Effect of ball milling on structural and electrochemical properties of $(PEO)_n LiX$ ($LiX = LiCF_3SO_3$ and $LiBF_4$) polymer electrolytes

J.H. Shin[a], Y.T. Lim[a], K.W. Kim[a,*], H.J. Ahn[a], J.H. Ahn[b]

[a]Department of Metallurgical and Materials Engineering, Advanced Materials Research Institute, Gyeongsang National University, Chinju 660-701, South Korea
[b]Department of Chemical Engineering, Gyeongsang National University, Chinju 660-701, South Korea

Abstract

Polymer electrolytes consisting of poly(ethylene oxide) (PEO) and lithium salts, such as $LiCF_3SO_3$ and $LiBF_4$ are prepared by the ball-milling method. This is performed at various times (2, 4, 8, 12 h) with ball:sample ratio of 400:1. The electrochemical and thermal characteristics of the electrolytes are evaluated. The structure and morphology of PEO–LiX polymer electrolyte is changed to amorphous and smaller spherulite texture by ball milling. The ionic conductivity of the PEO–LiX polymer electrolytes increases by about one order of magnitude than that of electrolytes prepared without ball milling. Also, the ball milled electrolytes have remarkably higher ionic conductivity at low temperature. Maximum ionic conductivity is found for the PEO–LiX prepared by ball milling for 12 h, viz. 2.52×10^{-4} S cm^{-1} for $LiCF_3SO_3$ and 4.99×10^{-4} S cm^{-1} for $LiBF_4$ at 90 °C. The first discharge capacity of Li/S cells increases with increasing ball milling time. $(PEO)_{10}LiCF_3SO_3$ polymer electrolyte prepared by ball milling show the typical two plateau discharge curves in a Li/S battery. The upper voltage plateau for the polymer electrolyte containing $LiBF_4$ differs markedly from the typical shape. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Polymer electrolyte; Poly(ethylene oxide); Ball milling; Lithium battery; Sulfur

1. Introduction

Lithium polymer batteries are considered as promising systems not only for electronic devices, such as electro-chemical sensors, but also for electric vehicles. This is due to the high specific energy and geometry flexibility of the polymer electrolyte [1,2]. Polymer electrolytes may play an important role in the performance of lithium batteries and much effort has been focused on improvement of the polymer electrolyte in terms of the ionic conductivity and the mechanical properties. The ionic conductivity of poly (ethylene oxide) (PEO) polymer electrolytes containing alkali metal salt was first demonstrated in 1975 [3] and Armand et al. [4] proposed their application as a solid polymer electrolyte (SPE) for lithium batteries [3,4]. Although, many types of SPE have been studies during the past several years, PEO is still one of the most promising SPEs [5,6].

PEO polymer electrolytes unfortunately have some problems, such as poor mechanical properties and low ionic conductivity at low temperature for lithium polymer rechargeable batteries [7]. Several methods are well known to resolve these problems. One is to decrease the crystal-linity of the polymer to improve the polymer chain mobility and increase the mechanical properties. In particular, this is achieved by the introduction of an inorganic ceramic filler (nanosize) in the PEO polymer electrolytes. Recently, Croce et al. [7] have demonstrated that nanocomposite polymer electrolytes have a very stable lithium electrode interface and an enhanced conductivity at low temperature, both features are combined with good mechanical properties. The other method is to increase the carrier concentration (e.g., lithium ions) in order to increase the ionic conductivity. The increase in carrier concentration can be achieved either by increase in lithium salt or by introduction of lithium salts with high dielectric value.

Our approach of increasing the ionic conductivity is different to that of the previous studies discussed above. We have focused on a decrease in the crystallinity of the PEO polymer electrolyte by preparation of the polymer electrolyte with a ball milling method. This is because ball milling can partially change the PEO structure into low crystallinity due to break down of the PEO chain by introduction of high energy.

* Corresponding author. Tel.: +82-55-751-5305; fax: +82-55-759-1745.
E-mail address: kiwonkim@nongae.gsnu.ac.kr (K.W. Kim).

Lithium–sulfur batteries give a theoretical specific capacity of 1672 mAh g^{-1} of active material and a theoretical specific energy of 2600 W h kg^{-1}, but rapid fade of capacity with repeated charge–discharge cycling limits the performance of such cells [8]. In this study, we have examined a PEO–LiX (LiX = LiCF$_3$SO$_3$ and LiBF$_4$) polymer electrolyte prepared by ball milling as the electrolyte of lithium–sulfur cells. Not only the ionic conductivity of the electrolyte in stainless-steel (SS)/polymer electrolyte/SS cells is evaluated but also the interfacial property between lithium and electrolyte in lithium/polymer electrolyte/lithium cells with PEO–LiX polymer electrolytes prepared by ball milling for 2–12 h with a ball:sample ratio of 400:1.

2. Experimental

All samples were prepared in an argon-filled glove box in order to prevent their exposure to the atmosphere. The amount of moisture in the glove box was kept below 10 ppm. The PEO (relative molar mass $M_w = 4 \times 10^6$, Aldrich) was vacuum dried for 24 h at around 50 °C before use. LiCF$_3$SO$_3$ (Aldrich) and LiBF$_4$ (Acros organics) were also dried for 24 h at around 100 °C under vacuum, and acetonytrile (Junsei) was used as received. Dry PEO was dissolved into acetonitrile with LiCF$_3$SO$_3$ or LiBF$_4$. The [EO]:[Li] ratio is the stoichiometric proportion of ether oxygen to Li ions. EO is related to the PEO ether unit. The [EO]:[Li] ratio for two kinds of lithium salt is give in Table 1. The polymer electrolyte consisted of 80 wt.% PEO an 5 wt.% lithium salt. The slurry was mechanically mixed by the ball milling method for 2–12 h. A ball-to-powder ratio of 400:1 was employed and hardened SS balls with diameter of 7.5 mm were used. After ball milling, the slurry was cast on a glass plate and then dried until the solvent was evaporated completely. The dried film was punched into a prototype with cork borer and then dried under vacuum in desiccator at 50 °C for 24 h. Sulfur, carbon, lithium salt and PEO were simultaneously dissolved in acetonitrile. The following procedure of sulfur electrode preparation is same with electrolyte preparation. The configuration of the Li/S cells was Li (350 μm thick, Aldrich)/polymer electrolyte/50% sulfur. All assemblies of the cells were carried out in

argon-filled glove box. The area and thickness of sulfur electrodes were approximately 0.8 cm^2 and 8 μm, respectively, and the weight of the sulfur electrode was of the order of 2.4 mg. Cell tests were conducted under galvanostatic conditions using a WBCS3000 and a Bitrode SCN battery cycler.

The polymer electrolyte for ac impedance measurement was prepared as a 1.54 cm^2 prototype and sandwiched between two SS or lithium electrodes. The ac impedance measurements were then performed with an amplitude of 10 mV over a frequency range of 10^5–1 Hz at 10 points per frequency decade using a CMS100 electrochemical measurement system (Gamry Instruments Inc.). Analyses of Nyquist plots were conducted by means of CMS300 electrochemical impedance spectroscopy software. The ionic conductivity as a function of temperature was determined by ac impedance measurements on a SS/electrolyte/SS cell over the temperature range 20–100 °C. The cell was kept at each measuring temperature for 30 min to assure equilibrium of temperature of the sample before measurement and the measurements were conducted at the open-circuit potential. The interfacial resistance between the electrolyte and the lithium electrode was measured by impedance response of Li/electrolyte/Li cells over a frequency range from 10^5 to 0.01 Hz under open-circuit conditions. The area of the lithium electrode was about of 0.8 cm^2. The transference number of the lithium ion was measured by an impedance–polarization coupling technique [9] in a symmetrical cell with a non-blocking lithium electrode of prototype 0.8 cm^2.

Cyclic voltammetry measurements were conducted at elevated temperature at a scanning rate of 10 mV s^{-1} by means of a PAR Potentiostat/Galvanostat model 263A(EG&G Instruments Inc.). The melting point (T_m) of the polymer electrolyte was measured by differential scanning calorimetry (DSC) under an argon stream of 60 ml min^{-1} and a heat flow of 2 °C min^{-1} using a DSC2010 (TA Instrument Inc.). X-ray diffraction (XRD) phase analysis of the polymer electrolyte was conducted using a Rigaku diffractometer. Cu Kα radiation was used in all experiments and a step scanner was employed at a scanning rate of 2° min^{-1}. The morphologies of the polymer electrolytes were observed with a XL30S (PHILIPS) and JSM6400 (JEOL) scanning electron microscopy (SEM) instrument.

Table 1
Lithium-ion transference numbers(t_{Li+}) of PEO–LiX(LiX = LiCF$_3$SO$_3$ and LiBF$_4$) polymer electrolytes prepared by ball milling

Electrolyte	Ball milling time (h)	t_{Li+}	Conductivity (S cm^{-1})	[EO]:[Li] ratio[*]	Temperature (°C)
PEO–LiCF$_3$SO$_3$	0	0.41	9.17 × 10^{-5}	10	90
PEO–LiCF$_3$SO$_3$	4	0.56	1.51 × 10^{-4}	10	90
PEO–LiCF$_3$SO$_3$	12	0.64	2.52 × 10^{-4}	10	90
PEO–LiBF$_4$	0	0.24	3.70 × 10^{-4}	6	90
PEO–LiBF$_4$	4	0.31	4.49 × 10^{-4}	6	90
PEO–LiBF$_4$	12	0.39	5.00 × 10^{-4}	6	90

[*] [EO]:[Li] ratio is stoichiometric proportion of ether oxygen:Li-ion ratio.

3. Results and discussion

3.1. Influence of ball milling on morphology of PEO electrolyte

Complexes of high molecular weight PEO and the stoichiometric proportion of inorganic alkali salts are generally deposited unperturbed solutions in polar solvents, such as methanol or acetonitrile, with well-defined spherulitic morphologies. Fig. 1 shows the morphologies for PEO electrolyte containing (a) $LiCF_3SO_3$ and (b) $LiBF_4$ as the lithium salt where ball milling was conducted for 2, 4, 8 and 12 h with a ball:sample ratio of 400:1. The morphologies of the polymer electrolytes exhibit spherulitic texture, which consists of individual spherulitic ranging from several tens to hundred of micrometers in diameter. The dimension of the spherulitic depends on various factors which may control the nucleation density per unit area, such as purity of solution,

film thickness and rate and uniformity of solvent removal [10]. For PEO electrolyte without ball milling, the texture is typical of other well-organized PEO-alkali salt structures with a stoichiometric [EO]:[Li] proportion. It is noticeable that PEO–LiX polymer electrolytes prepared by ball milling tend to decrease the dimension of spherulitic with ball milling time. The results mentioned above may indicate that ball milling in the preparation of PEO electrolyte may give rise to poorly defined spherulitic.

For below 4 h of ball milling, polymer electrolytes showed spherulitic morphology with smaller dimensions than typical electrolytes. The spherulitic dimensions remarkably decreased from several tens to a few micrometers for about 8 h of ball milling. The boundaries of individual spherulites became indistinct with increasing ball milling regardless of the use of different lithium salts. According to MacCallum and Vincent [10] spherulitic occur via sporadical nucleation and grow radially until they impinge upon each other at
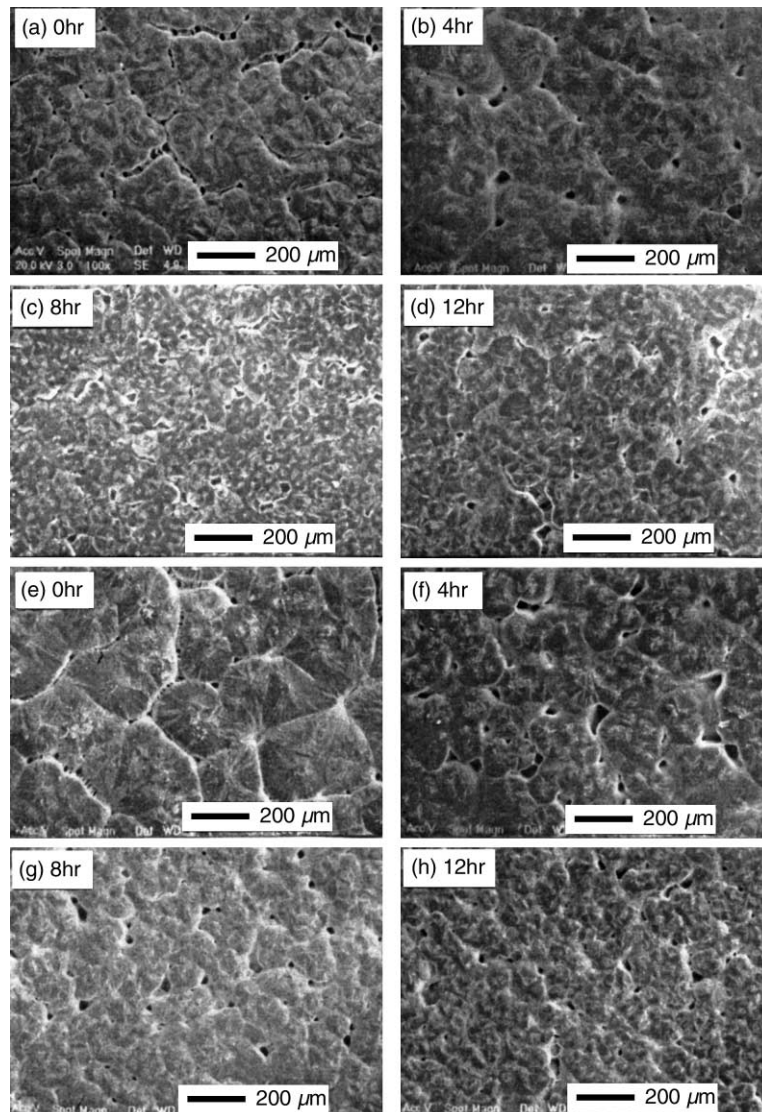

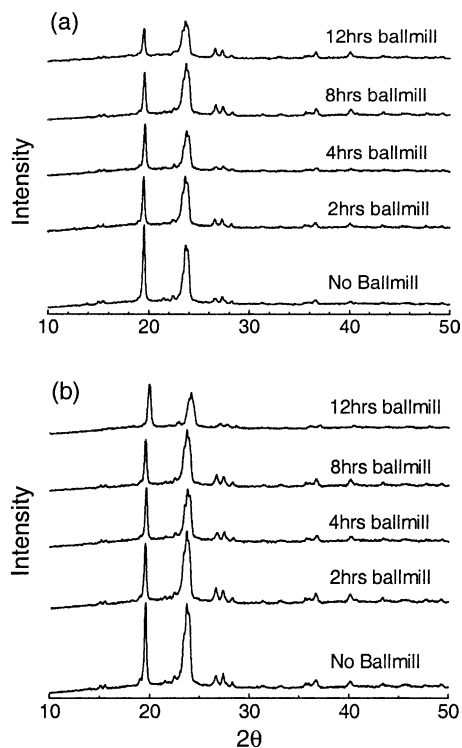Fig. 1. Scanning election micrographs of (a–d) $(PEO)_{10}LiCF_3SO_3$ and (e–h) $(PEO)_6LiBF_4$ polymer electrolyte prepared by ball milling for 0, 4, 8 and 12 h.

Fig. 2. XRD patterns of (a) $(PEO)_{10}LiCF_3SO_3$ and (b) $(PEO)_6LiBF_4$ polymer electrolyte prepared by ball milling.

Fig. 3. DSC curves of (a) $(PEO)_{10}LiCF_3SO_3$ and (b) $(PEO)_6LiBF_4$ polymer electrolyte prepared by ball milling.

straight boundaries. This is a typical phenomenon of the morphological behavior of crystalline polymers with flexible chains. These results may indicate that the crystallinity of polymer electrolyte may decrease with increasing time of ball milling because the chain of the PEO may be broken by mechanical operation.

3.2. Physical and thermal properties of PEO electrolyte with ball milling

The XRD pattern of a PEO polymer electrolyte containing $LiCF_3SO_3$ and $LiBF_4$ as lithium salt is shown in Fig. 2. The XRD analysis was used to evaluate the degree of crystallinity of the PEO polymer electrolyte. The crystalline peak for a PEO electrolyte without ball milling is strong and sharp as shown in Fig. 2. On the other hand, the peak for PEO electrolyte with ball milling changes into a broad and weak form as the time of ball milling is increased. For 12 h of ball milling, the intensity of crystalline peak decreases markedly. This behavior suggests that the PEO structure can be changed locally into an amorphous state by ball milling. Thus, the ambient ionic conductivity may be expected to increase compared with that obtained without ball milling.

DSC curves obtained from 30 to 80 °C for, a PEO polymer electrolyte prepared by ball milling are given in Fig. 3. There is an endothermic peak of the order of 64–67 °C which is attributed to the melting point of crystalline PEO. The melting point of PEO polymer electrolyte with ball milling is a little lower than that of polymer electrolyte without ball
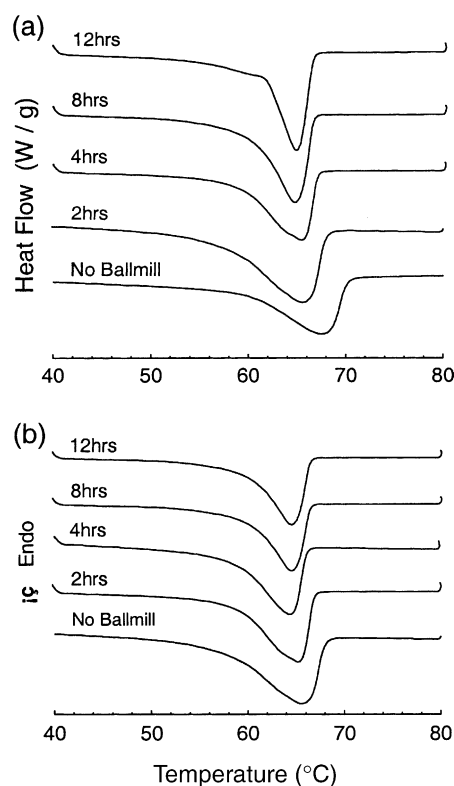
milling. This phenomenon may due to a local structural change of PEO from orderly arrangement to disorderly arrangement by ball milling. This result corresponds with the XRD findings mentioned above.

Cyclic voltammograms of Li/polymer electrolyte/Li cells at a scan rate of $10 m V s^{-1}$ at 90 °C are shown in Fig. 4. The peak potential and current density shift with increasing sweep number. The peak current increases with increasing time of ball milling. The lithium stripping peak in the vicinity of 0.5 V (versus Li) gradually sharpens with increasing time of ball milling. In the first sweep, the shape of lithium deposition and stripping curves is very sharp, but the curves become very broad during repetitive cycling to the 10th sweep. This phenomenon may indicate that the current density of lithium deposition and stripping may decrease due to the passivation layer formed by reaction between lithium electrode and polymer electrolyte. The lithium stripping peak does not shift with ball milling, but lithium deposition peak moves to more negative potentials during repetitive sweeping. Thus, lithium ions stripped from the lithium electrode are difficult to deposit on lithium during repetitive sweeping. The difference between the potentials of the anodic and cathodic peaks increases with increasing time of ball milling. The potential difference of PEO polymer electrolytes prepared by ball milling for 4–12 h is about 1.28 and 0.94 V, respectively. These results may indicate that the deposition and stripping of lithium in Li/polymer electrolyte/Li cells are relatively efficient for a polymer electrolyte prepared by ball milling.
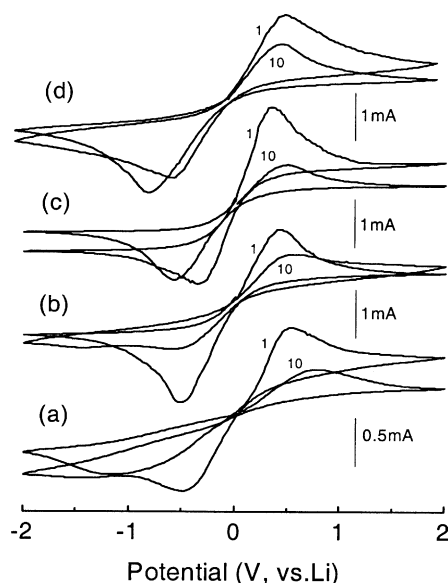
Fig. 4. Cyclic voltammograms for Li/polymer electrolyte/Li cells (at 90 °C and 10 mV s^{-1}) for the first to tenth sweeps. (PEO)$_{10}$LiCF$_3$SO$_3$ polymer electrolyte prepared by ball milling for (a) 0, (b) 4, (c) 8 and (d) 12 h.

Fig. 5. Ionic conductivity as function of storage time at 90 °C for (PEO)$_{10}$LiCF$_3$SO$_3$ (top) and (PEO)$_6$LiBF$_4$ (bottom) polymer electrolyte prepared by ball milling.

3.3. Influence of ball milling on conductivity of PEO electrolyte

The PEO electrolytes were prepared by ball milling as a function of time in order to investigate the effect of ball milling on ionic conductivity. The lithium-ion transference number (t_{Li+}) and ionic conductivity of the PEO–LiX electrolytes for various times of ball milling are shown in Table 1. Transference numbers are very important parameters for ionic conductors in terms of their practical application [11]. Although, many transference number measurements have been reported, however, a reliable and universally acceptable technique for their measurement is still to be found, as pointed out by Bruce et al. [12]. In this study, we have determined the lithium-ion transference numbers by using the theory developed by Vincent and coworkers [9]. It is interesting that the lithium-ion transference number also increases as the conductivity increases with increasing time of ball milling. This may indicate that ball milling may affect both the ionic conductivity and the lithium-ion transference number.

The ionic conductivity as a function of storage time at 90 °C for PEO–LiX(LiX = LiCF$_3$SO$_3$ and LiBF$_4$) polymer electrolyte with ball milling for 2, 4, 8 and 12 h is presented in Fig. 5. The ionic conductivities of the polymer electrolytes are found to increase with increasing storage time, reach a maximum, and then maintain a steady-state value. The ionic conductivities of polymer electrolyte with ball milling reach to steady-state value faster than those for a polymer without ball milling, and when ball milling for 12 h the time to attain a steady-state decreases remarkably. As shown in Fig. 5, ball milling of PEO containing LiCF$_3$SO$_3$ as
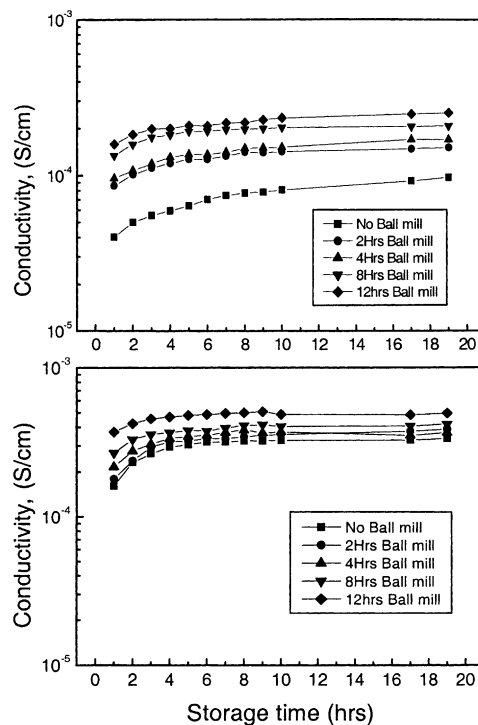
a lithium salt is more effective than in the case of LiBF$_4$. The ionic conductivities of (PEO)$_{10}$LiCF$_3$SO$_3$ with ball milling increase to almost an order of magnitude more than those without ball milling. It is very interesting that as the time of ball milling increases, the ionic conductivities of PEO–LiX also increase. These results indicate that ball milling may affect the ionic conductivity of the polymer electrolyte by changes in the microstructure and morphology. In this study, to account for the differences in the ionic conductivity with the ball milling, the grain boundaries and dimension effects of individual spherulites may be important.

The temperature dependence of the ionic conductivity in the range 20–100 °C during the first heating scan for the PEO–LiX polymer electrolyte with ball milling for 2, 4, 8, and 12 h is given in Fig. 6. The ionic conductivities of the polymer electrolytes with ball milling are higher than that without ball milling. For (PEO)$_{10}$LiCF$_3$SO$_3$ polymer electrolyte with ball milling, a remarkable increase in ionic conductivity can be observed at a low temperature below the melting point of the crystalline phase. Ball milling has a remarkable effect on ionic conductivity at low temperatures, as shown in Fig. 6. According to Krawiec et al. [13], the ionic conductivity of a composite polymer electrolyte containing microsized alumina increases by one order of magnitude above values an alumina-free polymer. In our study, the increase in ionic conductivity by ball milling is associated with the effect of inorganic ceramic filler in composite polymer electrolyte. The PEO-based polymer electrolyte generally shows the common break phenomenon in the
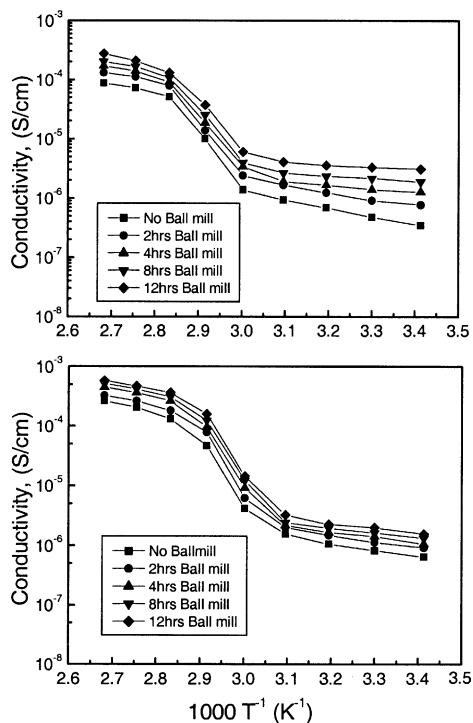
Fig. 6. Arrhenius plots of conductivity of $(PEO)_{10}LiCF_3SO_3$ (top) and $(PEO)_6LiBF_4$ (bottom) polymer electrolyte prepared by ball milling.

vicinity of the melting point and the break phenomenon for $(PEO)_{10}LiCF_3SO$ with ball milling is also observed. The slope of the curve for polymer electrolyte with ball milling however, is very different from that without ball milling.

3.4. Influence of ball milling on discharge capacity of PEO electrolyte

The discharge profiles of Li/polymer electrolyte/50% sulfur cells at a current of 100 mA g^{-1} sulfur at 90 °C for a PEO electrolyte containing $LiCF_3SO_3$ and $LiBF_4$ as lithium salts are presented in Fig. 7. The shape of discharge
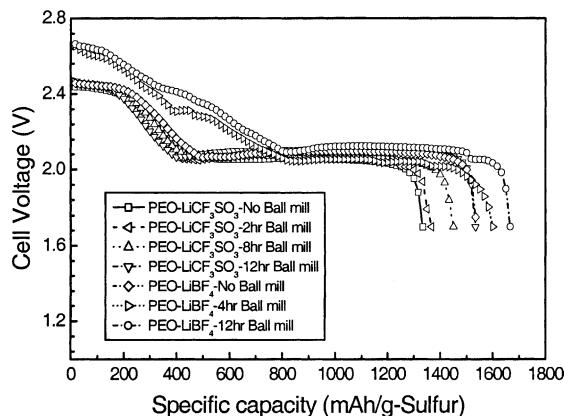
curves is very different for the two kinds of lithium salt. The discharge curves for $(PEO)_{10}LiCF_3SO_3$ polymer electrolyte display the typical stable upper and lower discharge plateau x that are well known for lithium–sulfur cells s_0. By contrast, the discharge curves for $(PEO)_6LiBF_4$ polymer electrolyte display unstable upper discharge plateau x. The weight of the sulfur electrode used in all discharge tests was 2.3 mg. The discharge capacity of cells using polymer electrolyte with ball milling is higher than that observed without ball milling and increase with the time of ball milling. These capacity results correspond with the ionic conductivity results discussed mentioned. This finding indicates that the interface resistance is not important factor in determining the capacity of cells on the first discharge.

3.5. Influence of ball milling on interfacial stability of PEO electrolyte

The interface property of the lithium electrode and the electrolyte determines the performance of rechargeable lithium batteries. The change in interfacial resistance versus time recorded at 90 °C for a PEO polymer electrolyte containing $LiCF_3SO_3$ and $LiBF_4$ sandwiched between two lithium electrodes is shown in Fig. 8. The charge-transfer resistance may be indicative of the interfacial stability and passivation phenomenon. The interfacial stability varies with the type of lithium salt and ball milling. The interface resistance of $(PEO)_6LiBF_4$ polymer electrolyte without ball milling increases rapidly after 6 days storage. The $(PEO)_6LiBF_4$ polymer electrolyte with ball milling experiences an increase of 1140 from 230 Ω cm^2 during storage for 24 h after the cell had been assembled, but rapid increase of interface resistance does not occur after 2 days of storage. The interface resistances of $(PEO)_{10}LiCF_3SO_3$ electrolytes are lower that those of $(PEO)_6LiBF_4$ electrolyte during storage. Thus, PEO polymer electrolytes prepared by ball milling exhibit good interfacial stability.
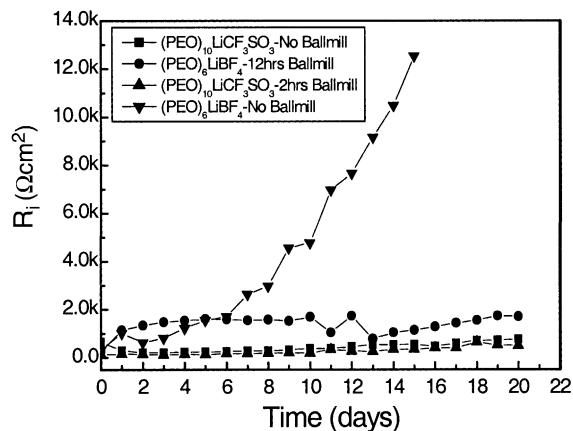

Fig. 7. Discharge profiles of Li/polymer electrolyte/50% sulfur cells at discharge current of 100 mA g^{-1} sulfur at 90 °C for PEO–LiX(LiX = $LiCF_3SO_3$ and $LiBF_4$) polymer electrolyte prepared by ball milling.

Fig. 8. Changes in interface resistance with time recorded at 90 °C for PEO–LiX(LiX = $LiCF_3SO_3$ and $LiBF_4$) polymer electrolyte prepared by ball milling.

4. Conclusions

(PEO)$_n$LiX ($n = 10$ and 6, LiX = LiCF$_3$SO$_3$ and LiBF$_4$) polymer electrolytes have been prepared by ball milling for 2, 4, 8 and 12 h with a ball:sample ratio = 400:1. The effects of ball milling effects have been evaluated from the electro-chemical and thermal characteristics. The structure and morphology of PEO–LiX polymer electrolyte changes into a partially amorphous and smaller spherulite texture by ball milling. The degree of crystallinity decreases due to the microstructure changing into a partially form on ball milling for 12 h. The ionic conductivity of a PEO polymer electrolyte prepared by ball milling increases about one order magnitude above that without ball milling, and also increases with ball milling time. The ionic conductivity at low temperature is increased markedly by ball milling for 12 h. The interface resistance between the polymer electrolyte and the lithium electrode is decreased by ball milling and it is very effective in decreasing the interface resistance of a (PEO)$_6$LiBF$_4$ polymer electrolyte prepared by ball milling for 12 h.

Acknowledgements

References

[1] D.F. Shriver, P.G Bruce (Eds.), Solid State Electrochemistry, Cambridge, 1995 (Chapter 5).

[2] B. Scrosati (Ed.), Applications of Electroactive Polymer, Chapman & Hall, London, 1983.

[3] D. Fenton, J.M. Parker, P.V. Wright, J. Polym. 14 (1973) 589.

[4] M.B. Armand, J.M. Chabagno, M. Duclot, in: Proceedings of the Second International Meeting on Solid Electrolytes, St. Andrews, Scotland, September, 1978 (Abstracts).

[5] S.R. Starkey, R. Frech, Electrochim. Acta 42 (1997) 471.

[6] H.J. Rhoo, H.T. Kim, J.K. Park, T.S. Hwang, Electrochem. Acta 42 (1997) 1571.

[7] F. Croce, L. Persi, F. Ronci, B. Scrosati, Solid State Ionics 135 (2000) 47.

[8] D. Mamorstein, T.H. Yu, K.A. Striebel, F.R. McLarnon, J. Hou, E.J. Cairns, J. Power Sources 89 (2000) 219.

[9] J. Evans, C.A. Vincent, P.G. Bruce, Polymer 28 (1987) 2324.

[10] J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Reviews, Vol. 2, Elsevier, London, 1989, p. 77.

[11] J.R. MacCallum, C.A. Vincent (Eds.), Polymer Electrolyte Reviews, Vol. 1, Elsevier, London, 1987, p. 55.

[12] P.G. Bruce, J. Evans, C.A. Vincent, Solid States Ionics 28–30 (1988) 918.

[13] W. Krawiec, L.G. Scanlon Jr., J.P. Fellner, R.A. Vaia, S. Vasudevan, E.P. Giannelis, J. Power Sources 54 (1995) 310.