Surface ion-activated polymer composite dielectrics for superior high-temperature capacitive energy storage†

Minhao Yang, Yanlong Zhao, Zepeng Wang, Huarui Yan, Zeren Liu, Qi Li* and Zhi-Min Dang†

Polymer dielectrics for high-temperature capacitive energy storage suffer from low discharge energy density and inferior efficiency owing to their exponential growth of conduction losses at elevated temperatures and electric fields. The electrode and bulk-limited conduction losses are two types of conduction mechanisms in polymer dielectrics. Unlike previous nanodielectric strategies that involve incorporating wide bandgap inorganic components inside the bulk phase or on the surface of polymer films, herein, we describe a surface ion-activated polymer composite dielectric composed of abundant surface polycarboxylate (RCOO−) ions to simultaneously inhibit the electrode and bulk-limited conduction losses. The strong electrostatic repulsion between the negatively charged dielectric surface and the metal electrode effectively alleviates the charge injection from the electrode and consequently leads to a reduction in the electrode-limited conduction loss. For the suppression of bulk-limited conduction loss, wide bandgap aluminium oxide nanoparticles in the bulk phase of dielectrics significantly increase the trap density and constrain the charge mobility, contributing to the suppression of conduction loss. Accordingly, the energy loss of polymer dielectrics at high temperatures and electric fields is thoroughly inhibited. Therefore, the discharge energy density with an efficiency of around 90% at 150 °C increases by 421.43% from 1.26 J cm−3 for the pure film to 6.57 J cm−3 for the ion-activated composites. More importantly, for the capacitive performance with an efficiency of ca. 90% at 200 °C, the activated composite sample exhibits a discharge density of 4.22 J cm−3, which increases by 1355.17% in comparison to 0.29 J cm−3 of the pristine film and outperforms those of most existing polymer dielectrics. The concept of employing ions to regulate the electrode/dielectric interfacial charge transport and the strategy of simultaneously inhibiting electrode and bulk-limited conduction losses in this contribution provide a novel perspective and approach for the improvement of the high-temperature capacitive performance of polymer dielectrics.

Broader context
Polymer dielectrics with superior high-temperature capacitive energy storage performance are urgently needed for modern power electronic devices and high-voltage electrical systems. However, the discharge energy density and charge–discharge efficiency severely degrade at elevated temperatures owing to the low glass transition temperature (Tg) of polymer dielectrics and exponentially increased conduction loss at high temperatures and electric fields. Therefore, inhibiting the conduction and energy losses of polymer dielectrics at high temperatures and electric fields is extremely important for the improvement of capacitive performance. Based on this, we pioneer utilizing the concept of electrostatic repulsion to fundamentally inhibit the charge injection from the electrode by the ion activation of the surface of polymer dielectrics. The surface of polymer dielectrics is composed of abundant inherent carboxylate (RCOO−) and traces of potassium (K+) ions. RCOO− could establish a negatively charged surface and the charge injection from the electrode would be sufficiently suppressed owing to the electrostatic repulsion. We also considered the contribution of bulk-limited conduction to the loss at elevated temperatures and simultaneously incorporated wide-bandgap Al2O3 nanoparticles into the polymer dielectric matrix to constrain the carrier mobility in the bulk phase of dielectrics. The concept of employing ions to regulate the electrode/dielectric interfacial charge transport and the strategy of simultaneously inhibiting electrode and bulk-limited conduction losses in this contribution provide a novel perspective and approach for the improvement of the high-temperature capacitive performance of polymer dielectrics.

† Electronic supplementary information (ESI) available. See DOI: https://doi.org/10.1039/d3ee03644h
1. Introduction

Flexible electrostatic capacitors using polymer films as the dielectric layer, represented by the commercially available biaxially oriented polypropylene (BOPP), have been extensively used in modern electronic and electrical systems owing to their fast charge/discharge rates, superior high-voltage endurance and graceful failure mechanism.\(^1\)–\(^8\) Recently, the explosion in demand for extreme-environment applications with a stringent working temperature requirement (> 150 °C) such as electric vehicles, oil/gas exploration and aerospace systems boosted the exploration of high-temperature polymer dielectrics.\(^9\)–\(^11\) Unfortunately, commonly used aliphatic polymer dielectrics suffer from relatively low operation temperatures due to their intrinsic low glass transition temperature (\(T_g\)) (< 150 °C) and unconfined macromolecular structure. A significant motion of polymer segments will inevitably occur as the temperature approaches \(T_g\), consequently leading to an abrupt increase in the conduction loss of dielectrics at high electric fields.\(^12\) Compared to the counterparts of aliphatic polymers, aromatic polymers exhibit a rigid benzene backbone structure where the motion of segments is significantly restricted because of the steric-hindrance effect, accordingly leading to a higher \(T_g\) (> 200 °C). Nevertheless, the conjugated structures of aromatic polymers seriously restrain their use at elevated temperatures due to a dramatic increase in conduction loss even when the temperature is well below their \(T_g\). The noticeably increased conduction loss of polymer dielectrics will consequently give rise to inferior charge-discharge efficiency (\(\eta\)) and low discharge energy density (\(U_c\)). Additionally, the Joule heat arising from conduction loss may cause a thermal runaway of the capacitor.\(^9\) From this, inhibiting the conduction loss at elevated temperatures and electric fields is found to be of vital importance for the high-temperature capacitive performance of polymer dielectrics.

The exponential increase in conduction loss of polymer dielectrics at elevated temperatures and electric fields is mainly attributed to the injected charges from metal electrodes and thermally activated carriers inside the bulk phase of dielectrics.\(^13\) The Schottky emission dominates the interfacial conduction source where thermally activated electrons in metal electrodes can overcome the barrier at metal electrodes and dielectrics and subsequently inject into the polymer dielectrics. Substantial efforts have been made to augment the barrier height by coating the polymer dielectrics with a physical block layer composed of wide-bandgap inorganic or organic composites.\(^14\)–\(^19\) The construction of a dense and defect-free block layer is extremely challenging and harsh conditions of a high vacuum degree and toxic chemical reactants are usually unavoidable. Moreover, the weak adhesion and huge Young’s modulus mismatch between the coating layer and polymer dielectrics may cause severe delamination, subsequently resulting in an increase in structural defects and conduction loss or even bringing about the failure of the capacitor.\(^4\) Radiation treatment of polymer dielectrics with high-energy sources such as gamma rays, electron beams and ultraviolet can effectively overcome the aforementioned shortcomings since this approach can fundamentally alter the surface properties of films and is easy to implement owing to the advantages of superior remote controllability, free of toxic additives and potential industrial uptake.\(^20\)–\(^21\) Although the underlying interaction mechanism between the radiation source and macromolecules containing surface grafting of polar groups, scission or crosslinking of polymer chains is thoroughly understood, clear and consentaneous evidence is still lacking. More importantly, the potential degradation of polymers during radiation may induce the formation of low molecular weight species and accordingly give rise to an increase in conduction loss and failure of the capacitor.\(^4\)

Herein, we differ from prior work by utilizing the concept of electrostatic repulsion to block the charge injection from a metal electrode to polymer dielectrics. Compared with the wide bandgap inorganic coating layer, the negatively charged surface of polymer dielectrics should be more favorable to inhibiting the injected charges from the metal electrode. As a class of polyimide (PI) derivatives, polyetherimide (PEI, Ultem\textsuperscript{TM}) developed by General Electric company for capacitor films has been widely regarded as the most promising high-temperature polymer dielectric since the benzene ring conjugation effect has been eliminated due to the introduction of ether linkage in the aromatic backbone.\(^9\)–\(^22\) Unfortunately, the exponential increase in conduction loss of PEI dielectrics at high temperatures and electric fields is still unavoidable. Therefore, we used PEI resin as a representative polymer dielectric and negatively charged the surface of PEI through a simple hydrolysis process. The targeted cleavage of imide bonds in the aqueous alkaline solution can induce the formation of potassium polyamate on the surface of PEI dielectrics containing abundant polycarboxylate (RCOO\(^–\)) anions and traces of potassium cations (K\(^+\)). The resultant polyanion layer can effectively inhibit the charge injection from the electrode. More than that, we also reduced the bulk-limited conduction loss by incorporating the commercially available aluminium oxide (Al\(_2\)O\(_3\)) nanoparticles into the PEI matrix. Coupled with this, the conduction and energy losses were fundamentally suppressed and the surface ion-activated Al\(_2\)O\(_3\)/PEI composite films exhibited a superior high-temperature capacitive performance, far outperforming that of the most existing high-temperature polymer dielectrics.

2. Results and discussion

Fig. S1 (ESI\textsuperscript{†}) illustrates the surface ion-activation process of PEI films. The PEI films were firstly hydrolyzed in a heated potassium hydroxide solution and the imide bonds in the macromolecular chains were broken to form carboxylate (RCOO\(^–\)) anions and potassium (K\(^+\)) cations. After that, the hydrolyzed PEI (H-PEI) films were thoroughly rinsed with deionized water (DI) to remove the residual potassium hydroxide solution until the pH reached 7. We also controlled the rinse procedure to obtain the different surface structures of PEI films (Fig. S1, ESI\textsuperscript{†}). To figure out the structural changes of the
PEI films after hydrolysis, Fourier transform infrared (FT-IR) and X-ray photoelectron spectroscopy (XPS) analyses were carried out. The peaks at 1780 cm$^{-1}$, 1715 cm$^{-1}$ and 1370 cm$^{-1}$ are attributed to the C=O asymmetric, C=O symmetric and C–N–C imide ring stretches, respectively, which are the typical peaks of pristine PEI films.23–25 Peaks at 1650 cm$^{-1}$ and 1550 cm$^{-1}$ represent amide I and II vibrations, respectively, which indicate that the imide bonds have been ruptured.24 Comparing the FT-IR curves of PEI and H-PEI films clearly shows that the peak intensity at 1715 cm$^{-1}$ is significantly weakened after hydrolysis. To quantify the degree of hydrolysis, the FT-IR spectra were normalized with respect to the peak at 1010 cm$^{-1}$, which is attributed to the in-plane C–H benzene ring breathing. As summarized in Fig. 1a, b and Fig. S2 (ESI†), the hydrolysis temperature and time have a great influence on the surface structure of H-PEI films. At lower temperatures of 40 °C and 60 °C, the peak intensity at 1715 cm$^{-1}$ is gradually reduced and reaches a stable platform with increasing hydrolysis time, which indicates that the hydrolytic degree reaches a saturation state (Fig. 1a, b and Fig. S2a, b, ESI†). Nevertheless, for the hydrolysis at 80 °C, the intensity of the peak at 1715 cm$^{-1}$ monotonically decreases with hydrolysis time, which indicates that the hydrolysis process will continue to occur and the saturation state will not occur (Fig. S2c and d, ESI†). A gradual decrease in the intensity of the peak at 1715 cm$^{-1}$ for the PEI and H-PEI films with increasing hydrolysis temperature at a fixed time of 60 s further demonstrates that the temperature can significantly accelerate the hydrolysis process (Fig. 1c). From this, a mild and effective hydrolysis temperature of 60 °C was chosen for the treatment of pristine PEI and Al₂O₃ incorporated PEI (Al₂O₃/PEI) composites films since the accelerated hydrolysis at high temperatures may introduce undesirable voids or defects on the surface of the dielectric film. As displayed in Fig. S3 (ESI†), a similar decrease in the peak intensity at 1715 cm$^{-1}$ is observed, which suggests that the Al₂O₃/PEI film has been successfully hydrolyzed.
Moreover, a smooth and uniform morphology of PEI and Al₂O₃/PEI films is still maintained after the hydrolysis process even if a long hydrolysis period is applied (Fig. S4 and S5, ESI†). Compared with the pristine PEI film, no obvious changes in the intensity of C, O and N elements are observed (Fig. S6a–c and e–g, ESI†). Interestingly, a significant enhancement of K element intensity is observed in the energy dispersive spectra (EDS) of the H-PEI film (Fig. S6d and h, ESI†), which indicates that the surface ion activation of the PEI films has been successfully achieved. The occurrence of K₂s and K₂p peaks in the XPS survey spectrum of H-PEI films with different hydrolysis periods further demonstrates that the PEI films have been hydrolyzed (Fig. S7a, ESI†). Fig. 1d–g shows the C₁s XPS of pristine PEI and H-PEI films. Upon prolonging the hydrolysis time, the peak intensities of K-1 and K-2 firstly increase and stay unchanged, which indicates that a saturation state exists in the hydrolysis process and is in accordance with the FT-IR results. The C₁s spectrum could be deconvoluted into three peaks at 284.6 eV for C-1, 286.2 eV for C-2 and 288.3 eV for C-3 (Table S1, ESI†). The red shift of the N₁s peak for the H-PEI films is mainly attributed to the breakage of the O—C=N imide group. The peak intensity of C-3 gradually decreases and remains unchanged with increasing hydrolysis time, which is due to the breakage of O—C=N imide groups and the existence of a hydrolysis saturation point. In the O₁s spectrum, a slight enhancement of peak intensity at 533.2 eV for O-2 is observed for the H-PEI films owing to the formation of a C—O— single bond (Fig. S7b–e, ESI†). The red shift of the N₁s peak for the H-PEI films is mainly attributed to the breakage of the O—C=N imide group (Fig. S7f, ESI†). The bandgap slightly increases from 3.383 eV for the pristine PEI film to 3.403 eV for H-PEI. For the Al₂O₃/PEI composites, the bandgap increases from 3.395 eV to 3.400 eV after hydrolysis. The broadened bandgap is helpful for the enhancement of the insulation properties of polymer dielectrics at elevated temperatures and fields. More importantly, the transmittance of the hydrolyzed films displays an obvious decline in the wavelength range from 400 nm to 500 nm when compared to that of un-hydrolyzed films, which indicates that the photons with energy lower than that of the optical bandgap are absorbed in the hydrolyzed films. Accordingly, the forbidden band of PEI films is split and extra trap energy levels are generated in the bandgap. This phenomenon will be further confirmed by the analysis of thermally stimulated depolarization current (TSDC).

In order to figure out the effects of the rinse process on the surface structural changes of H-PEI, we prolonged the rinse time with DI water and used HCl to rinse the H-PEI films. After the hydrolysis, we use DI water to remove the residual potassium hydroxide solution until the PH reaches 7. This rinse process removes most free K⁺ on the surface of the H-PEI film, accordingly leading to the formation of a more negatively charged surface. The surface H-PEI films are composed of abundant RCOO⁻ anions and a small quantity of K⁺ cations, which exist in the free volume of the H-PEI surface. The electrostatic potential distribution of several PEI repeat units is calculated by density functional theory (DFT) computation (Fig. 2a). The results reveal that the surface of H-PEI films with abundant RCOO⁻ anions is negatively charged, suggesting their strong repulsion nature to extra injected electrons. When the H-PEI films are rinsed with HCl, the RCOO⁻ anions are converted to RCOOH and the electrostatic potential moves to the positive direction. The XPS survey spectra of PEI, H-PEI, H-PEI-HCl and H-PEI-L films are displayed in Fig. 2b. It is observed that the prolonging of the rinse time with DI water can reduce the amount of K⁺ cations, but can not absolutely eliminate K⁺ from the surface of the H-PEI film, which is in accordance with previous results. In contrast, the rinse process with HCl can eliminate the residual K⁺ cations. The C₁s spectrum further confirms that the concentration of K⁺ can be well regulated by controlling the rinse procedure (Fig. 2c and d). The XPS O₁s and N₁s spectra are displayed in Fig. S10 and S11 (ESI†). The enhanced intensity of the O-2 peak (Fig. S10, ESI†) and the redshift of the N₁s peak (Fig. S11, ESI†) for the hydrolyzed films further demonstrate that the PEI films have been successfully hydrolyzed. The increase in the zeta potential from −32.97 mV for the H-PEI film to −57.19 mV for the film rinsed with HCl is mainly attributed to the conversion...
from the RCOO\(^-\) anion to RCOOH groups. Moreover, by prolonging the rinse time with DI water, the zeta potential slightly decreases from \(-72.97\) mV for the H-PEI film to \(-74.06\) mV for the H-PEI-L film owing to the reduction in the amount of K\(^+\). Upon further prolonging the rinse period, the peak of the K element still exists in the XPS spectrum of the H-PEI-Longer film (Fig. S12, ESI\(^\dagger\)). The rinsing process can not eliminate K\(^+\) from the surface of the hydrolyzed film. Only those K\(^+\) cations in the shallow region can be removed while those K\(^+\) cations in the deep area are difficult to be eliminated. In comparison to the XPS results of the H-PEI-L film, the peak intensity of the K element for the H-PEI-Longer film stays almost unchanged, which indicates that a saturation point exists in the rinse process (Fig. S13, ESI\(^\dagger\)). The optical bandgap of the H-PEI-Longer film also has a little change (Fig. S14, ESI\(^\dagger\)). The existence of negative RCOO\(^-\) ions on the surface of the hydrolyzed films is of importance in regulating the capacitive energy storage performance of PEI dielectrics. Table S2 (ESI\(^\dagger\)) summarizes the atomic percentages of pristine and hydrolyzed films. The percentage changes of O and K elements confirm that the hydrolysis and rinse processes can be well controlled.

The capacitive energy storage performance of polymer dielectrics is strongly related to the dielectric and electrical insulation properties at elevated temperatures and electric fields. The dielectric spectrum reveals that the dielectric constant of hydrolyzed films gradually increases with hydrolysis time (Fig. S15a and S16, ESI\(^\dagger\)) and temperatures (Fig. S15b, ESI\(^\dagger\)) owing to the increase in the fraction of polar groups during the hydrolysis process.\(^{20}\) The dielectric loss remains almost unchanged with a magnitude of \(10^{-3}\) compared with the un-hydrolyzed films. Additionally, the dielectric constant and loss of hydrolyzed films exhibit a stable frequency-dependent behavior. As displayed in Fig. 3a and Fig. S17 (ESI\(^\dagger\)), the H-Al\(_2\)O\(_3\)/PEI film shows the highest dielectric constant owing to the simultaneous improvements in the bulk and surface polarization intensity, which is beneficial to increasing polarization intensity and discharge energy density. The breakdown strength of H-PEI films firstly increases from 463 MV m\(^-1\) for pure PEI to 598 MV m\(^-1\) for the saturated H-PEI film, which is followed by a decrease with further prolonging the hydrolysis time. The increased breakdown strength is mainly attributed to the suppressed charge injection while the decrease in the breakdown strength results from the introduced voids or defects during a long hydrolysis period. Fig. 3b demonstrates that the breakdown strength is strongly related to the hydrolysis temperatures and an appropriate hydrolysis temperature is critically important for the improvement of insulation properties. The breakdown strength increases from 463 MV m\(^-1\) for the pristine PEI film to 574 MV m\(^-1\) for the hydrolyzed film at 60 °C, followed by a decrease to 544 MV m\(^-1\) for the film hydrolyzed at 80 °C. Higher hydrolysis temperatures may produce more defects on the surface of the film while lower temperatures can not sufficiently activate the surface with abundant ions to suppress charge injection. For the Al\(_2\)O\(_3\)/PEI composite films, an appropriate concentration of Al\(_2\)O\(_3\) nanoparticles in the PEI matrix is necessary to ensure the optimal insulation property. The PEI composite with 1 vol% loading of Al\(_2\)O\(_3\) nanoparticles shows the highest breakdown strength with a value of 526 MV m\(^-1\) (Fig. S18a, ESI\(^\dagger\)). The hydrolysis time-dependent breakdown strength behavior for the H-Al\(_2\)O\(_3\)/PEI films exhibits a similar tendency in that the breakdown strength firstly increases with hydrolysis time and then decreases with further prolonging the hydrolysis period (Fig. S18b, ESI\(^\dagger\)). The H-Al\(_2\)O\(_3\)/PEI film displays the highest
breakdown strength of 608 MV m\(^{-1}\) at 150 °C (Fig. S19, ESI\(^†\)) and 528 MV m\(^{-1}\) at 200 °C (Fig. 3d). As shown in Fig. S20 (ESI\(^†\)), the hydrolysis process does not significantly affect the mechanical properties of polymer dielectric films since Young’s modulus and elongation at break stay almost unchanged. Nevertheless, the incorporation of Al\(_2\)O\(_3\) nanoparticles in the polymer matrix contributes to an increase in Young’s modulus and a decrease in elongation at break owing to the rigid feature of the inorganic component. The improvement in Young’s modulus is helpful for the increase in the breakdown strength. From this, a simultaneous increase in the dielectric constant and breakdown strength of the H-Al\(_2\)O\(_3\)/PEI film help ameliorate the capacitive performance. The conduction loss of polymer dielectrics at high temperatures and electric fields is directly determined by the leakage current. It is observed from Fig. 3e and Fig. S21 (ESI\(^†\)) that the leakage current for the hydrolyzed films gradually decreases with hydrolysis time. The reduced conduction loss is mainly attributed to the suppressed charge injection from the electrode, which originates from the electrostatic repulsion between the electrode and the negatively charged surface. The experimental results for the leakage current of the H-PEI films are well-fitted with the Schottky emission model\(^{13}\), which is a typical mechanism for electrode-limited conduction at high temperatures and relatively low fields. The calculated charge injection barrier height increases from 1.019 eV for pristine PEI to 1.028 eV for the H-PEI film with a hydrolysis time of 480 s (Fig. S22, ESI\(^†\)). We also carried out ultraviolet photoelectron spectroscopy (UPS) measurement to figure out the changes in band diagrams at the interface of electrode/polymer dielectric (Fig. S23–S25, ESI\(^†\)). Fig. S23 (ESI\(^†\)) shows the schematic diagram of the UPS spectrum for a polymer dielectric and the results of the UPS spectrum are displayed in Fig. S24 (ESI\(^†\)). The barrier height for electrons (\(\phi_b\)) increases from 2.10 eV for pristine PEI to 2.36 eV for the H-PEI film (Fig. S25a and b, ESI\(^†\)), which is in good agreement with the tendency calculated from the leakage injection barrier height and hopping distance of PEI, H-PEI, Al\(_2\)O\(_3\)/PEI and H-Al\(_2\)O\(_3\)/PEI films from the fitting results of Schottky emission and hopping conduction models. (i) TSDC curves of PEI, H-PEI, Al\(_2\)O\(_3\)/PEI and H-Al\(_2\)O\(_3\)/PEI films.
current. The augmented barrier height suggests that the ion activated surface can effectively regulate the electrode/dielectric interfacial charge transport. The resultant carboxylate anions can construct a negatively charged surface and the charge injection from the electrode is suppressed because of the strong electrostatic repulsion. More importantly, the reduction in electron affinity (E_{A_b}) from 3.10 eV for pristine PEI to 2.84 eV for the H-PEI film (Fig. S23a and b, ESI†) further indicates that the ion-activated surface can effectively inhibit the charge injection from the electrode. Fig. 3f reveals that the leakage current monotonously decreases with hydrolysis temperature due to the enhanced electrostatic repulsion. As summarized in Fig. 3g, the H-Al_2O_3/PEI film exhibits the lowest leakage current at high temperatures and fields, which is attributed to the simultaneous suppression of electrode and bulk-limited conduction losses. The hopping conduction, a typical mechanism of bulk-limited conduction, is usually determined by the bulk insulation property of polymer dielectrics and it can be effectively suppressed by incorporating wide bandgap Al_2O_3 nanoparticles into the bulk phase of dielectrics. The Al_2O_3 NPs can generate deep traps inside dielectrics and dissipate the kinetic energy of injected or thermally activated carriers during the collision. The resultant deep traps can constrain the carrier mobility, accordingly leading to a reduction in the hopping conduction loss. The experimental results of leakage current at high electric fields are well-fitted with the hopping conduction model. In comparison to the pristine PEI film, the barrier height augments from 1.071 eV to 1.151 eV while the hopping distance decreases from 0.81 nm to 0.66 nm (Fig. 3h). The calculated \( \phi_{G} \) and E_{A_b} for Al_2O_3/PEI and H-Al_2O_3/PEI films further demonstrate that the charges are difficult to transfer from the metal electrode to the surface of polymer dielectric (Fig. S25c and d, ESI†). The reduced hopping distance is resulted from the increased trap density. The thermally stimulated depolarization current (TSDC) analysis was performed to figure out the trap characteristics (Fig. 3i). Compared with the pristine PEI film, the H-PEI film exhibits an apparent peak at lower temperatures in the TSDC curve. The generated new peak indicates that new trap energy levels are formed after the film was simultaneously incorporated with the H-PEI films. As summarized in Fig. 4b, the H-PEI films exhibit a monotonous reduction in the remanent polarization, which is mainly attributed to the relatively lower zeta potential of the PEI bulk phase. Fig. S33 (ESI†) displays the \( D-E \) loops of PEI, H-PEI, Al_2O_3/PEI and H-Al_2O_3/PEI films as a function of electric field at 200 °C. As summarized in Fig. 4e, the remanent polarization of PEI films was significantly suppressed after the film was simultaneously incorporated with the
Al₂O₃ nanoparticles and hydrolyzed in KOH solution. Moreover, the H-Al₂O₃/PEI film exhibits a higher polarization value than the H-PEI film due to the increased dielectric constant. The summarized energy loss as a function of electric field at 200 °C calculated from the D–E loops indicates that the energy loss at high temperatures and electric fields is fundamentally suppressed in the H-Al₂O₃/PEI film owing to the suppressed conduction loss as previously discussed (Fig. 4f) while the pristine PEI film exhibits an apparent exponential growth in the energy loss at higher electric fields. From this, at 150 °C, the H-Al₂O₃/PEI film displays a maximum \( U_e \) of 6.57 J cm\(^{-3}\) with a \( \eta \) of 89.70% while the pristine PEI film merely exhibits a maximum \( U_e \) of 2.55 J cm\(^{-3}\) with a \( \eta \) of 58.35%. As for discharge density with a \( \eta \) of around 90%, \( U_e \) is increased by 421.43% from 1.26 J cm\(^{-3}\) for pure PEI to 6.57 J cm\(^{-3}\) for the H-Al₂O₃/PEI film (Fig. 4g). Upon increasing the temperature from 150 °C to 200 °C, the capacitive performance of the PEI film degrades rapidly due to the exponential growth of conduction loss. At 200 °C, the pristine PEI film could merely deliver a maximum \( U_e \) of 1.01 J cm\(^{-3}\) with a \( \eta \) of 14.08%. Conversely, the maximum \( U_e \) for the H-Al₂O₃/PEI film is 4.77 J cm\(^{-3}\) with a \( \eta \) of 85.62%. As for the capacitive performance with a \( \eta \) of around 90%, \( U_e \) is increased by 1355.17% from 0.29 J cm\(^{-3}\) at 150 MV m\(^{-1}\) for the PEI film to 4.22 J cm\(^{-3}\) at 520 MV m\(^{-1}\) for the H-Al₂O₃/PEI film (Fig. 4h). As summarized in Fig. 4i, the insulation and capacitive performances of PEI films at elevated temperatures and electric fields are significantly improved by simultaneously inhibiting the electrode and bulk-limited conduction losses.

The distinctive insulated and capacitive features of H-Al₂O₃/PEI at elevated temperatures and electric fields are mainly attributed to the simultaneous inhibition of electrode and bulk-limited conduction losses. The incorporation of wide bandgap Al₂O₃ NPs introduces additional trap sites in the PEI matrix, which has been demonstrated by the reduction in the calculated hopping distance. The increased trap density is beneficial to the restriction of carrier mobility, consequently leading to the reduction in the bulk-limited conduction loss. A schematic illustration of using ions to regulate the interfacial
charge transport and inhibit electrode-limited conduction loss in this contribution is displayed in Fig. 5a. The generated RCOO\(^{-}\) anions on the surface of the hydrolyzed film offer the electrode/dielectric interface strong electrostatic repulsion, which can effectively suppress the charge injection from the electrode. The reference films employing different rinse procedures further demonstrate the mechanism proposed in this work. As displayed in Fig. 5b, an apparent temperature increase, simulated by the finite-element analysis, is observed for the capacitor with the pristine film and the maximum temperature is approximately 490 K, far exceeding the \(T_g\) of PEI resin, which may cause the thermal runaway and breakdown of the capacitor. Conversely, the temperature in the capacitor with the H-Al\(_2\)O\(_3\)/PEI film stays almost unchanged owing to the suppressed conduction loss and Joule heat and the maximum temperature inside the capacitor is merely 479 K, well below the \(T_g\) of PEI resin. The cyclic charge/discharge results further demonstrate that the H-Al\(_2\)O\(_3\)/PEI film exhibits excellent stability and reliability (Fig. 5c). Even after 50,000 cycles, the capacitive performance still remains stable. The discharge energy densities of the H-Al\(_2\)O\(_3\)/PEI film with an efficiency of \(\sim 90\%\) at 150 °C (6.57 J cm\(^{-3}\)) and 200 °C (4.22 J cm\(^{-3}\)) achieved in this work outperform those of most of the previously reported results for PEI-based composites (Fig. 5d and e).\(^{10,14,15,31,36-44}\) In comparison to other non-PEI-based composites, the capacitive performance obtained in this work is also superior to that of most other non-PEI dielectrics (Fig. S34, ESI†).

3. Conclusion

In summary, we have constructed a negatively charged layer on the surface of polymer dielectrics through a controlled hydrolysis process and the resultant anions could effectively regulate the charge transport in the interface of the metal electrode and polymer dielectric at elevated temperatures and electric fields. Carboxylate anions could establish a negatively charged surface and the charge injection from the electrode has been suppressed owing to the electrostatic repulsion. From this, the electrode-limited conduction loss has been distinctly inhibited. Additionally, the bulk-limited conduction loss has also been considered and suppressed by incorporating Al\(_2\)O\(_3\) nanoparticles into the polymer dielectric matrix owing to the increase in the density of charge-trapped sites. Therefore, the conduction loss of polymer dielectrics at high temperatures and fields has been fundamentally inhibited. The resultant capacitive energy storage performance with a discharge energy density of 4.22 J cm\(^{-3}\) and 90% efficiency at 200 °C outperforms that of most of the existing polymer dielectrics. The concept of using anions to regulate the electrode/dielectric interfacial charge transport could be easily extended to other polymer dielectrics for high-temperature capacitive performance.

4. Methods

4.1. Materials

Polyetherimide (PEI, Ultem1000) resin particles were provided by SABIC company. Potassium hydroxide (KOH) pellets and aluminium oxide nanoparticles (Al\(_2\)O\(_3\) NPs) with an average diameter of 40 nm were purchased from Macklin. Other reagents and solvents were obtained from Beijing Chemical Reagents Company. For the preparation of PEI and Al\(_2\)O\(_3\)/PEI films, the Al\(_2\)O\(_3\) NPs with an appropriate fraction were dissolved in \(n\)-methyl pyrrolidone (NMP) by tip ultrasonication for 1 h to form a homogeneous solution. After that, PEI particles...
were added to the above solution and the mixture was magnetically stirred for 24 h at 50 °C. The obtained suspensions were subsequently spin-coated onto a clean glass substrate and the films were placed in a vacuum oven at 120 °C for 12 h, which was followed by a further drying procedure at 200 °C for 3 h to eliminate any residual solvent. Finally, the PEI or Al2O3/PEI films were peeled off from the substrate in deionized water and then dried in a vacuum oven at 70 °C for 30 min to remove the moisture. The thickness of the obtained film is about 10–12 μm. As for the hydrolysis process, PEI or Al2O3/PEI films were firstly ultrasonically cleaned in isopropanol for 20 min to remove any organic pollutants, followed by being thoroughly washed with deionized water and dried in a vacuum oven. After that, the films were immersed in 15 M KOH aqueous solution at the desired temperature for a certain period. The obtained hydrolyzed films were ultrasonically treated with excess deionized (DI) water several times to remove the residual KOH on the surface of films until the PH reached 7. Finally, the samples were dried under vacuum at 70 °C with 6 h. The H-PEI-L film was prepared by prolonging the rinse period with DI water to reduce the amount of K+ ions. The H-PEI-HCl film was prepared by soaking the H-PEI film in 0.2 M HCl solution to convert RCOO− to RCOOH and excess HCl was removed by ultrasonication in DI water until the pH reached 7.

4.2. Characterization

Scanning electron microscopy (SEM) images of the surface morphologies of the pristine and hydrolyzed films were taken using a Quattro scanning electron microscope (Thermo Scientific). Fourier transform infrared spectroscopy (FT-IR) analysis was performed on a Nicolet 5700 spectrometer. XPS characterization was conducted with a near ambient pressure photoelectron spectroscopy system (SPECS ProvenX-NAP). Zeta potential was carried out on a SurPASS 3 (Anton Paar). UV-vis spectroscopy was carried out on a Shimadzu UV-2600 spectrophotometer. Ultraviolet photoelectron spectroscopy (UPS) was performed on a Thermo Scientific ESCALab 250Xi with He-I (21.2 eV) as the light source and the Fermi level was calibrated using clean Au. The rectangle-shaped films with a length of 10 mm and a width of 8 mm were stretched on INSTRON 3343 at a rate of 200 mm min⁻¹ until being fractured and Young’s modulus and elongation at break were obtained. Dielectric analysis was measured using a Novocontrol Concept 80 dielectric spectroscopy meter. Dielectric breakdown strength was measured on a BOHER high-voltage supply. The breakdown data were analyzed using a two-parameter Weibull statistic (ESI†). The leakage current was obtained from a measurement platform composed of a power supply (Keithley, 2290-10) and a current source meter (Keithley, 2635B). TSDDC measurement was performed using the Novocontrol platform integrated with an electrostatic/high-resistance measuring instrument (Keysight 2985B). The films were firstly polarized under a DC electric field of 30 MV m⁻¹ at 200 °C for 30 min. Subsequently, the polarized films were rapidly cooled down to −10 °C with the applied electric field. After that, the films were placed at −10 °C for 3 min and then the electric field was removed. Finally, the films were short-circuited and heated to 250 °C at a heating rate of 3 °C min⁻¹ with the current recorded. Unipolar displacement–electric field (D–E) hysteresis loops were measured using a modified Sawyer–Tower circuit under a unipolar wave at a frequency of 50 Hz. The cyclic fast charge–discharge tests were carried out using a modified Sawyer–Tower circuit. Gold electrodes with a diameter of 4 mm were sputtered on both sides of the polymer films for electrical measurements.

4.3. Simulations

The potential distribution of the repeat unit is determined by density functional theory (DFT). DFT calculations are carried out based on first-principles calculations, and the calculated molecular wave function is determined from the Schrödinger equation. In this work, DFT calculations were performed in Materials Studio using the DMOl3 module. The structure of PEI repeat units was optimized using the Perdew–Burke–Ernzerhof (PBE) exchange and general gradient approximation (GGA) functions. After that, their electrostatic potentials were obtained and analyzed in a color-mapped isosurface of electrostatic potential distribution.

The temperature distribution for a capacitor composed of pristine and hydrolyzed PEI films at elevated temperatures was obtained using a finite element analysis method on COMSOL Multiphysics. The mathematical models of films are governed by the following heat transfer model,

\[ ρ \cdot C \frac{∂T}{∂t} = K \nabla^2 T + Q \]

where \( ρ, C, T, t, K \), and \( Q \) represent the density, specific heat capacity, temperature, time, thermal conductivity and thermal power density, respectively. \( Q \) was computed by the energy loss with the equation \( Q = U_{loss} f \); \( U_{loss} \) was the energy loss in the D–E loop of films at 300 MV m⁻¹ and \( f \) was the frequency. The shape of the capacitor was set as cylindrical with a height of 10 mm and a diameter of 20 mm. The ambient temperature was set to 473.15 K and the boundary condition was set as convective heat flux with a heat transfer coefficient of 120 W m⁻² K⁻¹.

Data availability

The data that support the findings of this study are available from the corresponding authors on request.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

The authors gratefully acknowledge the support from the National Natural Science Foundation of China (Grant no. 52007060, 51937007 and 52127812), National Key Research and Development Program of China (Grant no. 2021YFB2401503) and Fundamental Research Funds for the Central Universities (2021MS049).
References