in the epoxy matrix [102]. Interestingly, they showed that breakdown strength of the composites became more reliable after incorporation of fillers but still lower than 120 MV/m. The low breakdown strength may come from the lack of surface functionalization of CCTO. Another disadvantage of CCTO is a high energy loss.
associated with the composites because of the higher dielectric loss of CCTO [94,103]. Current researchers are trying to increase breakdown strength and decrease the energy loss of the CCTO nanocomposites, but this type of material is not the subject of this work.

Another ABO$_3$ body-centered cubic oxide is Ba$_x$Sr$_{1-x}$TiO$_3$ [20,104], which is a solid solution of BaTiO$_3$ and SrTiO$_3$ that transfers from a cubic phase to a tetragonal phase when the Sr fraction decreases. In the Ba$_x$Sr$_{1-x}$TiO$_3$ solid solution, transformation occurs from the ferroelectric phase to the paraelectric phase when the Ba molar fraction decreases below 0.7 (x<0.7) and begins to show low remnant polarization around room temperature [105,106]. The use of high dielectric filler such as a Ba$_x$Sr$_{1-x}$TiO$_3$ can provide high dielectric constant while eliminating the remnant polarization to improve efficiency of the capacitor. A novel high energy density nanocomposite capacitor with Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs with fast discharge speed will be prepared in Chapter 4.

Beyond high dielectric permittivity fillers, relatively low dielectric constant fillers are also studied to prepare nanocomposite capacitors for energy storage, such as TiO$_2$ [17], ZrO$_2$ [13] and kaolinite [18]. Li et al. reported high energy density nanocomposites based on surface-functionalized TiO$_2$ nanorods into P(VDF-TrFE-CTFE) [17], as shown in Figure 1-19. It is interesting that the incorporation of TiO$_2$ did not improve the dielectric permittivity but increased the electric displacement of the nanocomposites. For the composites with 10 vol.% TiO$_2$, the energy density was 6.9 J/cc at 200 MV/m, which was 45% higher compared to polymer matrix (4.7 J/cc at 200 MV/m). They argued that the improved energy density was due to the coalescing of the interface region and a reduction of the interface effect.
Figure 1-19. Nanocomposites with TiO$_2$ nanorods for energy storage: A) SEM image of nanocomposite with 30 vol.% TiO$_2$, B) the stored energy of nanocomposites with different applied electric field. (Reprinted with permission from Li et al. [17])

 Compared to most composites base on functionalized fillers, a new route toward high energy density nanocomposites was reported based on chain-end functionalized ferroelectric polymers [13]. As shown in Figure 1-20a, ferroelectric polymers were first modified with phosphonic acid end coupling, and then allowed to react with terminal groups of ZrO$_2$. With the formation of covalent coupling between the fillers and matrix, the fillers had great stability and uniform dispersion in the nanocomposites. As a result of the intimate coupling, the interfacial interaction regions between the nanoparticles and polymer matrix produced high energy density. The improvement of the energy density was mainly attributed from the polymer microstructures and the rise of the electric displacement was induced by the nanoparticles. As shown in Figure 1-20b, for the composites with 9.1 wt.% ZrO$_2$, the energy density was 11.2 J/cc at 270 MV/m, which was a 60% increase compared to the neat polymer matrix. It is noted that the energy density began to decrease when the filler concentration was higher than 9.1 wt.%, since the breakdown strength was highly decreased.
For practical applications, it is desirable to not only have a high energy density, but also maintain a high efficiency. In order to improve the efficiency and enhance the energy density of nanocomposites, Tomer et al. explored a promising route to improve the energy storage performance of PVDF, through a synergy of hexafluoropropylene (HFP) co-monomers and kaolinite clay nanofillers [18]. It should be noted that kaolinite fillers have lower dielectric constant (~3) compared to the P(VDF-HFP) matrix (~10), and have a layered structure enabling their high breakdown strength. The addition of these kaolinite fillers was expected to decrease the electric displacement of the nanocomposites, but markedly enhanced the breakdown strength as shown in Figure 1-21. The D-E loop was closer to a linear capacitor at a high volume fraction of kaolinite. Specifically, these composite films exhibited reduced high field losses, markedly
increased breakdown strength (780 MV/m), thus, ultra-high energy density value of 19 J/cc was achieved.

Figure 1-21. D-E loops and breakdown strength of P(VDF-HFP) and its nanocomposites with kaolinite fillers. A) D-E loops, B) Weibull distribution and observed dielectric breakdown strength of the stretched P(VDF-HFP) and its nanocomposite films with 5 wt.% kaolinite. (Reprinted with permission from Tomer et al. [18])

The papers detailed in this section have shown some of the important research for fabrication nanocomposite capacitors for energy storage. Most of the papers detailed have improved dielectric constant of the nanocomposites by incorporation of high dielectric permittivity ceramic fillers. However, the decreased breakdown strength because of the increased defect limits the final energy density. Therefore, the integration and geometry of the fillers must be optimized along to reach the maximum possible energy density of the nanocomposites. This dissertation will investigate the fabrication of nanocomposites based on high aspect ratio nanowires rather than the equiaxial particles as discussed by other researchers. The relationship between the filler’s structure (aspect ratio and orientation) and the energy storage of nanocomposites will be investigated. Finally, the dissertation will fabricate ultra-high energy density nanocomposites base on the findings.
Dissertation Overview

The following two sections will present the contribution of this research to high energy density nanocomposite capacitors and provide a detailed description of the research performed in each chapter.

Contributions

High power capacitors form a critical technology for numerous electronic applications; however, the current state-of-the-art technologies suffer from low energy density making them bulky and costly [2,6,7,107]. With the requirement of high energy density, fast discharge time and low loss in pulsed-power capacitors, much of the attention in high power capacitors has been applied to this class of materials [2,6,7,107]. One method to increase the energy density of these systems is through the use of polymer nanocomposites as an alternative to polymeric and ceramic dielectrics, which are commonly used for electrostatic energy storage [13,15-18,55]. Nanocomposites derive their high energy density from the use of a high dielectric filler and a high breakdown strength polymer. Additionally, the use of nanocomposites adds a degree of tunability to the capacitor allowing intricate configurations for electronic and electric devices in addition to the film thickness [13,15-18,55]. Therefore, nanocomposites are promising candidates for the next generation of high power capacitors that reach unprecedented energy density. This dissertation investigates the relationship between the structure (aspect ratio and orientation) and energy density of nanocomposites. The research performed here serves as a novel approach for the development of high energy density nanocomposite capacitors with high aspect ratio nanowires.
The first contribution lies in the development of a novel technique that allows for large-scale production of wide ranging compositions of perovskite NWs, many of which have never been demonstrated in this form, such as PZT, BaTiO$_3$ and Ba$_x$Sr$_{1-x}$TiO$_3$. Besides these synthesis methods, a process to control the aspect ratio of the BaTiO$_3$ NWs is demonstrated for the first time by tuning the hydrothermal reaction temperature. Additionally, a facile approach to the growth of high aspect ratio Ba$_x$Sr$_{1-x}$TiO$_3$ NWs with high yield and control over the stoichiometry of the solid solution is successfully developed. These three methods of large-scale production of the pervoskite NWs are significant contribution to the ferroelectric and nanomaterials communities.

Following the synthesis of high aspect ratio PZT NWs, the effect of the aspect ratio on the energy storage of the nanocomposites is investigated. It is demonstrated that the dielectric constant and energy density of the nanocomposites are both improved by PZT NWs compared to PZT NRs. The improvement of the dielectric constant is also found by using high aspect ratio BaTiO$_3$ and Ba$_{0.2}$Sr$_{0.8}$TiO$_3$. The relationship between the dielectric constant of the nanocomposites and the aspect ratio of the fillers is also quantified for the first time in this dissertation. These synthesis methods and results have generated high quality papers published in Nanotechnology, Nano Letter and a best paper award at ASME’s 2010 Best Paper in Materials and Material Systems.

Furthermore, this dissertation has also investigated the effect of the orientation on the energy density of the nanocomposites. Experimental results show that the dielectric constant and energy density of the nanocomposites are improved with 3-direction alignment. Additionally, a novel strategy to tune the orientation factor of NWs
by controlling the draw ratio during uniaxial force assembly can be used in any form of thermoplastic matrix. In order to characterize the NWs orientation factor, a method is proposed by Herman’s Orientation Factor based on the fast Fourier transform analysis of SEM images. This represents the first time the relationship between the filler’s orientation factor and the dielectric constant of the nanocomposites has been quantified. All these results present a new solution to improve the energy density and dielectric constant of the nanocomposites.

Finally, ultra-high energy density nanocomposites with fast discharge speed are developed based on high aspect ratio Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs. The energy density reaches to 14.86 J/cc at 450 MV/m, which has more than an order of magnitude higher energy density than commercial B OPP capacitors (1.2 J/cc at 640 MV/m) with faster discharge time to peak power and vastly improved power density.

In summary, this dissertation has made contributions in synthesis of perovskite NWs, and the fabrication, testing and evaluation of high energy density nanocomposites with fast discharge speed. The findings of this dissertation could lead to enhanced interest in nanowire based nanocomposites due to their potential application in achieving next generation energy storage devices and future pulsed-power capacitors.

**Chapter Summary**

Chapter 1 provides an introduction to previous work in the areas related to the research in this dissertation. It starts with the motivation of this dissertation. It is detailed that there has been an increasing demanding for the development of high energy capacitor to meet the requirement of the pulsed-power device. Nanocomposites are promising candidate for fabricating high energy density capacitors since they can combine the high dielectric permittivity from filler and high breakdown strength from the
polymer. However, the current nanocomposites still do not reach the desirable energy density. Therefore, the motivation of this research is to develop high energy density nanocomposite capacitors through high aspect ratio and aligned NWs. The Chapter 1 then moves on to detail fundamentals of capacitors. Following, a literature review of the previously research related to nanocomposites for energy storage has been performed. The Chapter 1 finishes with an outline of the work that has performed using NWs synthesis, fabrication and characterization of high energy density nanocomposites.

Chapter 2 investigates the effect of the aspect ratio on the dielectric constant and energy density of the nanocomposites. It begins with a detailed synthesis and characterization of two different aspect ratio particles: PZT NWs and PZT NRs. Nanocomposites are then prepared using the two different aspect ratio fillers. Experiment results are demonstrated that the dielectric constant and energy density of the nanocomposites are improved by high aspect ratio. Many researchers are following this route to make high dielectric permittivity nanocomposites, however, the relationship between the aspect ratio of filler and dielectric constant of nanocomposites is still not quantified in the literature. In order to quantify this relationship, a method to control the aspect ratio of the BaTiO$_3$ NWs is proposed. The results demonstrated that the dielectric constant of the nanocomposites increases with increasing the aspect ratio of the fillers. These findings open a new route to prepare high dielectric constant and high energy density composites.

In order to further enhance the energy density of the nanocomposites, Chapter 3 investigates the effect of the filler orientation on the energy storage of the nanocomposites. It begins with a literature review of the effect of alignment on the
dielectric constant of the nanocomposites along with various alignment methods. In this regard, a novel strategy to align nanowires in a thermoplastic matrix by uniaxial force assembly is developed. The results demonstrate that the increased dielectric constant of the aligned filler in nanocomposites can provide a platform to obtain materials with greater energy density. However, no experimental research is conducted to investigate the relationship between the fillers’ orientation factor and the dielectric constant of the nanocomposites. Here, the orientation degree of the nanowires in the nanocomposites is controlled by the draw ratio. The orientation degree is characterized by Herman’s Orientation Factor based on the fast Fourier transform analysis of cross-sectional SEM images of the nanocomposites. This is the first time to quantify the relationship between the filler’s orientation factor and the dielectric constant of the nanocomposites. Through alignment control, the effective dielectric permittivity of the nanocomposite can be tuned without requiring additional fillers. This finding provides another way to improve the effective dielectric constant and the energy storage performance of the nanocomposites.

Based on Chapter 2 and Chapter 3’s findings, Chapter 4 develops two techniques for developing high energy density nanocomposites based on high aspect ratio NWs. The first technique is based on nanocomposites composed of high aspect ratio BaTiO$_3$ NWs in P(VDF-TrFE-CFE). The results show that the energy density reaches to 10.48 J/cc at 300 MV/m. However, this type of nanocomposites exhibits polarization saturation and high ferroelectric loss from ferroelectric filler and matrix, which limits the improvement of energy density. In order to overcome these limitations, another technique is developed. A new synthesis process is developed to provide a
facile approach to the growth of high aspect ratio nanowires with high yield and control over the stoichiometry of Ba$_{x}$Sr$_{1-x}$TiO$_3$ NWs. The paraelectric phase Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ is chosen for the NWs combined with quenched PVDF to fabricate high energy density nanocomposite capacitors. Compared to BaTiO$_3$/ P(VDF-TrFE-CFE) nanocomposites, this type of nanocomposite can maintain high polarization with no saturation, high breakdown strength and also reduced ferroelectric loss. Therefore, the results demonstrate that high aspect ratio nanowires can be used to produce nanocomposite capacitors with greater performance than the neat polymers thus providing a novel process for the development of the next generation energy storage devices.

The final chapter of this dissertation is Chapter 5, which starts with a brief overview of the results found throughout this dissertation. After the overview, a discussion of the contribution in this dissertation is made and how will they affect the future research in nanocomposites are presented. The final section of this chapter and this thesis describes the future work that could be conducted in further the research.
CHAPTER 2
THE EFFECT OF FILLER ASPECT RATIO ON THE ENERGY DENSITY OF NANOCOMPOSITES

Chapter Introduction

This chapter focuses the effects of the filler aspect ratio on the dielectric constant and energy storage performances of the nanocomposites. The hypothesis of this chapter is that the aspect ratio of the filler will impact the dielectric permittivity of the nanocomposites, which in turn influences their energy density. In order to investigate the effect of the filler’s aspect ratio on the dielectric constant of the nanocomposites, this chapter will first develop a hydrothermal procedure to produce a high yield of high aspect ratio PZT nanowires (NWs), while the low aspect ratio PZT nanorods (NRs) are obtained by decreasing the PZT NWs by mortal pestle. Then, the effect of the filler’s aspect ratio on the dielectric constant and the energy storage performance of nanocomposites will be investigated. It will demonstrate that the dielectric constant and energy density of the nanocomposites can be improved by high aspect ratio fillers. This method provides a solution to fabricate high dielectric constant nanocomposites. However, there is no research to quantify the relationship between the filler aspect ratio and the dielectric constant of nanocomposites, especially at high aspect ratio. In order to quantify this relationship, a novel method is developed to synthesize and control the aspect ratio of BaTiO$_3$ NWs based on a two-step hydrothermal reaction by adjusting reaction temperature. Using the different aspect ratio BaTiO$_3$ NWs, the relationship between the filler’s aspect ratio and the dielectric constant of the nanocomposites will be quantified. Finally, the chapter will conclude with identifying relationship between the aspect ratio of NWs and the energy storage of nanocomposites.
Investigation of the Effects of Filler Aspect Ratio on the Energy Storage of Nanocomposites

Many theoretical models have demonstrated that the aspect ratio of the fillers play an important role in the dielectric permittivity of the composites [123,124,73], however, there is few experimental research to demonstrate this point. Most of current composites are based on equiaxial particles, since the high aspect ratio NWs are unavailable until recently. This section will focus on the fabrication nanocomposites with nanowires to improve the energy density. A method allowing for large-scale production of different aspect ratio fillers (PZT NWs and PZT NRs) with will be presented. The effect of filler aspect ratio on the dielectric constant and energy density of the nanocomposite will be experimentally investigated to provide a new route for fabricate high energy density capacitor in the future.

Preparation of Different Aspect Ratio Fillers: PZT NWs and PZT NRs

PZT NWs were synthesized through the following hydrothermal process [55,56,60,108]. Briefly, a mixture of 0.08 M (C₄H₉O)₄Ti (Alfa Aesar, 98%) ethanol solution and 0.10 M ZrOCl₂ (Alfa Aester, 98%) water solution were co-precipitated by the dropwise addition of a 0.15 M ammonia solution (Ricca Chemical Company, 28.0-30.0%). The precipitated ZrₓTi₁₋ₓO₂·nH₂O (ZTO) gel was washed with deionized water through centrifugation (Eppendorf, centrifuge 5810) and vortex (Fisher Scientific) mixing three times, and then dispersed into deionized water under stirring. Then, 0.11 M of Pb(NO₃)₂ (Alfa Aesar, 99%), 0.5M of KOH (Mallinckrodt Chemicals, ACS, 88%), and 0.4 g/L of poly(vinyl alcohol) (PVA) water solution were dissolved in the ZTO solution. The final mixture was transferred into a 150ml Teflon lined stainless steel autoclave with a fill factor of 80%. The reaction vessel was kept at 200 °C for 4 hours under vigorous
stirring. After the hydrothermal process was complete, the precipitate was removed from the reactor and washed with water for four times through centrifugation and vortex mixing, and subsequently dried on a hotplate at 80 °C overnight. The resulting powder was a PX phase of PZT nanowires (PX is used to note the non-perovskite phase because of similarity to phase of PbTiO$_3$). The powder was then heated at 600 °C for 2 hours to transform PX phase to perovskite PbZr$_{0.2}$Ti$_{0.8}$O$_3$ phase [108].

In order to effectively evaluate the effect of the filler aspect ratio on the dielectric constant and energy storage performance of nanocomposites, the PZT NWs were ground with a sapphire mortal pestle for 30 minutes in ethanol to form low aspect ratio PZT NRs, then dried overnight at 80 °C. The morphology of the separated PZT NWs and NRs are shown in Figure 2-1 (a) and (b), respectively. It should be mentioned that there has been a great deal of research devoted towards the synthesis of PZT NWs due to their excellent ferroelectric and piezoelectric properties. However, control over the morphology and yield of as grown PZT NWs still poses a challenge in the field of nanotechnology. Here, a hydrothermal reaction was developed to procedure high yield and high quality PZT NWs. The aspect ratio of the acicular PZT particle was analyzed using SEM images through ImageJ software as shown in Figure 2-2. The PZT NWs are measured to have an aspect ratio of approximately 14 with a mean diameter of 160 nm and a mean length of 2.2 μm, while the PZT NRs have an aspect ratio of approximately 3 with a mean diameter of 200 nm and a mean length of 0.6 μm. Using the PZT nanoparticles with different aspect ratios allows for the characterization of the effect of the filler aspect ratio on the dielectric constant and energy storage performance of the nanocomposites.
In order to demonstrate that the phase of PZT has not changed during grinding, both the PZT NWs and PZT NRs are characterized using XRD as shown in Figure 2-3.
From the XRD trace it can be determined that the crystalline structure of the PZT before (NWs) and after (NRs) grinding is unchanged and closely match the structure of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (JCPDS No. 01070-4261). The Zr/(Zr+Ti) ratio can be verified using the XRD characterization along the Gaussian fitting to determine the structure of PZT. The (002) and (200) planes are used to calculate the lattice parameters (a, c) as well as the c/a ratio. The Gaussian function is used to fit the peaks that account for the 002 and 200 diffraction peaks as shown in Figure 2-4. The lattice parameters can be calculated by using Bragg’s law:

\[ 2dsin\theta = n\lambda \]

where \( d \) is the lattice plane distance, \( \theta \) is the scattering angle, \( n \) is an integer determined by the order given, and \( \lambda \) is the wavelength of the X-ray source (Cu K\( \alpha \), 0.1541 nm). It shows that the calculated lattice parameters of PZT are: \( a=3.935 \text{ Å}, \) \( c=4.135 \text{ Å} \) and \( c/a=1.051 \). Funakubo et al [109] performed a detailed study regarding the relationship between Zr/(Zr+Ti) ratio and c/a ratio as shown in Figure 2-4c, which indicates that the c/a ratio is approximately 1.051 when the Zr/(Zr+Ti) is about 0.2. Additionally, these lattice parameters (\( a=3.935 \text{ Å}, \) \( c=4.135 \text{ Å} \)) closely match the data found in the literature for PbZr$_{0.2}$Ti$_{0.8}$O$_3$ [110,111]; therefore, the composition of the PZT NWs synthesized here is PbZr$_{0.2}$Ti$_{0.8}$O$_3$. From the SEM and XRD, it can be seen that the only difference between the PZT NWs and PZT NRs is the aspect ratio of the particles, while the crystal structures of PZT NWs and NRs are the same. The next step is to verify the particle dispersion in the matrix by SEM observation and also the crystal phase of the PVDF matrix by FTIR. Following these analyses, the effect of the filler
aspect ratio on the dielectric properties and energy density of the nanocomposites can be studied more thoroughly.

Figure 2-3. XRD patterns of PZT NWs and PZT NRs.

Figure 2-4. Gauss fit of XRD. A) (002) plane XRD data with gauss fit, B) (200) plane XRD data with gauss fit, C) Zr/(Zr+Ti) ratio dependency of c/a ratio, report data from PZT powder by Funakubo et al [109].
Fabrication of Nanocomposites with Different Aspect Ratio Fillers

The nanocomposites were prepared by dispersing the PZT particles into a PVDF/DMF solution by sonicating for 30 minutes, then solution cast onto a glass plate and dried at 60 °C under vacuum overnight. In order to decrease the thickness and obtain smooth void free films, the resulting films were further hot pressed at 170 °C for one hour allowing a final film thickness of 0.1-0.2 mm. Finally, silver paint was applied to the top and bottom surfaces of the samples to act as the corresponding electrodes for electrical measurement.

The microscopic homogeneity of the nanocomposite is observed by imaging their top surfaces as shown in Figure 2-5. It is clearly shown that both of the PZT NWs and PZT NRs show homogeneous dispersion in the PVDF matrix. Each volume fraction is characterized using the same procedure and all demonstrated a homogeneous dispersion. As the previous study indicated, the dispersion of inorganic fillers in these fluorinated polymers is problematical due to the low surface energy of the polymers [14-16,19-21]. Agglomeration of the ceramic in the composites will significantly lower the energy density due to a reduction of the breakdown strength. A good dispersion of PZT NWs and NRs in the polymer is required to ensure high energy density of nanocomposite as well as the generation of reproducible measurements.
In order to demonstrate that fillers with different aspect ratios do not influence the phase of the polymer, Fourier-transform infrared (FTIR) spectroscopy was performed with a Nicolet 10 FTIR with a Smart Orbit ATR accessory to characterize the phase of PVDF in nanocomposite with different aspect ratio fillers, as shown in Figure 2-6. The FTIR spectrum of the nanocomposites with PZT NWs and NRs are very similar and clearly shows that the phase of PVDF does not change in either nanocomposite, while both PVDF matrices are predominantly in the β phase [112,113]. The nanocomposites differ only in the aspect ratio of the fillers, since the crystal structure of the two PZT particles and the PVDF do not change during the preparation and both fillers have good dispersion in matrixes. Therefore, the samples with PZT NWs and NRs in PVDF can be used to investigate the effect of aspect ratio on the dielectric property and energy storage performance.
The Effect of Filler Aspect Ratio on the Dielectric Constant

The dielectric constants of nanocomposites with various volume fractions of PZT NWs and NRs are compared with values predicted by the Maxwell model, as shown in Figure 2-7. It indicates that the dielectric constant of the composites increase with an increasing volume fraction of either NWs or NRs. This increase is attributed to the higher dielectric constant of PZT fillers compared to the PVDF matrix. More importantly, the nanocomposites with high aspect ratio PZT NWs have higher dielectric constant than the samples with low aspect ratio PZT NRs. For example, the dielectric constant of the nanocomposite containing PZT NWs is 21% larger than that of a nanocomposite containing PZT NRs at 50 vol.%. 

Many theoretical models have been developed to predict the effective dielectric constant of a 0-3 composite system. For nanocomposites, a third phase in the composite, such as grain boundaries and interfaces, are substantial and cannot be neglected. The Maxwell Model is formulated to include such broad assumptions and is based on the mean field theory of a single spherical inclusion surrounded by a
continuous polymer matrix [71]. Maxwell’s model is valid for volume fractions between 10-50%, which is the range of interest for this study. In a 0-3 composite system, the effective dielectric constant ($\varepsilon_{\text{eff}}$) can be expressed as

$$
\varepsilon_{\text{eff}} = \varepsilon_1 \frac{\varepsilon_2 + 2\varepsilon_1 - 2\phi(\varepsilon_1 - \varepsilon_2)}{\varepsilon_2 + 2\varepsilon_1 - \phi(\varepsilon_1 - \varepsilon_2)}
$$

where $\varepsilon_1$ and $\varepsilon_2$ represent the dielectric permittivity of the polymer matrix and the ceramic filler, respectively, and $\Phi$ is the volume fraction of the filler. In this model, $\varepsilon_1$ and $\varepsilon_2$ are chosen as typical values of 10 and 1600, respectively. From Figure 2-7, it can be seen that better agreement is exhibited for the composites with NRs compared to NWs. Since the Maxwell model considers the filler as a single spherical inclusion, it makes sense that dielectric constant is much closer to the model when the aspect ratio decreases from PZT NWs to PZT NRs. With increasing aspect ratio of the fillers, the dielectric constant of the nanocomposites diverges from the Maxwell model, as shown in Figure 3-7 [55,56,67,72-74].

![Figure 2-7](image-url)

Figure 2-7. Comparison of measured dielectric constant (at 1 KHz) of nanocomposites as a function of PZT NWs and NRs volume fractions with predicted values from Maxwell model.
Figure 2-8 shows the dielectric constant of the nanocomposites with various PZT volume fractions over a frequency range of 1 kHz to 1 MHz. It shows that the dielectric constant of the composites increases with an increase in the concentration of filler. Also, the dielectric constant decreases with increasing the frequency. At low frequency, the dipoles can move sufficiently fast to follow the electric field. However, as the frequency increases the dipole cannot shift orientation sufficiently fast as the applied electric field exceeds its relaxation frequency, resulting in a decrease in the dielectric constant at high frequency [31]. Additionally, the dielectric constant of nanocomposites with a high volume fraction of fillers decreases much faster than those with a lower volume fraction of filler. This occurs due to the high dielectric permittivity of PZT fillers which results due to orientation polarization and space charge polarization, which decrease faster at high frequency compared to PVDF matrix [31].

![Figure 2-8. Dielectric constants of nanocomposites with different PZT volume fraction depended on the frequency: A) PZT NWs/PVDF nanocomposites, B) PZT NRs/PVDF nanocomposites.](image)

The loss tangent of nanocomposites with varying volume fraction of PZT particles is shown in Figure 2-9. It is demonstrated that the loss tangent increases with frequency and decreases with increasing volume fraction of the PZT fillers.
dielectric loss is mainly due to a resonance of the matrix; therefore, the high volume fraction of PZT particles in the polymer matrix leads to a low loss tangent [15]. At high frequency, the loss tangent of the nanocomposite with NWs is lower than that with NRs, especially at high volume fractions such as 50% PZT NWs. According to Figure 2-9a, the loss tangent of the 50% PZT NW sample is 0.031 at 1 kHz, which is smaller than other nanocomposites currently reported in the literature [16,17].

![Dielectric loss tangent of different PZT volume fraction in PVDF from 1 kHz to 1 MHz: A) PZT NWs/PVDF nanocomposites, B) PZT NRs/PVDF nanocomposites.](image)

The Effect of Filler Aspect Ratio on the Energy Density

In order to characterize the energy storage capability of the nanocomposites, the electric displacement-electric field (D-E) loops of the nanocomposites were measured using a Sawyer-Tower circuit, which allowed for the direct computation of the energy density [33,114]. As shown in Figure 2-10, the sample capacitor and linear sensing capacitor are in series in the circuit, and connected to a high voltage source and oscilloscope. The voltage on the sensing capacitor is recorded on an oscilloscope. In the series circuit, the charge is the same across the sample and capacitor, since the capacitors are in series as shown in Figure 2-10. Therefore, the charge on the tested
sample can be obtained from the sensing capacitor. The electric displacement can be calculated by dividing the charge to the area of the sample.

![Diagram](image1.png)

**Figure 2-10.** The Sawyer Tower circuit and mechanism

Based on the measurement of the Sawyer-Tower circuit, a typical hysteresis curve of the nanocomposite sample can be obtained as shown in Figure 2-11. The energy density of the nanocomposites can be calculated from the D-E loops based on the integration of the discharge curve of the D-E loop as the shaded area in Figure 2-11,

![Diagram](image2.png)

**Figure 2-11.** Typical hysteresis loop and energy density calculation of nanocomposites.

Typical D-E loops measured at different electric field and various volume fractions are presented in Figure 2-12. The PZT particle concentration notably raises the electric displacement, which is attributed to the high polarization of the PZT fillers.
compared to PVDF matrix. Also, the electric displacements of the nanocomposites increase with the applied electric field, which indicates that the energy density can be achieved at higher electric field. It should be noted that the PZT NW nanocomposites have a larger electric displacement than the PZT NR samples. For example, at an electric field of 15kV/mm and a 50% volume fraction, the NWs achieve an electric displacement of 0.787 μC/cm², while NRs only have an electrical displacement of 0.471 μC/cm². This difference shows an increase of 67.1% for nanocomposites with high aspect ratio fillers compared to the lower aspect ratio materials.

![Figure 2-12. Electric displacement-field (D-E) loop measured under different applied fields at room temperature and 100 Hz for the polymer and nanocomposite: A) PZT NWs/PVDF nanocomposites, B) PZT NRs/PVDF nanocomposites.](image)

Figure 2-13 presents the stored electrical energy density of the PZT nanocomposites calculated from the D-E loops of Figure 2-12. It indicates that that the energy density of the nanocomposites is strongly dependent on the concentration of PZT particles and clearly shows that the energy density increases with the electric field. Most importantly, high aspect ratio NW improves the energy density more than lower aspect ratio NR. For example, the energy storage of a 40% PZT NW nanocomposite is nearly equal to that of a 50% PZT NR nanocomposite. The measured energy density of
a nanocomposite with 50% NWs at an electric field 15 kV/mm is 0.0528 J/cm$^3$, which is 77.8% larger than that of the 50% NR sample (0.0297 J/cm$^3$).

![Graph showing the dependence of energy density on the PZT volume fraction in a PVDF matrix under 15 kV/mm: PZT NWs/PVDF nanocomposite (blue) and PZT NRs/PVDF nanocomposite (red).]

Figure 2-13. The dependence of energy density on the PZT volume fraction in a PVDF matrix under 15 kV/mm: PZT NWs/PVDF nanocomposite (blue) and PZT NRs/PVDF nanocomposite (red).

Results of this study indicate that the aspect ratio of the filler significantly affects the dielectric constant and energy density of the nanocomposites. The nanocomposites with high aspect ratio PZT NWs exhibits improved energy density, which is attributed to the increased dielectric constant with NWs compared to NRs. It is well known that a material with higher dielectric permittivity will have higher energy density at the same electric field, since the energy density is linearly related to the dielectric constant.

In this work, the dielectric constant of nanocomposites with NWs is shown to be larger than nanocomposites consisting of lower aspect ratio NRs. The phase of the matrix and PZT inclusions are the same from the FTIR and XRD characterization, respectively. Therefore, it is implied that the aspect ratio of the PZT NWs is responsible for the change in the dielectric constant of nanocomposites. Additionally, the Brunauer-Emmet-Teller (BET) surface analysis can conclude that the aspect ratio plays a critical
role in defining the dielectric constant and energy density of the nanocomposite. BET surface area of PZT NWs and NRs are 3.46 m$^2$/g and 5.07 m$^2$/g, respectively, which means that nanocomposites with NRs have higher interfacial area than the samples with NWs. Some researchers have proposed that the dielectric constant of the composite increases with an increase in the interfacial area between the filler and matrix [115-117]. The PZT NRs have higher surface area compared to NWs and therefore, the interfacial area is not responsible for the increased dielectric permittivity and energy storage in this case. Consequently, the aspect ratio plays important role in enhancing the dielectric permittivity in this work.

A study of the electrical conductivity of composites consisting of insulating polymer and conductive filler, results concludes that it does not increase monotonically with increasing filler concentration. A critical volume concentration exists for these composites and is also called the percolation threshold [118-120]. When the concentration reaches the percolation threshold, the properties are drastically changed due to the formation of a connective passage that resembles a continuous filler network. For example, the insulating state could be changed to a semiconducting or a conducting state at percolation threshold [118-120]. Previous research has also shown that the percolation threshold is strongly related to the aspect ratio of filler with a larger aspect ratio leading to a smaller percolation threshold [118-120]. Therefore, the high aspect ratio filler (nanowire) reach the percolation threshold at a lower volume fraction than a low aspect ratio filler (nanorod or nanoparticle).

The dielectric properties of composites can be enhanced by several orders of magnitude depending on the manner in which connections are made [121], when the
fillers reach the percolation threshold. Therefore, the dielectric constant of the nanocomposites with PZT nanowires is much higher than that with PZT nanorods, since the NW is much easy to reach the percolation threshold in the polymer compared to NR. Additionally, the high aspect ratio nanowires can improve the dielectric constant of the composites due to the large dipole moment [122]. Previous BET results have demonstrated that high aspect ratio fillers had a lower surface area than low aspect ratio fillers, which helps to reduce the surface energy and thus prevent agglomeration in the nanocomposites. Considering all these reasons, the NWs with large aspect ratio are more effective enhancements of the dielectric constant of the nanocomposites. Thus, the nanocomposites with PZT NWs have higher energy density than that with PZT NRs because of the improvement in the effective dielectric permittivity. The results presented here clearly indicate that the use of high aspect ratio fillers can lead to significant improvement in energy storage density, which will be employed to fabricate high energy density nanocomposite capacitors.

**Quantification of the Relationship between the Filler Aspect Ratio and Dielectric Constant of the Nanocomposites**

The previous research has demonstrated that high aspect ratio (AR) fillers can improve the dielectric constant of the nanocomposites more efficiently compared to the spherical fillers. Also, many theoretical models have shown that high aspect ratio fillers can improve the dielectric constant of the nanocomposites [123,124,73]. This discovery has led many researches to follow this route to prepare composites with improved dielectric permittivity [21,125-127]. However, high AR fillers still have not been investigated as extensively as spherical fillers because of challenges in manufacturing NWs, especially for AR>15. Here, the relationship between the AR of the filler and the
The dielectric constant of the nanocomposites is quantified in this work. A novel and simple method has been developed to tailor the AR of BaTiO$_3$ NWs with an AR as high as 45.8. The dielectric constant of the nanocomposites with 30 vol.% and an AR of 45.8 NWs can be as high as 44.3, which is 3.5 times larger than the neat PVDF polymer. Therefore, the research performed here can be applied to manufacture high dielectric constant capacitors and provide a solution for the improvement of energy storage performance of future nanocomposites.

The synthesis of BaTiO$_3$ NWs was accomplished through a two-step hydrothermal reaction [128,129]. First, high aspect ratio sodium titanate nanowires were synthesized. Typically, 1.88g of anatase titanium dioxide powder (Sigma-Aldrich, ACS, 99%) was mixed with 91ml of a 10M sodium hydroxide (Fisher, ACS, 99%) aqueous solution. Then, the mixed solution was transferred into a 130ml Teflon-lined autoclave. The solution was sealed in a stainless steel autoclave and stirred at certain temperature for 24 hours. After the autoclave was cooled to room temperature, the obtained sodium titanate NWs were washed with water then soaked in diluted 0.2M hydrochloric acid (Fisher, 37%) for 4 hours to yield hydrogen titanate NWs. The resulting powder was then washed with water four times through centrifugation and vortex mixing with subsequent drying on a hotplate at 60 °C overnight. In order to adjust the aspect ratio of the hydrogen titanate NWs, the hydrothermal temperature is changed from 150 °C to 240 °C. Figure 2-14 shows the SEM images of the hydrogen titanate NWs synthesized at different temperatures. It is shown that the precursor sodium titanate is free-standing NWs. With an increase in temperature, the length of the NWs is increased much greater compared to the diameter, resulting in a higher AR.
The BaTiO$_3$ NWs were synthesized from the hydrogen titanate NWs by a second hydrothermal reaction in an aqueous with barium ions source. After the hydrothermal process was completed, the precipitate was collected and washed with 0.2M diluted HCl aqueous solution, water and ethanol to yield BaTiO$_3$ NWs. The second hydrothermal process was designed to specifically maintain the morphology of the nanowires since the morphology is highly dependent on the hydrothermal reaction parameters, such as the temperature, duration and nature of the precursors and as can be seen by Scanning Electron Microscopy (FE-SEM; 6335F, JEOL). Figure 2-15 shows the free-standing BaTiO$_3$ NWs after second hydrothermal transformation from the precursor hydrogen...
titanate. The surfaces of BaTiO$_3$ NWs are much rougher compared to precursor hydrogen titanate, which is because the Ba ions diffuse into the precursors and forms particles on the surface. It should be mentioned that the morphology of the BaTiO$_3$ is highly dependent on conditions of the second hydrothermal process, such as the temperature, duration and nature of the precursors. The BaTiO$_3$ can be varied from cubic, starfish-like, and snow flake-like during the second hydrothermal transformation.

Figure 3-13 shows that the morphology of BaTiO$_3$ was preserved from the hydrogen titanate with free-standing NWs. Additionally, the aspect ratio of BaTiO$_3$ NWs increases with increasing reaction temperature of the hydrogen titanate (Figure 2-16).

Figure 2-15. SEM images of BaTiO$_3$ NWs prepared at different temperature. A) 150 °C, B) 180 °C, C) 200 °C, D) 240 °C.
Figure 2-16. BaTiO$_3$ particle size distribution dependent on the hydrothermal temperature: A) 150 °C, B) 180 °C, C) 200 °C, D) 240 °C.
Chemical composition of nanowires was studied by an energy-dispersive X-ray spectroscopy (EDX, GENESIS), as shown in Figure 2-17a. The successful transformation of BaTiO$_3$ nanowires after diffusion of the Ba ions into the precursor NWs during the hydrothermal reaction is confirmed due to the presence of Ba, Ti and O. It should be mentioned that the it is hard to clearly observe the of the separate peaks of Ba and Ti, since the main peaks of Ba (L-edge) and Ti (K-edge) overlap in the energy range of 4.5-5 keV [130]. XRD equipped with a curved position sensitive detector (CPS120, Inel) with Cu Kα radiation was used to determine the structure of the BaTiO$_3$ NWs and is shown in Figure 2-17b. All the diffraction peaks can be assigned to the BaTiO$_3$ crystal structure (JCPDS, 81-2203) without any indication of crystalline by-products such as BaCO$_3$ or TiO$_2$. Therefore, the BaTiO$_3$ NWs were successfully transformed by the second hydrothermal reaction.

![Figure 2-17. Verification of BaTiO$_3$ NWs. A) typical EDS spectra, B) XRD patterns.](image)

The BaTiO$_3$ NWs are transformed directly from the precursor of hydrogen titanate, therefore, the aspect ratio distributions of BaTiO$_3$ NWs are dependent on the hydrothermal temperature of the precursor. The aspect ratio of BaTiO$_3$ are analyzed.
from SEM pictures by using ImageJ software and summarized in the Figure 2-18. It shows that the aspect ratio of the BaTiO$_3$ NWs is dependent on the hydrothermal temperature used to synthesize the precursor NWs. From the Figure 2-18, it is clearly shown that the length of NWs increases at a faster rate than the diameter of the NWs. The aspect ratio is increased from 9.5 to 45.8 with a corresponding increase in temperature from 150 °C to 240 °C, respectively, as shown in Figure 2-18.

![Graph showing aspect ratio vs. temperature](image)

**Figure 2-18.** The relationship between the aspect ratio of BaTiO$_3$ NWs and hydrothermal reaction temperature.

In order to increase compatibility and improve dispersion of the fillers in the matrix, the BaTiO$_3$ NWs were surface functionalized with ethylenediamine. The powder was mixed with ethylenediamine by vortex mixing, sonicated for 1 hour, and heated in a 90 °C water bath for another hour. The NWs were separated by centrifugation and dried at 70 °C on a hotplate overnight. FTIR spectroscopy was performed with a Nicolet 10 FTIR with a Smart Orbit ATR accessory to confirm the functionalization of the nanowires. Figure 2-19a shows the FTIR spectra of the BaTiO$_3$ NWs before and after the surface modification with ethylenediamine. Evidence of ethylenediamine binding
can be confirmed by an amine group (N-H) adsorption around 1450 cm\(^{-1}\)[131], which is known to act as a bridge to bind BaTiO\(_3\) with a PVDF matrix as shown in the Figure 2-19c. The nanocomposites were prepared by first dispersing the BaTiO\(_3\) NWs into a 7 wt.% PVDF in dimethylformamide (DMF) solution through 1 hour of sonication. Then the solution was cast onto a glass plate to obtain thin films. The films were then dried at 80 °C under vacuum overnight. The obtained films were heated at 200 °C for 10 min, and then dried at room temperature for 24 hours and peeled from the glass plate. Figure 2-18b shows the top surface of a nanocomposite with 10 vol.% BaTiO\(_3\) NWs. It indicates that the functionalized fillers have been homogenously dispersed in the PVDF matrix without voids in the film. Because of the surface-modification of BaTiO\(_3\) NWs using amine groups, there is an increase in the compatibility between filler and matrix, and a homogenous dispersion in the PVDF matrix is formed as shown in Figure 2-19b.

![Figure 2-19](image)

Figure 2-19. BaTiO\(_3\) NWs functionalization and nanocomposites. A) FTIR spectra of BaTiO\(_3\) NWs and modified BaTiO\(_3\) NWs by ethylenediamine, B) SEM topography of the nanocomposites with 10% BaTiO\(_3\) NWs, C) schematic image of the functionalized BaTiO\(_3\) by ethylenediamine reacting with PVDF.
The dielectric constants of the nanocomposites were measured with an Agilent 4980A LCR meter at a frequency of 1 kHz with a parallel equivalent circuit at room temperature. Gold electrodes with a thickness of approximately 10 nm were sputtered onto both surfaces of the film and served as contact points for the dielectric constant measurements. The dependency of the nanocomposite’s dielectric constant on volume fraction and aspect ratio of the fillers is shown in Figure 2-20. The dielectric constant of the nanocomposites increases with increasing volume fraction of filler due to the higher dielectric permittivity of BaTiO$_3$ as compared to PVDF polymer. Figure 2-20 clearly demonstrates that the dielectric constant of the nanocomposite can be significantly increased through an increased aspect ratio of BaTiO$_3$ NWs. It should be noted that the dielectric constant of the nanocomposite with 30 vol.% BaTiO$_3$ NWs (aspect ratio 45.8) can reach a dielectric constant as high as 44.3, which is 30.7% higher than samples with a low aspect ratio (9.3) and 352% larger than the polymer matrix. This technique efficiently improves the dielectric property of the nanocomposites without the need for additional fillers.

Figure 2-20. Dielectric constant of the nanocomposites as a function of aspect ratio and volume fraction of BaTiO$_3$ NWs.
This section has determined the relationship between the aspect ratio of fillers and the dielectric constant of the nanocomposites. The result clearly shows that the dielectric constant of the nanocomposites can be improved through increasing higher aspect ratio of the filler. Various theoretical models have correlated improved dielectric constant with high aspect ratio fillers [73,74,123]. The benefits of using high aspect ratio fillers can be also explained through the following aspects. First, the high aspect ratio fillers reach the percolation threshold at lower volume fraction than low aspect ratio nanowires, which allows connectivity in the system and improves the dielectric properties of the nanocomposites [118,119]. Additionally, the high aspect ratio nanowires can improve the dielectric constant of the composites because of their large dipole moment [122]. Finally, Brunauer-Emmer-Teller (BET) surface area analysis, detailed in this chapter, has also demonstrated that high aspect ratio fillers have lower surface area than low aspect ratio fillers, which helps reduce the surface energy and thus prevents agglomeration in the nanocomposites. All these aspects work to make high aspect ratio nanowires more effective in increasing the dielectric constant of the nanocomposites.

**Chapter Summary**

This chapter has demonstrated that the energy density of nanocomposites can be enhanced through high aspect ratio NWs. Specifically, nanocomposites are prepared by using two different aspect ratio fillers in a PVDF matrix: PZT NWs and PZT NRs. It was demonstrated that the high aspect ratio PZT NWs can improve the dielectric constant of the nanocomposites resulting higher energy density. The high aspect ratio PZT NWs show a 77.8% increase in energy density over the lower aspect ratio PZT NRs under an electric field of 15 kV/mm and at a 50 vol.%. 

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This chapter presented a highly efficient method for the large-scale synthesis of high quality PZT NWs. In addition, a novel synthesis method based on a two-step hydrothermal reaction is presented to achieve a high yield of BaTiO$_3$ NWs. This work is the first time to report the control of aspect ratio of the BaTiO$_3$ NWs by changing the hydrothermal reaction temperature from 150 °C to 200 °C, which corresponding to the AR from 9.3 to 45.8, respectively. Based on these different aspect ratio BaTiO$_3$ NWs, the relationship between the dielectric constant of nanocomposites and the aspect ratio of the fillers is quantified. The dielectric constant of the nanocomposites is significantly enhanced by using higher aspect ratio NWs. Nanocomposites with a 30 vol.% of BaTiO$_3$ NWs (aspect ratio 45.8) can reach a dielectric constant as high as 44.3, which is 30.7% higher than samples with an aspect ratio of 9.3 and 352% larger than the PVDF matrix.

The results presented in this chapter demonstrate that the use of high aspect ratio NWs is an effective way to tune and improve the dielectric and energy storage performance of nanocomposite capacitors. Future work related to Chapter 2 includes the synthesis of NWs and development of the high energy density nanocomposite capacitors based on the fundamental finding in this chapter. The Chapter 3 will investigate the effects of the orientation of the fillers in the matrix and how it influences the dielectric constant and energy storage performance of the nanocomposites.
CHAPTER 3
THE EFFECT OF FILLER ORIENTATION ON THE ENERGY DENSITY OF NANOCOMPOSITES

Chapter Introduction

Chapter 2 has demonstrated that high aspect ratio fillers can improve the energy density of the nanocomposites. This chapter focuses the effects of the filler orientation on dielectric constant and energy storage performances of the nanocomposites. It begins with a review of the effects of filler orientation on the dielectric property of the composites. Then, a novel method is proposed to align the NWs in a thermoplastic matrix by uniaxial force assembly. By using the NWs aligned in the polymer, the effects of the NWs’ orientation on dielectric constant and energy density of the nanocomposites are studied through three different directions: random, 1-direction alignment and 3-direction alignment. It will be shown that the orientation plays an important role in the dielectric property and energy density of the nanocomposites. Additionally, a new characterization method is proposed to quantify the NWs’ orientation factor by Herman’s Orientation Factor based on the fast Fourier transform analysis of cross-sectional SEM images of the nanocomposites. The orientation factor of nanowires is controlled by the draw ratio of the nanocomposites. Finally, the relationship between the orientation factor and the dielectric constant of the nanocomposites is quantified for the first time. The key contribution of Chapter 3 is to provide another solution to improve the energy density of nanocomposites by controlling the orientation of NWs.

Alignment Methods and Their Effects

Past research has been demonstrated composites with aligned filler can influence the dielectric properties of a material, specifically the dielectric constant and breakdown strength [72,132,133]. Andrew et al. [74] and Patil et al.[134] have
developed finite element models and the equivalent capacitance model, respectively, to show that the fillers aligned in the electric field direction can improve the dielectric constant of composites. Bowen et al. created anisotropic fillers for composites by using a dielectrophoretical assembly process [72]. The samples with aligned fillers had a dielectric constant approximately three times higher than that with randomly distributed fillers. However, the improved dielectric permittivity came at the expense of the breakdown strength [9]. This drop in breakdown strength has also been reported in the case of composites with randomly dispersed ceramic filler. Tomer et al. used the dielectrophoretical assembly method to obtain aligned BaTiO$_3$ in a silicone elastomer thermoset polymer and found the dielectric constant in the applied electric field direction was much larger than random sample [132]. However, the breakdown strength decreased when compared to a nanocomposite with random orientation. Later, Tomer et al. aligned high aspect ratio organomontmorillonite (MMT) in a polyethylene (PE) matrix and demonstrated the improvement in both the dielectric constant and breakdown strength, leading to higher energy density [133]. These results indicate that the fillers’ orientation must be carefully controlled to obtain high dielectric constant and breakdown strength to achieve materials with high energy density.

Alignment of NWs has been achieved by many methods, such as dielectrophoresis [72,132,133,135], extrusion methods [136,137], Langmuir-Blodgett troughs [138,139], microfluidics [140,141], blown-bubble-films [142,143], strain-release assembly [144,145] and contact printing [146,147]. However, most of these methods only align the NWs on the surface or in the plane of the substrate, making them unsuitable for preparing bulk nanocomposites. Furthermore, while the use of
dielectrophoresis can obtain bulk nanocomposites with aligned filler, only samples with low volume fraction of filler can be aligned [132,148,149]. It is especially difficult to align NWs in the composites since NWs occupy more space compared to equiaxial particles at the same weight.

Here, a simple and useful strategy for aligning NWs in a thermoplastic matrix is proposed. The nanocomposites with aligned PZT NWs are prepared by uniaxial force assembly. This chapter mainly covers the effects of orientation of PZT NWs on the dielectric constant and energy density of the nanocomposite. The alignment of the NWs in electric field direction leads to energy density up to 51.6% greater than nanocomposites with random alignment at 20 vol.%. Finally, the relationship between the orientation factor and dielectric constant of the nanocomposite is quantified. The study here indicates that aligned NWs in the electric field direction can be used to improve the energy density of the nanocomposites and have promising potential to produce high energy density nanocomposite capacitors in the future.

**Preparation of Nanocomposites with Aligned PZT NWs**

PZT NWs were synthesized through a hydrothermal process as described in Chapter 2. The nanocomposites were prepared by dispersing the PZT NWs into a PVDF (Kynar 301 F)/dimethylformamide (DMF) solution through bath sonication for at least one hour. The solution was cast onto a glass plate and dried under vacuum at 60 °C overnight. The resulting films were cut into small pieces and transferred to a stainless steel mold to be laminated in a hot press at 185 °C for one hour. This process was used to obtain void-free nanocomposites. The dimension of the final sample was 42 mm × 6.4 mm × 3.2 mm. Nanocomposites with aligned PZT NWs were prepared through uniaxial force assembly as shown in Figure 3-1(a). The samples with randomly
oriented PZT NWs were first loaded into the wedge grips of Instron 5969 electromechanical load frame as shown in Figure 3-1(b). Then, the samples were heated to 150 °C using a heat gun and stretched to 20% draw ratio. Finally, the stretched samples were cooled down to room temperature. The samples were released and final samples showed a dog bone shape with a necked section in the center of the sample (Figure 4-1(b)). Due to the brittle nature of the nanocomposites with 40 vol.% filler, the random films were first stretched to obtain films with aligned PZT NWs, and then were placed into a mold and hot pressed together at 180 °C for one hour.

Figure 3-1. Alignment of PZT NWs in nanocomposites. A) Illustration of the alignment of PZT NWs in PVDF matrix, B) Set up of alignment for PZT NWs in the composite under uniaxial force.

Figure 3-2(a) shows the free-standing high aspect ratio PZT NWs and the crystalline structure of the synthesized PZT NWs is PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (JCPDS No. 01070-4261) as shown in Figure 3-2(b). The microscopic homogeneity of the nanocomposite is investigated by imaging its top surface as shown in Figure 3-2 (c), which indicates
that the sample with 10 vol.% PZT NWs has a homogeneous dispersion in the PVDF matrix. Well dispersed PZT NWs in the PVDF matrix is required to ensure a high energy density as well as reproducible measurements. In order to observe the aligned PZT NWs in the nanocomposite, the uniaxial stretched samples were soaked in liquid nitrogen then snapped to break the samples and image the cross section of samples. After uniaxial force assemble, the PZT NWs are aligned in the PVDF matrix along the axis of the applied force as shown in Figure 3-2 (d). Each volume fraction is characterized using the same procedure and all are demonstrated homogeneous dispersion and uniform alignment of NWs in the nanocomposites.

![Figure 3-2. SEM images and XRD patterns of PZT NWs and nanocomposites. A) SEM images, B) XRD patterns of PZT NWs, C) SEM images of nanocomposites with 10% random PZT NWs, D) 10% aligned PZT NWs under uniaxial force.](image)
The Effect of Filler Orientation on the Dielectric Constant

The dielectric constant of the nanocomposites under different orientations (random, 1-direction alignment and 3-direction alignment) with various volume fractions of PZT NWs are shown in Figure 3-3. The 3-direction alignment is along the electric field direction, while the 1-direction is perpendicular to the electric field as shown in Figure 3-3. It shows that the effective dielectric constant values increase with increasing volume fraction of NWs. This is attributed to the higher dielectric permittivity of the PZT fillers compared to the PVDF matrix. More importantly, the dielectric constants of 3-direction aligned PZT NW samples are much larger than that of random and 1-direction aligned PZT NW samples at the same volume fraction. The dielectric constants of 3-direction aligned PZT NWs samples are 35.7% and 15.0% larger than the samples with random PZT NWs at 30 vol.% and 40 vol.%, respectively. The drop in dielectric constant of the nanocomposites with aligned NWs perpendicular to the electric field is expected and observed in prior studies [67,74,150,151] as well as through theoretical modeling [67].

Figure 3-3. Comparison of measured dielectric permittivity (at 1 kHz) of nanocomposites under different orientation (random, 1-direction alignment and 3-direction alignment) as a function of PZT NWs volume fractions
Figure 3-4 shows the dielectric constant of the nanocomposites under different orientation directions with various volume fractions of PZT NWs over the frequency range of 1 kHz to 1 MHz. It is indicated that the dielectric constant of the nanocomposites decrease with the frequency due to the dipole mobility, which is not sufficiently mobile to displace as the frequency of the applied electric field exceeds the relaxation frequency [31].

![Dielectric constant vs frequency](image)

Figure 3-4. Dielectric constants of different PZT volume fraction in PVDF from 1 KHz to 1 MHz. A) 3-direction aligned PZT NWs/PVDF nanocomposites, B) random PZT NWs/PVDF nanocomposites, C) 1-direction aligned PZT NWs/PVDF nanocomposites.

**The Effect of Filler Orientation on the Energy Density**

The effects of the filler orientation on the energy storage performance of the nanocomposites can be investigated by D-E loop characterized by a Sawyer-Tower circuit. Figure 3-5 presents the typical D-E loops measured at various volume fractions.
under different orientations (random, 1-direction alignment and 3-direction alignment). The concentration of PZT fillers notably raises the electric displacement, which is attributed to the higher dielectric permittivity of PZT compared to the PVDF matrix. It is also shown that the 3-direction aligned PZT NW nanocomposites have larger electric displacement than the random and 1-direction aligned PZT NW nanocomposites as a result of the higher dielectric permittivity of the samples. For example, with a field of 15 kV/mm and 40 vol.%, the 3-direction aligned nanocomposites achieve an electric displacement of 0.61 μC/cm², while the random and 1-direction aligned PZT NW nanocomposites have an electrical displacement of 0.47 μC/cm² and 0.31 μC/cm², respectively.

Figure 3-5. D-E loop measured under different applied fields at room temperature and 100 Hz for the polymer and nanocomposite. A) 3-direction aligned PZT NWs-PVDF nanocomposites, B) random PZT NWs-PVDF nanocomposites, C) 1-direction aligned PZT NWs-PVDF nanocomposites.
Figure 3-6 presents the stored electrical energy density of 3-direction aligned and random PZT NWs in PVDF calculated from each D-E loop. It demonstrates that the energy density of the nanocomposites is dependent on the orientation of the PZT NWs. Figure 3-6 indicates that the energy density increases with higher electric field and PZT concentration. The energy density of 3-direction aligned PZT NW composites is higher than that of random PZT NW composites throughout the entire volume fraction range considered. For example, the nanocomposite with 40 vol.% PZT NWs aligned in the field direction has an energy density of 0.0431 J/cm$^3$ at an electric field of 15 kV/mm, which is 36.0% larger than that of the 40% random PZT NWs composite (0.0317 J/cm$^3$).

![Figure 3-6](image)

Figure 3-6. The dependence of energy density on the PZT orientation and volume fraction in the PVDF under 15 kV/mm: 3-direction alignment PZT NWs/PVDF (red) and random PZT NWs/PVDF nanocomposites (blue).

In this work, the dielectric constant of nanocomposites with NWs aligned in the electric field direction is shown to be larger than that of nanocomposites with random orientation. In order to eliminate the influence of PVDF orientation on the dielectric property of nanocomposites, the phase of the PVDF is characterized. Figure 3-7 shows that the FTIR patterns of PVDF in the nanocomposites before and after stretching are
similar, which means that the uniaxial force does not change the structure of the PVDF. The filler orientation is the only parameter changed in the experiment; therefore, the filler’s alignment is responsible for the change of the dielectric constant. By aligning PZT NWs in single direction as shown in Figure 3-2, the poling direction and dipole can be more easily oriented in the electric field direction. Also, some researchers have proposed models that consider cubic particles in aligned chains as capacitors in series and showed that nanocomposites with aligned particles have higher dielectric constant than random ones [21,67,72]. Bowen proposes that aligned fillers in the matrix experience stronger interactions than randomly dispersed fillers leading to higher dielectric constant [72,151]. Considering all these points, nanocomposites with aligned PZT NWs will have higher dielectric constant than the samples with random inclusions. The improvement of dielectric constant yield higher energy density at the same electric field, since the energy density is linearly related to the dielectric constant.

![Figure 3-7. FTIR patterns of 10% PZT NWs-PVDF nanocomposites before and after stretching.](image)

Based on the findings in the Chapter 2 and 3, the current results demonstrate that higher aspect ratio fillers and 3-direction alignment shows the enhancement of
dielectric constant with potential to improve the energy density of nanocomposites. The relationship between the structure of the filler and dielectric constant of the nanocomposites are summarized in Figure 3-8, which represents the first report in the literature and has generated significant interest in this community. The ability of the dielectric constant of nanocomposite is listed as following: 3-direction alignment PZT NWS> random PZT NWs> random PZT NRs>1-direction alignment PZT NRs.

![Figure 3-8. Comparison of measured dielectric constant of nanocomposites with different structures (aspect ratio and orientation) as a function of volume fraction of PZT particle.](image)

**Quantification of the Relationship between the Filler Orientation Factor and the Dielectric Constant of Nanocomposites**

Prior research has demonstrated that filler alignment in the electric field direction can improve the dielectric constant more efficiently than randomly oriented fillers or fillers oriented perpendicular to the electric field direction. There are many theoretical models that have shown an improved dielectric constant by aligning the fillers in the electric field direction of the sample [72,74,123,152]. Currently, many researchers are using the alignment method to fabricate high dielectric constant composites.
However, the quantification of the orientation factor of filler in nanocomposites is still a challenge using experimental analysis. Here, the orientation factor of nanowires is successfully controlled by draw ratio of the nanocomposites. Additionally, a method is described to characterize the orientation factor of the fillers. Finally, the relationship between the dielectric constant and orientation factor is experimentally quantified.

It has been demonstrated that NWs can be aligned via shear forces on the NWs when the specimen is subjected to uniaxial force. This approach is employed here to tune the NWs’ orientation factor by varying the draw ratio of the samples, as shown in Figure 3-9. It is predicted that the orientation factor which represents the alignment of nanowires will be increased by increasing the draw ratio of the nanocomposites. However, the orientation factor will reach a saturation point when most of the NWs have been aligned, and further extension will not change the NWs’ orientation. Here, the orientation factor is characterized by Herman’s Orientation Factor (HOF) based on 2-dimensional (2-D) fast Fourier transform (FFT) analysis of a cross-sectional SEM image of the nanocomposites. Through orientation factor control, it is expected that the effective dielectric constant of the nanocomposite can be tuned without requiring additional fillers, which add defects into the nanocomposite. This method provides another solution to improve the energy density of the capacitors in addition to quantifying the relationship between the filler orientation and dielectric constant of the nanocomposites for the first time.
The orientation factor of embedded NWs in the polymer matrix can be obtained by performing FFT analysis on the cross-sectional SEM image of the nanocomposites (Figure 3-10). In this case, the Fourier transform maps the original grayscale levels of the SEM image from real space into frequency space (Figure 3-10c). The pattern of FFT intensity is identical to the degree of alignment distribution of the components in the original SEM image [153-155]. As shown in Figure 3-10b, the FFT intensity profile can be utilized to describe the distribution of the NWs’ orientation factor at a specified radius by extracting the intensity profile of each half circle projection. The peak and its sharpness in the intensity profile illustrate the orientation factor of the majority of NWs and the quality of the distribution of the aligned NWs, respectively. It is observed that perfectly aligned vertical NWs show a sharp peak at 90° while randomly distributed NWs do not illustrate a distinctive peak in the FFT profiles. It is worth mentioning that the edge effect in the SEM image adds fictitious information to the FFT intensity plot and consequently to the orientation factors [154]. The error of the edge effect appears...
as crossed lines in the FFT as shown in Figure 3-10d. In order to avoid this type of error, the edges of the SEM images are blurred by using a Gaussian low pass filter as shown in Figure 3-10a. Filtering the edge effects in the SEM image leads to less noise in the FFT output and consequently the intensity profiles (Figure 3-10c). Thus, the blurred images are utilized to determine the orientation factor of NWs based on the HOF with the procedure that will be described in detail.

Figure 3-10. FFT of the SEM images of the nanocomposites. A) Edge blurred SEM image of 20 vol.% PZT NWs nanocomposites under 25% draw ratio. B) radial projection representing normalized intensity profile. C) FFT of the edge blurred SEM image. D) corresponding FFT representing the edge effect.
Since the FFT intensity profile does not quantify the distribution of the NWs’ orientation factor, HOF is used to quantify the orientation factor of NWs in the nanocomposites based on the FFT intensity profiles. HOF as an orientation factor is a mathematical construction that describes the line structures relative to another direction of interest. Based on the definition, HOF can vary between -0.5 and 1. By defining a reference direction, -0.5 and 1 represent perfect alignment in perpendicular and parallel directions, respectively, while 0 represents random orientation of components. After performing a FFT on the SEM image, an azimuthal average of the output FFT image is performed to obtain the intensity-azimuthal angle curve, which is used to calculate the HOF. The details are as follows:

The HOF is defined as the standard formulation commonly used in polymer science to quantify orientation of semi-crystalline polymers:[156,157]

\[
HOF = \frac{1}{2} (3 < \cos^2 \varphi > -1)
\]

where the angular brackets indicate a spatial average to account for the spatial distribution of the orientation degree and can be expressed as:

\[
< \cos^2 \varphi > = \frac{\int_0^{\pi/2} I(\varphi) \cos^2 \varphi \sin(\varphi) d\varphi}{\int_0^{\pi/2} I(\varphi) \sin(\varphi) d\varphi}
\]

where azimuth angle \( \varphi \) is the angle between the orientation reference axis and component’s direction (Figure 3-11a), and \( I(\varphi) \) is the intensity profile of anisotropy as a function of \( \varphi \) from zero to \( \pi/2 \). The HOF is estimated by employing the averaged FFT intensity profiles as a function of azimuth angle and integrating numerically from zero to 90° to determine the spatial average. As shown in Figure 3-11, the profile intensities vary with respect to the distance from center; however, they show the same trends.
(profiles 1 to 4). At a distance far from center, the projected profile does not contain useful information due to the resolution limitations (profile 6). Here, the HOF is estimated by averaging the effective profile intensities based on cross sectional SEM images of the nanocomposites. Only minor variations in the determined HOF are observed by altering the range and increments of the averaged profiles. For aligned PZT NWs in the nanocomposite, the components are embedded PZT NWs. Ideally, all the individual PZT NWs should be exposed on the surface of the composite when the sample is prepared. Then, theoretically, the HOF determination should be performed for each individual NW; however, this is nearly impossible by SEM observation of the nanocomposites in this study.

Figure 3-11. The Determination of HOF. A) FFT image with defined axes azimuth angle. B) Extracted intensity profiles at different frequencies.

Different draw ratios are applied on the samples in order to control the orientation factor of the NWs. Here, the nanocomposites with 20 vol.% PZT NWs are used to investigate the effects of the filler orientation factor on the dielectric constant of the nanocomposites. Four different samples are cut to the same size and loaded into the wedge grips of an Instron 5969 electromechanical load frame as shown in Figure 3-1(b).
Then, the samples are heated to 150 °C using a heat gun and stretched to the desired draw ratio. Figure 3-12 shows the SEM images of the nanocomposites with different draw ratios under uniaxial force accompanied by their respective FFT analyses. Before stretching, randomly dispersed PZT NWs are observed in the PVDF matrix (Figure 3-12a). The corresponding FFT image shows the pixel distributed in a symmetrical and circular shape, which indicates all the specific pixel intensities are theoretically identical in any direction and the fillers are randomly distributed in the polymer matrix. After stretching, the PZT NWs begin to align in the draw direction. The FFT analysis of the aligned NWs results in an image distributed as an elliptical shape, which indicates that the pixel intensities are preferentially distributed with a specific orientation thus the NWs are aligned in the composites (Figure 3-12b). With increasing draw ratio, both the SEM images and their corresponding FFT intensity outputs indicate that the NW orientation factor increases (Figure 3-12).
Figure 3-12. SEM images of cross section of the 20. vol% PZT NWs nanocomposites along with their FFT under various draw ratio. A) 0%, B) 5%, C) 10%, D) 20%, E) 25%.
As shown in Figure 3-13, the HOF of the nanocomposites increases with increasing draw ratio. The HOF is 0.044 for the unstretched samples, which implies the NWs are completely randomly distributed. After stretching about 5%, the orientation factor increases sharply to 0.22, which means the NWs begin to align in the draw direction. With increasing draw ratio, the HOF of the NWs continues to increase however at a decreasing rate. Finally, the HOF of NWs reaches saturation because most of the NWs are aligned. It is noted that the HOF of the embedded NWs in the polymer matrix reaches 0.481 at 25% draw ratio. Previous research has shown that the HOF values of 0.3 to 0.6 are reached for a high volume fraction of aligned carbon nanotubes in composites or aligned carbon nanotube forest, which are shown to have good alignment in the SEM observation [158-160]. Therefore, the HOF (0.481) indicates that most of PZT NWs are aligned in the PVDF matrix.

![Figure 3-13. HOF as a function of the draw ratio for the nanocomposites with 20 vol.% PZT NWs.](image.png)

The dielectric constant of the nanocomposites is measured at a frequency range of 1 kHz to 1 MHz by an Agilent 4980A LCR meter. The frequency dependence of the
dielectric constants with various HOFs is shown in Figure 3-14. It is clearly shown that the dielectric constant increases with increasing orientation factor of PZT NWs in the nanocomposites. The dielectric constant of the nanocomposite with 20 vol.% PZT NWs reached as high as 28.7 at a HOF of 0.481, which is 1.48 times that of the randomly oriented PZT NWs with a dielectric constant of 19.4. Thus, it is demonstrated that the filler orientation factor plays a significant role in controlling the dielectric constant of the nanocomposites, and the proposed technique is able to efficiently improve the dielectric constant of the nanocomposites without the need for additional fillers.

Figure 3-14. Dielectric constant of the nanocomposites as a function of HOF at the 20 vol.% PZT NWs

**Chapter Summary**

In this chapter, the relationship between orientation factor of the filler and energy storage performance of the nanocomposites was investigated. It showed that the dielectric constant and the energy density of nanocomposites were enhanced through alignment of the NWs in the applied electric field direction. Nanocomposites with aligned PZT NWs were prepared through uniaxial force and compared to samples with
randomly distributed NWs. The results demonstrated that nanocomposites with NWs aligned in the electric field direction have higher dielectric constants than samples with randomly dispersed NWs. The increased dielectric constant of the aligned nanocomposites provided a platform to obtain materials with greater energy density. The alignment of the NWs led to energy densities up to 51.6% greater than nanocomposites with random alignment at 20 vol.%. These results showed that controlling the orientation of the filler could be used to improve the energy density of the nanocomposites.

This chapter also included details about a simple and useful strategy for aligning NWs in a thermoplastic matrix. The degree of NW orientation was tuned by varying the draw ratio of the samples through uniaxial force. The HOF was utilized to quantify the orientation factor of NWs based on 2-D FFT analysis of cross sectional SEM images of the nanocomposites. It was observed that HOF initially increased sharply after stretching and saturated when most of the NWs were aligned. The HOF varied from 0.044 to 0.481, corresponding to the draw ratios of 0 to 25%. It was demonstrated that the dielectric constant of the nanocomposites increased with increasing degree of NW orientation. The dielectric constant of the nanocomposite with 20 vol.% PZT NWs and a HOF of 0.481 reached as high as 28.7, which is 1.48 times larger than samples with randomly oriented PZT NWs (19.4). The relationship between the orientation factor of the fillers and dielectric constant of the nanocomposites was quantified for the first time.

The results presented in this chapter combined with my prior demonstration that high aspect ratios produce significant performance gains over spherical fillers provides a methodology to achieve vastly improved capacitive materials. The Chapter 4 will
introduce the fabrication of high energy density nanocomposite capacitors based on high aspect ratio NWs.
CHAPTER 4 HIGH ENERGY DENSITY NANOCOMPOSITES

Chapter Introduction

Based on the finding of Chapter 2 and 3, this chapter will develop and characterize nanocomposites with higher energy density and faster discharge rate than any appearing prior to the work of this dissertation. Two particular cases will be considered, one utilizing a high dielectric PVDF terpolymer matrix and BaTiO$_3$ NWs and a second using conventional PVDF and Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs. The first type of high energy density nanocomposite capacitor is fabricated with high aspect ratio BaTiO$_3$ NWs in poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) (P(VDF-TrFE-CFE)). It is shown that these nanocomposite capacitors have a high energy density up to 10.3 J/cc. However, this form of nanocomposite capacitor shows polarization saturation and high ferroelectric loss, which is attributed to the ferroelectric properties of BaTiO$_3$ fillers and P(VDF-TrFE-CFE) matrix. In order to achieve higher energy density, it is necessary to overcome the ferroelectric properties of the nanocomposite while maintaining high dielectric permittivity and high breakdown strength. Therefore, it is hypothesized that the fabrication of a nanocomposite without ferroelectric behavior will yield higher energy density. In order to achieve this goal, a new method is first developed to synthesize high aspect ratio Ba$_x$Sr$_{1-x}$TiO$_3$ NWs with different molar ratios of barium and strontium ions. In the Ba$_x$Sr$_{1-x}$TiO$_3$ solid solution, transformation occurs from the ferroelectric phase to the paraelectric phase when the Ba mole fraction decreases below 0.7 ($x<0.7$) and shows little hysteresis behavior at room temperature and above. Here, the paraelectric phase Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ is chosen for the NWs combined with quenched PVDF to fabricate high energy density nanocomposite capacitors, which can reach an energy density as high as 14.86 J/cc. This rivals or
exceeds those reports for ceramic/polymer composites [15-17,19,20] and is 1138% greater than the energy density of 1.2 J/cc at 640MV/m for commercial biaxially oriented polypropylene (BOPP).

**High Energy Density Nanocomposite Capacitors Using BaTiO₃ NWs and P(VDF-TrFE-CFE)**

High aspect ratio BaTiO₃ NWs are used in this case as filler for the fabrication of nanocomposites. Figure 4-1a shows the free standing BaTiO₃ NWs. The size of BaTiO₃ particles are analyzed from SEM pictures by using ImageJ, and shown that they have a mean length of 14.7 μm and a mean diameter of 470 nm, with an aspect ratio of approximately 31. A representative XRD pattern of the BaTiO₃ NWs is shown in Figure 4-1b. All diffraction peaks can be assigned to the BaTiO₃ crystal structure (JCPDS, 81-2203) without any indication of crystalline byproducts such as BaCO₃ or TiO₂.

When working with nanocomposites, the high surface area to volume ratio leads to large interfacial area that can produce defects in the polymer creating a situation where the overall dielectric strength is significantly compromised. In order to improve the compatibility between the filler and matrix and thus increase the breakdown strength, surface modification of the fillers is often used to improve the performance of the nanocomposite system [9,15-17]. Figure 4-1d shows the FTIR spectra of BaTiO₃ NWs before and after surface functionalization with ethylenediamine. The binding of ethylenediamine is evidenced by the adsorption around 1450 cm⁻¹, which corresponds to amine groups (N-H) [131]. The coordination of the amine group on the functionalized BaTiO₃ with the P(VDF-TrFE-CFE) matrix is schematically shown in Figure 4-1d. The presence of amine groups has been shown to increase the compatibility between the
filler and matrix and allow the formation of a homogenous dispersion in the P(VDF-TrFE-CFE) matrix more readily [161].

Figure 4-1. Morphology, structure and functionalization of BaTiO$_3$ NWs. A) SEM image, B) XRD patterns, C) FTIR spectra of BaTiO$_3$ NWs and modified BaTiO$_3$ NWs by ethylenediamine, D) schematic image of the functionalized TiO$_2$ by ethylenediamine reacting with P(VDF-TrFE-CFE).

Nanocomposites were prepared by dispersing the BaTiO$_3$ NWs into a 10 wt.% of P(VDF-TrFE-CFE) (63/29/8% mole ratio, Piezotech S.A.S, France) in dimethylformamide (DMF) solution through sonication for 1 hour then solution casting onto a glass plate to obtain thin films approximately 10µm thick. The films were then dried at 60 °C under vacuum overnight. The films were peeled from the glass substrates and further dried in a vacuum oven at 120 °C for 24 hours to make sure the solvent was completely removed. Finally, gold electrodes approximately 10 nm thick
were sputtered onto both surfaces of the film for low field measurements and high
electric field D-E loop measurements. The microscopic homogeneity of the
nanocomposite is investigated by imaging its top surface as shown in Figure 4-2. It
indicates that the BaTiO₃ NWs have a homogenous dispersion in the PVDF terpolymer
matrix, and no void exists in the film, which is required to ensure a high energy density
as well as reproducible measurements. The good dispersion of BaTiO₃ NWs is
attributed to the compatibility between the PVDF terpolymer and functionalized BaTiO₃
NWs with ethylenediamine.

Figure 4-2. SEM image of 10 vol.% BaTiO₃-P(VDF-TrFE-CFE) nanocomposites.

**Dielectric Property of the Nanocomposites**

The increased dielectric constant resulting from NWs over low aspect ratio
particles can be seen in Figure 4-3a. It clearly demonstrates that the use of high aspect
ratio filler more efficiently imparts its high dielectric permittivity to the bulk
nanocomposite than the low aspect ratio particles used by Wang et al [16]. The
dielectric constant can reach as high as 69.5 at 17.5 vol.% of BaTiO₃ NWs, while the
dielectric constant is only around 52 at a high concentration of 30 vol.% of nanoparticles
in a similar matrix. Considering the energy storage scope of this dissertation, high
energy density capacitors need to simultaneously have high breakdown strength as well as high dielectric permittivity. It is well-known that increasing the volume fraction of the filler decreases the breakdown strength of the capacitor [15,55]. In addition, the remnant polarization of the nanocomposite increases with the volume fraction of the ferroelectric fillers, which decreases the energy density of the material [16]. Therefore, this dissertation is focused on using a low concentration of fillers to maintain improved dielectric permittivity and high breakdown strength to create high energy density capacitors. It is also noted that the dielectric loss of the nanocomposite is around 0.09 and is almost independent of the low volume fraction of the BaTiO$_3$ NWs (Figure 4-3b). In addition, Figure 4-4 indicates that the effective dielectric permittivity of the nanocomposites decreases with increasing frequency. At low frequency, the dipoles can move sufficiently fast to follow the electric field. However, as the frequency increases the dipole cannot shift orientation sufficiently fast as the applied electric field exceeds its relaxation frequency, resulting in a decrease of dielectric constant at high frequency [31].

Figure 4-3. Dielectric properties of nanocomposites: A) comparison of measured dielectric permittivity (at 1kHz) of BaTiO$_3$ NWs nanocomposites as a function of BaTiO$_3$ NWs and nanoparticle volume fractions [16], B) dielectric permittivity and loss tangent (at 1kHz) of BaTiO$_3$ NWs nanocomposites.
Figure 4-4. Dielectric permittivity constants of different BaTiO$_3$ NWs volume fractions in P(VDF-TrFE-CFE) from 1kHz to 1 MHz.

**Energy Storage Performance of the Nanocomposite Capacitors**

The D-E loops measured with a Sawyer-Tower circuit under a unipolar 100 Hz field with varying peak electric field are shown in Figure 4-5. It shows that the electric displacement of the nanocomposite increases with the applied electric field, which indicates that it is reasonable to obtain a larger electric displacement at a higher electric field. Also, the electric displacement of the nanocomposite increases with the volume fraction of BaTiO$_3$ NWs. This is attributed to the fact that BaTiO$_3$ has a higher dielectric permittivity than PVDF terpolymer. It can also be observed that the remnant polarization of the D-E loops increase with the concentration of the fillers since the ferroelectric ceramic BaTiO$_3$ NWs has a much higher remnant polarization. For energy storage, the high remnant polarization will decrease the discharge energy of the material since the integrated area of the D-E loops will decrease. This is one of the reasons that the nanocomposites used here have been prepared with low volume fractions of BaTiO$_3$ NWs in the nanocomposites.
Figure 4-5. Unipolar electric displacement-electric field (D-E) loops for nanocomposites with different BaTiO$_3$ NWs volume fractions in P(VDF-TrFE-CFE) matrix.

The energy densities are summarized in Figure 4-6. It shows the energy densities of nanocomposites calculated from the D-E loops as a function of applied field at different volume fractions. It indicates that the energy density of the nanocomposites increases with increasing electric field and volume fraction of the BaTiO$_3$ NWs. The incorporation of BaTiO$_3$ NWs into the terpolymer greatly increases the energy density of the nanocomposites. Figure 4-6 clearly shows that BaTiO$_3$ NWs can improve the energy density of the nanocomposite compared to a neat polymer. The 17.5 vol.% nanocomposite show a increase in energy density of more than 45.3% over that of the P(VDF-TrFE-CFE) polymer (10.48 J/cc compared to 7.21 J/cc). This value is significant because it exceeds those reported for the conventional polymer-ceramic composites [9,15-17,61] and is also more than seven times larger than high-performance commercial polypropylene capacitors (1.2 J/cc).
Figure 4-6. Energy density of the nanocomposite with different volume fractions as a function of electric field calculated from D-E loops.

For pulsed-power applications, the capacitor needs to not only have high energy density but also high power density. Therefore, it is important to characterize the discharge speed of the capacitor to calculate discharged power density. The discharge speed and discharge power are measured by using a self-designed, high-speed capacitor discharge circuit similar to that reported in the literature [162-164] and shown in Figure 4-7.

First, the nanocomposite sample is charged with a given voltage. After that, by closing a high speed (<500 ns) high voltage switch (Behlke HTS81), the stored energy in the nanocomposite capacitor is discharged across a load resistor $R_L$. The dielectric materials can be modeled as an equivalent series resistor (ESR) as shown in Figure 4-8 [6,162,163]. It will be shown that most of the stored energy in the capacitor will be delivered to the load when the $R_L$ is much larger than the ESR. Therefore, the measurement of the energy density from the load resistor can be close to the stored energy of the tested sample. The voltage across $R_T$ is monitored with an oscilloscope.
through a high voltage probe as shown in Figure 4-7. The discharged energy can be calculated from the voltage on $R_T$ as a function of time, as shown in the following equation:

$$U = \int \frac{1}{VR_L}V(t)^2 dt$$

where $U$ is the energy density of the sample, $R_L$ is the resistor, $V(t)$ is the voltage from the oscilloscope, $t$ is the time and $V$ is the volume of the measured capacitors. Finally, the power density of the nanocomposite can be calculated by dividing the discharge energy by the discharge time.

Figure 4-7. Discharge circuit of energy density and discharge speed characterization.

Figure 4-8. An equivalent circuit of a dielectric sample.
It is well-known that the commercial polypropylene capacitor has fast discharge speed. In order to compare the discharge speed of the prepared nanocomposites with existing commercial materials, a nanocomposite with 17.5 vol.% BaTiO$_3$ NWs and a commercial biaxially oriented polypropylene having the same capacitance (73 pF) are discharged across a 20 kΩ load as shown in the Figure 4-9a. The experimental discharge time $\tau_{0.9}$ is defined as the time for the discharged energy under load to reach 90% of the final value from the discharge profiles. Figure 4-9a shows the discharging time is around 7.08 µs, which is comparable to the discharge speed of 5.68 µs for commercial polypropylene. More notably, the discharge energy density of the nanocomposites is 4.8 J/cc at an electric field of 175 MV/m, which is close to the result measured by the D-E loop and 17.5 times larger than a commercial polypropylene capacitor with 0.26 J/cc at 175 MV/m. In addition, the power density of the nanocomposites can reach as high as 1.2 MW/cc at 1.52 µs, which is 14 times larger than commercial polypropylene (0.08 MW/cc at 0.6 µs). Therefore, the high energy density nanocomposite capacitors with fast discharge speed can satisfy the application requirements for pulsed-power devices.

Figure 4-9. Discharge energy density and power density of nanocomposites: A) discharged energy density, B) power density profiles for nanocomposites with 17.5% BTO NWs and commercial polypropylene, respectively. The load resistor $R_L$ is 20 kΩ and the electrical field is 175 MV/m.
In this section, high energy density nanocomposite capacitors were successfully fabricated by using surface functionalized high aspect ratio BaTiO$_3$ NWs and P(VDF-TrFE-CFE) polymer. The nanocomposites exhibited increased dielectric permittivity at low volume fractions of the fillers and withstood high electric field for energy storage. The 17.5 vol.% nanocomposites showed a significant increase in energy density, more than 45.3% higher than that of the neat P(VDF-TrFE-CFE) polymer (10.48 J/cc compared to 7.21 J/cc) at electric field 300 MV/m. This value is significant and exceeds those reported for the conventional polymer-ceramic composite and is more than seven times larger than a high-performance commercial polypropylene capacitor. In addition, the nanocomposites have rapid discharge speed reached a power density of 1.2 MW/cc at 175 MV/m, which is 14 times larger than commercial polypropylene. This simple approach to obtain high energy density capacitors with fast discharge speed can be applicable to other ferroelectric nanowires, such as PZT and lead titanate.

**Ultra High Energy Density Nanocomposite Capacitors Using Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs**

The previous section has shown that nanocomposites prepared with BaTiO$_3$ NWs and P(VDF-TrFE-CFE) could achieve high energy density and fast discharge speed. However, it is shown that this type of nanocomposite capacitor has polarization saturation and high ferroelectric loss because of the ferroelectric properties of the BaTiO$_3$ and P(VDF-TrFE-CFE) (Figure 4-5) limiting the max energy recovered. Therefore, it is critical to avoid saturation of the polarization below the breakdown field [165]. Li et al. demonstrated that the γ-PVDF phase can be obtained by quenching the film in ice water and showed it exhibited higher energy density than β-PVDF or α-PVDF due to improved breakdown strength and the absence of early polarization saturation.
Ferroelectric fillers, such as PZT and BaTiO$_3$, are defined by their high remnant polarization and polarization saturation, both of which reduce the maximum energy density [19,20,165,166]. Other ceramics can be designed such that they have a non-ferroelectric structure but high dielectric properties, such as Ba$_x$Sr$_{1-x}$TiO$_3$ (BST), which can be tuned to obtain a desired hysteresis behavior by varying the stoichiometry [104,106]. In the Ba$_x$Sr$_{1-x}$TiO$_3$ solid solution, transformation from the ferroelectric phase to the paraelectric phase occurs when the molar fraction of Ba decreases below 0.7 (x<0.7) and shows little hysteresis behavior at room temperature and above [104-106].

The use of high dielectric fillers such as BST can provide a high dielectric permittivity while eliminating the remnant polarization, ultimately increasing the energy storage efficiency of capacitor.

A second technique to prepare high energy density nanocomposite capacitors with fast discharge speed is proposed. The nanocomposites are prepared with high aspect ratio Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs in PVDF and are quenched in ice water to achieve high breakdown strength and energy storage properties. To the best of my knowledge, these nanocomposites have the largest breakdown strength (>450 MV/m) and highest energy density of any nanocomposite incorporating a high dielectric filler reported in the current literature while also having low hysteresis and sub-microsecond discharge [15-17,19,20]. The maximum energy density calculated from the D-E loop is 14.86 J/cc, exceeding the state-of-the-art commercially available capacitors (1.2 J/cc at 640 MV/m) by more than an order of magnitude [48].

**Synthesis of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs and Preparation of Nanocomposites**

The synthesis of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs was approached by a two-step hydrothermal reaction [128]. First, the precursors of sodium titanate NWs were
synthesized by hydrothermal reaction. Typically, aqueous sodium hydroxide (Fisher, ACS, 99%) was added to a Teflon-lined autoclave followed by the addition of titanium dioxide powder (anatase, Sigma-Aldrich, ACS, 99%) and then bath sonicated for 20 min. The stainless steel autoclave was sealed and stirred at 200 °C for 24 hours. After the autoclave was cooled to room temperature, the obtained powder was sequentially washed with water and then soaked with 0.2M hydrochloric acid (Fisher, 37%) aqueous solution for 3 hours. Then, the powders were washed with water four times through centrifugation and vortex mixing, and subsequently dried on a hotplate at 60 °C overnight. Subsequently, the hydrogen titanate nanowires were converted to Ba$_x$Sr$_{1-x}$TiO$_3$ NWs by a second hydrothermal reaction with an aqueous solution containing barium and strontium ion sources. The precipitate was collected, washed with 0.2M HCl aqueous solution, water and ethanol.

The precursor to the Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ phase is sodium titanate synthesized by hydrothermal reaction as shown in Figure 4-10a. The precursor nanowires are free standing and have high aspect ratio. The second hydrothermal process is designed to specifically maintain the morphology of the nanowires and as can be seen by Figure 4-10b that the morphology of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ is preserved. Chemical composition of nanowires was studied by an energy-dispersive X-ray spectroscopy (EDX, GENESIS), as shown in Figure 4-10c. The successful transformation of Ba$_x$Sr$_{1-x}$TiO$_3$ nanowires after diffusion of the Ba and Sr ions into the precursor NWs during the hydrothermal reaction is further confirmed due to the presence of only Ba, Sr, Ti and O. It should be mentioned that the it is hard to clearly observe the of the separate peaks of Ba and Ti, since the main peaks of Ba (L-edge) and Ti (K-edge) overlap in the energy range of 4.5-
The crystal structure verification of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ is performed by XRD. As shown in the XRD patterns of Ba$_x$Sr$_{1-x}$TiO$_3$ NWs (Figure 4-10d), it clearly demonstrates the crystal structure of Ba$_x$Sr$_{1-x}$TiO$_3$ NWs after diffusion of the Ba and Sr ions into the precursor nanowires. The (110) diffraction peak of Ba$_x$Sr$_{1-x}$TiO$_3$ gradually shifts from 31.48 to 32.24 degree as the molar fraction of barium initially in solution decreases from 1 to 0.20, since the radius of a Ba$^{2+}$ ion (1.61 Å) is larger compared to radius of a Sr$^{2+}$ ion (1.44 Å). Using Bragg’s law, the lattice parameters of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs is calculated as 3.922 Å, which closely matches reported data (3.920 Å) [[167,168]].
Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ nanowires. Figure 4-11a shows the individual nanowire has a straight cylindrical shape and single crystalline structure with growth along the [100] axis, as evidenced by clear lattice fringes in the high-resolution TEM (HRTEM) image of Figure 4-11b. The interlayer distances between adjacent lattice fringes in the HRTEM image of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ nanowire is measured to be 3.915Å ± 0.005Å, which is consistent with XRD data and corresponds closely to the reported distance between two adjacent [100] Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ crystal planes (3.920Å) [(167,168)]. The Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ has paraelectric phase and shows little hysteresis behavior at room temperature and above, [104,105] which directly decreases the ferroelectric loss and should increase the energy density of the nanocomposites. This result demonstrates a unique process for the growth of high aspect ratio nanowires of any Ba$_x$Sr$_{1-x}$TiO$_3$ stoichiometry.

![Figure 4-11. TEM analysis of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs. A) TEM image, B) representative HRTEM image showing clear crystal lattice fringes.](image)

The surface of the Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs was functionalized with ethylenediamine to improve the dispersion and interaction with the PVDF matrix. The functionalization was carried out by mixing the BST powder with ethylenediamine followed by vortex
mixing for 5 minutes then sonicating for 1 hour followed by heated the solution to 90 °C in a water bath for one hour. The precipitate was separated by centrifugation and dried at 70 °C under vacuum overnight. Figure 4-12a shows the FTIR spectrum of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs before and after treatment with ethylenediamine. The presence of the amine groups on the surface of the Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs following functionalization is evidenced through the appearance of the transmission at 1450 cm$^{-1}$ [131], which acts as the bridge between the Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs and PVDF matrix as shown in Figure 4-12c. After functionalizing the BST NWs using ethylenediamine, they can be homogenously dispersed in the PVDF polymer matrix, as shown in Figure 4-10b, which also shows the absence of voids in the film following annealing and quenching.

The quenching process is used to modify the crystallization of the PVDF in the nanocomposites to improve the breakdown strength and decrease the ferroelectric loss. Therefore, FTIR has been collected for PVDF before and after quenching as shown in

![Figure 4-12. BST NWs functionalization and nanocomposites. A) FTIR spectra of BST NWs and functionalized BST NWs by ethylenediamine, B) top surface of 5% Ba$_{0.2}$Sr$_{0.8}$TiO$_3$/PVDF nanocomposites, C) schematic image of the functionalized BST by ethylenediamine reacting with P(VDF-TrFE-CFE).]
Figure 4-13a. From the FTIR spectrum, the quenched PVDF is primarily in the γ phase (840, 812, 775 cm\(^{-1}\)), while the untreated PVDF is dominated by the β phase. This result is as expected and desirable [166], since the γ-PVDF has reduced ferroelectric loss and higher breakdown strength [166]. Figure 4-13b summarizes the characteristic breakdown strength of the quenched PVDF, untreated PVDF and commercial biaxial oriented polypropylene (BOPP). Following the quenching of the PVDF film in ice water, the dielectric strength is improved to 536.1 MV/m, while the untreated PVDF is 443.8 MV/m. It should be noted that the breakdown strength of the quenched PVDF is close to commercial BOPP from Milwek Company with 646.8 MV/m. Additionally, the γ-PVDF reduced ferroelectric loss to yield high energy storage efficiency and high energy density of the nanocomposites, which will be discussed in the energy storage part.

![FTIR spectra and breakdown strength of quenched PVDF](image)

**Figure 4-13.** FTIR spectra and breakdown strength of quenched PVDF. A) FTIR spectra of untreated PVDF, quenched PVDF, B) Weibull distribution analysis of breakdown strength of untreated PVDF, quenched PVDF and BOPP

**Dielectric Property of the Nanocomposites**

The breakdown strength of the nanocomposites decreases with increasing concentration of the filler, especially at high volume fraction [15,55]. In order to improve the dielectric property of the nanocomposite while maintaining high breakdown strength,
the nanocomposites are fabricated at a low volume fraction of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ NWs ranging from 2.5%-7.5%. In addition, the high aspect ratio $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ NWs are ground to form low aspect ratio $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ nanorods (NRs) to effectively demonstrate the effect of the filler's aspect ratio on the dielectric constant of the composite. Figure 4-14a shows that the dielectric constant of the samples increases at low electric field with increasing volume fraction of $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ NWs in the nanocomposites, since the $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ fillers have a higher dielectric constant than the PVDF matrix. Also, it is clearly demonstrated that the nanocomposites with BST NWs have a higher dielectric constant than the samples with BST NRs, which has also been demonstrated in the prior research [19,55]. Building off these findings, the high energy density capacitors developed here will use high aspect ratio $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ NWs. Figure 4-14b shows the relationship between the dielectric constant of the nanocomposite and the frequency. The dielectric constant decreases with increasing frequency due to the fact that the dipole cannot shift orientation direction as the frequency of the applied electric field exceeds the relaxation frequency [31,31].

Figure 4-14. Dielectric properties of the nanocomposites: A) comparison of measured dielectric constant (at 1 kHz) of nanocomposites with different aspect ratios of BST NWs and BST NRs, B) dielectric constant of different BST NWs volume fractions in PVDF from 1 kHz to 1 MHz.
The breakdown strength was measured using an electrostatic pull-down method [165,169,170]. A diagram of the setup is shown in Figure 4-15. Pull-down between the conductive substrate and a brass dome typically occurs at an electrical field of 10 MV/m and is maintained until breakdown occurred over the test area. The pull-down method was chosen over a point-contact method to avoid any mechanical force that might cause premature breakdown at the contact point. Breakdown testing is performed in silicon oil to avoid electric arcing and was performed using an Acopian high voltage supply (PO30HP2M) by sweeping the applied voltage from 60 V\text{DC} at approximately 500 V/sec until sample failure, as evidenced by spurious current changes.

![Diagram of breakdown strength test using an electrostatic pull-down method.](image)

Figure 4-15. Diagram of breakdown strength test using an electrostatic pull-down method.

The dielectric breakdown strength is analyzed using a two parameter Weibull cumulative probability function: 

$$P(E) = 1 - \exp\left[1 - \left(E/E_{BD}\right)\beta\right]$$

where $P(E)$ is the cumulative probability of failure occurring at the electric field lower or equal to $E$ [18,75]. The $E_{BD}$ is the scale parameter for experimental breakdown strength with a 63.2% probability for failure, $\beta$ is the shape parameter associated with the linear regressive fit of the data distribution. The dielectric breakdown strength is then extracted from a fit using Weibull failure statistics across at least 15 tests per sample. Figure 4-16 summarizes the characteristic breakdown strength of the nanocomposites with different volume fractions.
of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs, PVDF, quenched PVDF and BOPP. Following quenching of the PVDF film in ice water, the dielectric strength is improved to 536.1 MV/m, which is close to commercial BOPP from Milwek Company with 646.8 MV/m. As the volume fraction of the BST NWs increases from 2.5% to 7.5%, the dielectric breakdown strength decreases from 505.1 to 450.1 MV/m, since the introduction of the fillers into the polymer results in defects that initiate failure and decrease the breakdown strength. It should be noted that while the breakdown decreases, compared to other composites [15-17,19,20], all nanocomposites maintain relatively high breakdown strength at a low volume fraction of the filler, which provides the opportunity for nanocomposites with very high energy density.

![Figure 4-16. Weibull distribution and observed dielectric breakdown strength of nanocomposites with different volume fractions of BST, quenched PVDF and commercial polypropylene films.](image)

Energy Storage Performance of the Nanocomposite Capacitors

The polarization loop was measured by the Sawyer-Tower circuit under a unipolar 100 Hz electric field with increasing peak electric field as shown in Figure 4-17 for the neat PVDF and each volume fraction of NWs. The addition of the Ba$_{0.2}$Sr$_{0.8}$TiO$_3$
NWs into the PVDF polymers greatly increases the maximum polarization of the nanocomposites. Most notably, it increases sharply at a high volume fraction of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs compared to pure PVDF. It should also be noted that the hysteresis increases slowly with increasing concentration of the filler; however, the hysteresis is considerably smaller than the results presented in prior research efforts utilizing nanocomposites with ferroelectric fillers [19,20]. Hysteresis is important since it leads to reduced efficiency, internal heating and ultimately limits the maximum energy density and operational frequency of the capacitor.

![Unipolar electric displacement-electric field (D-E) loops for nanocomposites with different BST NWs volume fractions.](image)

Figure 4-17. Unipolar electric displacement-electric field (D-E) loops for nanocomposites with different BST NWs volume fractions.

Figure 4-18a summarizes the energy density of BST nanocomposites calculated from the D-E loop. It shows the use of the BST nanowires leads to improved energy densities compared with neat PVDF polymer at high electric field. For the composites with 7.5% Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs, the energy density is 14.86 J/cc at 450 MV/m, which represents a 42.9% increase in comparison to the PVDF with an energy density of 10.4 J/cc at the same electric field. This energy density rivals or exceeds those reports for
ceramic/polymer composites [15-17,19,20], and is 1138% greater than the 1.2 J/cc energy density at 640MV/m for commercial BOPP [48,171]. The measured breakdown strength over 450 MV/m is the highest breakdown strength reported for nanocomposites incorporating a high dielectric filler ceramic/polymer capacitor, all of which are well below 250 MV/m [15-17,19,20].

For practical applications, it is desirable to not only have a high energy density, but also maintain a high efficiency ($\eta$). It is well known that the energy losses in the capacitor leads to heating, and consequently, to detrimental effects on the performance and reliability of the capacitor. Figure 4-18b shows the efficiency (discharge energy/charge energy) of the nanocomposites with different NW concentration at high electric field, as calculated from the D-E loops in Figure 4-17. It is clearly shown that the efficiency decreases with the applied electric field, particularly above 100 MV/m, which is highly related to conduction loss [172]. As the concentration of the filler increases, the efficiency of the capacitor decreases due to the larger hysteresis in the polarization. However at fields below 100 MV/m, the efficiency is greater than 90% and greater than 60% at an electric field of 450 MV/m, which are higher than the nanocomposite capacitors reported in the literature [19,20]. The improved efficiency is attributed to the non-ferroelectric structure of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs and the quenching process to obtain $\gamma$-PVDF phase [104,166]. The efficiency results demonstrate that the nanocomposites developed here can capitalize upon the combination of inorganic materials of large permittivity with polymers of high breakdown strength to achieve high energy density and high efficiency.
Figure 4-18. Energy density and efficiency of nanocomposites with Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs. A) Energy density of the nanocomposite with different volume fractions as a function of electric field calculated from D-E loops; B) Efficiencies of the nanocomposites with different volume fraction as function of electric field.

The discharge speed and discharged energy were measured using a specially designed, high-speed capacitor discharge circuit as shown in Figure 4-7. In order to compare with the discharge speed of commercial capacitors, the nanocomposites and commercial polypropylene films are designed to have the same capacitance 26 pF at 1 kHz. Both samples are charged to 200MV/m followed by discharge across a 20 kΩ load, as shown in the Figure 4-19a. It is demonstrated that the nanocomposites have a discharge speed of approximately 2.3 µs, which is faster than commercial polypropylene (2.8 µs) that is noted for its fast discharge. Additionally, nanocomposites can discharge more energy at the same electric field compared to polypropylene. The electric field used here was limited for safety thus the delivered energy should not be the full energy density of the material. The rate of discharge is also primarily driven by the RC time constant thus the discharge rate is highly dependent on the load resistance. However, the nanocomposites have faster discharge than commercial BOPP when the RC time constant is identical. The discharge speed demonstrates that nanocomposites can be applied to the design of pulsed-power capacitors with ultra-high energy density and fast
discharge time. It can be seen that the energy density measured from the discharge measurement (Figure 4-19a) and the D-E loop measurement (Figure 4-17) has consistent results (around 3.5 J/cc at electrical field 200 MV/m). The power density calculated from the discharge curve is shown in Figure 4-19b and demonstrates that the nanocomposites can reach 2.38 MW/cc at 0.6 µs while the BOPP can only deliver 0.164 MW/cc at 0.92 µs.

![Figure 4-19. Discharged energy density and power density of nanocomposites with Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs. A) discharged energy density, B) power density profiles for nanocomposites with 7.5% BST NWs and commercial BOPP, respectively. The load resistor $R_L$ is 20 kΩ and the electrical field is 200 MV/m.](image)

In this section, a novel method for the preparation of high energy density nanocomposite capacitors with fast discharge speed has been developed. It was shown that the quenched PVDF and Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs can improve the breakdown strength of the nanocomposites with the absence of polarization saturation. The energy density with 7.5% Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs reached 14.86 J/cc at 450 MV/m, which represented a 42.9% increase in comparison to the PVDF (10.4 J/cc at 450 MV/m) and 1138% greater than commercial capacitor BOPP (1.2 J/cc at 640MV/m). To the best of my knowledge, this energy density is the highest reported for any nanocomposite incorporating a high dielectric filler ceramic/polymer capacitor in the literature [9,15-}
17,61]. Furthermore, the discharge speed of the nanocomposites is only 2.3 µs across a 20 kΩ resistor, which is faster than commercial BOPP at the same RC time constant. Furthermore, the efficiency of the nanocomposite is high due to the use of a paraelectric phase of barium strontium titanate and quenched PVDF.

**Chapter Summary**

This chapter has studied two techniques to prepare high energy density nanocomposites. The first technique is based on high aspect ratio BaTiO$_3$ NWs and the ferroelectric polymer P(VDF-TrFE-CFE). A 17.5 vol.% of BaTiO$_3$ nanocomposite showed a significant increase in the energy density, more than 45.3% higher than that of the neat P(VDF-TrFE-CFE) polymer (10.48 J/cc compared to 7.21 J/cc) at an electric field of 300 MV/m. However, this type of nanocomposite capacitor exhibits polarization saturation and high ferroelectric loss, which limits the maximum energy density of the nanocomposite. In order to overcome these limitations and obtain high energy density nanocomposite capacitors, a second technique is developed focusing on the elimination of the ferroelectric properties. Specifically, the second technique is based on choosing paraelectric phase Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ nanowires as fillers along with a quenched PVDF matrix. Compared to BaTiO$_3$/ P(VDF-TrFE-CFE) nanocomposites, this type of nanocomposite capacitor can maintain high polarization with no saturation, high breakdown strength and also reduced ferroelectric loss. The energy density of the nanocomposite with 7.5% Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs reaches to 14.86 J/cc at 450 MV/m, which represents a 42.9% increase in comparison to the PVDF with an energy density of 10.4 J/cc at the same electric field. The capacitors have more than an order of magnitude higher energy density than commercial BOPP capacitors (1.2 J/cc at 640 MV/m) and exhibit faster time to peak power and vastly improved power density. The
techniques presented in this chapter demonstrate that the use of high aspect ratio nanowires can be used to produce nanocomposite capacitors with greater performance than the neat polymers thus providing a novel process for the development of future pulsed-power capacitors.
CHAPTER 5
CONCLUSIONS

The demand for materials with high energy density and fast discharge speed is rapidly rising due to the requirement of pulsed-power devices. An example of a research area within the scope of this topic is high energy density and pulsed-power capacitors. The energy density of a capacitor is linearly related to its dielectric permittivity and quadratically to the breakdown strength. However, monolithic materials are not meeting the increasing demand for flexible, lightweight and compact high energy density capacitors. The limitation in energy density is due to the trade-off between the dielectric permittivity and breakdown strength. Nanocomposites containing high dielectric permittivity ceramics embedded in high breakdown strength polymers are currently of considerable interest as a solution for the development of high energy density capacitors. Compared to conventional ceramic or polymer capacitors, nanocomposite capacitors can not only provide lightweight, compact and cost-effective devices with higher energy density capabilities, but can also be inexpensively fabricated as large, mechanically flexible and intricate configuration devices using polymer processing techniques.

Most current nanocomposites are based on a high dielectric permittivity filler in high breakdown strength polymer matrix to improve the energy density. However, the improvement of the dielectric permittivity comes at the expense of the breakdown strength, which in turn limits the energy density of the capacitor. Therefore, the integration and geometry of the fillers must be optimized together to reach the highest possible energy density of the nanocomposites. This dissertation has explored the relationship between structure (aspect ratio and orientation) of the filler and energy
density of the nanocomposites. High energy density nanocomposite capacitors were fabricated by using high aspect ratio nanowires rather than equiaxial particles as discussed by other researchers. The highest energy density of the nanocomposites fabricated in this work reached as high as 14.86 J/cc, which was an order of magnitude higher energy density than commercial BOPP capacitors (1.2 J/cc at 640 MV/m) and exhibited faster discharged time resulting in higher power density. This dissertation provides a novel process for the development of future pulsed-power nanocomposite capacitors by using high aspect ratio nanowires with greater performance than the neat polymers.

Brief Summary of Dissertation and Results

This dissertation has investigated the development of high energy density nanocomposite capacitors with fast discharge speed. Initially, the effect of filler’s aspect ratio on the energy density of nanocomposites was investigated. High aspect ratio PZT NWs were synthesized by hydrothermal reaction, while low aspect ratio PZT NRs were obtained by decreasing PZT NWs using mortal pestle. The experimental results demonstrated that both dielectric constant and energy density of the nanocomposites were improved by the high aspect ratio fillers. The PZT NWs showed a 77.8% increase in energy density over PZT NRs, under an electric field of 15 kV/mm and 50 vol.%. This finding generated a lot of interest in this community and many researchers followed this method to prepare high dielectric constant nanocomposites, however, there was no research to quantify the relationship between the filler’s aspect ratio and the dielectric constant of the nanocomposites. In order to quantify this relationship, a method to control the aspect ratio of BaTiO$_3$ NWs was the first time to be proposed by adjusting the hydrothermal reaction temperature. The aspect ratio of BaTiO$_3$ NWs was varied.
from 9.3 to 45.3 with respect to the hydrothermal reaction temperature from 150 °C to 240 °C. The results exhibited that the dielectric constant of the nanocomposites increased with increasing aspect ratio of the filler. Nanocomposites with 30 vol.% BaTiO$_3$ NWs (aspect ratio 45.8) reached a dielectric constant as high as 44.3, which was 30.7% higher than samples with low aspect ratio (9.3) and 352% larger than the PVDF matrix. Therefore, using high aspect ratio NWs was an effective way to control and improve the dielectric constant and energy density of the nanocomposites.

In order to continue to improve the energy density, the effect of filler’s orientation on the dielectric constant and energy storage performance was studied. The NWs were aligned in the PVDF matrix by using uniaxial force assembly. The results showed that the dielectric constant and energy density of the nanocomposites were improved by the aligned fillers in the electric field direction. The increased dielectric constant with aligned NWs led to an energy density up to 51.6% greater than nanocomposites with randomly aligned filler at 20 vol.%. Additionally, the NWs’ orientation factor was successfully controlled by the draw ratio of the nanocomposites. Orientation factor was characterized by the Herman’s Orientation Factor based on the fast Fourier transform analysis of the cross-sectional SEM images of the nanocomposites. Following these tests, the relationship to the filler’s orientation factor to the dielectric constant of the nanocomposites was identified for the first time. The experimental results demonstrated that the dielectric constant of the nanocomposites increased with an increase in the filler orientation factor in the matrix. These results provided another solution to improve the dielectric constant and energy density of nanocomposites by controlling of the filler’s orientation.
Based on the prior findings, two technologies for fabricating high energy density nanocomposite capacitors were developed based on high aspect ratio NWs. The first nanocomposite capacitors were prepared by dispersing BaTiO$_3$ NWs into a P(VDF-TrFE-CFE) matrix. The nanocomposites with 17.5 vol.% BaTiO$_3$ NWs reached an energy density of 10.48 J/cc at an electric field 300 MV/m, which was 45.3% higher than that of the neat P(VDF-TrFE-CFE) polymer (7.21 J/cc at 300 MV/m). However, the high ferroelectric loss and polarization saturation from the filler and matrix limited the improvement of energy density of the nanocomposites. In order to overcome these limitations, a second technique was developed. Control over the stoichiometry of Ba$_x$Sr$_{1-x}$TiO$_3$ NWs was exhibited based on a two-step hydrothermal reaction. The paraelectric phase of Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ was chosen for NWs combined with quenched PVDF to fabricate high energy density nanocomposite capacitors. Compared to BaTiO$_3$/P(VDF-TrFE-CFE) nanocomposites, this type of nanocomposite maintained high polarization with no saturation, high breakdown strength and also reduced ferroelectric loss. The nanocomposites with 7.5% Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs were shown to have an ultra-high energy density of 14.86 J/cc at 450 MV/m, and provided microsecond discharge time quicker than commercial BOPP capacitors. The energy density of the nanocomposites exceeds those reported in the literature for ceramic/polymer composites, and was 1138% greater than the reported commercial capacitor with an energy density of 1.2 J/cc at 640 MV/m for the current state of the art BOPP. These results demonstrated that the high aspect ratio NWs could be used to produce nanocomposite capacitors with greater performance than the neat polymers thus providing a novel process for the development of future pulsed-power capacitors.
Contributions

Nanocomposites have generated substantial attention for high energy density capacitors; however the improved dielectric permittivity comes at the expense of the breakdown strength thus limiting the final energy density. This dissertation has investigated the structure-property relations in the nanocomposites for energy storage and has fabricated high energy density nanocomposite capacitors by using high aspect ratio nanowires. This work has made numerous contributions detailed in the following paragraph.

One-dimensional nanostructure of ferroelectric perovskite has been studied with increasing interest due to the potential application in microelectromechanical systems, nonlinear optics and sensors. The application of the nanowires is currently still in the initial phase, and one of the important steps is to produce high quality nanowires. This dissertation reported a series of novel methods allowing for large-scale production of wide ranging compositions of perovskite NWs, such as PZT, BaTiO$_3$ and Ba$_x$Sr$_{1-x}$TiO$_3$. Based on these methods, this dissertation is the first report of a simple route to control the aspect ratio of BaTiO$_3$ NWs by adjusting the hydrothermal reaction temperature. Additionally, the stoichiometry and structure of Ba$_x$Sr$_{1-x}$TiO$_3$ NWs were successfully controlled in achieving the desired properties for applications, such as the paraelectric phase Ba$_{0.2}$Sr$_{0.8}$TiO$_3$. These methods for large-scale and high quality production of ferroelectric perovskite NWs were expected to provide new alternatives for fabricating new electric devices in the future.

Unlike previous theoretical models regarding the effect of aspect ratio, this dissertation experimentally investigated the effect of the filler’s aspect ratio on the energy density of nanocomposites. The experimental results showed that the aspect
ratio played an important role in the energy storage of nanocomposites. Both energy
density and dielectric constant were improved by high aspect ratio PZT NWs. This
finding was also verified by using high aspect ratio BaTiO$_3$ NWs and Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs
in this dissertation. This fundamental discovery has led many researchers to follow this
route to prepare composites with improved dielectric permittivity. However, high aspect
ratio fillers still have not been investigated as extensively as spherical fillers because of
challenges in manufacturing NWs, especially for aspect ratio larger than 15. Based on
the different aspect ratio BaTiO$_3$ NWs, the relationship between the filler’s aspect ratio
and dielectric constant of the nanocomposites was experimentally quantified for the first
time. The results clearly showed that the dielectric constant of the nanocomposites was
improved with increasing aspect ratio of the NWs. It paved a new way to fabricate high
dielectric constant and energy density nanocomposites based on high aspect ratio NWs.

Furthermore, this dissertation investigated the effect of the filler’s orientation on
the energy density of nanocomposites. Compared to conventional alignment of NWs on
the substrate, a novel method was proposed to align any NWs in any thermoplastic
matrix by uniaxial force assembly. The orientation factor was easily controlled by
adjusting the draw ratio of the samples. The experimental results showed that the
dielectric constant and energy density of the nanocomposites were improved by the
aligned NWs in the electric field direction. Additionally, this dissertation detailed an
image processing method to characterize the NWs’ orientation by the Herman’s
Orientation Factor based on fast Fourier transform analysis of SEM images. Unlike
other methods requiring complex sample preparation, this method can easily
characterize the NWs’ orientation factor using easily obtained SEM images.
Furthermore, the relationship between the filler’s orientation factor and the dielectric constant of the nanocomposites was experimentally quantified, which is useful for future nanocomposite design and evaluation of theoretical models. These results provided another solution to improve the dielectric constant and energy density of the nanocomposites.

Following the prior findings, this dissertation has developed two techniques to fabricate high energy density nanocomposite capacitors based on high aspect ratio NWs, which have never been demonstrated in this form. The first technique was prepared by dispersing high aspect ratio BaTiO₃ NWs in ferroelectric polymer P(VDF-TrFE-CFE), which produced the energy density 10.48 J/cc, 45.3% higher than that of the neat P(VDF-TrFE-CFE) (7.21 J/cc) at an electric field of 300 MV/m. However, this type of nanocomposite exhibited polarization saturation and high dielectric loss that limited the maximum energy density. In order to alleviate these restraints, a second technique was developed focusing on the elimination of the ferroelectric properties. The nanocomposites were based on paraelectric phase Ba₃Sr₀.₆TiO₃ nanowires along with a quenched PVDF matrix. The energy density reached 14.86 J/cc at 450 MV/m with microsecond discharge speed. These values were significant, since it had more than an order of magnitude higher energy density than commercial BOPP capacitors (1.2 J/cc at 640 MV/m) with faster discharge time to peak power and vastly improved power density. These methods will open a new door to fabricate high energy density nanocomposite capacitors in the future.

In closing, this dissertation has made numerous contributions in the fabrication, and characterization of high energy density nanocomposite capacitors. The synthesis
of ferroelectric nanowires provided a facile method for producing large-scale and high quality nanowires to meet the desired properties of NW applications in the future. The investigation of the relationship between structure (aspect ratio and orientation) and energy density provided a baseline for fabricating nanocomposites by using high aspect ratio NWs. The use of high aspect ratio NWs and their alignment in the electric field direction provided a new route to fabricate high dielectric constant and high energy density of nanocomposite capacitors. Furthermore, the Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ NWs allowed the fabrication of nanocomposites capacitors with an energy density as high as 14.86 J/cc at 450 MV/m with microsecond discharge speed. This ultra-high energy density demonstrated a new way to produce high energy density nanocomposite capacitors based on high aspect ratio nanowires.

**Recommendations for Future Work**

This dissertation has performed fundamental research for the development of high energy density nanocomposite capacitors. The highest energy density of the nanocomposite capacitors reached 14.8 J/cc at 450 MV/mm with an efficiency of 62%. However, the existing energy loss in the capacitor leads to heating, and consequently degrades the commercial potential, performance and reliability of a capacitor. Therefore, the first recommendation for future work is to develop high energy density nanocomposite capacitors with low loss. The suggested nanocomposites can be fabricated by dispersion non-ferroelectric filler into polypropylene matrix, which is a commercial linear capacitor and has very low loss. It is expected that this nanocomposite capacitor will have high energy density, low loss and fast discharge speed.
In the case of fabrication high energy density nanocomposites, only the ferroelectric nanowires were chosen as fillers in this dissertation. As mentioned in Chapter 1, there are four different types of D-E loops: linear, relaxor ferroelectric, ferroelectric and anti-ferroelectric. Anti-ferroelectric material has low remnant polarization and relatively narrow D-E hysteresis loop, which implies higher energy storage ability with high efficiency. Therefore, it is necessary to fabricate the nanocomposites with high aspect ratio anti-ferroelectric nanowires. Hopefully, this can provide another route to fabricate high energy density nanocomposite capacitors with low loss.

Lastly, other properties of the nanocomposites could be investigated due to the active fillers PZT. The piezoelectric strain coefficient ($d_{33}$) and sensitivity of the nanocomposites could be studied in the future work. The goal of this research has been to develop a composite that can perform a wide range of functions including high energy storage and electromechanical coupling. This will allow the material system with application structural health monitoring, power harvesting and sensor.
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BIOGRAPHICAL SKETCH

Haixiong Tang was born in Hunan, China. He completed his high school at Shaodong No.1 High School in Hunan, China. In the year of 2003, Haixiong entered Harbin Institute of Technology (HIT) to start his first year of college, majored in materials science and engineering. Following four years of undergraduate study he received his Bachelors of Science degree in materials science in July of 2007. After graduation, he was recommended to go on to his master’s studies without the entrance exam in HIT. He spent two happy years in Institute of Advanced Ceramic under the supervision of Dr. Yu Zhou and Dr. Dechang Jia. He worked as both graduate assistant and teaching assistant, and focused on research of biomaterials. Following his master's studies in China, he came to USA and joined in Dr. Henry Sodano’s group to pursue his PhD degree in the mechanical engineering department at Arizona State University. In December 2010, he transferred to University of Florida with Dr. Henry Sodano to continue his research towards PhD degree in materials science and engineering. The topic of his PhD research is about investigation of structure-property relations for energy storage of nanocomposites. This research is trying to open a new door for high energy density capacitor with fast discharge speed used for future pulsed-power application. After 3 years 6 months, Haixiong defended his Doctor of Philosophy in the spring of 2013 and looks forward to a career pursuing new technologies for energy materials, nanotechnology field.