

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

Lishi Wang, Xingwang Li, Wensheng Yang*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history:

Received 28 August 2009
Received in revised form 24 October 2009
Accepted 2 November 2009
Available online 6 November 2009

Keywords:

Hot-pressing
Poly(ethylene oxide)
Nanocomposite polymer electrolyte
Interfacial property
All-solid-state lithium polymer battery

ABSTRACT

PEO₁₆-LiClO₄-ZnAl₂O₄ nanocomposite polymer electrolyte (NCPE) films prepared by hot-pressing method have been investigated. In order to compare with the hot-pressed NCPEs, the NCPE films have also been prepared using the conventional solution-casting method. Field emission scanning electron microscopy (FESEM), differential scanning calorimetry (DSC), conductivity (σ) and interface property studies have been carried out on above two kinds of films. The results show that the NCPE film prepared by hot-pressing method has smoother surface, higher interface stability, lower crystallization and melting temperature values than that prepared by solution-casting method. An all-solid-state lithium polymer battery using the hot-pressed NCPE film as electrolyte, lithium metal and LiFePO₄ as anode and cathode respectively, shows high discharge specific capacity, good rate capacity, high coulombic efficiency, and excellent cycling stability as revealed by galvanostatical charge/discharge cycling tests.

© 2009 Elsevier Ltd. All rights reserved.

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, interface 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

* Corresponding author. Tel.: +86 10 64435271; fax: +86 10 64425385.
E-mail addresses: yangws@mail.buct.edu.cn, yangws.buct@126.com (W. Yang).

at least 48 h before use. The ZnAl_2O_4 powders with particle sizes of 10–15 nm were prepared according to the reference [15] and were heated under vacuum at 150 °C for 48 h to remove water before use.

$\text{PEO}_{16}\text{-LiClO}_4\text{-ZnAl}_2\text{O}_4$ NCPE films were prepared by hot-pressing method and solution-casting method respectively, as follows:

Hot-pressing method: The electrolyte components (PEO, ZnAl_2O_4 , and LiClO_4) were carefully sieved and then introduced in their correct proportion (the amount of PEO and LiClO_4 were fixed with $[\text{EO}]/[\text{Li}]$ molar ratio at 16 according to the reported literature [21]) inside sealed Teflon bottles protected by N_2 and thoroughly mixed by ball-milling for at least 24 h to obtain homogeneous mixture of powders. The powders sandwiched by two Teflon sheets were hot pressed at 120 °C and 10 MPa 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 ZnAl_2O_4 powders of PEO was dispersed in acetonitrile with the aid of ultrasonic dispersion, followed by the addition of PEO and LiClO_4 with fixed $[\text{EO}]/[\text{Li}]$ molar ratio of 16 [21]. The solution was stirred at room temperature for 24 h 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. Finally, the samples were dried under vacuum at 50 °C for 48 h. The films obtained were 150–200 μm in thickness. They were stored under argon-filled dry box for subsequent measurements.

The NCPEs containing ZnAl_2O_4 are designated as $\text{PEO}_{16}\text{-LiClO}_4\text{-}x\text{wt.}\% \text{ZnAl}_2\text{O}_4$, where x denotes 0, 8.

2.2. Characterization of samples

Differential scanning calorimetry (DSC) was employed to determine the melting temperature (T_m), recrystallization enthalpy (ΔH_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 10 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 2 h 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 $\sigma = L/(R_b A)$ 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 2 h 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.

Table 1

Melting temperature (T_m), recrystallization enthalpy (ΔH_m) and crystallinity (X_c) values of pure PEO and polymer electrolyte $\text{PEO}_{16}\text{-LiClO}_4\text{-}x\text{wt.}\% \text{ZnAl}_2\text{O}_4$ ($x = 0, 8$) prepared by solution-casting method and hot-pressing method respectively.

Sample	Preparation technique	T_m (°C)	ΔH_m (J g^{-1})	X_c^a (%)
Pure PEO	Powder	67.5	107.1	50.2
$\text{PEO}_{16}\text{-LiClO}_4$	Solution-casting	64.0	82.18	38.45
$\text{PEO}_{16}\text{-LiClO}_4$	Hot-pressing	60.2	67.95	31.80
$\text{PEO}_{16}\text{-LiClO}_4\text{-}8\% \text{ZnAl}_2\text{O}_4$	Solution-casting	62.8	51.11	23.92
$\text{PEO}_{16}\text{-LiClO}_4\text{-}8\% \text{ZnAl}_2\text{O}_4$	Hot-pressing	47.7	43.7	20.45

$$^a X_c = (\Delta H_m / \Delta H_m^*) \times 100, \text{ where } \Delta H_m^* = 213.7 \text{ (J g}^{-1}\text{)}.$$

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, LiFePO_4 (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 ($\text{O}_2 < 1$ ppm; $\text{H}_2\text{O} < 1$ ppm).

3. Results and discussion

3.1. Physical properties of polymer electrolyte

Table 1 lists T_m , ΔH_m and X_c values of pure PEO and polymer electrolyte $\text{PEO}_{16}\text{-LiClO}_4\text{-}x\text{wt.}\% \text{ZnAl}_2\text{O}_4$ with $x = 0, 8$ prepared by hot-pressing method and solution-casting method. From Table 1, we can see that the dispersal of ZnAl_2O_4 nanoparticles in $\text{PEO}_{16}\text{-LiClO}_4$ substantially influences T_m , ΔH_m and X_c values of the NCPE. It also can be observed that the T_m , ΔH_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 $\text{PEO}_{16}\text{-LiClO}_4\text{-}x\text{wt.}\% \text{ZnAl}_2\text{O}_4$ 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 $\text{PEO}_{16}\text{-LiClO}_4$ 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 $\text{PEO}_{16}\text{-LiClO}_4\text{-}8\text{wt.}\% \text{ZnAl}_2\text{O}_4$ 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.

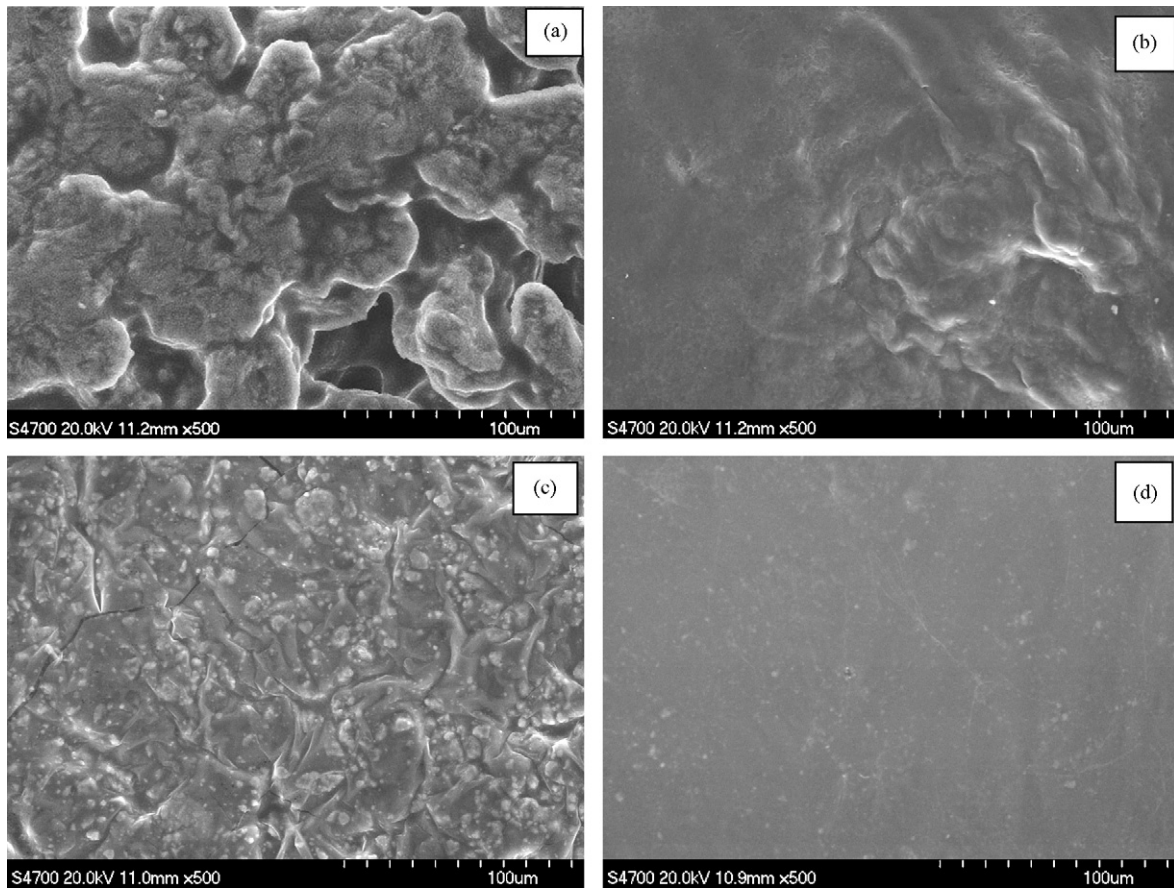


Fig. 1. FESEM images of polymer electrolyte films of $\text{PEO}_{16}\text{-LiClO}_4\text{-}x\text{ wt.}\% \text{ZnAl}_2\text{O}_4$: (a) $x=0$ (solution-cast), (b) $x=0$ (hot-pressed), (c) $x=8$ (solution-cast), and (d) $x=8$ (hot-pressed).

3.2. Ionic conductivity

Temperature dependence of ionic conductivity is measured for $\text{PEO}_{16}\text{-LiClO}_4\text{-}8\text{ wt.}\% \text{ZnAl}_2\text{O}_4$ 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

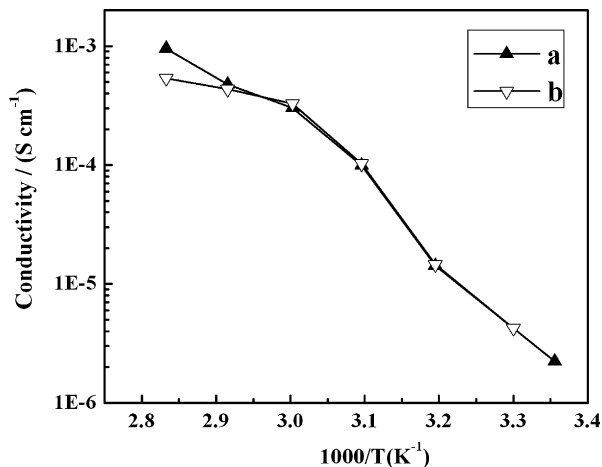


Fig. 2. Temperature dependence of ionic conductivity for $\text{PEO}_{16}\text{-LiClO}_4\text{-}8\text{ wt.}\% \text{ZnAl}_2\text{O}_4$ NCPE films prepared by (a) solution-casting method and (b) hot-pressing method respectively.

ZnAl_2O_4 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 ZnAl_2O_4 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 $\text{PEO}_{16}\text{-LiClO}_4\text{-}x\text{ wt.}\% \text{ZnAl}_2\text{O}_4$ ($x=0, 8$) 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.% ZnAl_2O_4 as filler. It also can be observed that the presence of nanosized ZnAl_2O_4 particles in the NCPE films pre-

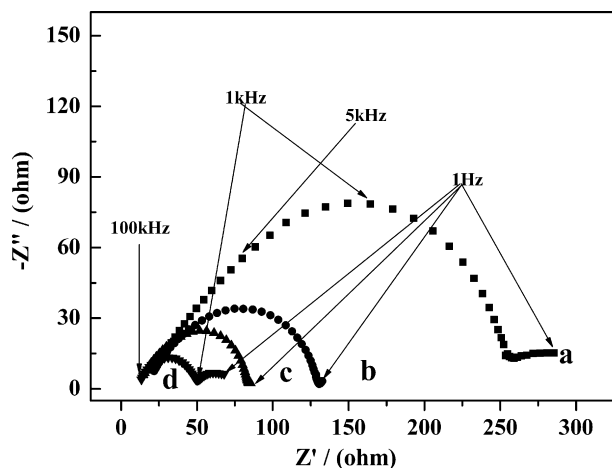


Fig. 3. Impedance spectra of Li/PEO₁₆-LiClO₄-*x* wt.% ZnAl₂O₄ NCPEs/Li cells kept at 70 °C for 2 h under open circuit potential with (a) *x*=0 (solution-cast), (b) *x*=0 (hot-pressed), (c) *x*=8 (solution-cast), and (d) *x*=8 (hot-pressed). Frequency range: 100 kHz to 1 Hz.

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

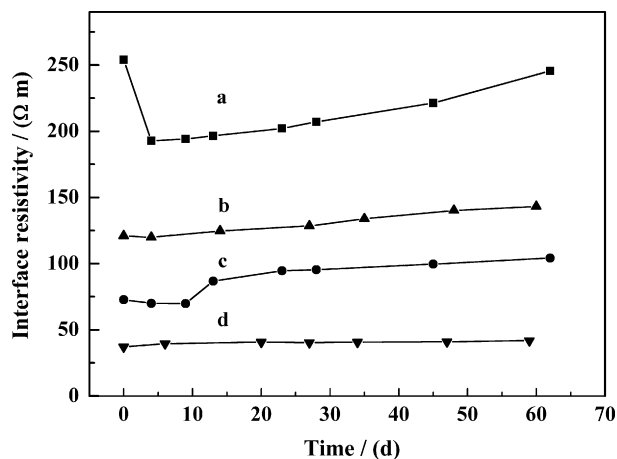


Fig. 4. Changes of interfacial resistivity as a function of time for Li/PEO₁₆-LiClO₄-*x* wt.% ZnAl₂O₄ NCPEs/Li cells at 70 °C under open circuit potential with (a) *x*=0 (solution-cast), (b) *x*=0 (hot-pressed), (c) *x*=8 (solution-cast), and (d) *x*=8 (hot-pressed). Frequency range: 100 kHz to 1 Hz.

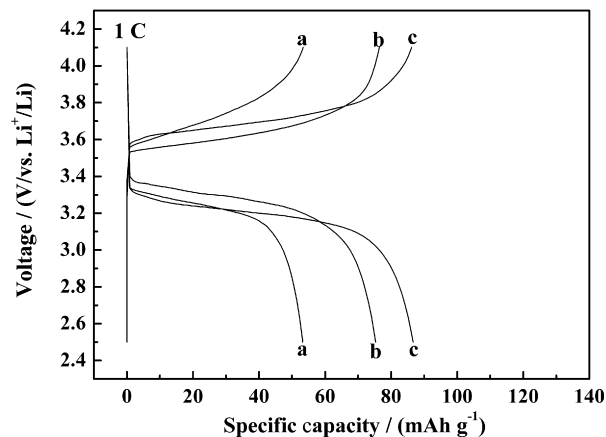
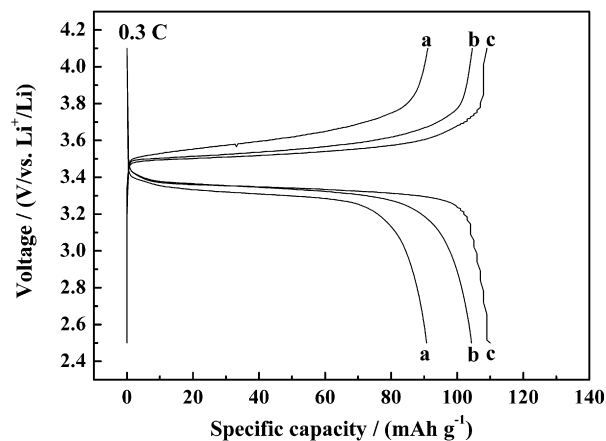
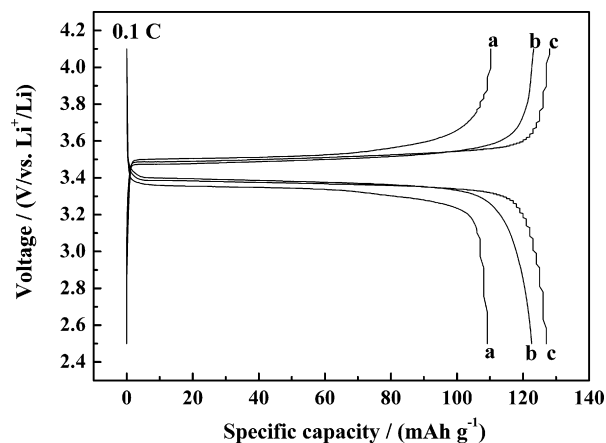


Fig. 5. The charge/discharge curves for the fifth cycles of the Li/polymer electrolyte/LiFePO₄ batteries at 65 °C with different charge/discharge rates (0.1, 0.3 and 1 C) using (a) hot-pressed PEO₁₆-LiClO₄, (b) solution-cast and (c) hot-pressed PEO₁₆-LiClO₄-8 wt.% ZnAl₂O₄ films as electrolytes.

polymer electrolytes. It indicates that hot-pressing method and nanosized ZnAl₂O₄ could primarily 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 Li/polymer electrolyte/LiFePO₄ batteries using different polymer electrolytes at 65 °C with different charge/discharge rates (0.1, 0.3 and 1 C). It is obvious that the charge/discharge curves of all batteries have flat voltage plateaus around 3.5 V (vs. Li⁺/Li).

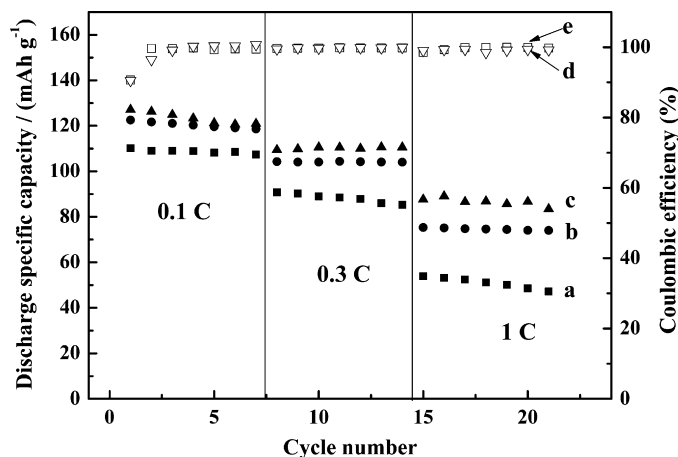


Fig. 6. The discharge specific capacity and coulombic efficiency of the Li/polymer electrolyte/LiFePO₄ batteries (a) hot-pressed PEO₁₆-LiClO₄, (b and d) solution-cast and (c and e) hot-pressed PEO₁₆-LiClO₄-8 wt.% ZnAl₂O₄ films as electrolytes, as a function of cycle number at 65 °C with different charge/discharge rates of 0.1, 0.3 and 1 C, respectively.

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/LiFePO₄ batteries using different polymer electrolytes as electrolytes as a function of cycle number at 65 °C with different charge/discharge rates (0.1, 0.3 and 1 C) are presented in Fig. 6(a–c). Li/hot-pressed PEO₁₆-LiClO₄-8 wt.% ZnAl₂O₄ NCPEs/LiFePO₄ batteries exhibit better cycling performance and higher discharge specific capacity with the cycle number increased and the discharge/charge rate enhanced than Li/hot-pressed PEO₁₆-LiClO₄/LiFePO₄ battery. Compared with Li/solution-cast PEO₁₆-LiClO₄-8 wt.% ZnAl₂O₄ NCPEs/LiFePO₄ batteries, they also exhibit better cycling performance and higher discharge specific capacity. It may be the reason that the battery using the hot-pressed PEO₁₆-LiClO₄-8 wt.% ZnAl₂O₄ NCPE film as electrolyte exhibits the best interfacial stability among the three batteries. The coulombic efficiency of the Li/polymer electrolyte/LiFePO₄ batteries using hot-pressed and solution-cast PEO₁₆-LiClO₄-8 wt.% ZnAl₂O₄ NCPE films as electrolytes, as a function of cycle number at 65 °C with different charge/discharge rates (0.1, 0.3 and 1 C) are presented in Fig. 6(d and e). In the first cycle, the coulombic efficiency of these two batteries is around 90%. The large irreversible capacity could be ascribed to the formation of a passivation film between the NCPE film and Li electrode [24]. After the first cycle it is estimated to more than 97%, and approaching 100% with the increase of the

cycles even at high rates. The high coulombic efficiency indicate that the batteries using the hot-pressed PEO₁₆-LiClO₄-8 wt.% ZnAl₂O₄ NCPE films as electrolytes have small internal resistance and high reversible capacity.

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.

4. Conclusions

A comparative study has been carried out on polymer electrolyte films of PEO₁₆-LiClO₄-x wt.% ZnAl₂O₄ with x = 0, 8 prepared by hot-pressing and solution-casting methods respectively. The results show that the properties of PEO-based NCPE films are enhanced by the addition of the nanosized ZnAl₂O₄ powder with mesoporous network than the filler-free polymer electrolytes prepared by not only the hot-pressing method but also the solution-casting method. The polymer electrolyte prepared by the hot-pressing method has smoother surface, higher interface stability, lower crystallization and melting temperature values than that prepared by the solution-casting method. The ion conductivity of hot-pressed NCPE film is very close to that of solution-cast film. The lithium polymer battery using the hot-pressed NCPE film as electrolyte, lithium metal and LiFePO₄ as anode and cathode respectively, shows high discharge specific capacity, good rate capacity, excellent cycling stability, and high coulombic efficiency as revealed by galvanostatical 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.

Acknowledgments

This work was supported by the National Natural Science Foundation of China, the Ministry of Science and Technology High Technology Development (863) Plan (Grant No. 2006AA03Z343), the 111 Project (Grant No. B07004), and the Program for New Century Excellent Talents in Universities (Grant No. NCET-08-0713).

References

- [1] D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer* 14 (1973) 589.
- [2] F. Croce, L. Persi, F. Ronci, B. Scrosati, *Solid State Ionics* 135 (2000) 47.
- [3] F. Croce, G.B. Appetecchi, L. Persi, B. Scrosati, *Nature* 394 (1998) 456.
- [4] G.B. Appetecchi, F. Croce, G. Dautzenberg, M. Mastragostino, F. Ronci, B. Scrosati, F. Soavi, A. Zanelli, F. Alessandrini, P.P. Prosini, *J. Electrochem. Soc.* 145 (1998) 4126.
- [5] Q. Li, H.Y. Sun, Y. Takeda, N. Imanishi, J. Yang, O. Yamamoto, *J. Power Sources* 94 (2001) 201.
- [6] B. Scrosati, F. Croce, S. Panero, *J. Power Sources* 100 (2001) 93.
- [7] A. Bac, M. Ciosek, M. Bukat, M. Marczewski, H. Marczevska, W. Wiecezorek, *J. Power Sources* 159 (2006) 405.
- [8] B.H. Lee, N.S. Choi, J.K. Park, *Polym. Bull.* 49 (2002) 63.
- [9] Q. Li, Y. Takeda, N. Imanishi, J. Yang, H.Y. Sun, O. Yamamoto, *J. Power Sources* 97–98 (2001) 795.
- [10] G.B. Appetecchi, F. Croce, L. Persi, F. Ronci, B. Scrosati, *Electrochim. Acta* 45 (2000) 1481.
- [11] J.Y. Xi, X.P. Qiu, M.Z. Cui, X.Z. Tang, W.T. Zhu, L.Q. Chen, *J. Power Sources* 156 (2006) 581.
- [12] L.Z. Fan, C.W. Nan, S.J. Zhao, *Solid State Ionics* 164 (2003) 81.
- [13] J.W. Kim, K.S. Ji, J.P. Lee, J.W. Park, *J. Power Sources* 119–121 (2003) 415.
- [14] F. Croce, S. Sacchetti, B. Scrosati, *J. Power Sources* 161 (2006) 560.
- [15] L.S. Wang, J. Wang, W.S. Yang, D.G. Evans, *Solid State Ionics* 180 (2009) 392.
- [16] F.M. Gray, J.R. MacCallum, C.A. Vincent, *Solid State Ionics* 18–19 (1986) 282.
- [17] P.P. Prosini, S. Passerini, R. Vellone, W.H. Smyrl, *J. Power Sources* 75 (1998) 73.
- [18] G.B. Appetecchi, S. Passerini, *Electrochim. Acta* 45 (2000) 2139.
- [19] C. Capiglia, J. Yang, N. Imanishi, A. Hirano, Y. Takeda, O. Yamamoto, *Solid State Ionics* 154–155 (2000) 7.
- [20] G.P. Pandey, S.A. Hashmi, R.C. Agrawal, *Solid State Ionics* 179 (2008) 543.
- [21] L.F. Hu, Z.L. Tang, Z.T. Zhang, *J. Power Sources* 166 (2007) 226.
- [22] B. Kumar, L.G. Scanlon, *Solid State Ionics* 124 (1999) 239.
- [23] J.H. Shin, F. Alessandrini, S. Passerini, *J. Electrochem. Soc.* 152 (2005) A283.
- [24] D. Fauteux, *Solid State Ionics* 17 (1985) 133.