Investigation of structure and ionic conductivity of (PEO)$_{12}$-SiO$_2$-LiClO$_4$ nanocomposite electrolyte for all solid-state lithium-ion battery

Y Z Li, Y P Yang*, R Y Lei, S D Fu, R G Wan and J Li

School of Materials Engineering, Shanghai University of Engineering Science, Shanghai 201620, People’s Republic of China

*E-mail: yangc0709@126.com

Abstract. Solid polymer electrolytes (SPEs), based on poly ethylene oxide (PEO) matrix and nano-sized SiO$_2$, are prepared by solution-casting method. The morphology, crystallinity, thermostability and ionic conductivity of nanocomposite polymer electrolyte are systematically investigated by field-emission scanning electron microscope (FE-SEM), X-ray diffraction (XRD), thermogravimetric analysis, and AC impedance spectroscopy. The result reveals that SiO$_2$ is uniformly dispersed in the SPE. Furthermore, the incorporation of nano-sized SiO$_2$ can restrict the crystalline behaviour of PEO effectively, leading to the improvement in amorphous state of PEO. With increasing the mass loading of SiO$_2$, the ionic conductivity of SPEs increase to a maximum value, about $3.03 \times 10^{-4}$ S·cm$^{-1}$ ($\chi_{(\text{SiO}_2/\text{PEO})} = 6.85\%$), and then fall down. Meanwhile, the initial decomposition of SPE reaches 335 ℃, showing the good thermal stability and potential application of SPEs for the next-generation all solid-state lithium-ion battery (LIB) with enhanced safety.

1. Introduction

Ionic conductive solid polymer electrolyte has the advantages of light-weight, flexible processing and good safety, therefore it has a wide application prospect in high energy density batteries, electrochemical devices and chemical sensors [1, 2]. In 1973, the ionic conductivity of coordination between PEO and alkali metal salt was reported for the first time in the literature [3]. The research on PEO based polymer electrolyte has aroused great interest, and it is the most widely studied polymer electrolyte system [4, 5]. As a polymer body, PEO has a special structure that can dissolve inorganic salts in large quantities, which is conducive to the transport of lithium ions, and can eventually obtain a high conductivity.

Due to the relatively high crystallinity of PEO, the ionic conductivity of such electrolytes is low at room temperature, which is far from meeting the requirements of practical application. How to improve the ionic conductivity of PEO-based SPE at room temperature even lower temperature, has become a crucial topic in recent days [6-8]. And there are two main ways to improve the ionic conductivity of SPE. One way is to add organic plasticizers such as propylene carbonate, ethylene carbonate, etc., to polymer electrolyte. Organic plasticizer can increase the movement of polymer chain segment and promote the migration of lithium ions. However, the addition of organic plasticizers can damage the mechanical properties of polymer electrolytes and react with lithium electrodes [9]. Another method is to add inorganic nanoparticles [7]. Commonly used inorganic nanoparticles include TiO$_2$ [10], SiO$_2$ [2], ZnO [11], ZrO$_2$ [12], Al$_2$O$_3$ [13], etc.. The benefits of adding inorganic nanoparticles into polymer
matrix are as follows: the order of the chain segments will be lowered, resulting in reducing the crystallinity of polymer matrix; furthermore, these inorganic additives can improve the mechanical properties and thermodynamic stability of SPE; at the same time, the stability of the interface between the polymer and the electrodes can be enhanced after adding nano-sized inorganic additives. Therefore, the addition of nano phase on the microstructure of polymer and the transport of conductive ions remains to be further studied.

In this work, nano-SiO₂ modified (PEO)₁₂-LiClO₄ is used to prepare SPEs, and the morphology, crystallization, thermal stability and ionic conductivity of the nano-composite all-solid polymer electrolyte are studied by FE-SEM, XRD, TGA and AC impedance methods. Therefore, this study is expected to provide ideas for the application of inorganic additives in solid polymer electrolyte, so as to improve the electrochemical performance of all-solid lithium ion batteries.

2. Experimental

2.1. Materials
PEO (molecular weight, \(M_w=1,000,000\), Aladdin), lithium perchlorate (LiClO₄, 99.99%, Aladdin), nanometer silica (nano-SiO₂, 99.8%, BET: 150 m²/g, Aladdin) and anhydrous acetonitrile (ACN, 99.8%, Aladdin) were purchased. All raw materials were dehydrated before use to a water content below 200 ppm. Finally, dry materials were putted into an Ar-filled glove box (\(H_2O\) and \(O_2\) ≤ 0.5 ppm) to avoid the effect of moisture on the raw material.

2.2. Preparation of SPEs
Dried PEO was dispersed into acetonitrile solution at room temperature. This mixture was vigorously stirred for 1 h to form uniform colorless transparent solution. The mass ratio \(\chi(\text{SiO}_2/\text{PEO})\) was controlled at 2% - 8% as indicated in Table 1, and a lithium/oxygen ratio was controlled at 12:1. Anhydrous LiClO₄ was then added and stirred for 12 h to obtain SPEs solution. After which, the solvent casting method was been used to obtained the (PEO)₁₂-LiClO₄ and (PEO)₁₂-SiO₂-LiClO₄ systems SPEs film. All SPE samples were dried in Ar-filled glove box for 24 hours at room temperature until the solvent was completely evaporated. The resulting sample film possesses a flat surface with an average thickness of 70-80 μm.

Table 1. The summary of the ionic conductivity (\(\sigma\)) and crystallinity (\(X_c\)) for PEO and various PEO-LiClO₄-SiO₂ system SPEs samples.

| Sample | \(\sigma\) (\(\times 10^{-4}\) S·cm⁻¹) | \(X_c\) (in %) |
|--------|---------------------------------|----------------|
| PEO    | 60.98 (1.51)                    |                |
| \(\chi(\text{SiO}_2/\text{PEO}) = 0\) | 2.24                          | 38.79 (0.71)   |
| \(\chi(\text{SiO}_2/\text{PEO}) = 2.85\%\) | 2.81                          | 20.56 (0.29)   |
| \(\chi(\text{SiO}_2/\text{PEO}) = 4.85\%\) | 2.90                          | 18.61 (0.25)   |
| \(\chi(\text{SiO}_2/\text{PEO}) = 6.85\%\) | 3.03                          | 17.01 (0.34)   |
| \(\chi(\text{SiO}_2/\text{PEO}) = 8.85\%\) | 2.68                          | 25.48 (0.42)   |

2.3. Material characterization

2.3.1. Field-emission scanning electron microscope. The surface morphology of the SPEs and the dispersion of nano-SiO₂ in the polymer matrix were observed by field emission scanning electron microscopy (FE-SEM, Hitachi Co., Japan).
2.3.2. X-ray diffraction (XRD). The crystallinity ($X_c$) of the SPEs were done with a Rigaku X-ray diffractometer (D/Max-2550 PC, Rigaku Co., Japan) equipped with Ni-filtered Cu $K_{\alpha}$ radiation. The step-interval was set at 0.02°. Furthermore, the diffraction curve was fitted with MDI Jade software for peak separation, and the following formula was used to calculate the $X_c$ of the SPEs [14]:

$$X_c \text{(in \%) = } \frac{A_c}{(A_a + A_c)} \times 100$$  \hspace{1cm} (1)

where $A_c$ is the crystalline area and $A_a$ is the amorphous area.

2.3.3. Thermogravimetric analysis (TGA). The thermal stability of SPEs were carried out with thermogravimetric analysis (TGA, TG209F1 Iris, Netzsch), and the SPE sample was heated in N$_2$ at a rate of 10 °C/min from 30 °C to 600 °C.

2.3.4. Ionic conductivity ($\sigma$). The AC impedance testing of a stainless steel (SS)/SPE/SS coin cell (CR2032) with SS gasket blocking electrodes was carried out in the frequency domain of 1 MHz ~ 0.01 Hz, and the Nyquist plots were displayed as an insert in Fig. 3(a). The obtained bulk impedance was used to calculate the ionic conductivity ($\sigma$) of SPE.

$$\sigma = \frac{l}{S \times R_b}$$  \hspace{1cm} (2)

Where $l$ is the thickness of the SPE film, $R_b$ is the bulk resistance obtained from the equivalent analog circuit, and $S$ is the surface area of the stainless steel gasket.

3. Result and Discussion

3.1. Morphology of the SPEs
The field-emission scanning electron microscopy images of the surface of the (PEO)$_{12}$-SiO$_2$-LiClO$_4$ system SPE ($\chi_{(SiO_2/PEO)} = 2.85\%$, 6.85%) are illustrated in figure 1. As can be seen from figure 1(a) and figure 1(b), the surface of the polymer electrolyte is relatively smooth with a few cracks, which may be caused by repeated expansion and contraction during the washing and drying process. In addition, the higher magnification FE-SEM images (figure 1(c) and figure 1(d)) for (PEO)$_{12}$-SiO$_2$-LiClO$_4$ system SPE shows that nano-SiO$_2$ particles are uniformly dispersed in PEO matrix without aggregation. Thereby, it is beneficial to the improvement of electrochemical performance for SPE as nano-SiO$_2$ doping is uniform. Furthermore, the fuzzy interface between the surface of the nanoparticles and the polymer matrix indicates that nano-SiO$_2$ particles have good compatibility with PEO matrix [8].

![Figure 1](image-url) FE-SEM images of the surface of the (PEO)$_{12}$-SiO$_2$-LiClO$_4$ system SPE (a, c: $\chi_{(SiO_2/PEO)} = 2.85\%$; b, d: $\chi_{(SiO_2/PEO)} = 6.85\%$).
3.2. Crystallinity of the SPEs

Figure 2 shows the XRD patterns of polymer electrolytes, including pure PEO, (PEO)$_{12}$-LiClO$_4$ and (PEO)$_{12}$-SiO$_2$-LiClO$_4$ ($\chi_{(SiO_2/PEO)}$ = 2.85%, 4.85%, 6.85%, 8.85%). The crystalline form of PEO has sharp diffraction peaks at 2θ = 19° and 23°, representing the characteristic diffraction peaks, which are assigned to the crystal planes (120) and (112) of crystallized PEO respectively [15, 16]. Moreover, the two crystallization peaks of (PEO)$_{12}$-LiClO$_4$ and (PEO)$_{12}$-SiO$_2$-LiClO$_4$ ($\chi_{(SiO_2/PEO)}$ = 2.85%, 4.85%, 6.85%, 8.85%) gradually weaken after the addition of LiClO$_4$ and nanometer SiO$_2$, indicating that the addition of LiClO$_4$ and nano-SiO$_2$ reduces the crystallinity of PEO, but does not change the crystalline form of PEO [17, 18].

In order to further explain the change of crystallization of SPEs, curve fitting procedure is applied for the XRD of the electrolyte. The results are listed in Table 1, and the calculation error is shown in brackets. After LiClO$_4$ is added, the $X_c$ drop rapidly from 60.98% to 38.79%, and further reduces with the addition of nano-SiO$_2$ particles. As shown in figure 2 and Table 1, the $X_c$ for the (PEO)$_{12}$-SiO$_2$-LiClO$_4$ system SPEs decreases with improved $\chi_{(SiO_2/PEO)}$. Moreover, the minimal $X_c$ is 17.01% when $\chi_{(SiO_2/PEO)}$ = 6.85% similar to previous report [19]. This phenomenon can be ascribed to the interact between nano-SiO$_2$ particles and PEO chain segment, resulting in a decrease in crystallinity of PEO and an increase in the amorphous phase of lithium ion transport. Thereby, it is conductive to lithium ion transport and ultimately leads to an increase in ionic conductivity.

![Figure 2. XRD patterns of SPEs.](image)

3.3. Ionic conductivity of SPEs

The electrical conductivity of SPEs was measured by AC impedance method. Figure 3(a) shows the influence of nano-SiO$_2$ content on the ionic conductivity of SPEs. As can be seen from figure 3(a), the ionic conductivity of SPEs increases continuously with the increase of nano-SiO$_2$ content. According to the analysis results in figure 2, doping nano-SiO$_2$ in PEO can effectively inhibit PEO crystallization and improve the amorphous degree of PEO. When $\chi_{(SiO_2/PEO)}$ = 6.85%, (PEO)$_{12}$-SiO$_2$-LiClO$_4$ system SPE has the highest ionic conductivity ($3.03 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$), suggesting that lower PEO crystallinity is beneficial to improve the ionic conductivity of SPE. On the other hand, an interface layer with higher conductivity can be generated between the surface of the nanoparticles and the polymer matrix, which increases the channel for the transmission of lithium ion, further allows lithium ions to pass through with lower activation energy [20]. As a consequence, the ionic conductivity of SPE increases. However, with the further increase of nano-SiO$_2$ content, the ionic conductivity of SPE decreases on the contrary. This is because the nano-SiO$_2$ content is too large, and agglomeration will occur under thermodynamic driving. Thus, the nano-SiO$_2$ is hard to disperse in PEO matrix, which hinders the migration of lithium ions in SPEs [21].
3.4. Thermal stability of SPEs

The thermal stability of a solid-state polymer electrolyte is directly related to the operating temperature and safety of the battery. Therefore, thermogravimetric analysis of SPE is performed. TGA scan of the (PEO)$_{12}$-SiO$_2$-LiClO$_4$ ($\chi$(SiO$_2$/PEO) = 6.85%) system SPE with analysis result is shown in figure 3(b). Due to water desorption, the first mass loss in the SPE occurs at low temperature. As the temperature rises further, the curve stays roughly the same. The result shows that the initial thermal decomposition temperature ($T_{onset}$) of the polymer electrolyte is as high as 335 ℃, which completely meets the application requirements of lithium battery at room temperature or high temperature.

![Figure 3](image_url)

**Figure 3.** (a) Variation of ionic conductivity of SPEs with $\chi$(SiO$_2$/PEO), inserting with the Nyquist plots; (b) TGA curves of SPEs ($\chi$(SiO$_2$/PEO) = 6.85%).

4. Conclusion

In this work, a simple solution casting method is used to prepare (PEO)$_{12}$-SiO$_2$-LiClO$_4$ all-solid polymer electrolyte. The effect of nano-SiO$_2$ on the microstructure and conductive properties of SPEs is systematically studied. Result indicates that nano-SiO$_2$ particles can reduce the crystallinity of PEO, thereby improving ion transport performance and increasing the ionic conductivity of (PEO)$_{12}$-SiO$_2$-LiClO$_4$ system SPE. When $\chi$(SiO$_2$/PEO) = 6.85%, the lithium ion conductivity reaches the maximum, about $3.03 \times 10^{-4}$ S·cm$^{-1}$. TGA analysis shows that the thermal decomposition temperature of SPE reaches 335 ℃, which exceeds the use requirement of the lithium ion battery electrolyte decomposition temperature of not less than 150 ℃, indicating that the (PEO)$_{12}$-SiO$_2$-LiClO$_4$ system SPE has excellent thermal stability.

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