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Review

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Modeling-guided understanding microstructure effects in energy storage dielectrics

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Abstract

Addressing the relationships between microstructures and properties is critical to the design of novel dielectric capacitors, which further enables widespread promising applications in electronic and electrical systems. The present review focuses on the role of different theoretical modeling techniques in understanding microstructural effects in energy storage dielectrics. State-of-the-art developments in the computational modeling of inorganics, polymers and their composite dielectrics are summarized. Diverse microstructural effects, including domain configurations, crystallization behavior and composite structures, are discussed with regards to different models. Theoretical modeling is not only essential for gaining fundamental insights into the underlying mechanisms behind experimental phenomena but can also be used to inversely engineer the design of dielectrics by prediction or optimization. Finally, to further promote innovative developments in dielectric capacitors, some future perspectives are provided to stimulate the in-depth consideration of the research paradigm between modeling and experiment.

Keywords: Theoretical modeling, microstructural effects, energy storage, dielectric capacitors

INTRODUCTION

With the rapid development of the global economy, the demand for energy continues to grow. Simultaneously, a series of problems, such as the fossil energy crisis, climate change and air pollution, have promoted the urgent need for high-performance materials for energy storage[1-4]. In existing electrical storage technologies, dielectric capacitors, which store and release energy by dipole polarization, have attracted increasing attention due to their fast charge/discharge rate and ultrahigh power density. As one of the most important electronic parts and components, dielectric capacitors have enabled widespread applications ranging from high-voltage direct-current transmission to high-power weapons, hybrid electric vehicles, medical equipment and other electrical/electronic systems[5,6]. Nevertheless, dielectrics with low energy density limit the further applications of capacitors under the increasing demands for miniaturization and portability. For example, the commercial dielectric biaxially oriented polypropylene (BOPP) usually exhibits a limited energy density of less than 2 J/cm^3, leading to a large volume and weight of capacitors in electrical equipment[7]. In addition, more electric power applications are required to be used in harsh environments with high temperature and voltage conditions, which puts forward strict requirements for dielectric capacitors with higher dielectric strength and rated temperature[8-10]. Therefore, dielectric materials with high energy density, efficiency and stability are highly desirable for electrostatic energy storage devices.

A simple dielectric capacitor consists of two metal electrodes with a dielectric material between them[3,11]. As shown in Figure 1, without an applied electric field, the dipoles in dielectrics are random. When an electric field is applied during charging, the electrostatic energy is stored by the dipoles aligning along the direction of the applied electric field. After removing the electric field, the oriented dipoles tend to be randomly distributed again and the stored electrostatic energy is released into the load. Therefore, the recoverable energy density of a dielectric can be obtained by the integral of the polarization and the electric field:

$$U_e = \int_{P_r}^{P_m} E\,dP \tag{1}$$

where P_m and P_r are the maximum polarization and remnant polarization, respectively. The hysteresis response of polarization to an electric field leads to a partial energy loss (U_{loss}) in dielectrics, so the energy storage efficiency η for a dielectric can be expressed as $\eta = U_e/(U_e + U_{loss})$.

For linear dielectrics with the dielectric constant independent of the electric field, the stored energy storage density is given by:

$$U_e = \frac{1}{2}\varepsilon_0\varepsilon_r {E_b}^2 \tag{2}$$

where ε_0, ε_r and E_b represent the vacuum dielectric constant, relative dielectric constant and breakdown strength, respectively. It can be seen from Equation (2) that in order to obtain high energy density, dielectrics with high polarization (i.e., a high dielectric constant) and breakdown strength and low dielectric loss are highly desired. However, one of the main problems of dielectrics is that the increase of E_b is usually at the expense of ε_r, due to the extremely high local electric field in dielectrics with high ε_r tending to weaken the polar dipoles, thereby making them easier to break[12,13]. Therefore, it is necessary to explore new strategies and rational designs to simultaneously improve the breakdown strength and dielectric constant of dielectric materials[14].

The intrinsic properties of a material are among the most basic principles to be considered in the design of energy storage dielectrics. Generally, according to the different responses of polarization to the applied electric field, dielectric materials can be divided into linear dielectrics, ferroelectrics, relaxor ferroelectrics and antiferroelectrics[15-17]. Their schematic dipoles, domain structures and polarization hysteresis loops are displayed in Figure 2. Linear dielectrics are characterized by linear polarization loops, high energy storage efficiency and negligible dielectric loss, but their low dielectric constant limits their further application.

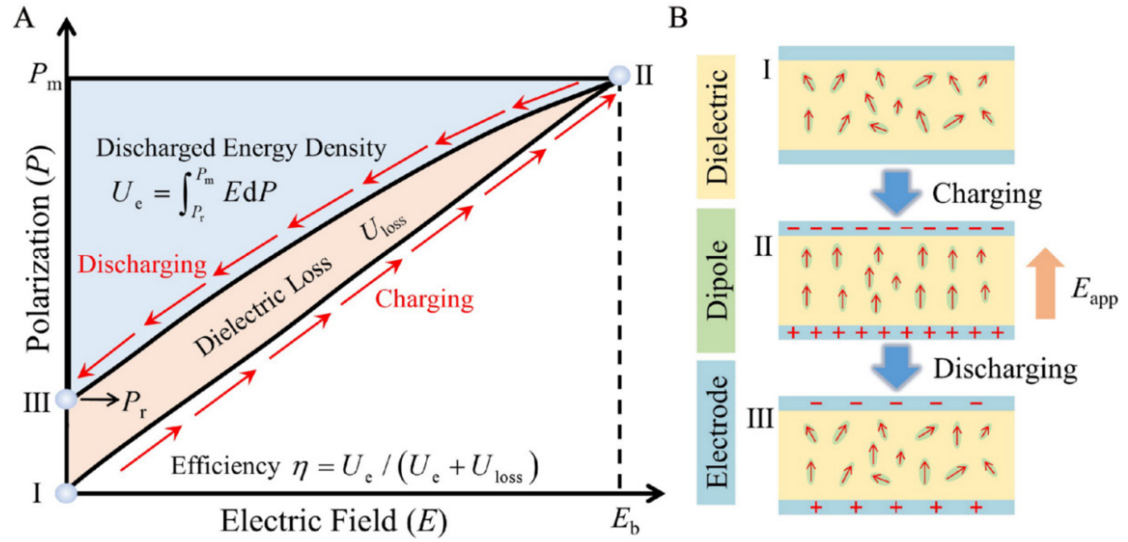

Figure 1. (A) Schematic of dielectric energy storage during a charge/discharge process. Points I to II represent the charge process, while points II to III represent the discharge process. (B) Corresponding local dipole states in the dielectrics of points I, II and III.

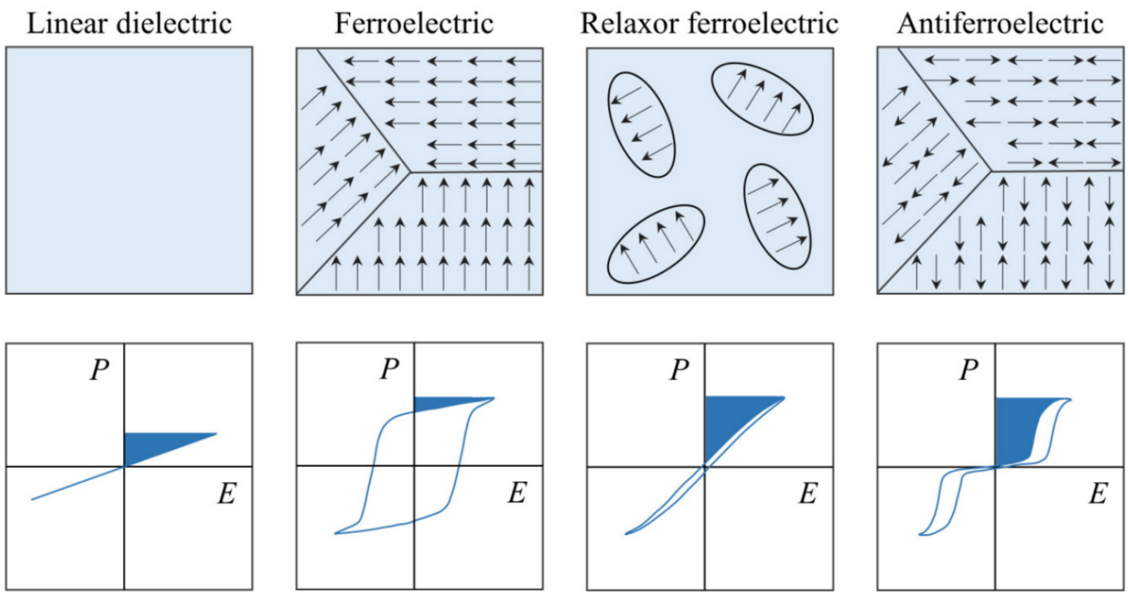

Figure 2. Schematic illustration of dipoles, domain structures and polarization hysteresis loops for linear dielectrics, ferroelectrics, relaxor ferroelectrics and antiferroelectric materials.

Ferroelectrics are widely studied due to their high dielectric constant, but their large remnant polarization is not conducive to achieving high energy density. Relaxor ferroelectrics and antiferroelectrics show excellent potential in optimizing energy storage efficiency and energy density, making them promising candidates for energy storage applications[4,18]. For example, there are nanodomains that can be freely flipped in relaxor ferroelectrics, resulting in lower remnant polarization and dielectric loss. Benefitting from the antiferroelectric-ferroelectric phase transition at high fields, antiferroelectrics exhibit double hysteresis loops, resulting in low coercive fields and high saturated polarization[19]. Therefore, the selection of suitable dielectrics can be used to effectively regulate the energy storage performance. On this basis, as illustrated in Figure 3, the diversity and complexity of microstructures at different scales in dielectrics open another perspective for regulating energy storage performance.

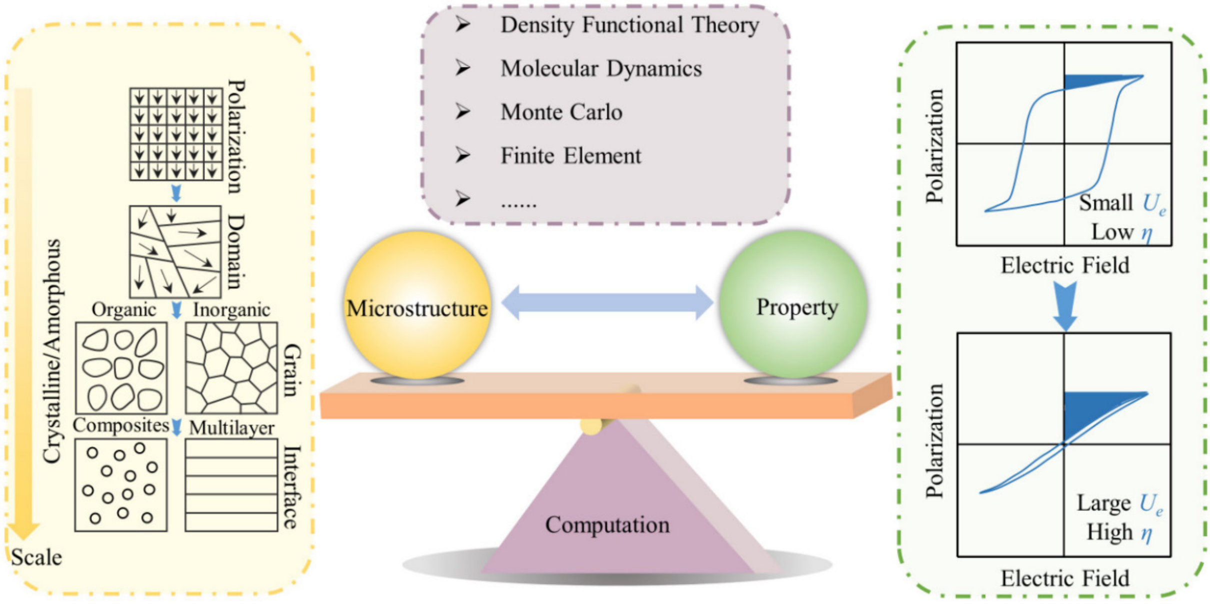

Figure 3. Schematic of the relationship between microstructures and ferroelectric properties and the role of theoretical modeling in guiding the multiscale design of microstructures in dielectrics.

In recent decades, a large number of studies have shown that regulating the microstructures in dielectrics represents a simple and effective method to improve the energy storage performance[6,20,21]. The variety of microstructures at different scales provides considerable opportunities for regulating performance, including domain configurations, crystallization behavior, composite structures and so on[3-5,11]. For example, at the nanoscale, ferroelectric materials respond to external field changes through domain switching. During the polarization switching process, the coupling effect between domains makes ferroelectrics exhibit nonlinear behavior, resulting in an increased energy loss. Some studies have shown that high energy density can be achieved by designing and controlling domain structures, such as the transformation of microscale domains into highly dynamic nanodomains[6,22]. When the scale increases to the micron level, taking inorganic dielectrics as examples, microstructural properties, such as grain size and grain boundaries, have a significant influence on the dielectric properties[23]. Fine ceramic grains with a uniform distribution can exhibit higher breakdown strength, leading to an enhancement in energy density.

With a further increase in scale, the heterogeneous structures in composite dielectrics have been proved to have substantial effects on dielectric properties by combining the advantages of all phases and some possible coupling effects, such as interfacial effects[21,24,25]. A great deal of composite structures have been designed to modulate the energy storage performance in experiments, such as core-shell, sandwich and multilayer structures, and polymer-based composites with inorganic nanofillers[7,26,27]. As a result, microstructural design has become a major research hotspot in the field of dielectric capacitors[1,28,29]. Beyond the limitations of material type, the diversity and complexity of microstructures at different scales provide a new level of design freedom for regulating the energy storage performance. However, this also brings more difficulties in clarifying the microstructure-property relationships and underlying mechanisms due to complicated and diverse influencing factors. Therefore, accurate knowledge of the relationships between the microstructures and properties of dielectrics is conductive to further promoting the development of high-performance dielectrics for energy storage.

With the continuous improvement of basic theories and the rapid development of computing power, theoretical modeling has become a burgeoning method in the exploration of the underlying microstructure-property relationships and the guidance of experimental optimization and design. In the field of dielectric materials for energy storage, complementary to experiments and characterization, ever more models are being developed to study microstructural effects. For example, density functional theory (DFT) and molecular dynamics (MD) can be used to determine some dielectric properties, including the electronic structure and intermolecular interactions, which are difficult to obtain experimentally[30-33]. In addition, some complex dielectric behavior, such as domain switching, dynamic processes of electric breakdown and interfacial effects, could be simulated by phase-field or finite element methods at the mesoscale[34-36]. In this review, we first briefly introduce the background to energy storage dielectrics. We then summarize some recent works on improving energy storage performance through microstructural design with the aid of theoretical modeling. These studies are organized into three areas, namely, inorganics, polymers and polymer-based composites. Finally, conclusions and future perspectives are provided. The main purpose of this review is to emphasize the importance of theoretical modeling and facilitate the cooperation of experiments and modeling.

INORGANIC DIELECTRICS

Compared with other dielectric materials, inorganic dielectrics have broad application prospects in energy storage due to their medium breakdown strength, high dielectric polarization and excellent temperature stability[4,37]. In recent decades, microstructural design in inorganic dielectrics, such as ferroelectrics, relaxor ferroelectrics and antiferroelectrics, have been extensively studied by domain engineering, grain regulation and the artificial design of core-shell or multilayer structures[22,38-44]. Although these microstructural designs can be achieved by advanced equipment and optimized fabrication processes, most of the underlying mechanisms of varying performance are poorly understood. Recently, theoretical modeling has gradually become an effective tool for clarifying microstructure-property relationships, including polymorphic nanodomain, grain and interfacial effects[35,45-48]. Here, some microstructural effects across different scales on the polarization and breakdown strength of inorganic dielectrics are analyzed from a modeling perspective.

At the nanoscale, domain configuration and switching behavior strongly affect the macroscopic ferroelectric properties[49]. Generally, microdomains in ferroelectrics tend to show strong ferroelectric hysteresis and large remnant polarization, resulting in high dielectric loss and low energy storage efficiency. On the contrary, weakly coupled polar nanodomains in relaxor ferroelectrics are highly dynamic and sensitive to the applied electric field. Therefore, relaxor ferroelectrics exhibit slim Polarization-Electric Field (P-E) loops with modest maximum polarization and negligible remnant polarization in the process of charging and discharging[50,51]. In recent decades, in order to achieve high energy density, increasing attention has been paid to the construction of nanodomains to promote the transformation of ferroelectrics into relaxor ferroelectrics[52-55]. However, due to the complexity of domain structures at the nanoscale, the reasonable construction of nanodomains has become a significant challenge in experimental design.

Based on Landau's theory, a phase-field model was properly developed to simulate domain structures and switching under external stimuli[56,57]. For instance, Pan *et al.*[58] proposed a polymorphic nanodomain strategy based on phase-field simulations. First, the domain structures of solid solutions were simulated, as shown in Figure 4A and B. It was found that the $0.45BiFeO_3$-$0.55SrTiO_3$ solid solution possesses rhombohedral domains while the $0.20BiFeO_3$-$0.25BaTiO_3$-$0.55SrTiO_3$ ternary system has a disordered structure with coexisting rhombohedral and tetragonal nanodomains. These polymorphic nanodomains with competitive free energy in ternary systems can effectively weaken the polarization anisotropy and reduce the domain switching barrier, leading to a higher polarization and lower dielectric loss. The energy density and efficiency of different components were then calculated to find the best composition in this system. Finally, under the guidance of simulation results, the optimized $0.25BiFeO_3$-$0.30BaTiO_3$-$0.45SrTiO_3$

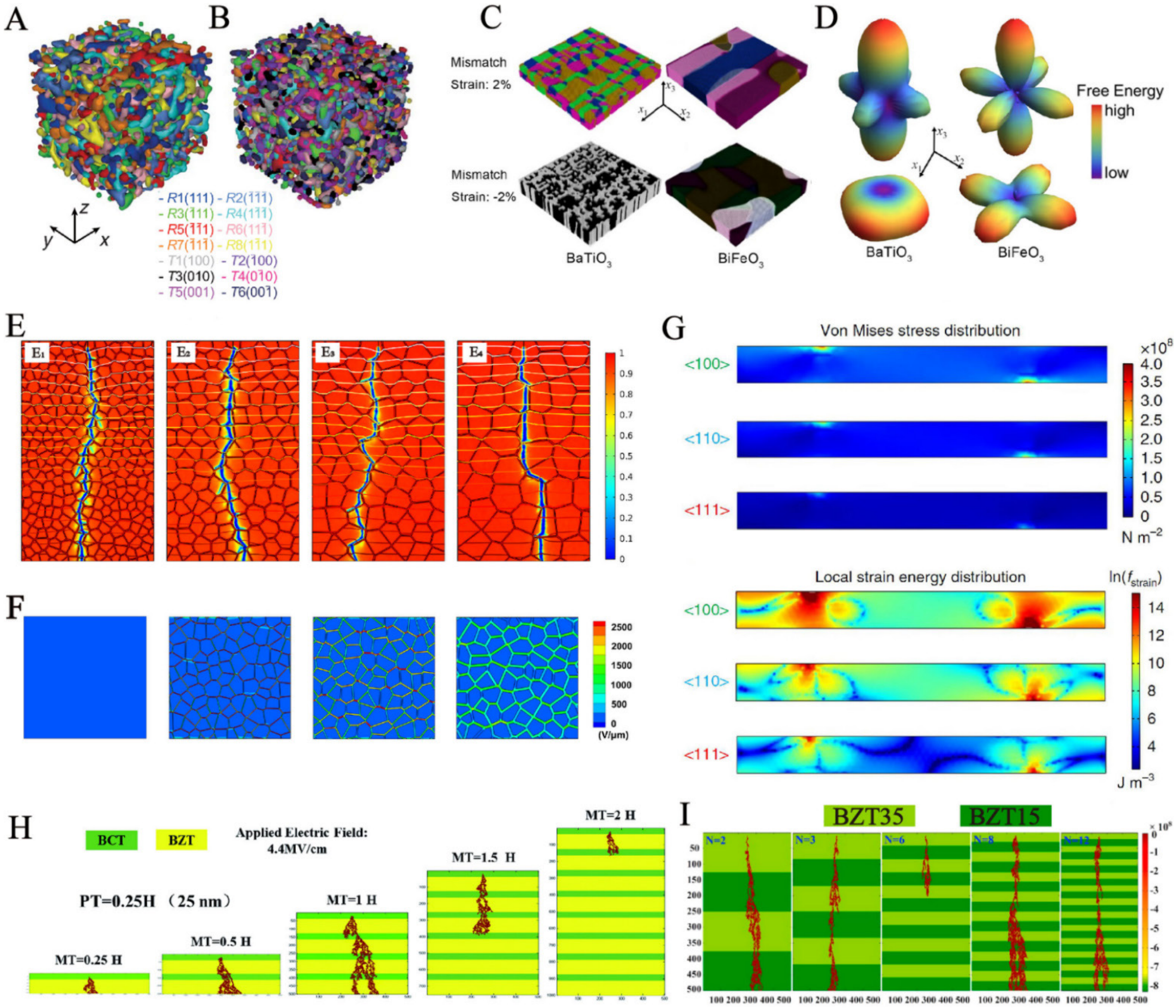

Figure 4. Simulated domain structures of (A) $0.45BiFeO_3$-$0.55SrTiO_3$ and (B) $0.20BiFeO_3$-$0.25BaTiO_3$-$0.55SrTiO_3$[58]. (C) Simulated domain structure of $BaTiO_3$ and $BiFeO_3$ thin films under mismatch strains of 2% and -2%. Black and white colors represent domains with stronger out-of-plane polarization components, while other colors represent domains with stronger in-plane polarization components[59]. (D) Free energy surfaces of $BaTiO_3$ and $BiFeO_3$ under mismatch strains of 2% and -2%, respectively[59]. (E) Breakdown path in dielectrics with different grain sizes[61]. (F) Local electric field distribution of virtual samples with different shell fractions under an external applied voltage of 200 V[68]. (G) Finite element simulation of the distribution of stress and elastic energy density in a single layer of a multilayer ceramic capacitor[72]. (H) Simulated development of electric trees in $Ba_{0.7}Ca_{0.3}TiO_3/BaZr_{0.2}Ti_{0.8}O_3$ multilayer films with different total thicknesses[74]. (I) Simulated evolution of electric trees in $BaZr_{0.15}Ti_{0.85}O_3/BaZr_{0.35}Ti_{0.65}O_3$ multilayer films with different stacking periodic numbers (N)[77].

composition exhibited minimized hysteresis while maintaining high polarization and achieved a giant energy density of 112 J/cm^3 with a high energy efficiency of ~80%.

In domain engineering, besides forming solid solutions, strain engineering is also widely used to tune the domain behavior. For example, Wang *et al.*[59] used the phase-field method to calculate free energy surfaces and predict the domain structures of ferroelectric oxide thin films under mismatch strains of 2% and -2%. Taking $BaTiO_3$ as an example, as shown in Figure 4C and D, a $BaTiO_3$ thin film under a 2% equibiaxial mismatch strain shows orthorhombic in-plane domains and the surface free energy is at a maximum when the polarization is along the out-of-plane [001] and [00$\bar{1}$] directions. Alternatively, a $BaTiO_3$ thin film under -2% equibiaxial mismatch strain shows out-of-plane tetragonal domains and the surface free energy is at maximum when the polarization is along the in-plane [00$\bar{1}$], [010], [$\bar{1}$00] and [0$\bar{1}$0] directions. Therefore, in-plane tensile strain reduces remanent polarization and out-of-plane tensile strain increases saturated polarization. Based on the predicted results of the strain effects on the domain structure and polarization, a bending strategy for optimizing the charge/discharge density was proposed. $PbZr_{0.52}Ti_{0.48}O_3$ with a high energy density of 182 J/cm^3 was then obtained by bending the substrate up and down during the charge/discharge process.

On a larger scale than the domain structure, crystallization behavior is another research hotspot[4,15]. For example, the grain size has a significant effect on dielectric properties, especially for the breakdown strength. In inorganic dielectrics, the relationship between the breakdown strength and grain size can be empirically described as[60]:

$$E_b \propto 1/\sqrt{G} \tag{3}$$

where G is the grain size. A decrease in grain size leads to an increase in grain boundary density, which can prevent the further migration of charge carriers and improve the breakdown strength. Furthermore, due to the quadratic correlation to the energy density, increasing breakdown strength can improve the energy density more effectively than increasing the dielectric constant. Increasingly more researchers have struggled to further elucidate the effect of crystallization behavior on the breakdown process[41,47,61]. However, it is difficult to characterize the breakdown process by experimental techniques because the dielectric breakdown is a complex nonequilibrium process.

Generally, the breakdown is often accompanied by a conductive path throughout the materials; thus, dynamic simulations of the breakdown path can help to better analyze the dielectric breakdown process[62]. As a result, many theoretical models have been proposed to simulate the generation and expansion of electric trees, such as the dielectric breakdown[63,64] and electron avalanche models[65]. For example, Cai *et al.*[61] established a phase-field model to study the effect of grain size on the breakdown path. As shown in Figure 4E, during the dielectric breakdown process, the breakdown path is hindered by the grain boundary due to the higher breakdown energy required. Therefore, inorganic dielectrics with fine grains show higher breakdown strength. Furthermore, the concept of core-shell dielectric ceramics was proposed, which is based on the use of highly insulating materials, such as SiO_2 and Al_2O_3[66,67], to coat ferroelectric ceramic grains. Wu *et al.*[68] employed the finite element method to investigate the effect of core-shell structures on dielectric properties in terms of the electric field distribution. It can be seen from Figure 4F that for a given electric field, the local field uniformity is enhanced with increasing shell fraction, which is conducive to higher dielectric breakdown strength. Likewise, Yuan *et al.*[69] designed core-shell $BaTiO_3$-$Bi(Mg_{0.5}Zr_{0.5})O_3$@SiO_2 relaxor ferroelectrics and found that the introduction of SiO_2 reduced the grain size of $BaTiO_3$-$Bi(Mg_{0.5}Zr_{0.5})O_3$.

Simultaneously, finite element simulations have showed that SiO_2 forms interfacial barriers to prevent the rapid development of electric trees. In addition, the electrostrictive strain under the external electric field also seriously affects the electromechanical breakdown of dielectric ceramics[70]. Studies have shown that due to the strong electrostrictive anisotropy, the electrostrictive strain produced by grains with different orientations varies greatly[71]. Recently, Li *et al.*[72] performed finite element simulations to investigate the effect of grain orientation on electric field-induced strain in textured ceramics. As displayed in Figure 4G, compared with other ceramics, <111>-textured ceramics exhibit much lower stress, local displacement and elastic energy, which is excepted to enhance the breakdown strength. To experimentally realize this concept, the authors fabricated high quality <111>-textured $Na_{0.5}Bi_{0.5}TiO_3$-$Sr_{0.7}Bi_{0.2}TiO_3$ ceramics by a template grain growth method. The <111>-textured ceramics show lower electric field strain, leading to a decrease in the failure probability and an increased breakdown strength of ~103 MV/m, which was ~65% higher than that of the corresponding randomly oriented ceramics.

In addition, the artificial design of multilayer inorganic dielectrics by stacking two layers of different components has been widely studied due to the existence of hierarchical interfaces in the multilayer structure[73-76]. Interfacial engineering has been shown to be effective in enhancing dielectric energy density. Simultaneously, researchers further used computational simulations to explain how the interface between the dielectric layers affects the growth of electric trees and the distribution of the electric field. For instance, Sun *et al*.[74] prepared multilayer films of $Ba_{0.7}Ca_{0.3}TiO_3/BaZr_{0.2}Ti_{0.8}O_3$ dielectrics and used theoretical models to study the effects of interfacial density and total multilayer film thickness on the dielectric breakdown. The development of electric trees was simulated by the finite element method for the multilayer films with the same period thickness with a different total thickness, as shown in Figure 4H. It can be seen from the simulation results that with increasing total thickness of the multilayer films, the suppression effect of the interface on the electric trees is enhanced. This phenomenon can be attributed to the increase in interfacial density, which can boost the ability to prevent the growth of electric trees. Analogously, Fan *et al.*[77] prepared a $BaZr_{0.15}Ti_{0.85}O_3/BaZr_{0.35}Ti_{0.65}O_3$ multilayer thin film by controlling the number of interfaces under a given total thickness. As presented in Figure 4I, the development of electric trees was simulated based on the finite element method. The simulation results can be explained from two perspectives. Firstly, the existence of the interface can block the electric trees penetrating in the film. Secondly, interfacial coupling becomes stronger with increasing interface number, which may weaken the interfacial blocking effect. Therefore, the breakdown strength achieves its maximum value when the period number N is 6.

As mentioned above, many studies have realized improved energy density by optimizing microstructures through domain engineering, grain engineering and multilayer structures. With the aid of theoretical modeling, the influence of microstructural changes on dielectric properties is analyzed, including polarization switching and dielectric breakdown. However, the low breakdown strength is still the main factor limiting for the increase in the energy storage density of inorganic dielectrics. Simultaneously, alleviating and breaking the coupling between polarization and breakdown strength are key challenges for further performance enhancement. The combination of theoretical modeling and experimental characterization is expected to explore unrevealed mechanisms and accelerate the discovery of novel inorganic dielectrics with excellent energy storage properties.

POLYMER DIELECTRICS

Compared with inorganic dielectrics, polymer dielectrics have the advantages of high intrinsic breakdown strength, good flexibility, lightweight and easy processing[3,8]. In recent years, to replace commercial BOPP film capacitors for device miniaturization and cost reduction, extensive research has been carried out to discover or create new polymer systems, such as ferroelectric polymers (e.g., PVDF, PVDF-HFP and PVDF-TrFE) and linear polymers (e.g., PI, PEI and PS)[26]. Meanwhile, researchers have found that microstructural regulation could be a direct and effective approach for improving the energy storage performance, such as molecular chain modification, crystalline/amorphous phase behavior and multilayer structures[78-83]. A growing number of studies have made excellent progress under the guidance of theoretical modeling. Here, we present several representative works to summarize the role of theoretical modeling in addressing the influence of microstructural effects on dielectric properties.

At the molecular level, DFT and MD are widely used to study the behavior of molecular chains in polymers[84,85]. Such behavior includes thermodynamic details, the interactions between molecular chains and the optimized molecular structure of the polymers[86-89]. For example, Wang *et al.*[90] used DFT simulations to investigate the role played by -OH functional groups and water molecules in two short-chain polyethylene oligomers (o-PE), as shown in Figure 5A. The dielectric constant increases from 2.3 for o-PE to 4.3 for o-PE-OH-$2H_2O$ due to the contribution of electrons and ions. Further simulation results have shown that the use of functionalized polymer chains is an effective path to improving the dielectric constant of polymers. Additionally, Thakur et al. reported that by blending poly(arylene ether

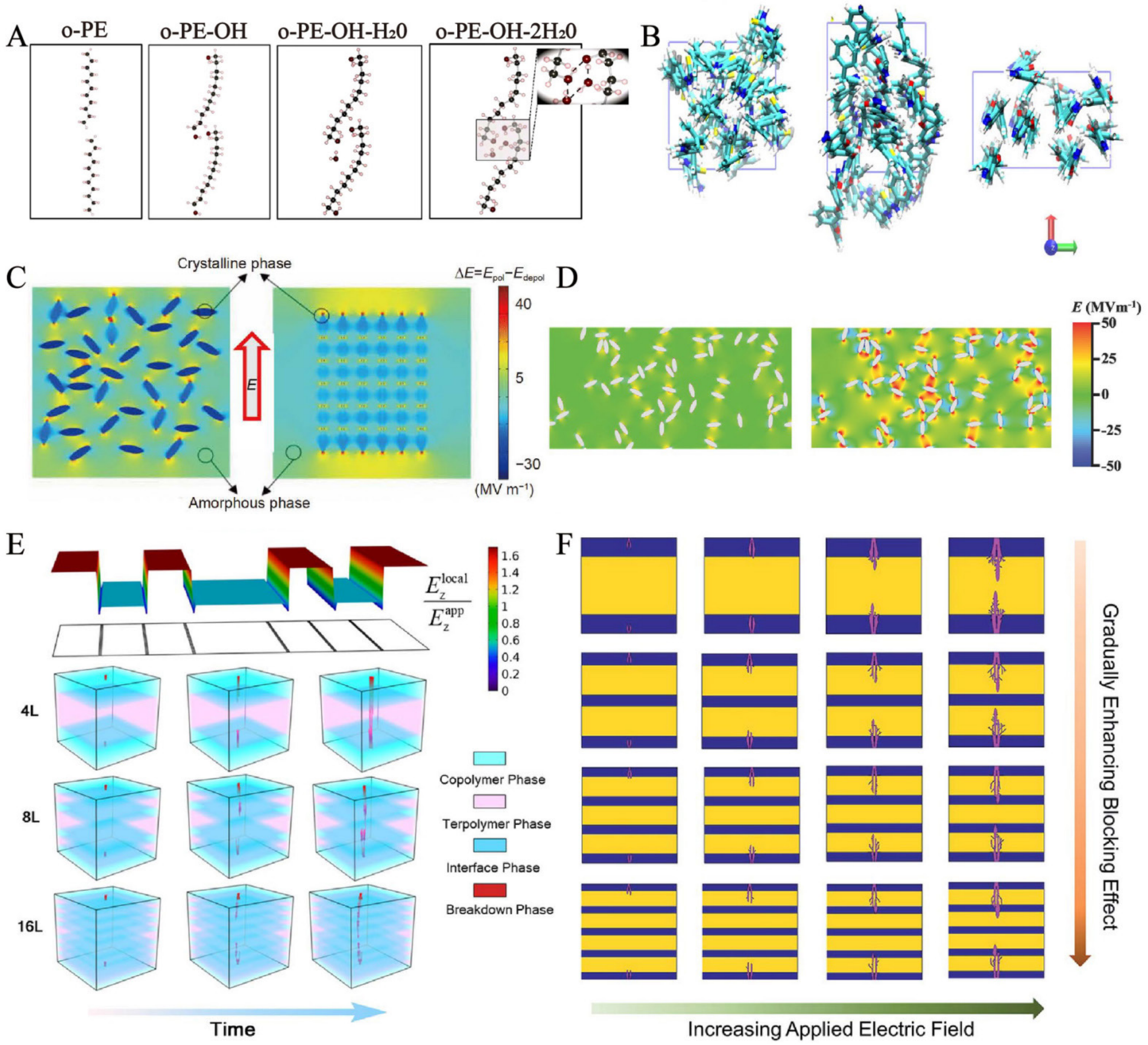

Figure 5. (A) Optimized structures of o-PE, o-PE-OH, o-PE-OH-H_2O and o-PE-OH-$2H_2O$, where black, white and red spheres represent C, H and O atoms, respectively[90]. (B) From left to right, top view of simulation unit cells of ArPTU, blend with a 1:1 PEEU:ArPTU ratio and PEEU, respectively[91]. (C) Simulated microscopic local electric field distribution of ΔE in polymer blends with random and ordered distributed amorphous phases[95]. (D) Internal field distribution inside the relaxor ferroelectric polymer blend before (left) and after int-biased (right) at 50 MV/m[96]. (E) Distribution of local electric field along the direction of the applied field in Co/Ter multilayer films with eight layers (top) and their breakdown evolution (bottom)[97]. (F) Breakdown evolution for multilayer films with different layers[98].

urea) (PEEU, ε_r = 4.7) and aromatic polythiourea (ArPTU, ε_r = 4.4) to form a nanomixture, the resulting blend exhibited a very high dielectric constant of 7.5[91]. As displayed in Figure 5B, the simulation results indicated that mixing of the two polymers causes an increase in the interchain spacing due to the mismatch of the polymer unit length and dipolar functional group locations. The increase in molecular chain spacing introduces additional free volume, which allows the dipole to rotate and align better with the electric field, thereby enhancing the dielectric response.

It should be noted that modifying molecular chain structures is a costly and complex process. Polymer blending is a general and scalable strategy to tune the ferroelectric behavior by controlling the composition and crystallization behavior[31,92-94]. For example, Zhang *et al.*[95] proposed a two-step process to generate a random distribution of P(VDF-TrFE) crystalline phases and break the coherent coupling of the ferroelectric domain between ordered crystalline phases. By performing phase-field simulations, the local electric fields ΔE in polymer blends with random and ordered configuration are simulated to find the underlying mechanism, as seen in Figure 5C. The simulation results demonstrated that the random configuration is much more capable of reducing the ΔE in the crystalline phase and is conducive to the inversion of the dipole, resulting in an ultrahigh electrical energy storage density of 20.4 J/cm^3 at 720 MV/m. In addition, Qian *et al.*[96] employed phase-field simulations to understand the effect of the internal DC bias field. In this work, they introduced a ferroelectric component in the nanophase form into the relaxor polymer matrix to establish an internal DC bias field in the polymer blends by controlling the properties of ferroelectric components. Figure 5D shows the distribution of remnant electric field established under an external of ΔE = 100 MV/m in the relaxor polymer matrix, which is unbiased and int-biased with E_{bias} of 50 MV/m. It can be seen from the simulation results that the int-biased blends exhibit a marked internal electric field in the terpolymer matrix due to the strong remnant polarization of the ferroelectric copolymer. As a result, the int-biased blends exhibit a high electrocaloric effect at low fields.

At larger scales, multilayer structures have been taken as another effective method to adjust the dielectric properties of polymer dielectrics[80]. With the assistance of theoretical modeling, some possible physical mechanisms are becoming clear, which greatly promote the design of novel multilayer structures. For example, dielectric or electrical mismatch among different polymer layers could cause the redistribution of the local electric field. Furthermore, the interfacial phase with a high dielectric constant induced by Maxwell-Wagner-Sillars interfacial polarizations changes the charge behavior, electrical conduction and electric polarization at the interface. Recently, Jiang *et al.*[97] fabricated P(VDF-HFP)/P(VDF-TrFE-CFE) multilayered films with extremely high charge/discharge efficiency (80%-85%) and high discharge energy density (~20 J/cm^3) through a non-equilibrium process. Phase-field simulations revealed the superiority of the multilayer structure in energy storage.

The top of Figure 5E exhibits the distribution of the local electric field along the direction of the applied field in multilayered films with eight layers. The interfacial phase with a high dielectric constant substantially weakens the local electric field at the interface, which can hinder the migration of carriers and greatly suppress the conduction loss. As the three-dimensional simulated breakdown path at the bottom of Figure 5E shows, the breakdown paths propagate faster in the nanocomposites with less layers than those with more layers and hence a higher breakdown strength was obtained with an increasing number of layers. Similarly, Zhang *et al.*[98] used a stacking method to prepare a series of alternating multilayer films with different layers of PMMA and P(VDF-HFP). A phase-field model was employed to determine the reasons for the improved performance by simulating the growth of electric trees in the multilayer films, as shown in Figure 5F. Deep traps at the interfaces between PMMA and P(VDF-HFP) can capture charge carriers and limit their further migration. In addition, the dielectric mismatch between layers can reduce the electric field in the P(VDF-HFP) layer and avoid early breakdown. Thus, with an increasing number of layers, the longitudinal growth and lateral expansion of the electric trees were inhibited. Therefore, optimization of the topological structure, phase composition, layer thickness and layer numbers of multilayer films can improve the energy storage performance of materials.

As summarized above, theoretical modeling has gradually become a common method in understanding microstructure-property relationships. By combining DFT, MD and the phase-field method, researchers have made significant progress in the microstructural design of polymer dielectrics, such as molecular chain modifications, polymer blending and multilayer structures. However, there are still some challenges facing polymer dielectrics. For example, the low dielectric constant of the polymer limits the energy density and the deterioration of polymer performance at high temperature is another important factor restricting the application of polymer dielectrics. In addition, there is a lack of in-depth analysis of some mechanisms or effects, such as the interfacial effect between crystalline and amorphous phases and high-temperature effects. In the future, it will be necessary to combine the results of theoretical calculations with experimental rules to further explore the relationship between microstructure and properties.

POLYMER-BASED COMPOSITE DIELECTRICS

Polymer-based composite dielectrics have the potential to combine both the advantages of the high dielectric constant of ceramic fillers and the high breakdown strength of polymer matrices and have attracted significant attention for energy storage applications[27,99]. Polyvinylidene fluoride and its copolymers and terpolymers are currently the most widely studied matrices in polymer-based composite dielectrics due to their high breakdown strength and medium dielectric constant[100,101]. Various ceramics with high dielectric constants are used as filler candidates, including $BaTiO_3$, $SrTiO_3$, TiO_2 and so on[102-105]. Furthermore, microstructural modulation has been proved to be a practical method to improve the dielectric constant and breakdown strength of nanocomposite dielectrics, such as interfacial modification[106-108], nanofiller structures and distribution[109-113] and multilayer structures[75,114,115]. Simultaneously, the rapid development of theoretical modeling has brought convenience for the efficient design of new nanocomposite structures[34,85,116,117]. The role of theoretical modeling in the materials selection and microstructural design of polymer-based composite dielectrics is discussed in this section.

When nanofillers with high specific surface area are added into the polymer matrix, a large number of interfacial regions are formed, which may alter the macroscopic properties of the composites[118,119]. For example, the existence of interfaces may change the distribution of space charges, thereby improving polarization. In addition, the interfaces in composites with a low content of nanofillers may act as traps to limit the migration of charges, resulting in a decrease in charge mobility and suppressed leakage current. Nevertheless, the interfacial regions in polymer-based composites with a high volume fraction of nanofillers are highly possible to overlap, which may lead to the aggregation of space charge and improved electrical conductivity. Therefore, a full understanding of the interface is favorable for tailoring the properties of composite dielectrics.

Although some theoretical interfacial models, such as Lewis's model[118] and Tanaka's model[120], have been proposed to explain the interfacial effects on nanocomposites, quantitative studies of interface-property relationships are still lacking. Recently, Shen *et al.*[121] employed theoretical modeling to investigate the interfacial space charge effects on the dielectric response of polymer nanocomposites with randomly distributed and aggregated nanoparticles, as shown in Figure 6A. When the nanofillers aggregate, a connected space charge region is formed, resulting in a high dielectric constant but also high dielectric loss and local electrical conductivity. In addition, modeling results indicate that the dielectric constant mismatch between the matrix and fillers can cause an obvious inhomogeneous local electric field at the interface, which can lead to a decrease in breakdown strength.

The introduction of low dielectric constant materials on the surface of high dielectric constant nanofillers as shell layers is an effective method for alleviating electric field distortion. For instance, Pan *et al.*[122] designed novel core-double-shell-structured $BaTiO_3@TiO_2@Al_2O_3$ nanofibers and incorporated them into a PVDF matrix. The finite element method was used to illustrate the effect of nanofibers with different structures on the local electric field distribution. It was found that $BaTiO_3@TiO_2@Al_2O_3$ nanofibers with a multilayer hierarchical interface can alleviate the local electric field and reduce leakage current obviously compared with composites with only $BaTiO_3$ or $BaTiO_3@TiO_2$ nanofibers. Furthermore, in order to better understand the effect of microscopic interfacial features on the macroscopic properties, Shen *et al.*[123] developed a data-driven interface design strategy based on high-throughput phase-field simulations to investigate the interfacial effect on dielectric properties. In this model, an interfacial phase with different thicknesses and permittivity was introduced to optimize the dielectric constant and breakdown strength of nanocomposites. As shown by the local electric field displayed in Figure 6B, the interface with higher or lower permittivity causes an obvious electric field distortion, leading to fast propagation of the breakdown path and early failure under a high electric field. Based on the calculation results, an interface optimized strategy with a core-shell structure in the PVDF-$BaTiO_3$ nanocomposite with $0.3r \le d \le r$ and $0.026\varepsilon_{\text{filler}} \le$

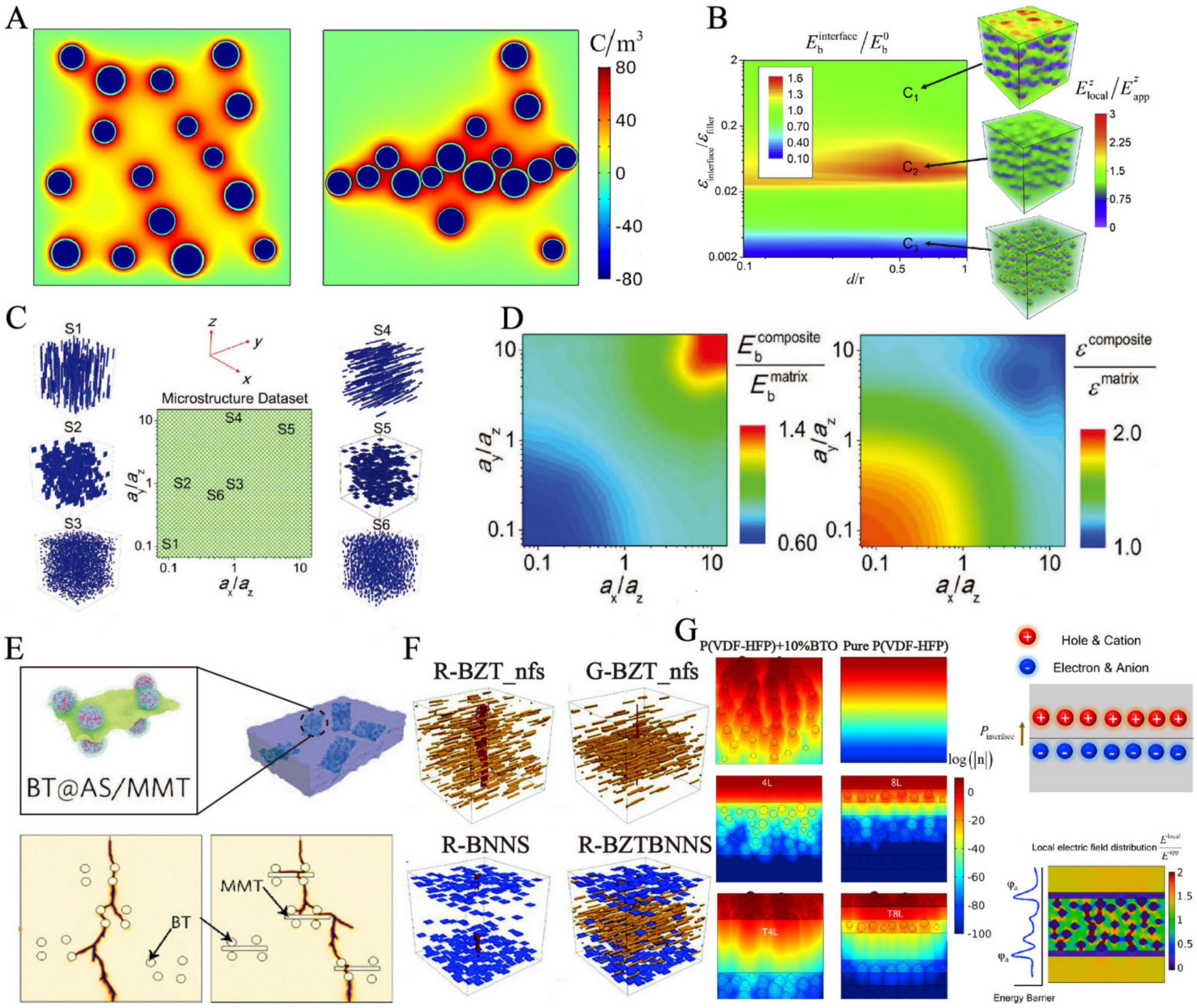

Figure 6. (A) Equilibrium distributions of space charge in a polymer nanocomposite with randomly distributed and aggregated nanoparticles[121]. (B) Map of breakdown strength with different interfaces in PVDF-$BaTiO_3$ nanocomposites[123]. (C) Definition of the microstructure dataset by assigning different length ratios of the nanofillers[124]. (D) Datasets of breakdown strength and the effective relative permittivity from high-throughput calculations[124]. (E) Simulated development of electric trees in polymer nanocomposites without and with aluminosilicate nanosheets (MMT)[130]. (F) Simulated development of electric trees in polymer nanocomposites with different nanofiller configurations[131]. (G) Distribution of charge density in different multilayered nanocomposites[134].

$\varepsilon_{\text{interface}} \leq 0.08\varepsilon_{\text{filler}}$ was obtained. This interface design strategy can also be applied to study interfacial issues in other functional nanocomposites.

The shape and orientation of nanofillers also strongly influence the dielectric properties of nanocomposites[110,124,125]. For example, one-dimensional nanofibers with a high aspect ratio increase the effective dielectric constant of the nanocomposites more obviously compared with zero-dimensional nanoparticles, and the enhancement effect is more significant when the nanofibers are parallel to the electric field direction[126]. A higher breakdown strength can be achieved in nanocomposites filled with highly insulating two-dimensional nanosheets perpendicular to the electric field direction[10,111,112]. In order to comprehensively understand the effect of nanofiller features on the local electric field distribution and breakdown strength in nanocomposites, high-throughput simulations based on a phase-field model were developed. As displayed in Figure 6C, Shen *et al.*[124] defined a microstructural dataset for nanocomposites by assigning different length ratios of the nanofillers. The breakdown strength and effective relative permittivity were then calculated with different microstructures, as shown in Figure 6D. The simulation results indicated that the shape and orientation of the nanofillers significantly affect the energy storage performance. For example, with the same volume fraction of the nanofiller, vertically distributed nanofibers make the electric field more concentrated at the ends of the fibers, resulting in higher polarization. In contrast, parallel nanosheets make the electric field more dispersed, which hinders the expansion of the breakdown phase. Therefore, the incorporation of parallel nanosheets into the polymer could increase the breakdown strength, while the incorporation of vertical nanofibers is beneficial for increasing the effective dielectric constant.

Based on the above conclusions, many hierarchical structures have been designed to improve energy storage performance[127-129]. For example, Luo *et al.*[130] proposed an effective strategy that utilizes superhierarchical structures and gradient interfaces in inorganic/organic nanocomposites to achieve ultrahigh energy density. The dynamic breakdown process of polymer nanocomposites without and with aluminosilicate nanosheets (MMT) was simulated by the phase-field method. As shown in Figure 6E, although $BaTiO_3$ nanoparticles with a layer of Al_2O_3 and SiO_2 (BT@AS) can improve polarization, their lower intrinsic breakdown makes the nanocomposites easier to breakdown. When BT@AS particles are located around MMT nanosheets, the nanosheets obviously change the direction of the breakdown path, thereby playing a role in hindering the propagation of the electric trees. As a result, a high energy density of 20 J/cm^3 and a high efficiency of 84% at a low electric field of 510 MV/m were achieved.

The design of three-dimensionally-distributed nanofillers has been proved to have excellent potential in tuning the energy storage properties of nanocomposites[3]. For example, the gradient distribution of nanofillers can be realized by adjusting the content in the out-of-plane direction and modeling has further verified the superiority of gradient structures in inhibiting charge injection and preventing the growth of electric trees. Recently, Jiang *et al.*[131] proposed polymer nanocomposites with a novel interpenetrating gradient structure by cofilling a PVDF matrix with $Ba(Zr_{0.21}Ti_{0.79})O_3$ fibers and BN nanosheets. Figure 6F presents the development of electric trees in nanocomposites simulated by the phase-field method. It can be seen that gradient distributed fillers (G-BZT_nfs and G-BNNS) are more effective in hindering the development of the breakdown phase than randomly distributed fillers (R-BZT_nfs). Furthermore, G-BZTBNNS nanocomposites with an interpenetrating gradient structure combine the advantages of G-BZT_nfs and G-BNNS nanocomposites, resulting in enhanced polarization and breakdown strength and suppressed dielectric loss.

In addition, the strategies of sandwich or multilayer structures also work in polymer-based nanocomposites[75,132]. The distribution of a local electric field in multilayered nanocomposite dielectrics can be adjusted by controlling the filler content in different layers. For instance, Wang *et al.*[133] prepared a sandwich-structured dielectric nanocomposite with a much improved breakdown field and energy density. Finite element simulations showed the redistribution of the electric field due to the different volume fractions of $BaTiO_3$ in each layer, with the weak electric field at the interface blocking the growth of the electric trees. Furthermore, Jiang *et al.*[134] fabricated multilayered polymer nanocomposites with interfaces of high structural integrity by a nonequilibrium processing method. They then employed a phase-field model to understand the influence of the interfaces between adjacent dielectric layers on the charge distribution in nanocomposites, as displayed in Figure 6G. In multilayer nanocomposites, polarized ions at the interface induce a strong depolarization field opposite to the applied electric field, which lowers the local electric field and increases the height of the potential barrier at the dielectric/dielectric interface. Moreover, compared with the pure P(VDF-HFP) layer close to the electrodes, the charge injection of the P(VDF-HFP)/$BaTiO_3$ composite layer close to the electrodes is more serious. Therefore, multilayered nanocomposites with a pure polymer layer close to the electrodes can exhibit lower leakage current and higher breakdown strength.

Through the reasonable design of microstructures with approaches such as interfacial modification, nanofiller structures and distribution, and multilayer structures, nanocomposite materials have made remarkable progress in enhancing energy density. With the aid of theoretical modeling, some underlying mechanisms and foundational relationships between microstructures and properties have gradually become clear. However, it is still too early to challenge the status of the BOPP capacitor because many issues, including poor charge/discharge efficiency and temperature stability, still exist in current polymer-based nanocomposites. Furthermore, the understanding of interfacial effects at the molecular and atomic levels is also insufficient. In the future, multiscale modeling and machine learning may become powerful weapons to break through these bottlenecks.

CONCLUSIONS AND OUTLOOK

As reviewed in this article, modeling has become an important component in the research and development of energy storage dielectrics from inorganics and polymers to their composites. The combination of experiment and modeling has yielded impressive developments in not only understanding the relationships between the microstructures and properties of dielectrics, but also in sparking novel design ideas for new dielectrics. However, to further enhance the guiding role of theoretical modeling in the process of materials discovery and innovation, the following strategies deserve increased attention.

Multiscale modeling

With the developments in basic theory and computing technology, many modeling methods at different scales have been widely used for materials research, including DFT, MD and phase-field simulations. However, these different models usually focus on one or limited scales of resolution. It remains highly challenging to simulate a multiscale process or hierarchical phenomenon in dielectrics using a single-scale modeling approach, such as the dielectric breakdown process and relaxation behavior. Therefore, to study one dielectric system at different levels of resolution and complexity with sufficient accuracy and appropriate efficiency, it is necessary to develop multiscale modeling approaches that bridge microscopic and macroscopic models. Such models will help us to further understand the direct relationships between microstructures and properties from an atomic/molecular level to macroscopic dielectric performance, such as linking P-E loops to atomic displacements or chemical fluctuations. However, some challenges remain to achieve the multiscale modeling of dielectric behavior, including multiscale theories and algorithms.

Microstructure-property databases

In recent decades, partly propelled by the Materials Genome Initiative, database technology has been extensively studied and developed, with many materials databases now available and open to the public, such as the Materials Project and AFLOWLIB. However, most databases focus on the information of chemical elements and crystal or molecular structures and thus lack microstructural data, such as domain configurations, polycrystalline structure and multiphase distribution, in the field of dielectrics. It is therefore imperative to build databases containing microstructures and the corresponding macroscopic properties of dielectrics, which could be important data for supporting the intelligent investigation of microstructure-property relationships. Due to the image data type of complicated microstructural information, some critical technologies still need to be improved. One of the major challenges is how to automatically acquire massive microstructural images from experiments and precisely generate virtual microstructures by algorithms. Other challenges include image storage and management technology and information mining technology.

Machine learning models

Under the data-driven research paradigm, machine learning is regarded as a promising tool for the discovery and design of novel materials for a broad range of applications. When studying microstructural effects on macroscopic properties, machine learning could also be a powerful approach for performance prediction, microstructure optimization and inverse design. In view of the diversity and complexity of microstructures, some updated technologies in machine learning models need to be developed. For example, establishing effective descriptors to characterize the graphical features of different microstructures with numerical data is the basis of finding mathematical expressions, predicting dielectric properties and designing new microstructures. Furthermore, introducing intelligent algorithms into the whole process of experimental preparation and characterization could make materials research and development faster, less expensive and more efficient.

DECLARATIONS

Authors' contributions

Conceived and designed the manuscript: Shen ZH
Drafted and revised the manuscript: Shen ZH, Wang J

Availability of data and materials

Not applicable.

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Conflicts of interest

Both authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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