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Nonlinear dielectric thin films for high power electric storage with energy density comparable with electrochemical supercapacitors

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Abstract

Although batteries possess high energy storage density, their output power is limited by the slow movement of charge carriers, and thus capacitors are often required to deliver high power output. Dielectric capacitors have the high power density with the fast discharge rate, but their energy density is typically much lower in comparison with electrochemical supercapacitors. Increasing the energy density of dielectric materials is highly desired to extend their applications in many emerging power system applications. Here we review the mechanisms and major characteristics of electric energy storage with electrochemical supercapacitors and dielectric capacitors. Three types of in-house produced ferroic nonlinear dielectric thin film materials with high energy density are described, including $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.90}\text{Sn}_{0.05}\text{Ti}_{0.05})\text{O}_3$ (PLZST) antiferroelectric ceramic thin films, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PZN-PMN-PT) relaxor ferroelectric ceramic thin films, and poly(vinylidene fluoride) (PVDF)-based polymer blend thin films. The results showed that these thin film materials are promising for electric storage with outstanding high power density and also fairly high energy density comparable with electrochemical supercapacitors.

Key Words – Energy storage, dielectric, ferroelectric, antiferroelectric, thin film, capacitors

I. Introduction

With the development and expanded applications of various new energy generation technologies, the devices for effectively storing, absorbing, and supplying electricity are highly demanded. Not only high energy storage density, but high power electric output is also essential for many applications. Commercial electrical energy storage and energy supply devices including fuel cells, batteries, electrochemical supercapacitors, and dielectric capacitors. Among them, fuel cells and batteries possess high energy density (200~1000 Wh/kg, and 10~300 Wh/kg, respectively), but their power density is quite low (typically below 500 W/kg) due to the slow movement of charge carriers, which limits their applications in many high power systems. Electrochemical supercapacitors are able to offer improved power density (10^1 - 10^6 W/kg) at moderate energy density (0.04 ~ 30 W.h/kg) and becoming very promising in many power system applications, but their charge or discharge process still requires period of seconds or even tens of seconds. In contrast, dielectric capacitors can offer much higher power density (up to 10^8 W/kg) due to their extremely high discharge speed (millisecond or microsecond) and thus are required for the energy storage applications when high power delivery or uptake is essential. Therefore, dielectric capacitors provide the technical solutions for high power electronics and systems including electric guns. [1-3] However, conventional dielectric capacitors only have very small energy density ($\sim 10^{-2}$ - 10^{-1} W.h/kg). If the energy density can be improved to be competitive with electrochemical supercapacitors, the applications of dielectric capacitors in the area of energy management will be greatly extended.

Currently, the commercial high-power capacitors are mainly made of linear dielectric polymer materials with low dielectric constant (e.g. polypropylene, polyethylene terephthalate and polyphenylene sulfide) because of their high dielectric breakdown strength. Their volume energy density is usually below 1 to 2 J/cm³ ($\sim 10^{-1}$ Wh/kg). Recently, progresses in PbZrO₃ based

antiferroelectric ceramic thin films [4, 5] and poly(vinylidene fluoride) (PVDF)-based ferroelectric polymers have been made with substantially improved energy density above 10 J/cm^3 . [6-9] In this paper, three types of our in-house produced ferroic nonlinear dielectric thin film materials with high energy density are described, including $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.90}\text{Sn}_{0.05}\text{Ti}_{0.05})\text{O}_3$ (PLZST) antiferroelectric ceramic thin films, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PZN-PMN-PT) relaxor ferroelectric ceramic thin films, and poly(vinylidene fluoride) (PVDF)-based polymer blend thin films. We also review the mechanisms and major characteristics of electric energy storage with electrochemical supercapacitors and dielectric capacitors. The results and discussion here have shown that ferroic nonlinear dielectric thin film materials are promising for extended electric energy storage applications due to their outstanding high power density and also energy density potentially comparable with electrochemical supercapacitors.

II. Mechanisms and characteristics of energy storage in capacitors

As the electrochemical supercapacitors are receiving great attention in many power system applications, it is interesting to compare the mechanisms and major characteristics of energy storage in electrochemical supercapacitors and dielectric capacitors. An electrochemical supercapacitor is typically based on electrochemical double-layer effects (EDLCs). [10, 11] As schematically illustrated in Fig. 1, the supercapacitor comprises of several basic elements, including a porous separator, a pair of porous electrodes, electrolyte in the porous separator and electrodes, and a pair of current collectors. With an external bias applied between the two electrodes, the electrical charges supplied at the electrodes attract the ions with opposite charges in the electrolyte at the respective electrode interfaces. As the porous electrodes have very high exposed surface area (up to $\sim 10^3 \text{ m}^2/\text{g}$) and thus an extremely high capacitance value, the amount of the charge and energy stored is dramatically enhanced.

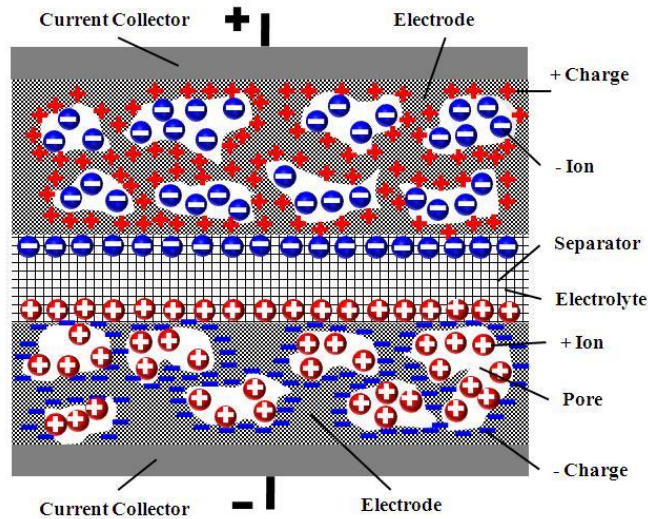


Fig. 1. A schematic illustration for an electrically charged electrochemical supercapacitor.

For a capacitor made of a dielectric material, the electric polarization mechanisms allow more charges to be stored since the dipoles created in the dielectric material under the external bias can bind more charges on the electrodes of the capacitor. There are different types of electric polarization mechanisms, including electronic polarization, ionic polarization, dipolar orientation polarization, and space charge polarization. Figure 2 schematically illustrates that the charges in the orientated electric dipoles under external bias contribute to bind the opposite charges at the respective electrode interfaces. As the polarization increases with the electric field, large amount of polarization and thus the charges bond at the electrode can be realized at large voltage. For many nonlinear dielectric materials in which the polarization does not just linearly increasing with the electric field, such as ferroelectrics and antiferroelectrics, the polarization and charges can be significantly enhanced at a large electric field. As the dielectric materials

have a large breakdown electric field, the dielectric capacitor can work at a high voltage, which can be up to several hundred volts or even higher.

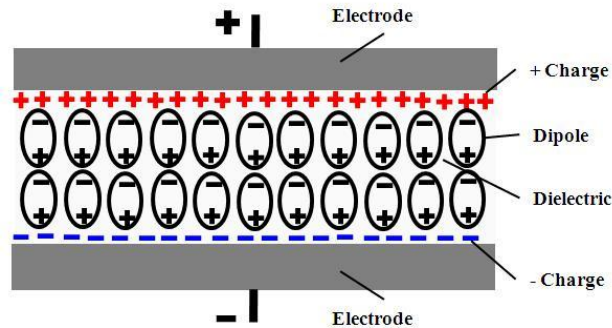


Fig. 2. A schematic illustration for an electrically charged dielectric capacitor in which the charges of the orientated electric dipoles under bias contribute to bind the opposite charges at the respective electrode interfaces.

The principles for the electrochemical supercapacitors and nonlinear dielectric capacitors determine their device characteristics. The electrochemical supercapacitors have capacitance value several orders of magnitude higher. However, the electrolyte cells have a rather small maximum working voltage, which is limited below 3.0 V. The low mobility of ions in the electrolytes restricts the charge/discharge rate (typically in the order of second), and thus the output power. The electrochemical supercapacitors also suffer from a limited cycling life ($\sim 10^5$) and often a high leakage current ($\sim \text{mA}$). The relatively complex structure also requires complicated fabrication process. The nonlinear dielectric capacitors exhibit many advantages in terms of maximum working voltage, charge/discharge rate, output power, cycling life, leakage current, and ease of the fabrication. However, the capacitance values of several orders of magnitude smaller seriously limit their energy storage density in comparison with electrochemical supercapacitors, as the stored energy U_e in a capacitor is proportional to the capacitance C as shown in Equation (1) as below,

$$U_e = \frac{1}{2}CV^2 \quad (1)$$

Nevertheless, it should also be highlighted in Equation (1) that the stored energy is proportional to the square of the voltage. Therefore, with reasonably improved capacitance value, energy density comparable with electrochemical supercapacitors could possibly be obtained as the working voltage for dielectric capacitors are significantly higher. Table I summarize the comparisons between the electrochemical supercapacitor and nonlinear dielectric capacitor.

Table I Comparisons between electrochemical supercapacitor and nonlinear dielectric capacitor.

Electrochemical supercapacitor	Nonlinear dielectric capacitor
Use of liquid electrolytes	Use of solid dielectric material
Large capacitance (~10,000 F)	Small capacitance (< 0.01 F)
Low maximum voltage (< 3 V)	High maximum voltage (> 300 V)
Slow charge/discharge (~sec)	Fast charge/discharge (~ μs-ms)
Medium power output (10^1 - 10^6 W/kg)	High power output (~ 10^8 W/kg)
Medium cycling life (~100,000)	Long cycling life (almost unlimited)
High leakage current (~ mA)	Low leakage (~0.1 mA)
Not easy to fabricate	Easy to fabricate
Medium energy density (0.04 ~ 30 Wh/kg)	Low to medium energy density (see Fig. 7)

III. Several nonlinear dielectric thin films for electric energy storage

A. $(Pb_{0.97}La_{0.02})(Zr_{0.90}Sn_{0.05}Ti_{0.05})O_3$ (PLZST) antiferroelectric ceramic thin films

Lanthanum-doped lead zirconate stannate titanate (PLZST) antiferroelectric (AFE) bulk ceramics and thin films have been investigated in the literature with interests in their large strain [12-17] and energy density [18-20]. For bulk ceramics, the switching between the AFE and

ferroelectric (FE) states occurs at low field (tenth of kV/cm), leading to small energy storage density (0.41 J/cm^3) [21]. For thin films, the large switching field (a few hundred kV/cm) results in much larger energy storage density (8.13 J/cm^3) [20, 22] compared to the bulk counterpart. However, it should be noted that secondary pyrochlore phase and even micro cracking often appear in these films with the complex compositions [23-25], which limit the electric breakdown voltage and energy density.

With our recent efforts for preparing $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.90}\text{Sn}_{0.05}\text{Ti}_{0.05})\text{O}_3$ (PLZST) thin films from an improved chemical solution approach, the secondary pyrochlore phase was effectively suppressed with the introduction of poly-ethylene glycol (PEG) in the precursor solution, and was further eliminated by applying a PbO capping layer on the film surface, as evident from the investigation with high resolution transmission electron microscopy [25]. With the improved quality of the PLZST ceramic thin films, double antiferroelectric hysteresis loop of electric displacement- field was able to obtain at a large electric field above 1300 kV/cm with a maximum electric displacement of $53 \text{ } \mu\text{C/cm}^2$ and a small remnant polarization of $3.5 \text{ } \mu\text{C/cm}^2$, as shown in Fig. 3.

The energy storage density U_e in the thin film is the area as shaded in Fig. 3, which is described in Equation (2) below,

$$U_e = \int E dD \quad (2)$$

in which E and D are the electric field and displacement, respectively. As the remnant polarization of the antiferroelectric is extremely small accompanied by the formation of the anti-parallel domain structure, energy stored in PLZST can be effectively released. Thus we obtained a large energy density of 14.0 J/cm^3 in our antiferroelectric PLZST thin films.

For comparison purpose, the hysteresis loop for a bulk PLZST ceramic as published in the literature [21] is also provided in Fig. 3, showing that the switching electric field and the energy density are significantly higher in our thin film sample than the bulk. It is estimated that the energy density in our PLZST thin film is about 30 times higher than the bulk material.

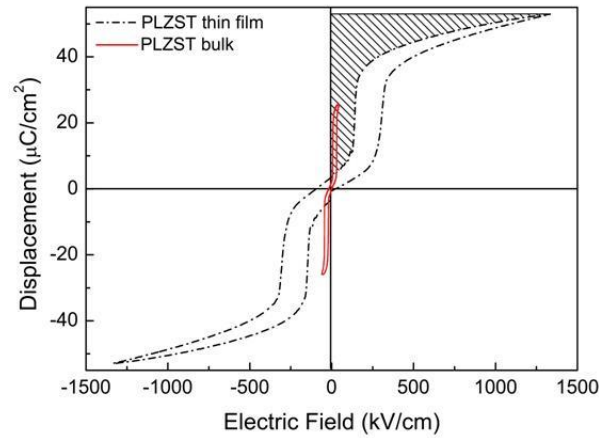


Fig. 3. The double hysteresis loop of electric displacement - field for a PLZST thin film in comparison with a bulk ceramic. The shaded area represents the energy storage density.

B. $Pb(Zn_{1/3}Nb_{2/3})O_3$ - $Pb(Mg_{1/3}Nb_{2/3})O_3$ - $PbTiO_3$ (PZN-PMN-PT) relaxor ferroelectric ceramic thin films

An ideal normal ferroelectric material with large remnant polarization is not suitable for energy storage application because the charges cannot be effectively released to the system. For achieving large useful energy stored in a ferroelectric material, a material with a large maximum polarization but small remnant polarization is desired. Therefore, relaxor ferroelectrics may be preferred to normal ferroelectrics for many energy storage applications. Here we examined the

potentials in energy storage for relaxor ferroelectric ceramic thin films with a composition of $0.462\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PMN-PT). The composition was reported near a morphotropic phase boundary, as claimed in bulk with perovskite structure [26]. However, due to the high concentration of PZN, pyrochlore phase rather than perovskite phase formed in the thin film samples by a chemical solution approach. We noted that PEG introduced in the precursor solutions of PZT and PZN exhibited the strong effects in promoting the perovskite phase while suppressing the pyrochlore phase in the resulting ceramic thin films [27, 28]. With the addition of PEG, ferroelectric PZN-PMN-PT thin films with perovskite structure were obtained on a $(\text{La,Sr})\text{MnO}_3$ (LSMO) -coated LaAlO_3 (LAO) substrate, [29] and a high dielectric constant above 4000 was demonstrated in the thin film samples. [30]

Figure 4 presents the slim hysteresis loop of electric displacement – field at an electric field of 700 kV/cm, showing a large maximum displacement of $108 \mu\text{C}/\text{cm}^2$ and a remnant polarization of $20 \mu\text{C}/\text{cm}^2$. The estimated energy density as represented by the shaded area in Fig. 4 is $15.8 \text{ J}/\text{cm}^3$ at an electric field of 700 kV/cm, in comparison with $14.0 \text{ J}/\text{cm}^3$ in the PLZST antiferroelectric thin film at 1300 kV/cm. It is expected that much higher energy density than that in antiferroelectric PLZST could be achieved in the relaxor PZN-PMN-PT thin films at the high electric field above 1000 kV/cm. However, the present relaxor PZN-PMN-PT have not been optimized to obtain high breakdown strength, and they exhibited a large leakage at higher electric field. We believe this problem could be solved with optimized PZN-PMN-PT thin films.

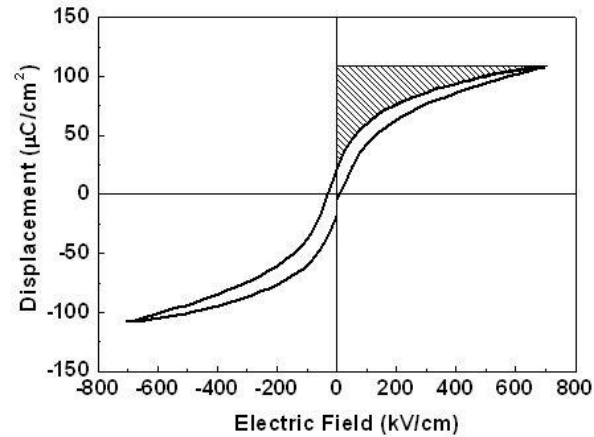


Fig. 4. The slim hysteresis loop of electric displacement – field for a PZN-PMN-PT relaxor ferroelectric thin film. The shaded area represents the energy storage density.

C. Poly(vinylidene fluoride) (PVDF)-based polymer blend thin films

Organic polymer materials typically have smaller polarization than inorganic ferroelectric material. However, commercial high-power capacitors are often made of dielectric polymer materials with low polarization and dielectric constant because of their higher dielectric breakdown strength. Poly(vinylidene fluoride) (PVDF)-based ferroelectric polymer materials with improved polarization and dielectric constant are currently receiving attention for energy storage applications. One strategy for enhancing the energy density is to transform normal ferroelectric PVDF-based polymers to ferroelectric relaxor by irradiation or adding bulky groups (e.g. chlorofluoroethylene (CFE) or chlorotrifluoroethylene (CTFE)) into the polymer chain. [6, 7, 9, 32] However, these irradiation and chemical synthesis (co- or terpolymerization) processes are either expensive or require strict process condition control, and may not be suitable for scaling up.

Our study demonstrated that, by simply blending the low-cost and readily available polymers such as PVDF homopolymer, VDF oligomer, poly(vinylidene fluoride/hexafluoropropylene) (P(VDF/HFP)) and/or poly(methyl methacrylate) (PMMA), the breakdown field and energy density of the PVDF-based blends were significantly enhanced. For example, the PVDF/P(VDF/HFP) blend film exhibited a breakdown field of 690 MV/m, which is much higher than the breakdown field of PVDF-based thin film materials without blending (typically 400-500 MV/m) [31]. When VDF oligomer was blended with P(VDF/HFP), a even higher breakdown field of 770 MV/m was achieved. As a result of the high breakdown field, the blends showed high energy densities about 15~23 J/cm³. Very recently, we observed a breakdown field above 800 MV/m in VDF oligomer and PVDF blend film and thus a high energy density more than 27 J/cm³ was obtained, which could be the highest among PVDF-based polymer systems as reported in the literature [32].

It should be noted that ferroelectric β phase could be effectively promoted with hydrated salts introduced in the precursor solution for PVDF-based polymer, and β -phase dominated PVDF homopolymer [33, 34] and P(VDF/HFP) [35] thin films could be obtained on a substrate without any mechanical stretch process. The β phase significantly improved the polarization, but could also reduce the electric strength, and therefore it did not always improve the energy density without the right design and processing.

Figure 5 shows a hysteresis loop of electric displacement – field for a PVDF/P(VDF/HFP) (10/90) blend film in comparison to the hysteresis loop of PVDF polymer film tested under the same condition. As the blend film showed a breakdown field much higher than PVDF, a significant larger energy density of 23 J/cm³ was obtained in the blend film, as represented in the shaded area in Fig. 5.

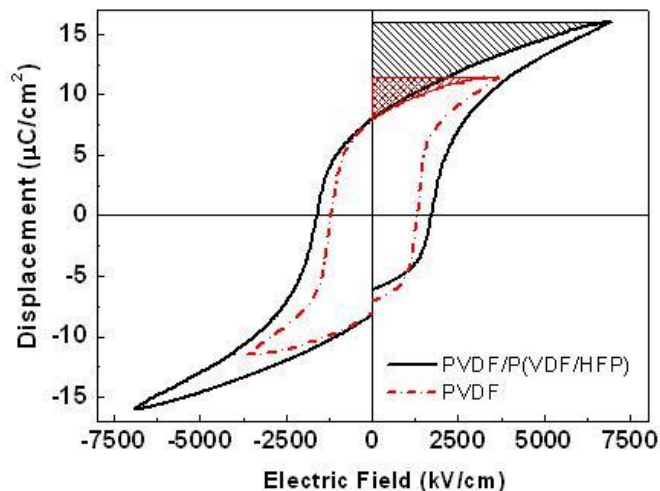


Fig. 5. A hysteresis loop of electric displacement – field for a PVDF/P(VDF/HFP) (10/90) blend film in comparison with the hysteresis loop of PVDF film tested under the same condition. The shaded area represents the energy storage density.

These ferroelectric and antiferroelectric materials have an extremely fast discharge speed, which is mainly determined by the RC (resistance-capacitance) delay in the electric circuit. As an example, a measured discharge curve is given in Fig. 6, with the discharging time is in the order of μsec . The discharge curve was measured with a circuit in which the sample was first charged by a high-voltage source, and then through a switch, the sample was discharged to external resistors monitored with an oscilloscope (TDS 3052C, Tektronix, Beaverton, OR). In this case, the capacitance of the P(VDF-HFP/PVDF) sample had a capacitance of 41.7 PF and the external load resistance was 47 K Ω without taking into account the internal resistance. The calculated relaxation time is 1.96 μs . Thus, the decay time of $\sim 2.1 \mu\text{s}$ was mainly determined by the RC delay. Inorganic antiferroelectrics and relaxor ferroelectrics should usually also have extremely fast discharging speed, which is determined by the nature of the fast domain

orientation. The discharging time will increase with the much larger capacitance and load resistance in practical applications.

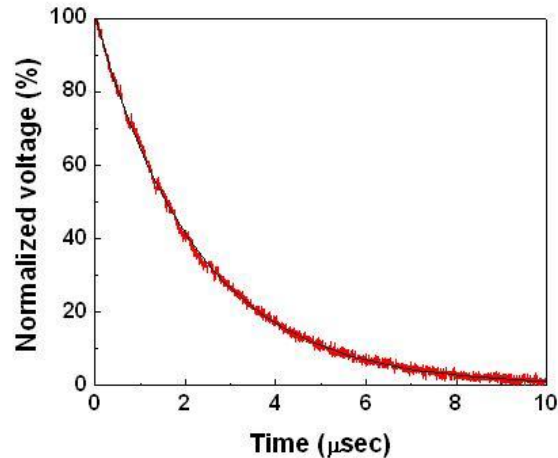


Fig. 6. The measured discharge curve for a PVDF/P(VDF/HFP) (10/90) blend film sample, with the exponential fitting curve.

D. Discussion

For the comparisons with various energy storage means, the power density and energy density for the nonlinear dielectric thin film materials as presented in this paper and the commercial dielectric capacitors, electrochemical capacitors, and batteries are summarized in Fig. 7. All the three types of thin film materials exhibited the outstanding power density, and an energy density potentially comparable with electrochemical supercapacitors but well below batteries. Here the calculated energy density values for the dielectric thin films did not take into account the weight of the substrate, electrodes, and any packages. The overall energy density for the packaged capacitors made of these ferroelectric and antiferroelectric thin films will be certainly much lower than that in Fig. 7. However, by implementing appropriate device structure, such as multilayer

configuration, it is possible that the energy density of the packaged dielectric capacitors are mainly determined by the energy density of these dielectric thin layers. Therefore, the results in Fig. 7 show the potentials for producing capacitors with these nonlinear dielectric thin films with outstanding power density and also energy density comparable with electrochemical supercapacitors.

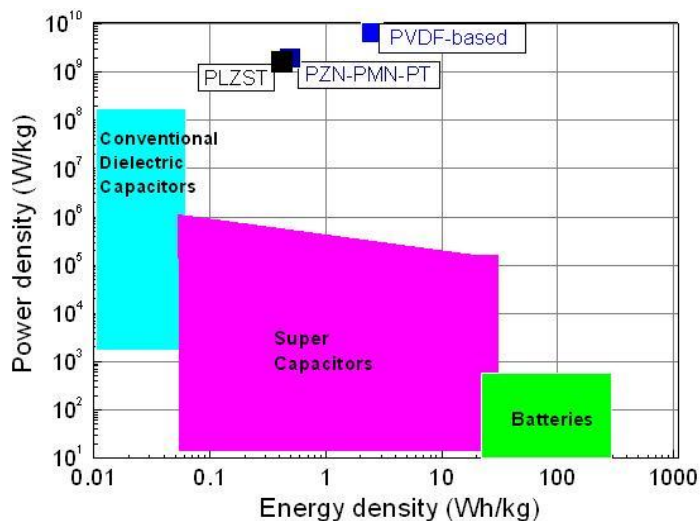


Fig. 7. Power density and energy density for the PLZST, PZN-PMN-PT, and PVDF-based polymer blend thin films, in comparison with the commercial dielectric capacitors, electrochemical capacitors and batteries.

As analyzed in Section II and summarized in Table I, dielectric capacitors have many advantages over the electrochemical capacitors, such as the large working voltage and high charge/discharge rate, high output power, long cycling life, low leakage current, and ease of the fabrication, while the major disadvantage is the lower energy density. With the exhibition of the high energy density potentially comparable with that of electrochemical capacitors, the ferroelectric and antiferroelectric nonlinear dielectric thin films could be promising for producing capacitors competitive to electrochemical capacitors for electric energy storage.

The PVDF-based ferroelectric polymer blends exhibited a slight higher energy density in term of weight than the PZN-PMN-PT ferroelectric ceramic thin films and PLZST antiferroelectric ceramic films. As the polymer has a substantially smaller density than the inorganic ceramic, the energy density in term of weight for the polymer blends becomes even significantly larger. The higher energy density in ferroelectric polymers than the inorganic antiferroelectrics is attributed to their higher electrical breakdown strength, which outweighs the negative effect of their relatively lower polarization. However, as the PVDF-based polymers become unstable at a high temperature, the inorganic materials may be required for the applications at an elevated temperature. The development of high temperature and high energy density dielectric materials is also one of the new challenges currently attracting research interests. [36]

It should be highlighted that antiferroelectric and ferroelectric thin film samples could exhibit dramatically improved energy density compared with their bulk counterparts. One of the reasons is that thin films usually have a larger switching field for antiferroelectric and a larger coercive field for ferroelectric thin films in comparison with the respective bulk materials. In addition, thin film samples also exhibit substantially higher electric strength, and their electric polarization also tends to saturate at higher electric field.

The bipolar cycling stability for ferroelectric thin films is mainly limited by the polarization switching fatigue behavior. However, for energy storage applications, the nonlinear dielectric capacitors often work under a unipolar cycling condition in which the polarization fatigue is very minor. Thus, the ferroelectric-based capacitors can have an extremely long cycling life in principle if no electric breakdown occurs.

Another nonlinear dielectric material currently explored for high energy density application is ceramic-polymer composites. [37-39] Currently, the electric strength of these composites are often lower than those of the unfilled polymer materials, which limits the energy density of the composites. The understanding on the interfaces between the different phases and the geometric factor of the fillers is being improved to design appropriate composites with further improved energy density.

IV. Conclusions

Three types of our in-house produced ferroic nonlinear dielectric thin film materials with high energy density are described, including $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.90}\text{Sn}_{0.05}\text{Ti}_{0.05})\text{O}_3$ (PLZST) antiferroelectric ceramic thin films, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PZN-PMN-PT) relaxor ferroelectric ceramic thin films, and poly(vinylidene fluoride) (PVDF)-based polymer blend thin films. We also review the mechanisms and major characteristics of electric energy storage with electrochemical supercapacitors and dielectric capacitors. The results and discussion here have shown that ferroic nonlinear dielectric thin film materials are promising for extended electric energy storage applications due to their outstanding high power density, fairly high energy density potentially comparable with electrochemical supercapacitors, and many other advantages such as high charge/discharge rate, long cycling life, low leakage current, and ease of the fabrication. It should also be highlighted that antiferroelectric and ferroelectric thin film samples could exhibit dramatically improved energy density compared with their bulk counterparts because they typically have higher electric strength and the electric polarization tends to saturate at higher electric field. The PVDF-based ferroelectric polymer blends exhibited significantly larger energy density in term of weight than the inorganic ceramic thin films due to

their high dielectric strength and low density. However, the inorganic materials may be required for the applications with a broaden temperature range.

VI. Acknowledgement

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