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Enhanced electrochemical properties of PEO-based composite polymer electrolyte with shape-selective molecular sieves

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Abstract

ZSM-5 molecular sieves, usually known as shape-selective catalyst in a great deal of catalysis fields, due to its special pore size and two-dimensional interconnect channels. In this work, a novel PEO-based composite polymer electrolyte by using ZSM-5 as the filler has been developed. The interactions between ZSM-5 and PEO matrix are studied by DSC and SEM techniques. The effects of ZSM-5 on the electrochemical properties of the PEO-based electrolyte, such as ionic conductivity, lithium ion transference number, and interfacial stability with lithium electrode are studied by electrochemical impedance spectroscopy and steady-state current method. The experiment results show that ZSM-5 can enhance the ionic conductivity and increase the lithium ion transference number of PEO-based electrolyte more effectively comparing with traditional ceramic fillers such as SiO₂ and Al₂O₃, resulting from its special framework topology structure. The excellent performances such as high ionic conductivity, good compatibility with lithium metal electrode, and broad electrochemical stability window suggesting that PEO–LiCIO₄/ZSM-5 composite polymer electrolyte can be used as candidate electrolyte materials for lithium polymer batteries.

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1. Introduction

PEO-LiX (X = ClO_4^- , I^- , BF_4^- , PF_6^- , $CF_3SO_3^-$, etc.) based solid polymer electrolytes (SPEs) have received extensive attentions for its potential capability to be used as candidate material for traditional liquid electrolytes [1–6], since Wright et al. found that the complex of PEO and alkaline salts had the ability of ionic conductivity in 1973 [7]. Lithium polymer batteries may be one of the best choices for electrochemical power source of the future characterized by its high energy densities, good cyclability, reliability and safety [8–11]. Development of PEO-based electrolytes capable of combining high ionic conductivity and lithium ion

transference number, superior interfacial stability towards the lithium metal anode, and good mechanical properties are the key problems for the R&D of all solid-state lithium polymer batteries [1,11]. General concept of the transport of Li⁺ cations in the polymer electrolyte are coupled with the local relaxation and segmental motion of the PEO chains, which conditions can only be obtained when PEO is in its amorphous state, however, due to its particular structure, PEO often shows much higher crystalline ratios at sub-ambient temperature regions, and then its ionic conductivity is lower than 10^{-7} S cm⁻¹ [1,12–16]. This limitation is, of course, a drawback for its applications in the consumer electronic market, such as cell phone and notebook PC. On the other hand, ionic conductivity of PEO based polymer electrolytes can reach to the appreciable level (about 10^{-4} to 10^{-3} S cm⁻¹), an advantage for numerous other applications such as elec-

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Fig. 1. Schematic representation of the shape-selective molecular sieves ZSM-5 and two types of its channels.

tric vehicles (EV), hybrid electric vehicles (HEV), energy storage, and load levering, when the operation temperature is higher than the melting point ($\sim 65 \,^{\circ}$ C) of the PEO [17–19].

When the third component, such as inorganic fillers, was introduced into the PEO-based electrolytes to form the composite polymer electrolytes (CPEs), all of above performances could be improved [20,21]. The fillers have been used in CPEs in previous research works can be generally classified into four families:

- (1) ceramic and/or nano-oxides, e.g., SiO₂ [22–24], Al₂O₃ [25–27], TiO₂ [28], ZnO [29,30], ZrO₂ [31,32], etc.;
- (2) layered clays, e.g., montmorillonite [33–35];
- (3) organic-inorganic hybrid materials [36-38];
- (4) ordered mesoporous materials (OMMs), e.g., MCM-41 [39,40] and SBA-15 [41,42].

Inorganic fillers help to increasing the conductivity of CPE in two ways [1]: (1) increasing the ratios of the amorphous phase of PEO matrix, which was beneficial for the transport of Li⁺, by lowering of the PEO reorganization tendency and (2) providing novel Li⁺ conducting pathways at the surface regions of the fillers through the microcosmic interactions, such as Lewis acid–base interactions, among different species in the CPEs.

Microporous molecular sieves [43,44] and ordered mesoporous materials [45–48] have attracted much attention because of its potential for advanced applications in selective absorption and separation technologies, catalysis, electronic engineering, and nanoscience, due to their well-ordered microstructure and special pore size. Porous materials have several advantages compared with traditional ceramic fillers, which may influence the lithium transport properties in the CPEs because of their tunable pores/cages size and base/acid sites [43–48]. ZSM-5 molecular sieves, usually known as shape-selective catalyst in a great deal of catalysis fields, has two-dimensional interconnect channels, as shown in Fig. 1 [49]. The cation-exchange centers resulting from the periodic replacement of [AlO₄]⁻ for [SiO₄] in the framework of ZSM-5 suggesting that Li⁺ cation can be ion-exchanged into the well-defined cages or channels for charge balance, which may provide a contribution for the lithium transport properties. In addition, the Lewis acid sites of ZSM-5 frameworks may provide another contribution in increasing the lithium transport properties through Lewis acid–base interactions, like the case of other ceramic fillers [1].

In this work, a novel composite polymer electrolyte PEO–LiClO₄/ZSM-5 has been developed, in which ZSM-5 as the filler can obviously enhance the room temperature ionic conductivity and improve other electrochemical properties of the electrolyte at the same time. The enhancement mechanisms of ZSM-5 on PEO-based electrolyte were also studied by differential scanning calorimeter (DSC), scanning electron microscopy (SEM) and electrochemical methods.

2. Experimental

Poly(ethylene oxide), PEO, $M_w = 1,000,000$ (Shanghai Liansheng Chem. Tech. Co. Ltd.) and LiClO₄, A.R. (Shanghai Second Regent Company) were vacuum dried for 24 h at 50 and 120 °C, respectively, before use. Acetonitrile, A.R. (Shanghai Chemical Regent Company), dehydrate by 4A molecular sieves before use. SiO₂ (10 nm) and Al₂O₃ (60 nm) (Zhoushan Nano Co. Ltd., China) were vacuum dried for 24 h at 200 °C prior to use. ZSM-5 was obtained by ion exchange method from H-ZSM-5 (SiO₂/Al₂O₃ = 25, from Nankai University Catalyst Company).

The preparation of CPE involved first the dispersion of the filler and LiClO₄ in anhydrous acetonitrile at room temperature, followed by the addition of the PEO. The resulting slurry was cast onto a Teflon plate and then the plate was placed into a self-designed equipment, under the sweep of dry air with a flow rate of 10 L min^{-1} , in order to let the solvent slowly evaporate. Finally, the result films were dried under vacuum at 50 °C for 24 h to get rid of the residue solvent. These procedures yielded translucent homogenous films of thickness ranging from 100 to 200 µm. All the CPE films were stored in an argon atmosphere glove box before test. The CPE samples used in this study were denoted as PEO₁₀–LiClO₄/*x*% filler, in which the EO/Li ratio was fixed to 10 for all samples and the content of filler, *x*, ranged from 0 to 30 wt.% of the PEO weight.

SEM images of the surface and cross-section of CPEs were observed on Hitachi S-2150 with gold sputtered-coated films. CPEs films were broken in liquid nitrogen to obtain a cross-section.

Differential scanning calorimeter (DSC) measurements were carried out on a Perkin-Elmer Pyris-1 analyzer. The measurements were carried out at a heating rate of $10 \,^{\circ}\text{C} \,\text{min}^{-1}$ from -60 to $100 \,^{\circ}\text{C}$ in the heating cycle and from 100 to $-20 \,^{\circ}\text{C}$ in the cooling cycle.

Ionic conductivity of the CPEs was determined by ac impedance spectroscopy. The film was sandwiched between two stainless steel (SS) blocking electrodes (with a diameter of 1 cm) to form a symmetrical SS/CPE/SS cell. The cell was placed into a self-designed oven coupled with a temperature controller. For each temperature, at least 30 min were waited before the impedance response was recorded. The impedance tests were carried out in the 1 MHz to 1 Hz frequency range using a Solartron 1260 Impedance/Gain-Phase Analyzer coupled with a Solartron 1287 Electrochemical Interface.

Lithium ion transference number, t_{Li^+} , was evaluated using the method of ac impedance combined with steady-state current technique, proposed by Vincent and Bruce [50–52]. The CPE was sandwiched between two lithium-unblocking electrodes to form a symmetrical Li/CPE/Li cell. The cell was assembled and sealed in an argon-filled UNILAB glove box (O₂ < 0.1 ppm; H₂O < 0.1 ppm).

Electrochemical stability window of the CPEs were determined by running a linear sweep voltammetry in threeelectrode cells using stainless steel as the blocking working electrode, lithium as both the counter and the reference electrode and the CPE film as the electrolyte. A Solartron 1287 Electrochemical Interface was used to run the voltammetry at a scan rate of 1 mV S^{-1} .

3. Results and discussion

SEM is often used to study the compatibility between various components of the CPEs through the detection of phase separations and interfaces [53,54]. The compatibility between the polymer matrix and the inorganic fillers has great influence on the properties (mechanical, thermal, ionic conductivity, and interface with the lithium anode) of the PEO-based composite electrolytes.

Both Li salt and ZSM-5 modified the surface morphology of the PEO electrolytes. Fig. 2a is the surface image of pure PEO film. The image shows a rough morphology with a great deal of micropores, a common occurrence for PEO-based electrolytes prepared by the solvent casting method. These small pores are caused by the fast evaporation of the acetonitrile solvent during the preparation process. A dramatic



Fig. 2. Surface SEM images of pure PEO. (a), PEO₁₀-LiClO₄ (b) and PEO₁₀-LiClO₄/x%ZSM-5 composite polymer electrolytes: (c) x = 3; (d) x = 7; (e) x = 10; (f) x = 30.



Fig. 3. Cross-section SEM images of PEO₁₀–LiClO₄ (a) and PEO₁₀–LiClO₄/x%ZSM-5 composite polymer electrolytes: (b) x=3; (c) x=7; (d) x=10; (e) x=15; (f) x=30.

improvement of surface morphology from rough to smooth is found after the addition of Li salt (Fig. 2b). The smooth surface morphology is closely related to the reduction of PEO crystallinity through the interaction between PEO segments and lithium cations [28]. Incorporation of enough ZSM-5 in PEO₁₀–LiClO₄ complex further improves the smooth morphology (Fig. 2d–e). Although the distribution of ZSM-5 in PEO is difficult to visualize by surface SEM since these two phases do not differ significantly in their ability to radiate secondary electrons upon incidence by the analytical electron beam [53], no aggregation of ZSM-5 can be observed in Fig. 2c–e suggesting that ZSM-5 dispersed homogeneously in the films. However, the morphology of the electrolyte becomes rough when the content of ZSM-5 further increased (Fig. 2f), which can be explained by the aggregation of ZSM-5 at high loading content.

Cross-section SEM images (Fig. 3) of PEO_{10} -LiClO₄/x%ZSM-5 composite polymer electrolytes show that ZSM-5 can disperse homogeneously in PEO matrix even when its content up to 15% of PEO weight (Fig. 3b–e),

Sample	Glass point T_g (°C)	Melting point $T_{\rm m}$ (°C)	Melting enthalpy ^a $\Delta H_{\rm m} (\rm J g^{-1})$	Crystallinity ^b X_c (%)		
PEO ₁₀ -LiClO ₄	-34.8	54.4	83.3	39.0		
PEO10-LiClO4/5%ZSM-5	-37.5	51.8	71.4	33.4		
PEO ₁₀ -LiClO ₄ /10%ZSM-5	-41.9	50.4	49.7	23.3		
PEO10-LiClO4/20%ZSM-5	-45.1	48.7	45.3	21.2		
PEO10-LiClO4/30%ZSM-5	-45.4	44.3	44.7	20.9		

 $Thermal \ properties \ of \ PEO_{10}-LiClO_4 \ and \ PEO_{10}-LiClO_4/x\% ZSM-5 \ composite \ polymer \ electrolytes \ obtained \ from \ DSC \ analysis \$

^a The data have been normalized to the weight of the PEO matrix.

^b $X_{\rm c} = (\Delta H_{\rm m}^{\rm sample} / \Delta H_{\rm m}^{*}) \times 100$, where $\Delta H_{\rm m}^{*} = 213.7 \text{ (J g}^{-1})$.

Table 1

suggesting the good compatibility between ZSM-5 and PEO matrix. When ZSM-5 content is higher than 30% of PEO weight, obviously phase separation between the polymer matrix PEO and inorganic component ZSM-5 can be observed (Fig. 3f).

DSC traces of PEO, PEO₁₀–LiClO₄, and PEO₁₀–LiClO₄/*x*%ZSM-5 are displayed in Fig. 4. For all samples, the endothermic peak between 20 and 80 °C at heating scan of DSC curves are corresponding to the melting of the crystalline PEO. The relative percentage of crystalline PEO, X_c , can be calculated with the equation $X_c = \Delta H_m / \Delta H_m^*$, where ΔH_m^* is the melting enthalpy of a completely crystalline PEO sample [55]. The calculated data of X_c and other thermal properties of all samples are summarized in Table 1.

It can be seen from Fig. 4 and Table 1 that both the melting temperature ($T_{\rm m}$) and the crystallinity of PEO ($X_{\rm c}$) decrease obviously when ZSM-5 is added in PEO₁₀–LiClO₄ complex. $T_{\rm m}$ of PEO₁₀–LiClO₄/x%ZSM-5 decreases from 54.4 to 44.3 °C when the content of ZSM-5 increases from 0 to 30 wt.%. On the contrary, $X_{\rm c}$ of PEO₁₀–LiClO₄/x%ZSM-5 first decreases with the increase of ZSM-5 content and then



Fig. 4. DSC traces of PEO (a), PEO₁₀–LiClO₄ (b), and PEO₁₀–LiClO₄/x%ZSM-5 composite polymer electrolyte: (c) x=5; (d) x=10; (e) x=20.

maintains at the value of about 21% when ZSM-5 content is higher than 10%. In addition, ZSM-5 can also decrease the T_g of PEO effectively. The lowest T_g of about -45 °C are obtained when the content of ZSM-5 ranges from 20 to 30 wt.% of PEO weight. The decrease of T_g and X_c will increase the flexibility of the PEO chains and the ratio of amorphous state PEO, respectively. And as a result, the ionic conductivity should be enhanced at low temperature regions.

Pure PEO, due to its particular chain structure, shows a strong recrystallize tendency when cooling from high temperature, corresponding to the strong narrow exothermal peak at about 45 °C in the cooling scan of DSC trace (Fig. 4a). The area of the recrystallization peak of PEO decreases after the addition of Li salt and ZSM-5 filler, suggesting that both Li salt and ZSM-5 can inhibit the reorganization of PEO chains through the coordination interactions between the ether O atoms of PEO and Li⁺, and Lewis acid–base interactions between ether O atoms of PEO and Liewis acid sites of ZSM-5, respectively. In addition, the recrystallizing temperature, T_c , of PEO in PEO₁₀–LiClO₄ complex and PEO₁₀–LiClO₄/x%ZSM-5 composite polymer electrolyte also shift to the low temperature regions comparing with pure PEO sample (Fig. 4b–e).

Fig. 5 shows the temperature dependence for ionic conductivity of PEO_{10} -LiClO₄/x%ZSM-5. All samples show a break around the temperature range of 45–60 °C corresponding to the melting of crystalline PEO and the degree of this



Fig. 5. Temperature dependence for the ionic conductivity of $PEO_{10}-LiCIO_4/x\%ZSM$ -5 composite polymer electrolytes.

Temperature (°C)	t _{Li} ^{+ a}	t _{Li} + ^a					
	PEO ₁₀ -LiClO ₄	PEO10-LiClO4/10%SiO2	PEO10-LiClO4/10%Al2O3	PEO10-LiClO4/10%ZSM-5			
70	0.198	0.238	0.246	0.355			
90	0.196	0.240	0.251	0.360			

Lithium ion transference numbers of pristine PEO10-LiClO4 and PEO10-LiClO4/10% filler composite polymer electrolytes

^a All tests were repeated at least three times and the value of t_{Li^+} were reproducible within 0.01.

break decreases with the increasing of ZSM-5 content, agree well with the DSC (Fig. 4 and Table 1) results mentioned above. In addition, the sample PEO_{10} -LiClO₄/10%ZSM-5 has the highest ionic conductivity at all testing temperature regions.

Fig. 6 displays the effect of ZSM-5 content on the enhancement of ionic conductivity of PEO_{10} -LiClO₄/x%ZSM-5 at different temperatures. Croce et al. suggested that ceramic fillers help to increase the ionic conductivity of composite polymer electrolyte in two ways [1]: (1) increasing the ratios of the amorphous phase of PEO, which is beneficial for the transport of Li⁺ cation; (2) providing special Li⁺ conducting pathways at the fillers' surface regions through the Lewis acid-base interactions among different species in the composite polymer electrolytes. The former reason can explain the enhancement of ionic conductivity induced by ZSM-5 at the temperature regions lower than $T_{\rm m}$ (25 and 50 °C in Fig. 6), ~65 °C, of PEO, consistent with DSC (Fig. 4) results, which show that ZSM-5 can decrease the crystallinity of PEO effectively. On the contrary, the conductivity enhancement at temperature regions higher than the $T_{\rm m}$ of PEO (70 °C in Fig. 6) should only be attributed to the latter reason that the Lewis acid-base interactions between the Lewis acid sites



Fig. 6. Enhancement in the ionic conductivity of PEO_{10} -LiClO₄/x%ZSM-5 composite polymer electrolytes comparing with pristine PEO_{10} -LiClO₄ at different temperatures.

on the framework of ZSM-5 and ether O of PEO chains may provide novel conducting pathway for Li⁺.

The enhancement of ionic conductivity first increase with ZSM-5 content and reach at the maximum value that is nearly 100 times higher than the pristine PEO_{10} -LiClO₄ (at 25 °C), by 10% loading content of ZSM-5. When ZSM-5 content increases further, ionic conductivity decreased. The enhancement of ionic conductivity decreases with the increasing temperature can be attributed to the melting of crystalline PEO and the increase of the ratio of amorphous PEO when temperature increasing. The existence of the maximum value of ionic conductivity indicates that there are two opposing effects of ZSM-5 on ionic conductivity of PEO₁₀-LiClO₄/x%ZSM-5 composite polymer electrolyte. The active effect induces by ZSM-5, as mentioned above, can increase the ionic conductivity of the composite polymer electrolyte. On the other hand, when the content of ZSM-5 is too high, the blocking effect on the transporting of charge carriers resulting from the aggregating of the ZSM-5 (see Fig. 2f), may decrease the ionic conductivity of the composite polymer electrolyte. However, the conductivity decreasing tendency in the case of ZSM-5 is relative small compared with ceramic fillers such as SiO2 and Al2O3 [20]. The interconnect channels of ZSM-5 may act as the conducting pathway of part of the charge carriers can explain this result.

Lithium ion transference number, t_{Li^+} , is one of the most important parameters for rechargeable lithium ion batteries. A relative high t_{Li^+} can eliminate the concentration gradients within the battery and ensure the battery operation at high current density [1]. t_{Li^+} of the PEO₁₀–LiClO₄ before and after the addition of inorganic fillers are compared in Table 2. It is obviously that the t_{Li^+} of the polymer electrolytes are independent of testing temperature and can be increased in different degrees by the addition of inorganic fillers.

In PEO–LiClO₄ complex, Li⁺ can coordinate not only with the ether O in PEO but also with the O atoms in ClO₄⁻, and then its transport ability are restricted, result in a very low t_{Li^+} value (<0.2) [1], consistent with our result in Table 2. After the addition of SiO₂ and Al₂O₃, t_{Li^+} can be increased slightly through the well-known Lewis acid–base interactions [1,12]. The Lewis acid sites on the surface of SiO₂ and Al₂O₃ can interact with O atoms in PEO and ClO₄⁻ (Lewis base), and hence weaken the interactions between these O atoms and Li⁺. And as a result, more "free" Li⁺ ions are released and t_{Li^+} are enhanced. In the case of ZSM-5, t_{Li^+} can also be enhanced by the same Lewis acid–base interactions, but the even more important fact is that, ZSM-5, as one kind

Table 2



Fig. 7. Time evolution of the interfacial resistance R_{inter} between polymer electrolyte and Li electrode evaluated from the impedance response of Li/polymer electrolyte/Li cells at 70 °C.

of microporous molecular sieves, has two-dimensional open channels, which are interconnected by each other. The pore sizes of ZSM-5 are 0.53 nm × 0.56 nm for straight channel and 0.51 nm × 0.55 nm for Z type channel, as shown in Fig. 1. The diameters of Li⁺ and ClO₄⁻ are 0.152 and 0.474 nm [56], respectively, and as a result, Li⁺ can enter and path through the channels of ZSM-5 more easily than ClO₄⁻, in other words, ZSM-5 has a selective actions on the transporting of different charge carriers, which is beneficial for enhancing the t_{Li^+} . In addition, the negative charge environments in the channels of ZSM-5 are in favor of the entrance of Li⁺, on the contrary, ClO₄⁻ are hard to enter the channels of the ZSM-5 due to the electrostatic excluding effect. The composite polymer electrolyte containing ZSM-5 has the highest t_{Li^+} (see Table 2) proves the above hypothesizes.

One of the remaining problems to assure the successful operation of lithium polymer batteries is the reactivity of the lithium metal interface. Scrosati et al. have demonstrated that this reactivity can be greatly reduced by dispersing inorganic fillers in the PEO-LiClO₄ complex [1,12]. The stability of the interface between polymer electrolytes and the lithium metal electrode can be studied by monitoring the impedance response of symmetric Li/polymer electrolyte/Li cells stored under open circuit condition at constant temperature. Fig. 7 shows time evolution of the interfacial resistance of Li/PEO₁₀-LiClO₄/Li cell and Li/PEO₁₀-LiClO₄/10%ZSM-5/Li cell stored at 70 °C. For the case of PEO₁₀–LiClO₄ complex, the interfacial resistance increases very fast during the whole test time. Residual solvent and/or other liquid impurities in the polymer electrolyte are expected to react most easily with the Li electrode. The increasing of interfacial resistance may be associated with the formation and the growth of a passivation layer on the Li electrode surface [1]. On the contrary, interfacial resistance of Li/PEO10-LiClO4/10%ZSM-5/Li cell do not increase consistently with time and remains at a very low value even under the prolonged storage time. It is possible to assume that, ZSM-5, due to its high surface area and pore volume, has strong ability of trapping the trace residual liquid impurities in the composite polymer electrolyte, and thus enhances



Fig. 8. Current–voltage response of PEO_{10} –LiClO₄ and PEO_{10} –LiClO₄/ x%ZSM-5 composite polymer electrolytes at 90 °C on stainless steel working electrode at a scanning rate of 1 mV s⁻¹.

the stability of the interface between the electrolyte and Li electrode.

Electrochemical stability window of the polymer electrolyte can be obtained by the method of linear voltage sweep. Fig. 8 displays the linear voltage sweep curves of pristine PEO₁₀–LiClO₄ and PEO₁₀–LiClO₄/x%ZSM-5 composite polymer electrolytes at 90 °C. The irreversible onset of the current determines the electrolyte breakdown voltage, which in the case of PEO₁₀–LiClO₄ only extends to about 4.0 V versus Li. The decomposition voltage of PEO₁₀–LiClO₄/x%ZSM-5 content and exceed 4.8 V versus Li when the content of ZSM-5 up to 5 wt.%. The sample PEO₁₀–LiClO₄/30%ZSM-5 shows a decomposition voltage lower than the pristine PEO₁₀–LiClO₄ can be attributed to the phase separation between PEO matrix and ZSM-5 filler occurs at high ZSM-5 loading content, as shown in Fig. 3f.

4. Conclusions

A novel PEO-based all solid-state composite polymer electrolyte, by using shape-selective molecular sieves ZSM-5 as filler is obtained for the first time. A combination of thermal analysis, scanning electron microscopy (SEM), and electrochemical impedance techniques show that ZSM-5 can reduce the crystallinity of PEO effectively through the Lewis acid-base interactions between the Lewis acid sites on the framework of ZSM-5 and ether O in PEO chains, resulting the obviously enhancement of ionic conductivity of PEO-LiClO₄/ZSM-5 composite polymer electrolyte. In addition, ZSM-5 can also enhance other electrochemical properties such as lithium ion transference number, interface compatibility with lithium metal electrode, and electrochemical stability window of the composite polymer electrolyte, which may be explained by the special framework topology structure and pore size of ZSM-5. The excellent electrochemical properties such as high room temperature ionic conductivity and lithium ion transference number combined with wide electrochemical stability window ensures the use of PEO–LiClO₄/ZSM-5 composite polymer electrolyte as candidate electrolyte materials for all solid-state rechargeable lithium polymer batteries.

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