Enhancement of electrochemical properties of hot-pressed poly(ethylene oxide)-based nanocomposite polymer electrolyte films for all-solid-state lithium polymer batteries

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1. Introduction

Advantages such as no-leakage of electrolyte, high energy density, good cyclability, flexible geometry, mechanical strength and safety have drawn the attention of many researchers to the development of all-solid-state lithium polymer batteries. Poly(ethylene oxide)/PEO-based polymer electrolytes have been found to be one of the best candidates as electrolytes for lithium polymer batteries in view of ionic conductivity and mechanical property since the discovery of ionic conductivity in the complex of PEO and alkaline salts in 1973 [1]. However, some problems still exist for all-solid-state lithium polymer batteries based on PEO–LiX electrolytes. There are bad interface property, due to the reactivity of the lithium metal anode [2]; and temperature of operation, due to thermal dependence of the lithium ion transport in the polymer electrolyte [3]. An effective approach for solving these problems is that of dispersing inorganic powders in the polymer electrolyte bulk [4–14].

In a previous paper, we investigated a novel PEO16–LiClO4–ZnAl2O4 nanocomposite polymer electrolyte (NCPE) prepared by the solution-casting method, in which nano-sized, high-surface-area ZnAl2O4 with mesoporous network as the filler. The ionic conductivity and lithium ion transference number of the PEO-based NCPE were enhanced [15]. However, the conventional solution-casting method has some disadvantages so that it may influence the interfacial property of polymer electrolyte and the performance of all-solid-state polymer battery because of the rudimental solvent in the polymer electrolyte. Hot-pressing method has been suggested for casting polymer electrolyte membranes originally by Gray et al. [16], followed by other workers [17–19]. This technique promises several advantages over the conventional solution-casting method and has been recognized as a rapid, least expensive and dry procedure to prepare solvent-free polymer electrolyte films [20].

In this work, PEO16–LiClO4–ZnAl2O4 NCPE films have been prepared by the hot-pressing method and conventional solution-casting method respectively in order to carry out direct comparison. The effects of two methods on the properties of the NCPE films such as surface property, interfacial stability, crystallization, melting temperature and conductivity have also been investigated. The discharge specific capacity, cycling stability, and coulombic efficiency of the lithium polymer battery using polymer electrolyte as electrolyte, lithium metal and LiFePO4 as anode and cathode respectively, have been revealed by galvanostatical charge/discharge cycling tests.

2. Experimental

2.1. Preparation of PEO16–LiClO4–ZnAl2O4 NCPE films

PEO with molecular weight 100,000 and LiClO4 supplied by Alfa Aesar, were dried under vacuum at 50 and 100 °C, respectively, for...
at least 48h before use. The ZnAl2O4 powders with particle sizes of 10–15 nm were prepared according to the reference [15] and were heated under vacuum at 150 °C for 48h to remove water before use.

PEO16–LiClO4–ZnAl2O4 NCPE films were prepared by hot-pressing method and solution-casting method respectively, as follows:

- **Hot-pressing method**: The electrolyte components (PEO, ZnAl2O4, and LiClO4) were carefully sieved and then introduced in their correct proportion (the amount of PEO and LiClO4 were fixed with [EO]/[Li] molar ratio at 16 according to the reported literature [21]) inside sealed Teflon bottles protected by N2 and thoroughly mixed by ball-milling for at least 24h to obtain homogeneous mixture of powders. The powders sandwiched by two Teflon sheets were hot pressed at 120 °C and 10MPa pressure in a dry room. Homogeneous rigid membrane samples, having thickness ranging from 100 to 200 μm were obtained after hot-pressing.

- **Solution-casting method**: A certain amount of ZnAl2O4 powders of PEO was dispersed in acetonitrile with the aid of ultrasonic dispersion, followed by the addition of PEO and LiClO4 with fixed [EO]/[Li] molar ratio of 16 [21]. The solution was stirred at room temperature for 24h until complete homogenization of the mixture had occurred. The slurry was then cast onto a self-designed Teflon plate and solvent was evaporated slowly at room temperature for 24 h. The films obtained were 150–200 μm in thickness. They were stored under argon-filled dry box for subsequent measurements.

The NCPEs containing ZnAl2O4 are designated as PEO16–LiClO4–x wt.% ZnAl2O4, where x denotes 0, 8.

### 2.2. Characterization of samples

Differential scanning calorimetry (DSC) was employed to determine the melting temperature ($T_m$), recrystallize enthalpy ($\Delta H_m$) and crystallinity ($X_c$) values of the polymer electrolyte by using a NETZSCH-DSC-204-F1 instrument. The measurements were carried out at a heating rate of 10 °C min⁻¹ from −60 to 100 °C. A flow of nitrogen gas was maintained over the perforated pan to avoid any contact with atmospheric moisture. The sample weights were maintained in the range of 3–5 mg and an empty aluminum pan was used as a reference.

Sample morphology was investigated using a Hitachi S4700 field emission scanning electron microscope (FESEM). The ionic conductivity of the samples was measured by sandwiching the samples between two stainless steel blocking electrodes using AC impedance techniques. The measurements were performed using an electrochemical workstation (IM6e, Germany) between 100 kHz and 1 Hz at various temperatures ranging from 80 to 25 °C. A thermostatic bath (Julabo Labortechnik GmbH, Germany) was utilized to control the temperature to within ±0.1 °C of the target value. The samples were thermally equilibrated at each temperature for at least 2h prior to the measurements. The bulk resistance ($R_b$) was obtained by reading the intercept of the impedance spectrum, and the ion conductivity was calculated from the expression $\sigma = \frac{L}{R_b A}$ where $L$ is the thickness of the electrolyte film and $A$ represents the electrode area.

Symmetric nonblocking cells for interfacial stability measurements were formed by sandwiching a polymer electrolyte between two lithium electrodes in an argon-filled glove box. The cells were thermally equilibrated at 70 °C for at least 2h prior to the measurements to optimize the contact at the interface between the electrode and the polymer electrolyte, and then were measured under open circuit potential using an IM6e electrochemical workstation at the frequency range from 100 kHz to 1 Hz.

### 2.3. Li/LiFePO4 polymer battery

The coin-type (CR2032) all-solid-state lithium polymer batteries were prepared using the hot-pressed NCPE films as electrolytes, LiFePO4 (Valence, USA) and lithium metal as cathode and anode materials respectively. Electrochemical measurement was carried out using an Arbin MSTAT4+ multichannel galvanostat/potentiostat. The polymer batteries were galvanostatically charged and discharged between 4.1 and 2.5 V (vs. Li⁺/Li⁺) at different current densities.

All the above batteries were assembled and sealed in an argon-filled UniLab glove box (O2 < 1 ppm; H2O < 1 ppm).

### 3. Results and discussion

#### 3.1. Physical properties of polymer electrolyte

Table 1 lists $T_m$, $\Delta H_m$ and $X_c$ values of pure PEO and polymer electrolyte PEO16–LiClO4–x wt.% ZnAl2O4 with x = 0, 8 prepared by hot-pressing method and solution-casting method. From Table 1, we can see that the dispersal of ZnAl2O4 nanoparticles in PEO16–LiClO4 substantially influences $T_m$, $\Delta H_m$ and $X_c$ values of the NCPE. It also can be observed that the $T_m$, $\Delta H_m$ and $X_c$ values of the polymer electrolyte prepared by the hot-pressing method are lower than those prepared by the solution-casting method not only for filler-free polymer electrolyte but also for NCPE. It can be explained that the hot history to the polymer electrolyte influences the crystallinity of PEO [22], namely, hot-pressing method can reduce the crystallinity of PEO effectively than solution-casting method. The reduction of crystallinity of PEO also corresponds to the low $T_m$ of hot-pressed NCPE.

Fig. 1(a–d) shows the FESEM images for solution-cast and hot-pressed polymer electrolyte PEO16–LiClO4–x wt.% ZnAl2O4 with x = 0, 8. The image of Fig. 1(a) shows a rough morphology with a great deal of micro-pores, a common occurrence for PEO16–LiClO4 polymer electrolyte prepared by solution-casting method. These small pores are caused by the fast evaporation of acetonitrile solvent during the preparation process. This phenomenon disappears in Fig. 1(b), which indicates that the polymer electrolyte prepared by hot-pressing method can avoid the influence of acetonitrile solvent. The spherulites stand for the crystallinity of PEO is less and smaller compared Fig. 1(b) with (a), which means amorphous regions of PEO increased. From Fig. 1(c–d), we can also find that the surface morphology of PEO16–LiClO4–x wt.% ZnAl2O4 NCPE film prepared by the hot-pressing method is smoother than that prepared by the solution-casting method. The smooth surface morphology and amorphous structure are closely related to the reduction of PEO crystallinity [20] which is also caused by the hot history to the polymer electrolyte.
3.2. Ionic conductivity

Temperature dependence of ionic conductivity is measured for PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE films prepared by both solution-casting and hot-pressing methods to determine the effect of preparation procedure, as shown in Fig. 2. The NCPE films prepared by both solution-casting and hot-pressing methods show a very similar temperature-dependent ionic conductivity behavior below $T_m$. The possible reason is that low PEO crystallinity can enhance the conductivity of the hot-pressed NCPE, while the ZnAl2O4 aggregates can reduce the conductivity of the hot-pressed NCPE. When the temperature is higher than $T_m$, the ionic conductivity of the NCPE film prepared by solution-casting method is slightly higher than that prepared by hot-pressing method, therefore, a change around 3.0 (1000/K) in the temperature-dependent ionic conductivity in Fig. 2(b) is observed. The function of ultrasonic is a possible explanation for the slightly higher conductivity of the NCPE film prepared by solution-casting method. Because of the ultrasonic, more nanosized ZnAl2O4 particle can be obtained, and more conducting pathways for the transference of Li$^+$ cations can be provided.

3.3. Interfacial property

Fig. 3 shows the impedance spectra of Li/polymer electrolyte/Li cells by using solution-cast and hot-pressed PEO16–LiClO4–x wt.% ZnAl2O4 ($x = 0, 8$) as electrolytes respectively, after 2 h storage time at 70°C under open-circuit potential condition. The shapes of the impedance responses are similar for all of the polymer electrolytes. A slightly depressed semicircle, corresponding to the interfacial resistance consisting of the passivation layer and charge transfer resistance, is followed at lower frequency by a linear spur associated with the diffusion of lithium in the polymer electrolyte [22]. However, substantial differences are detected among different polymer electrolytes in terms of interfacial impedance evolution. From Fig. 3, we can obviously find that the interfacial resistance of polymer electrolytes prepared by hot-pressing method is much smaller than that prepared by solution-casting method for both filler-free and 8 wt.% ZnAl2O4 as filler. It also can be observed that the presence of nanosized ZnAl2O4 particles in the NCPE films pre-
pared not only by solution-casting method but also by hot-pressing method appears to be useful to their lithium interfacial characteristics.

Fig. 4 shows the interfacial resistance as a function of time for Li/polymer electrolyte/Li cells with polymer electrolytes prepared by solution-casting and hot-pressing methods under open circuit potential at 70 °C. The interfacial resistances are obtained by fitting the impedance spectra using simulation software of IM6e. In general, the solution-cast and hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE films exhibit lower interfacial resistance ($R_i$) than the filler-free ones, which show a stable and low value over the entire storage time. It is because nanosized ZnAl2O4 can decrease the crystallinity of PEO and make the surface of NCPE film smoother than the filler-free one. The hot-pressed polymer electrolytes exhibit a better interfacial stability than the solution-cast polymer electrolytes. It is because hot-pressing method is a dry procedure to prepare solvent-free polymer electrolyte films. No residual solvent and/or other liquid impurities in the polymer electrolyte are expected to react with the lithium electrode [23]. Thus, the stability of the interface between the electrolyte and lithium electrode is enhanced. The hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE film exhibits the lowest interfacial resistance and remains at a very low value even under the prolonged storage time among the four polymer electrolytes. It indicates that hot-pressing method and nanosized ZnAl2O4 could primely improve the interfacial property of the polymer electrolyte.

3.4. Performance of Li/polymer electrolyte/LiFePO4 battery

Fig. 5 shows the charge/discharge curves for the fifth cycles of the Li/polymer electrolyte/LiFePO4 batteries at 65 °C with different charge/discharge rates (0.1, 0.3 and 1 C) using (a) hot-pressed PEO16–LiClO4, (b) solution-cast and (c) hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 films as electrolytes.
All the batteries using hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE films as the electrolytes achieve higher charge and discharge specific capacities than those using the filler-free polymer electrolytes as the electrolytes at charge/discharge rates of 0.1, 0.3 and 1 C respectively. Especially, the discharge specific capacity of the battery using hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE film as electrolyte maintains 89 mAh g\(^{-1}\) when discharge/charge rate raises to 1 C, however, it declines to 53.9 mAh g\(^{-1}\) by using the filler-free polymer electrolyte film as electrolyte (Fig. 5(c)). It also can be observed that the batteries using hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE films as electrolytes achieve higher charge and discharge specific capacities than those using solution-cast PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE films as electrolytes at charge/discharge rates of 0.1, 0.3 and 1 C respectively. Thus, the battery using the hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE film as electrolyte has the best rate capacity. It may be the reason that the battery using the hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 NCPE film as electrolyte possesses high lithium ion transference number and good interfacial property. The discharge specific capacities of the Li/polymer electrolyte/LiFePO\(_4\) batteries using different polymer electrolytes as electrolytes as a function of cycle number at 65 °C with different charge/discharge rates of 0.1, 0.3 and 1 C, respectively.

![Fig. 6. The discharge specific capacity and coulombic efficiency of the Li/polymer electrolyte/LiFePO\(_4\) batteries (a) hot-pressed PEO16–LiClO4, (b and d) solution-cast and (c and e) hot-pressed PEO16–LiClO4–8 wt.% ZnAl2O4 films as electrolytes, as a function of cycle number at 65 °C with different charge/discharge rates of 0.1, 0.3 and 1 C, respectively.](image)

In general, the high charge/discharge specific capacity, high coulombic efficiency and excellent cycling stability suggest that the hot-pressed PEO16–LiClO4–ZnAl2O4 NCPE film can be used as a candidate electrolyte film for lithium polymer battery. The polymer electrolyte prepared by the hot-pressing method has a very close to that of solution-cast film. The lithiuim polymer battery using the hot-pressed NCPE film as electrolyte, lithium metal and LiFePO\(_4\) as anode and cathode respectively, shows high discharge specific capacity, good rate capacity, excellent cycling stability, and high coulombic efficiency as revealed by galvanostatic charge/discharge cycling tests, which suggests that the hot-pressed PEO16–LiClO4–ZnAl2O4 NCPE film is a viable candidate electrolyte film for all-solid-state lithium polymer batteries.

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### References