Dielectric materials for high-temperature capacitors

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Abstract: Dielectric materials with excellent energy storage capability at elevated temperatures are critical to meet the increasing demand of electrical energy storage and power conditioning at extreme conditions such as hybrid electric vehicles, underground oil industries and aerospace systems. This review study summarises the important aspects and recent advances in the development of nanostructured dielectric materials including ceramics, polymers and polymer composites for high-temperature capacitor applications. The advantages and limitations of current dielectric materials are discussed and analysed. Ongoing research strategies to suppress the conduction loss and optimise the high-temperature capacitive performance of dielectrics have been highlighted. A summary and outlook will conclude this review.

1 Introduction

With the increasing demand of electrical energy storage devices used under extreme conditions such as hybrid electric vehicle (HEV), underground oil industries and aerospace power systems, the explorations on dielectrics with excellent thermal stability and remarkable energy density have attracted considerable attention. Fig. 1 shows some typical temperature ratings for various applications [1–4]. High working temperatures pose a new challenge for the development of high-performance dielectric materials [5–7]. Energy density (\(U_c\)) and charge–discharge efficiency (\(\eta\)) are basic performance parameters to evaluate capacitors [8–10]. Recently, considerable efforts have been placed to improve the \(U_c\) and \(\eta\), which are crucial for the miniaturisation of electronics and electrical power systems [10–13]. For high-temperature applications, there exist additional challenges for dielectric materials, e.g. temperature stability, thermal conductivity and electrical resistivity. One of the most important issues in designing high-temperature capacitors is to avoid the electrical/thermal ageing which is related to dielectric loss [3, 14, 15]. Owing to the competing mechanism between the dielectric permittivity (\(\varepsilon_r\)) and dielectric loss (tan \(\delta\)), an increased \(\varepsilon_r\) would cause an increase in tan \(\delta\), especially at high applied electric fields and elevated temperatures. Dielectrics with a relatively lower \(\varepsilon_r\) have the potential for further modification without resulting in high tan \(\delta\). In general, linear dielectrics with relatively lower values of \(\varepsilon_r\) and tan \(\delta\) are investigated for operations at high temperatures. The conduction loss plays a determining role in \(\eta\) of dielectrics operating at high-temperatures. Thus, the control of conduction loss is critical for high-temperature dielectrics in order to maximise the discharged energy density [5, 16, 17].

Various classes of dielectric materials have been developed for high-temperature capacitors, but each has its own limitations. Normally, ceramics can withstand high temperature and exhibit high \(\varepsilon_r\), but low breakdown strength (\(E_b\)) and large variation of dielectric properties versus temperature limit their applications. Glasses always possess high \(E_b\) and relatively good thermal stability, but their low \(\varepsilon_r\) impedes the increment in energy storage density. Although high \(E_b\) and low loss of polymers are beneficial for capacitive performance, the maximum working temperature is significantly limited by their thermal stability such as glass transition temperatures (\(T_g\)) [18–22]. For example, the commercial state-of-the-art biaxially oriented polypropylene (BOPP) polymer film capacitors have a working temperature <80°C [23]. Extensive studies have been carried out to modify dielectric materials to address their intrinsic shortcomings for high-temperature applications.

Herein, we first summarise the working principles of dielectrics for capacitor applications. Second, for the convenience of discussion, we categorise the high-temperature dielectrics into inorganic bulk dielectrics, polymer dielectrics and nanocomposites. The structure design, composition-property correlation and development of processing methods are highlighted in this paper.

2 General features of dielectrics for high-temperature capacitors

The dielectric materials are generally divided into four categories according to the D–E loops. Fig. 2 shows the schematic D–E loops of four typical dielectrics, e.g. linear dielectrics, relaxors, ferroelectrics and anti-ferroelectrics (AFE). The integrated pink areas represent the discharged energy storage density (\(U_d\)) [24–28].

As seen in Fig. 2a, the dielectrics possess linear loops which are typical characteristics of linear dielectric and paraelectric dielectrics. These materials usually exhibit high \(E_b\) and extremely...
low loss which would benefit their applications at elevated temperatures. In comparison to linear dielectrics, ferroelectrics exhibit high polarisation and moderate $E_b$. The non-linear characteristic leads to higher hysteresis loss and larger remnant polarisation which result in the decrement of $\eta$ [27, 29]. The non-linear behaviour also makes them difficult to reach high $U_e$, as shown in Fig. 2c. As the temperature rises above the Curie temperature ($T_c$), ferroelectrics undergoes a phase transition from ferroelectric state (FE) to paraelectric state and results in enhanced energy efficiency, but the variation of dielectric properties versus temperature would limit their practical uses at high temperatures [30–32].

Relaxor ferroelectrics have been extensively studied for energy storage capacitors [33, 34]. High $\varepsilon_r$ of relaxor dielectrics is responsible for achieving high saturation polarisation and the slim $D–E$ hysteresis loops are conducive to enhance the energy efficiency due to the low remnant polarisation. Dielectrics with relaxor behaviour always possess higher polarisation than linear dielectrics and much lower hysteresis loss compared with ferroelectrics and AFE, which make them promising for high-temperature capacitor applications.

AFE exhibits lots of advantages in energy storage applications such as largely saturated polarisation, very small remnant polarisation and moderate $E_b$. Unlike the dipoles oriented in the same direction in ferroelectrics, the adjacent dipoles in AFE are aligned in the opposite orientation and result in zero polarisation at the initial state [35, 36]. With the increase of the external electric field, the opposite orientate dipoles are aligned along the direction of the electrical field. When the applied field is above the phase transition (AFE–FE) switching field, the ferroelectric phase is formed. Consequently, double hysteresis loops are found in AFE [37, 38]. As shown in Fig. 2d, linear behaviours at low electric fields and double hysteresis features at high electric fields are found in $D–E$ loops. These unique behaviours in AFE materials would induce higher recoverable energy density compared with normal ferroelectrics and linear dielectrics. AFE exhibits the similar temperature-dependent characteristics and transition behaviours to ferroelectrics. It undergoes a phase transition from AFE to FE states, which is related to the crystal structure changing from orthorhombic/tetragonal AFE phase to rhombohedral FE phase as temperature is above $T_c$. The phase transition behaviours are temperature dependent and thus greatly influence the polarisation with a variation of temperature [39]. Therefore, for AFE whose $T_c$ is within the working temperature, their phase transition behaviours may deteriorate temperature stability.

Table 1 summarises the common high-temperature dielectric materials. Considerable progress has been achieved in both ceramics and polymer films for high-temperature capacitors over the past decades. More recently, polymer-based nanocomposites are emerging as promising high-temperature dielectrics [40, 41].

### 3 High-temperature inorganic dielectrics

In comparison to polymer dielectrics with lower thermal stability, bulk ceramic/glass capacitors possess the great potential to meet the requirements for high-temperature capacitive applications.
However, low $E_b$ of ceramics and low $\epsilon_r$ of glass, unstable temperature-dependent permittivity, the increasing hysteresis and conduction loss are limiting factors for high-temperature capacitors. A variety of inorganic bulk and thin films dielectrics have been exploited for high-temperature applications. In this part, we will review the recent progress in inorganic dielectrics and their application in aerospace power conditioning capacitors.

3.1 High-temperature linear/paraelectric dielectrics

The features of linear dielectric such as high intrinsic $E_b$, low loss and large bandgap are favourable for high-temperature applications. The main bottleneck of linear dielectric is their low $\epsilon_r$, which needs to be increased without sacrificing $E_b$ in order to achieve high-energy density at high temperatures. Similarly, ferroelectric in paraelectric or non-polar phase state exhibits suppressed polarisation, moderate $\epsilon_r$ and high $E_b$. Unfortunately, the temperature-dependent dielectric properties deteriorate their stability over the wide-temperature range.

Both linear and paraelectric dielectrics are thus promising materials. Typically, as typical linear dielectrics, glasses are applicable for high-temperature energy storage applications due to their excellent thermal stability, outstanding insulating properties and self-healing ability [42, 43]. For example, the high melting temperature ($T_m>1400°C$) and $T_g$ ($>550°C$) of alkali-free glasses as well as their unique disordered molecular structures make them high-temperature resistant [44]. Furthermore, the glasses always have the advantages of defined composition, formability, homogeneity, easy processing and easy modification.

Randall et al. [7] compared the temperature-dependent dielectric properties of alkali-free glasses (63%SiO$_2$·12%BaO·16%B$_2$O$_3$·9%Al$_2$O$_3$) with the alkali glasses (69%SiO$_2$·8%B$_2$O$_3$·7%Na$_2$O·5%K$_2$O·5%ZnO·3%Al$_2$O$_3$·3%TiO$_2$) and found that alkali-free glasses exhibit higher conduction activation energy and enhanced bond dimensionality in the structure. Recently, alkali-free glasses (e.g. boroaluminosilicate, aluminoborosilicate etc.) have been studied for high-temperature capacitor applications [7]. The modification of composition (e.g. doping of calcium oxide, barium oxide and sodium oxide) and the control of structure (e.g. addition of network former: silicon dioxide (SiO$_2$), boron trioxide, germanium dioxide and phosphorus pentoxide) have been applied to improve $\epsilon_r$ and $E_b$ [45–47]. In addition, it is found that thickness is closely related to $E_b$, which decreases from 1200 to 400 MV/m as the thickness increases from 5 to 50 mm due to the randomly distributed bulk defects [42]. High $E_b$ up to 1200 MV/m and $U_e$ of 35 J cm$^{-3}$ were obtained in thin alkali-free barium boroaluminosilicate substrates at room temperature [43]. To achieve high $U_e$, Manoharan et al. [44] invented flexible glass film for high-temperature capacitors. Very high $U_e$ (10–35 J cm$^{-3}$), high efficiency (>90%) and excellence $E_b$ (>700 MV/m) over a broad temperature range (25–150°C) were obtained in alkali-free aluminium borosilicate glasses films. Subsequently, 10 μm thick commercial boroaluminosilicate glasses (OA-10G, NEG, Shiga, Japan) were tested and compared with conventional high-temperature polymers. As a result, OA-10G exhibits excellent stability of energy storage properties up to 200°C, $U_e$ > 11.3 J cm$^{-3}$ and $\eta$ of 95%, which are almost three times higher than polyetherimide (PEI) [48]. The dielectric performance of low alkali of alkali-free glasses exceeds the known polymer dielectrics.

Calcium zirconate (CaZrO$_3$)-based solid solutions have gained great attention due to their controlled capacitance (~30) and loss (<0.1%) over a broad temperature change (~55 to 150°C). Furthermore, high $E_b$ (>10 MV/m) is another important advantage for high-temperature applications [49]. An $U_e$ of 4.8 J cm$^{-3}$ was obtained in CaZrO$_3$-based class-I dielectric material multilayer ceramic capacitors (BME X9G MLCC) at room temperature, which shows stable temperature-dependent dielectric performance up to 250°C [50]. However, low $\epsilon_r$ of CaZrO$_3$ (~30) limits its recoverable energy density [51]. Recent efforts have been focused on improving $\epsilon_r$ by solid solution method. For example, with the doping of titanium dioxide, 10 μm Ca(Zn$_{0.8}$Ti$_{0.2}$)O$_3$ single-layer capacitors exhibit high-$\epsilon_r$ ranging from 34 to 75, a large $E_b$ of 17.5 MV/m and a high $U_e$ of 4 J cm$^{-3}$ at 15 MV/m and 250°C [52]. As calcium titanate (CaTiO$_3$) exhibits a much higher ($\epsilon_r$=171) than CaZrO$_3$ (~30), the 0.8CaTiO$_3$–0.2CaHfO$_3$ (CHT) solid solution systems were designed to take the full advantage of high $\epsilon_r$ of CaTiO$_3$ and the large bandgap of CaHfO$_3$ (6.4 eV). High ambient $U_e$ of 9.0 J cm$^{-3}$ was reported in prototype CHT single-layer capacitors (~19 μm), which show poor stability above 100°C. Moreover, the instability of CHT at high temperatures can be improved by doping with 0.5 mol% manganese (Mn), which is favourable for large $E_b$ and high-temperature energy density (e.g. 9.5 J cm$^{-3}$ at 200°C and 6.5 J cm$^{-3}$ at 300°C) [51].

Recently, the temperature- and composition-dependent phase structures have been intensively investigated in the CaTiO$_3$–strontium titanate (SrTiO$_3$) binary systems [52–57]. Although the energy storage properties have not been extensively studied, the combined effect of high $\epsilon_r$ of SrTiO$_3$ (~240) and the wide bandgap of CaTiO$_3$ (3.4 eV) may suggest high $U_e$ with great thermal stability [58]. Promising results have been reported in the Mn- and hafnium(IV) oxide-doped Ca$_{90}$Sr$_{10}$TiO$_3$ bulk ceramics, whose energy density is about 1.0 J cm$^{-3}$ at 26 MV/m with good thermal stability [59, 60]. In addition, Na$_{1/2}$Bi$_{1/2}$TiO$_3$-based ferroelectric materials exhibit excellent temperature stability in dielectric properties over a wide range of temperature. However, these materials are rarely applied to capacitors due to their intrinsic ferroelectric property [61–63]. Chen et al. described a new method to expand the temperature range between $T_g$ (phase transition temperature from a ferroelectric phase to a high-temperature non-polar phase) and $T_m$ (the maximum temperature of the dielectric constant) and result in a smaller variation of $\epsilon_r$ and energy storage properties over a wider-temperature range. For example, with the introduction of Bi(Mg$_{1/2}$Ti$_{1/2}$)$_3$O$_7$ into (Na$_{1/2}$Bi$_{1/2}$)$_2$O$_9$Bi$_{0.8}$TiO$_3$ ceramics, high $U_e$ (~2 J cm$^{-3}$) and excellent $\eta$ (~88%) were obtained from 25 to 180°C [64].

3.2 High-temperature ferroelectric relaxors

Most relaxors used as high-temperature dielectrics have concentrated on lead-based (Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_7$ and Pb(Zn$_{0.5}$Nb$_{0.5}$)$_2$O$_7$)-based ceramics and films and Bi-based systems which contain BaTiO$_3$–Bi(MgO) [M: zirconium (Zr), scandium (Sc), yttrium (Y), Mg$_{1/2}$Ti$_{1/2}$ and Mg$_{2/3}$Nb$_{1/3}$] [65–67]. Excellent temperature stability has been reported in (1-x)Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_7$-xPbTiO$_3$ relaxor ferroelectric thin films with barely unchanged $U_e$ of 11.8 J cm$^{-3}$ and η of 72% as the film is heated from room temperature to 200°C [68]. However, the toxicity of lead limits the applications of lead-based relaxors in the future. Endeavours to develop lead-free alternatives which can be used at a wide-temperature range have been made all over the world. Bi-based ceramics have been vastly investigated during the past decades on their electromechanical properties after the Bi$_{0.5}$Na$_{0.5}$TiO$_3$–BaTiO$_3$–K$_{0.6}$Na$_{0.4}$NbO$_3$ (BNT-BT-KNN) system was reported. Good temperature stability (100–150°C) has been reported in 0.89BNT–0.06BT–0.05KNN ceramics with $U_e$ of 0.59 J cm$^{-3}$ [69]. Subsequently, Mn-doped Na$_{0.5}$Bi$_{0.5}$TiO$_3$-based relaxor ferroelectrics generate a high recoverable energy density of 1.06 J cm$^{-3}$ with excellent temperature stability from room temperature to 100°C [70]. Furthermore, Na$_3$NbO$_6$ was added to Bi$_{0.5}$Na$_{0.5}$TiO$_3$–SrTiO$_3$ matrix, resulting ergodic relaxor phase for improved energy storage properties. As shown in Fig. 3, while the polarisation exhibits slight decrease with the increase of temperature, the energy density maintains steady due to the offset effect of the reduced $U_e$ by decreased polarisation and enhanced $U_e$ by the increased efficiency [71, 72]. Similar to the phase transition behaviour of ferroelectrics and AFE, the BNT-based systems undergo a phase transition from FE to ergodic relaxor phase by varying composition and...
temperature. These phase transition behaviours are detrimental to the thermal stability. Efforts have been placed on the introduction of La(Mg$_{1/2}$Ti$_{1/2}$)$_2$O$_3$ with distorted cubic perovskite structure to induce non-ergodic–ergodic transformation. For example, excellent energy storage properties ($U_e$ ~1.6 J cm$^{-3}$, $\eta$ ~82%) were attained in La(Mg$_{1/2}$Ti$_{1/2}$)$_2$O$_3$-doped BiFeO$_3$-BaTiO$_3$ lead-free relaxor with desirable temperature stability from 25 to 180°C [73]. As $U_e$ of commercial ceramic dielectrics is typically <2 J cm$^{-3}$ due to their limited $E_b$. High $E_b$ of more than 150 MV/m has been achieved in Mn-doped BiFeO$_3$-SrTiO$_3$ thin films grown by pulsed laser deposition, which result in ultrahigh $U_e$ of ~51 J cm$^{-3}$. Excellent thermal stability of energy storage performance within ~40 to 140°C range and the high-energy density made them promising candidates as high-temperature dielectric materials [74].

3.3 High-temperature AFE

AFE generates higher $U_e$ than ferroelectrics, paraelectrics and linear dielectrics [75, 76]. In general, AFE is always divided into several groups, e.g. perovskite, liquids crystal and pyrochlore group [9]. Among these categories, the lead zirconate (PbZrO$_3$)-based anti-ferroelectric have attracted many attentions since 1961 when high-energy storage performance was predicted in PbZrO$_3$ by Jaffe [77]. Since then, numerous research on new perovskite AFE [e.g. PbHfO$_3$, NaNbO$_3$, (Na$_{0.3}$Bi$_{0.5}$)TiO$_3$-BaTiO$_3$-based composites] have been published [9, 78–80]. In 2015, spark plasma sintering was employed to suppress the diffusion behaviour between tetragonal phase and orthorhombic phase in (Pb$_{0.85}$Ba$_{0.15}$)$_{0.9}$La$_{0.02}$Ti$_{0.05}$O$_{3}$- (Zr$_{0.95}$Ti$_{0.05}$)O$_{3}$- (Pb$_{0.97}$La$_{0.03}$)O$_{3}$ at 280 MV m$^{-1}$ at room temperature. Both of these films can maintain high stability from 25 to 150°C [85]. However, the phase transition behaviour of AFE dielectric induces temperature instability. To solve this issue, Sr was doped into the PbZrO$_3$ anti-ferroelectric thin films to tune the $T_c$ to 251°C, resulting in excellent temperature stability from 25 to 210°C. A high $U_e$ of >7.5 J cm$^{-3}$ and a large $\eta$ of >72% can be obtained. Furthermore, outstanding temperature stability was found in compositionally graded multilayer Pb$_{1-3x}$La$_x$Zr$_{0.85}$Ti$_{0.15}$O$_{3}$ AFE thick films. The values of $U_e$ and $\eta$ in the upgrade thick films are varied from 19.2 to 17.9 J cm$^{-3}$ and 75 to 77%, respectively, as temperature increase from 25 to 150°C measured at an electric field of 90 MV m$^{-1}$ [86].

4. High-temperature dielectric polymers

The inherent advantages of lightweight, easy processing, scalability, high $E_b$ and excellent fatigue resistance make polymer dielectrics the materials of choice for room-temperature capacitors. On the other hand, polymers are always limited to relatively low working temperatures. Great efforts have been paid to develop various temperature-stable polymer dielectrics. Zhang et al. [5] have systematically investigated the dielectric properties of high-temperature resistant polymer dielectrics (HTPDs) and their applications in electrical/electronic insulation. For example, poly(ethylene terephthalate) (PET), poly(carbonate) (PC), polyetheretherketone (PEEK) and imide polymers including polyimide (PI), PEI, polyamideimide (PAI) etc. (Table 1). All these polymers exhibit low loss factor, high volume resistivity, high $T_g$ and high $E_b$, as well as good temperature stability. Thus, enormous attempts have been made to validate these polymers as high-temperature dielectrics.

Fig. 4 illustrates the structures of these HTPDs which are usually divided into several classes based on their structure, non-aromatic polymers including PP, poly(methyl methacrylate) (PMMA). Aromatic polymer including polystyrene, PC, aromatic polyurea (ArPU), poly(arylene ether) urea (PEEU), PET, PEEK, poly(ether ketone) (PEKK) etc. Heteroaromatic polymers including poly(phenylazinone) ether ketone (PPEK) (PEPK), PI, PEI, PAI, polybenzimidazole (PBI), polybenzoxazole (PBO), polyphenylenoxazine etc. Fluoropolymers such as polytetrafluoroethylene (PTFE), fluorine polyester (FPE), poly(tetrafluoroethylene-hexafluoroisopropylene) (PTFE–HFPP) etc. [5, 16, 21, 87–90].

The strong inter- and intra-molecular interactions induced by hydrogen bond (−NH−, −CO−NH− etc.), $\pi$ conjugarion in polymer chains (imide ring, imidazole ring etc.), aromatic/heteroaromatic molecular skeletons and high-strength chemical bonds (C–F etc.) are benefits for maintaining thermal ability of polymer at elevated temperatures [91]. The dielectric properties and capacitive performance of non-aromatic, aromatic, heteroaromatic polymers and fluoro resins that are controlled by molecular structures will be presented systematically in this section.

4.1 Non-aromatic dielectric polymers at high-temperatures

Non-aromatic polymer plays an important role in commercial capacitors due to their high $E_b$ (>500 MV m$^{-1}$) and high charge-
discharge efficiency. BOPP is applied to DC bus capacitors in HEVs at the temperature below 105°C. However, the main drawback of BOPP is the relatively low \( \varepsilon_r (\sim 2.2) \) which limits \( U_g \) to below 1.2 J cm\(^{-3} \) [23]. Liu et al. modified PMMA by introduction of high electrical resistivity boron nitride nanosheets (BNNSs), resulting in high \( E_h \) and good thermal stability within the temperature range from room temperature to 70°C. The maximum energy density of 3.5 J cm\(^{-3} \) was obtained in modified PMMA. Most non-aromatic polymer with low \( T_g \) exhibits relatively low temperature stability (<120°C), limiting their applications at elevated temperatures [92].

### 4.2 High-temperature aromatic dielectric polymers

Similar to the non-aromatic polymer working temperature, some aromatic polymer can only withstand the temperature below 140°C. For example, though PET films offer a reasonable dielectric constant (\( \sim 3.3 \)) and high \( E_h (>570 \text{ MV/m}) \), their relatively low dissipation factors at high temperatures prevent them from high pulse power applications. PC has its advantages in high \( E_h \) induced by extra high \( E_g \), but low \( U_g (<1 \text{ J cm}^{-3}) \) was obtained in solvent cast PC [16]. As a semi-crystalline aromatic polymer, PEEK is a class of easy-process engineering polymer with high mechanical/chemical resistance to high temperatures. The low \( T_g (143°C) \) and \( \varepsilon_r (>3.2) \) of PEEK limit its high-temperature dielectric application, i.e. only 0.5 J cm\(^{-3} \) energy was stored below \( T_g [93] \). Great efforts have been placed on improving the dielectric properties of aromatic polymers by modifying the chemical structures. As another semi-crystalline thermoplastic, PEEK has a similar chemical structure to PEEK. The substitution of ether group (–O–) by ketone group (–C=O) has increased the \( T_g \) to 155°C. The dielectric properties (\( \varepsilon_r = 3.6, \tan \delta = 0.0033 \) at 1 kHz) were found to be considerably stable with respect to temperature up to 150°C. Stable discharged energy densities (\( \sim 2.4 \text{ J cm}^{-3} \) at 400 MV m\(^{-1} \)) were also obtained [94]. Cheng et al. modified ArPU by replacing ethyl group (-CH\(_3\)) CH\(_2\) group with polar ether groups to form PEEU, resulting in higher \( \varepsilon_r \) without sacrificing thermal stability. As a result, high \( U_g \) of 13 and 9 J cm\(^{-3} \) were obtained at room temperature and 120°C, respectively [95]. However, further improvement of the operating temperatures of aromatic polymers is still limited by using chemical modification methods. It is expected that the formation of heteroring with the introduction of the heterocyclic atom in the backbone chains would give rise to higher \( T_g \).

### 4.3 High-temperature heteroaromatic dielectric polymers

It has been reported that incorporation of the rigid asymmetric phenyl phthalazine moiety into the polymer backbone yields dielectric polymer with high \( T_g \) and excellent mechanical properties. Pan et al. synthesised phenyl phthalazine containing PPEK and examined their dielectric properties at various temperatures. The heteroaromatic structure of PPEK (Fig. 4) yields high \( T_g (\sim 250°C) \), high decomposition temperature (\( \sim 490°C \)), low \( \varepsilon_r (\sim 3.5) \), low tan \( \delta (\sim 0.0063) \) and temperature-independent dielectric properties (25-240°C). A large \( U_g (\sim 2.8 \text{ J cm}^{-3}) \) and high \( \eta (>85\%) \) have been obtained at temperature ranging from room temperature to 130°C [90].

Typically, imide cyclic structure is favourable for high thermal stability, large mechanical strength and high electrical insulation. Thus, the imide polymers are promising dielectrics for high-temperature applications. As one of the most common thermal resistant dielectric polymers, PI films are widely used in electronic and electrical insulation applications. PI films (Kapton\(^\text{®} \) by Dupont, USA) provide an excellent thermal stability with a high \( T_g \) value (\( >350°C \)). Large dielectric strength (\( >300 \text{ MV m}^{-1} \)), high-temperature resistant, (\( >240°C \)) and high resistivity (\( >10^{17} \Omega \)) were obtained in 25 μm thick PI films. Uplex\(^\text{®-S} \) PI film from Ube (Japan) is another class of super-heat resistant films, which can be operated at 300°C without deterioration in electrical properties. All these desirable properties of PIs make them favourable candidates for high-temperature capacitor applications regardless of low \( \varepsilon_r (\sim 3 \text{ at 1 kHz}) \). However, PIs are difficult to process because of their insoluble and infusible nature. Other imide polymers such as PAI and PEI with good melt processability have been developed. For example, PAI plastics (\( T_g >300°C \)) inherit the advantages of PI and exhibit good processability. Similarly, PEI (Extem XH1005 by Sabic, Saudi Arabia \( T_g: 267°C \)) was commonly obtained by modifying PI with flexible ether linkages, which can be easily prepared by one-step polycondensation. As a result, the extruded PEI films discharge an \( U_g of 1.57 \text{ J cm}^{-3} \) with an \( \eta \) of 73.8% at 400 MV m\(^{-1} \) and 150°C, surpassing all the commercially available polymer dielectrics [5, 21, 96].

Polymer dielectrics with high \( T_g (>300°C) \) and high thermal stability will play an important role in providing electromechanical stability for wide-temperature power electronics applications. PBO has excellent thermal stability and the thermo-oxidative resistance, high electrical resistivity and temperature-stable dielectric strength. Temperature stability measurements have been performed on fluorinated PBO (OH–6F–PBO/12F–PBO copolymer). Small changes in film capacitance over a wide-temperature ranging from room temperature to 250°C have been found, suggestive of its intrinsic temperature-stable properties [5, 97].

As the highest thermal stable thermoplastics with a very high \( T_g (>400°C) \), PBI plastics (Celazole\(^\text{®} \) BPI U-60, USA) have been used in high-temperature electrical and power insulation due to their high mechanical strength, Young’s modulus and electrical resistivity. It has been reported that PBI exhibits temperature independent dielectric properties including stable \( \varepsilon_r \) and \( E_h \). These results motivate engineers to exploit the applicability of heteroaromatic polymer as high-temperature dielectric materials [98].

### 4.4 High-temperature fluoropolymer dielectrics

Compared to linear polymer dielectrics, poly(vinylidene fluoride) (PVDF)-based ferroelectric polymers with high permittivity have been extensively studied for room temperature capacitor applications [99, 100]. Defect strategies have been applied to achieve high \( \varepsilon_r \) and large \( U_g \), e.g. 10 and 17 J cm\(^{-3} \) have achieved in P[VDF–trifluoroethylene (TrFE)– chlorofluoroethylene (CFE)] terpolymers and P[VDF–chlorotrifluoroethylene (CTFE)] 91/9 mol % copolymers (TrFE, CFE and CTFE) [19, 101–103]. However, high dielectric loss arising from the polarisation hysteresis and electrical conduction limits their applications. At 70°C and 200 MV m\(^{-1} \), \( U_g \) of P(VDF–TrFE–CTFE) is degraded to only 1 J cm\(^{-3} \) with a low \( \eta \) of ~21% [21]. PMMA has been grafted onto P(VDF–TrFE–CTFE) chains to inhibit the temperature-dependent ferroelectric relaxation for broad temperature stability [104]. P(TFE–VDF)s (TFE) are designed by combining PVDF with high \( \varepsilon_r \) and PTFE with high-temperature stability. As a result, P(TFE–VDF) has a melting temperature of >260°C and maintains a high \( \varepsilon_r (>21\%) \) from 25 to 100°C. A large \( U_g \) of 6 J cm\(^{-3} \) at 500 MV m\(^{-1} \) and 110°C was obtained in the hot-pressed P(TFE-HIP) films, which is a promising substitution of BOPP (\( U_g of 2.1 \text{ J cm}^{-3} \) at 70°C) for high-temperature-pulsed power applications [105]. The temperature independent dielectric properties (\( \varepsilon_r = 3.5, \tan \delta <0.3\%) \) within the temperature range from room temperature to 200°C have been observed in FPE whose \( T_g \) is about 330°C [106]. FPE discharges a \( U_g of 1.3 \text{ J cm}^{-3} \) at 150°C and 350 MV m\(^{-1} \) with \( \eta \) of ~40% [21]. It is known that film thickness and quality have a critical influence on the capacitive performance of dielectric films. Tan et al. [16] have reviewed the development history of PEI films thickness reduction and found that thinner PEI films are favourable for improving \( E_h (>500 \text{ MV/m}) \) and achieving high \( U_g (3.5 \text{ J cm}^{-3}) \).
The advantages of the polymer matrix and ceramic fillers such as example, the PI/Al improvement in temperature to 200°C [108]. However, a large contrast incorporated fillers would either block charge injection from electrodes or scatter electron to reduce conduction loss at high fields and elevated temperatures [96, 109, 110].

The incorporation of high-$\varepsilon_r$ BaTiO$_3$ nanoparticles into PI polymer matrix render an enhanced energy density of 6.79 J cm$^{-3}$ at 120°C, much higher than that of pristine PI (i.e. 1.2 J cm$^{-3}$) [107]. The dielectric thermal stability has also been confirmed in the PI/BaTiO$_3$ composites within the temperature range from room temperature to 200°C [108]. However, a large contrast $\varepsilon_r$ between the fillers and polymer matrix leads to a highly inhomogeneous distribution of local electric fields and consequently a large reduction of $E_b$ [11]. Thakur et al. incorporated a series of low-$\varepsilon_r$ oxides including Al$_2$O$_3$, MgO, SiO$_2$ and iron(III) oxide into HTPDs matrix. They found that a significant increase in $\varepsilon_r$ can be achieved in polar polymer-based nanocomposites with the addition of nano-fillers, whose $\varepsilon_r$ is similar to that of the matrix. For example, the PI/Al$_2$O$_3$ composites exhibit a $\varepsilon_r$ enhancement of about 30%, while the PEI/Al$_2$O$_3$ composites have about 60% improvement in $\varepsilon_r$. The large enhancement in $\varepsilon_r$ contributes to excellent energy storage properties in the PEI/Al$_2$O$_3$ nanocomposites at high temperatures up to 150°C [6, 109, 110]. Fluoropolymer P(TFE–HFP–VDF) exhibits low loss and high-temperature stability. Insulating Al$_2$O$_3$ nano-fillers are introduced into the polymer to reduce the conduction loss at high temperatures [111]. With the introduction of nano-size aluminium nitride particles, a great enhancement of $\varepsilon_r$ (∼4.4) and high thermal stability up to 250°C were obtained [112]. The cross-linked divinyltetramethyldisiloxane bis(benzocyclobutene) (c-BCB) is emerging as high-performance dielectric materials when mixed with BNNSs. The structure of c-BCB can be seen in Fig. 5c. As shown in Figs. 5a and b, the dielectric properties ($\varepsilon_r$≥3.1, tan $\delta$ < 1.7%) that are stable over a broad range of temperature (room temperature to 300°C) and frequency (10$^2$–10$^6$ Hz) were found in c-BCB/BNNS nanocomposites, which can discharge a $U_e$ exceeding 2.2 and 2 J cm$^{-3}$ with a $\eta$ larger than 90 and 80% at 150 and 200°C at 400 MV m$^{-1}$, respectively [21].

To mitigate the local electric-field distortion between the polymer matrix and inorganic fillers in the dielectric polymer composites and further improve the dielectric properties and high-temperature capacitive performance, a variety of new approaches have been developed, e.g. using large-aspect-ratio fillers and modifying the interface layers [113, 114]. Particularly, the multilayered structures open additional flexibility in tuning chemical compositions and the spatial organisation of nano-fillers, thus presenting a promising route to high-performance dielectric materials [115–120]. As shown in Fig. 5d, Li et al. described sandwich-structured nanocomposites (SSNs) with c-BCB/BT as the central layers to improve the dielectric and stacked c-BCB/BNNS as the outer layer to block charge injection. This method integrates the advantages of high $\varepsilon_r$ from the central layer and high $E_b$ from outer layer as well as the excellent thermal stability of c-BCB matrix, resulting in stable $U_e$ of 0.93 J cm$^{-3}$ up to 150°C at 200 MV m$^{-1}$ (Fig. 5e) [121]. However, the high-cost polymer matrix and time-consuming preparation of BNNSs impede the mass production of the c-BCB/BNNS composites. Thus, a scalable chemical vapour deposition method for hexagonal BN (h-BN) is adopted to develop high-temperature polymer nanocomposite dielectrics. Superior high-temperature energy storage properties ($U_e$ of 1.19 J cm$^{-3}$ and $\eta$ >90%) were achieved at 200°C in h-BN-coated PEI nanocomposites [122]. It is envisioned that the excellent performance, along with the outstanding cyclability and dielectric stability at elevated temperatures, paves the way for the applicability of a wide range of engineering polymers in high-temperature electronics and energy devices.

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5 High-temperature dielectric nanocomposites

The dielectric polymer nanocomposites are designed to integrate the advantages of the polymer matrix and ceramic fillers such as high $E_b$ and facile processability from polymers and large $\varepsilon_r$ from ceramics such as BaTiO$_3$, for greatly enhanced $U_e$ [107, 108]. More recently, wide bandgap fillers such as BNNSs and low $\varepsilon_r$ fillers such as aluminium oxide (Al$_2$O$_3$), magnesium oxide (MgO) and SiO$_2$ have been added into polymers to improve the high-temperature capacitive performance. It is thought that the incorporated fillers would either block charge injection from electrodes or scatter electron to reduce conduction loss at high fields and elevated temperatures [96, 109, 110].

The dielectric thermal stability has also been confirmed in the PI/BaTiO$_3$ composites within the temperature range from room temperature to 200°C [108]. However, a large contrast $\varepsilon_r$ between the fillers and polymer matrix leads to a highly inhomogeneous distribution of local electric fields and consequently a large reduction of $E_b$ [11]. Thakur et al. incorporated a series of low-$\varepsilon_r$ oxides including Al$_2$O$_3$, MgO, SiO$_2$ and iron(III) oxide into HTPDs matrix. They found that a significant increase in $\varepsilon_r$ can be achieved in polar polymer-based nanocomposites with the addition of nano-fillers, whose $\varepsilon_r$ is similar to that of the matrix. For example, the PI/Al$_2$O$_3$ composites exhibit a $\varepsilon_r$ enhancement of about 30%, while the PEI/Al$_2$O$_3$ composites have about 60% improvement in $\varepsilon_r$. The large enhancement in $\varepsilon_r$ contributes to excellent energy storage properties in the PEI/Al$_2$O$_3$ nanocomposites at high temperatures up to 150°C [6, 109, 110]. Fluoropolymer P(TFE–HFP–VDF) exhibits low loss and high-temperature stability. Insulating Al$_2$O$_3$ nano-fillers are introduced into the polymer to reduce the conduction loss at high temperatures [111]. With the introduction of nano-size aluminium nitride particles, a great enhancement of $\varepsilon_r$ (∼4.4) and high thermal stability up to 250°C were obtained [112]. The cross-linked divinyltetramethyldisiloxane bis(benzocyclobutene) (c-BCB) is emerging as high-performance dielectric materials when mixed with BNNSs. The structure of c-BCB can be seen in Fig. 5c. As shown in Figs. 5a and b, the dielectric properties ($\varepsilon_r$≥3.1, tan $\delta$ < 1.7%) that are stable over a broad range of temperature (room temperature to 300°C) and frequency (10$^2$–10$^6$ Hz) were found in c-BCB/BNNS nanocomposites, which can discharge a $U_e$ exceeding 2.2 and 2 J cm$^{-3}$ with a $\eta$ larger than 90 and 80% at 150 and 200°C at 400 MV m$^{-1}$, respectively [21].

To mitigate the local electric-field distortion between the polymer matrix and inorganic fillers in the dielectric polymer composites and further improve the dielectric properties and high-temperature capacitive performance, a variety of new approaches have been developed, e.g. using large-aspect-ratio fillers and modifying the interface layers [113, 114]. Particularly, the multilayered structures open additional flexibility in tuning chemical compositions and the spatial organisation of nano-fillers, thus presenting a promising route to high-performance dielectric materials [115–120]. As shown in Fig. 5d, Li et al. described sandwich-structured nanocomposites (SSNs) with c-BCB/BNNS as the central layers to improve the dielectric and stacked c-BCB/BNNS as the outer layer to block charge injection. This method integrates the advantages of high $\varepsilon_r$ from the central layer and high $E_b$ from outer layer as well as the excellent thermal stability of c-BCB matrix, resulting in stable $U_e$ of 0.93 J cm$^{-3}$ up to 150°C at 200 MV m$^{-1}$ (Fig. 5e) [121]. However, the high-cost polymer matrix and time-consuming preparation of BNNSs impede the mass production of the c-BCB/BNNS composites. Thus, a scalable chemical vapour deposition method for hexagonal BN (h-BN) is adopted to develop high-temperature polymer nanocomposite dielectrics. Superior high-temperature energy storage properties ($U_e$ of 1.19 J cm$^{-3}$ and $\eta$ >90%) were achieved at 200°C in h-BN-coated PEI nanocomposites [122]. It is envisioned that the excellent performance, along with the outstanding cyclability and dielectric stability at elevated temperatures, paves the way for the applicability of a wide range of engineering polymers in high-temperature electronics and energy devices.
Conclusions and future perspectives

There have been many exciting developments in the field of dielectric materials targeted for high-temperature capacitors over the past several years. Various classes of high-temperature dielectric materials including ceramics, polymers and polymer composites have been developed. Prototype capacitors based on bulk ceramics and novel fabrication processes for dielectric ceramics continue to appear with an impressive performance. Unique advantages of dielectric polymers and dielectric polymer composites are being exploited for high-temperature capacitors. In particular, the latest results on polymer nanocomposites suggest unique features of this class of dielectrics for high-temperature applications. Dielectric polymer nanocomposites already complete structure design, is needed for the rational development of high-polar groups, simultaneously yield largely increased dielectric loss and low hysteresis loss (<0.1 J cm\(^{-3}\)) multilayer films at 150°C [123–126].

There is plenty of room for further improvement as many key issues remain to be addressed. Large-scale production has proven challenging for ceramic dielectrics. A multiscale approach, ranging from atomic defects, through nanoregions, to micro/macroscale structure design, is needed for the rational development of high-temperature ceramics. Efforts should also be paid to transfer the materials into multilayered ceramic capacitors and investigate the compatibility of ceramics with internal electrodes at high temperatures.

At present, current polymer dielectrics have not been optimised for operating at elevated temperatures and high applied electric fields. A systematic study of high-temperature high-field loss and breakdown mechanisms of dielectric polymers has not yet been carried out. The polymer structures have to be judiciously engineered to integrate contrast features such as high thermal stability, high \(\varepsilon_r\) and low loss for greatly improved collective performance. Current high-temperature polymer dielectrics possess relatively low \(\varepsilon_r\) values, i.e. below 4, which severely limits their energy densities. However, the popular approaches to enhance \(\varepsilon_r\) of polymer dielectrics such as functionalisation of polymers with polar groups, simultaneously yield large \(\Delta\varepsilon\) and moderate dielectric loss at elevated temperatures and high electric fields. On a fundamental level, a much-improved understanding of the structure–property relationship of dielectric polymers, e.g. polarity of functional groups versus dielectric permittivity/loss, under elevated temperatures and high electric fields is crucial. Thermal conductivity has been identified as a key factor in determining the performance of high-temperature polymer dielectrics. While polymers are well known for their thermal conductors, the thermal conductivity of polymers may be improved by optimising chain packing and controlling chain orientation.

Integration of carefully chosen inorganic fillers into polymers to form dielectric polymer composites is emerging as a promising approach with enormous potential for high-temperature capacitors. It remains challenging to process the dielectric polymer composites by utilising currently available scalable approaches. Low-cost large-scale methods for fabricating fully dense ceramic capacitor-grade thin films need to be demonstrated. Self-healing abilities of the composite films have to be investigated. The growing need for high-performance high-temperature capacitors in advanced electronics and electrical power systems will certainly encourage great improvements in current dielectric materials and inevitably catalyse the emergence of novel dielectric structures and fabrication techniques.

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