Int. J. Electrochem. Sci., 7 **(2012)** 12601 - 12609

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

PVDF-based Comoposite Polymer Electrolyte for Li/$LiFePO_4$ Batteries

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Received: 22 October 2012 / *Accepted:* 16 November 2012 / *Published:* 1 December 2012

In order to improve the mechanical strength of the PP/PE/PP membrane, a novel polymer membrane was prepared by introducing nano-SiO_2 filled PVDF polymer film. After soaking the liquid electrolyte (1 mol L^{-1} $LiPF_6$ (DMC:DEC:EC=1:1:1, w/w/w)), the composite polymer electrolyte was obtained and used as the electrolyte for Li/$LiFePO_4$ batteries.The properties of the composite polymer film/electrolyte were characterized by scan electronic microscopy, material test machine, scan voltammetry, electrochemical impedance spectroscopy, constant current charge/discharge test. The results showed that the composite polymer film owns higher electrolyte absorption ability (145 % absorbance) and improved mechanical strength than that of PP/PE/PP film. The ionic conductivity reached 1.12×10^{-3} Scm^{-1}, and its electrochemical stability window is about 4.5V. At 60℃, the capacity retention of Li/$LiFePO_4$ batteries with the obtained composite polymer electrolyte as electrolyte was 98 % after 100 cycles even at 1*C*. The excellent cyclability of Li/$LiFePO_4$ batteries at high temperature showed that the obtained composite polymer electrolyte could be a possible electrolyte candidate for Li/$LiFePO_4$ batteries used for electric vehicles and hybrid electric vehicles.

Keywords: Composition; Polymer electrolyte; Electrochemical properties; Mechanical properties; Li/$LiFePO_4$ batteries

1. INTRODUCTION

Since introduced by Sony in 1990s, lithium ion batteries have been one of the most popular power sources candidates in transportation and energy storage systems. The standard electrolyte most frequently used in commercial lithium ion batteries is the liquid electrolyte, which is mainly composed of lithium salts ($LiPF_6$, $LiCLO_4$, $LiBF_4$) and organic solvents (EC, DEC, DMC). Although lithium ion batteries contained the standard liquid electrolyte can meet most needs of the applications, the leakage is inevitable due to the fluidity nature of the liquid, especially in abuse conditions. On the other hand, the rigid package has to be adopted because of the liquid electrolyte, thus the weight specific energy of the lithium ion batteries will be limited. On the contrary, the polymer electrolytes can pack flexibly and eliminate leakage, which is attractive for safety improvement of lithium ion batteries. And the significant advantages in weight, volume specific capacity and the packaging cost can also be obtain by using polymer electrolytes[1-4]. So, more attentions are paid to the polymer electrolyte with acceptable ion conductivity by soaking the porous polymer film with organic liquid electrolyte[5-7]. Recently, $LiFePO_4$ is considered as one of the most suitable cathode material applied in Electric Vehicle(EV) and Hybrid Electric Vehicles(HEV) due to advantages such as low cost, good cycling performance at room temperature, high safety, non-toxicity and environmental friendliness[8,9]. However, though some efforts have been made to enhance the mechanical strength of the polymer electrolyte, such as introducing the inorganic metallic oxides Al_2O_3, SiO_2, TiO_2 and so on as the filling stuff[10,11], the mechanical strength of the polymer electrolyte is still not satisfied for the $Li/LiFePO_4$ batteries, especially during long cycled at high temperature.

In this paper, a PVDF-based composite polymer film with nano-SiO_2 filling stuff by incorporating the PP/PE/PP film to enhance the mechanical strength. After further soaking with standard electrolyte (1 mol L^{-1} $LiPF_6$ (DMC:DEC:EC=1:1:1, w/w/w)), the composite polymer electrolyte for $Li/LiFePO_4$ batteries was obtained. The composite polymer electrolyte was found to reveal excellent electrochemical properties and could be a promising electrolyte candidate for $Li/LiFePO_4$ batteries applied in EV and HEV fields.

2. EXPERIMENTAL

2.1 Materials

dibuty(o-)phthalate (DBP) and acetone was purchased from Tianjin Kermel Chemical Reagent Co., Ltd., China. $LiFePO_4$ was purchased from Changes scending Ent., Taiwan. N-methylpyrrolidone (NMP) was purchased from Tianjin Ruijinte Chemical Co., Ltd., China. Aforementioned reagents were used of analytical grade. Other materials were obtained from Zhejiang dongsheng energy technology development Co. Ltd. China.

2.2 Preparation of the PVDF-based composite polymer electrolyte

The PVDF polymer solution with nano-SiO_2 filling stuff was prepared as follows: PVDF powder was dried at 80℃ under vacuum for 12 hours before use. Then the PVDF powder、DBP and nano-SiO_2 powder (1.5:1:1.1 in weight) were mixed and dissolved in acetone, stirring homogeneously for 12 hours at 40℃. Afterwards, the commercial PP/PE/PP film was dipped into the above solution for 2 hours and taken out to be dried in air naturally. Finally, the dried composite polymer film was transferred into argon filled glove box and immersed into the standard electrolyte (1 mol L-1 LiPF6

(DMC:DEC:EC=1:1:1, w/w/w)) for 1 hour to obtain the composite polymer electrolyte. The excess liquid electrolyte on the surface of the film was removed by filter paper to get the composite polymer electrolyte.

2.3 Measurements of the PVDF-based composite polymer electrolyte

The morphologies of the dried composite polymer and the commercial PP/PE/PP films were observed by scanning electron microscopy (SEM, HITACHI S-4700).

The electrolyte absorbing ability (S_w) of the dried composite polymer film was evaluated by equation (1):

$$S_w = \frac{100(w - w_0)}{w} \qquad (1)$$

where w_0 is the mass of dried composite polymer film and w is the mass of composite polymer electrolyte.

The mechanical strength of the dried composite polymer film was measured by material test machine (USA Instron5569).

The ionic conductivity (σ) of the composite polymer electrolyte was obtained by electrochemical impedance spectroscopy (EIS) in configuration of blocking cells (SS/composite polymer electrolyte/SS, SS=stainless steel) within the frequency of 100k～0.01 Hz at the amplitude of 5 mV by electrochemical analyzer (CHI604b). The ionic conductivity (σ) was calculated according to the equation (2):

$$\sigma = \frac{l}{AR_b} \qquad (2)$$

where R_b is the bulk resistance obtained from the intercept of the Nyqiust plot with the real axis, l is the thickness of the composite polymer electrolyte and A is the electrode area (0.79 cm^2).

The electrochemical stability window of the composite polymer electrolyte was tested in three-electrode cell (SS as working electrode, Li metal as counter and reference electrode) by electrochemical analyzer (CHI660a) via linear scan voltammetry (LSV) technique in potential range of 0～5.5 V at the scan rate of 5 mV s^{-1}.

The charge-discharge behavior of the 2025-type coin cells (Li/LiFePO_4) tests were conducted at 60℃ using a oven thermostat. The tests were performed at the constant current mode, cycled at 1 *C* over the range of 2.7~4.2 V by Neware battery testing system.

2.4 Battery assembly

The performance of the composite polymer electrolyte was estimated with coin cell, where carbon treated LiFePO_4 was used as cathode, metal lithium was used as counter electrode and the composite polymer electrolyte was used as both electrolyte and separator. For comparison, the commercial PP/PE/PP film soaked with standard electrolyte (1 mol L^{-1} $LiPF_6$ (DMC:DEC:EC=1:1:1, w/w/w)) was also used as both electrolyte and separator in the same cell configuration. Cathode electrodes were prepared by mixing 80 wt% $LiFePO_4$ material power, 10 wt% PVDF and 10wt% acetylene black in N-methylpyrrolidone (NMP) solvent. The mixed slurry was then coated onto aluminum foil. After vacuum drying at 120℃ for 24 h, the dried electrode was cut into disks and compressed by a roller at room temperature to make a smooth and compact electrode structure. Disks of similar surface area, thickness and weight were selected and stored in an argon-filled glove box.

3. RESULTS AND DISCUSSION

3.1. Physical properties characterization

Fig. 1 shows the SEM images of the PP/PE/PP film and the dried composite polymer film. The PP/PE/PP film (Fig. 1 (a)) owns the porous structure with small pores distributed homogenously. After coated with the polymer, the surface is covered by the transparent polymer layer and the porosity nature of the PP/PE/PP film still exists (Fig. 1 (b)). The image of the polymer coating is magnified in Fig. 1 (c), the spongy and porous features of the polymer layer are obviously obtained, which will be beneficial for the ability of absorbing the electrolyte.

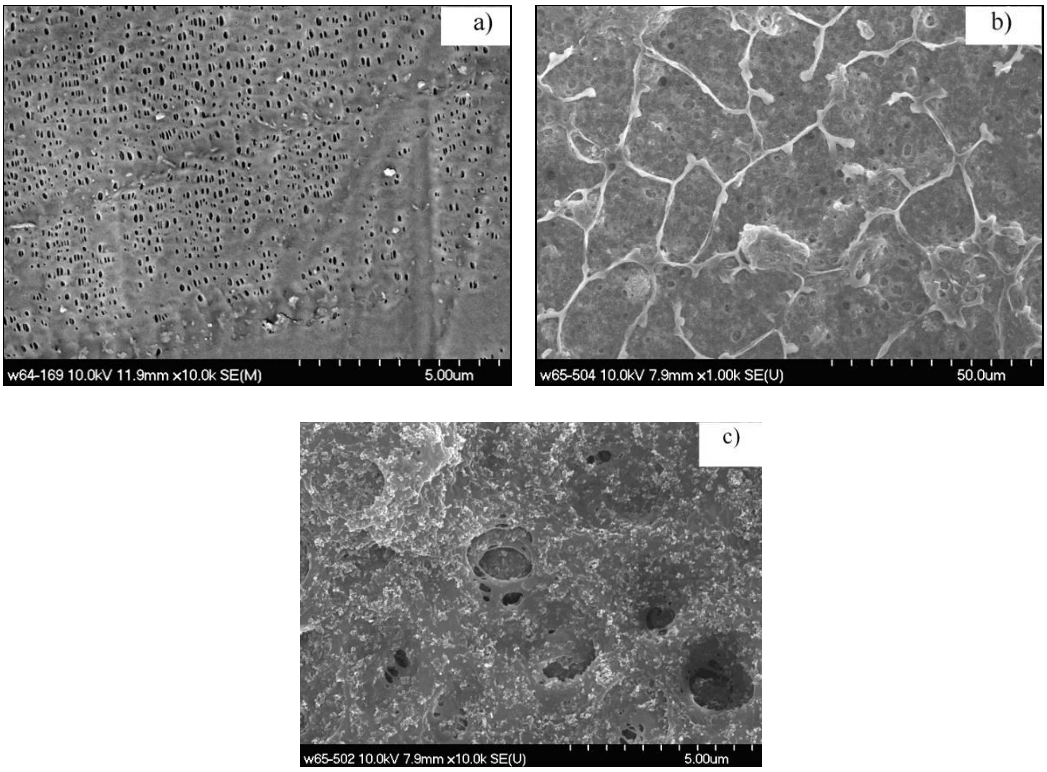

Figure 1. SEM images of (a) PP/PE/PP film, (b) dried composite polymer film (low magnification) and (c) dried composite polymer film (high magnification)

Before soaking the electrolyte, the weight (w_0) of the dried composite polymer film is 14.7 mg and the thickness is 48μm which is a little thicker than the PP/PE/PP film (34 μm). After soaking, the weight increases to 36.0 mg (w) and the thickness expands to 63 μm (l). By application of equation (1), the absorptance is calculated to be 145 %, which is larger than the 130 % of the PP/PE/PP film (whose w_0 and w is 14.4 mg and 33.1 mg respectively). This enhanced absorptance is supported by the spongy and porous features of the morphology observed in SEM images.

Fig. 2 shows the plot of the mechanical strength test and the parameters are summarized in Table 1.

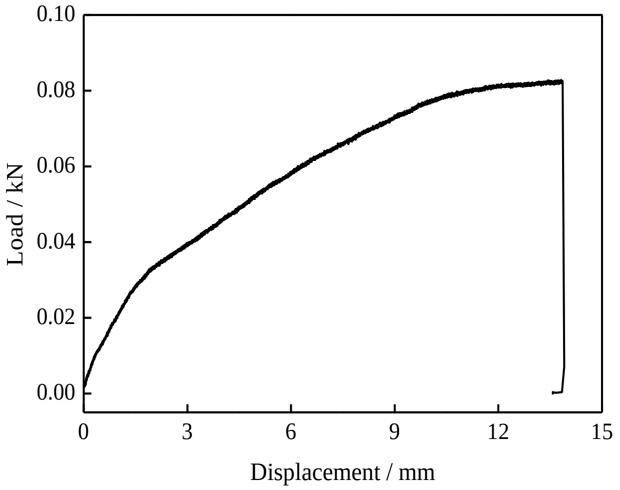

Figure 2. Mechanical strength test of the dried composite polymer film

Table 1. Mechanical strength parameters

Lengthways pull stress	Maximal load	Maximal displacement	Area	Pull strength
Dried composite polymer film	82.80 N	13.82 mm	7.5×10^{-7} m^2	110.40 MPa
PP/PE/PP film	88.84 N	3.84 mm	1.0×10^{-6} m^2	88.84 MPa

The maximal lengthways pull strength is the most important factor to evaluate the mechanical properties. As is shown in Table 1, the maximal lengthways pull strength of the composite polymer film is 110.40MPa, which is larger than that of PP/PE/PP film (88.84 MPa). By simple treated with the commercial PP/PE/PP film, the improved mechanical strength is obtained, which will be beneficial for the cycling performance of Li/$LiFePO_4$ batteries. As we all know， the maximal displacement associates with the elasticity and ductility of the materials. As is shown in Table 1, when the similar maximal load applied on the commercial PP/PE/PP film and the composite polymer electrolyte, the maximal displacement of the composite polymer film is 13.82 mm, which is larger than that of PP/PE/PP film (3.84 mm). This indicates that the composite polymer film is an elastic and ductile material and appropriate for flexible packing.

3.2 Electrochemical characterization

Fig. 3 shows the Nyqiust curve of the SS/composite polymer electrolyte/SS blocking cell. The measured Nyquist plot exhibits an approximately straight line from real axis, which reflects that Li^+ conductivity is mainly dependent on the liquid electrolyte encapsulated in the polymer film matrixes. From the intercept of the plot on the real axis, the value of R_b is found to be 7.42 Ω, thus the value of σ is 1.12×10^{-3} S cm^{-1}, which is comparative to the standard electrolyte for lithium ion batteries. In the previous reports, the ionic conductivity of some polymer electrolyte rarely reached 10^{-3} S cm^{-1} at room temperature[12-14]. The increased ionic conductivity of the composite polymer electrolyte is attributed to the improved ion transport properties of the composite polymer layer which is able to widen the ion-conductive pathways.

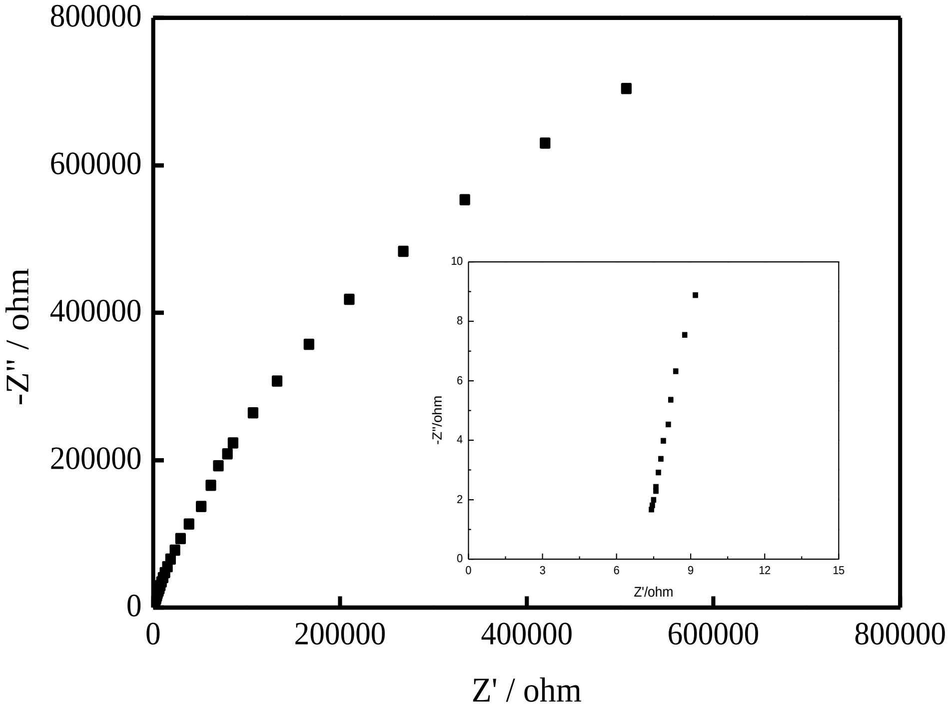

Figure 3. Nyquist plot of the blocking cell (SS/composite polymer electrolyte/SS)

Fig. 4 plots the LSV of the composite polymer electrolyte and there is no anodic spikes observed from 0V to 4.5V. The electrochemical stability window of the composite polymer electrolyte is about 4.5 V, which means that various cathodes, from relative low voltage to high voltage species, can be assembled with this composite polymer electrolyte. $LiFePO_4$ cathode material has the most suitable characteristics for application as EV and HEV batteries in terms of cost and stability. The work voltage of the $LiFePO_4$ is 3.4V[15], and the prepared composite polymer electrolyte can be assembled with the $LiFePO_4$ cathode.

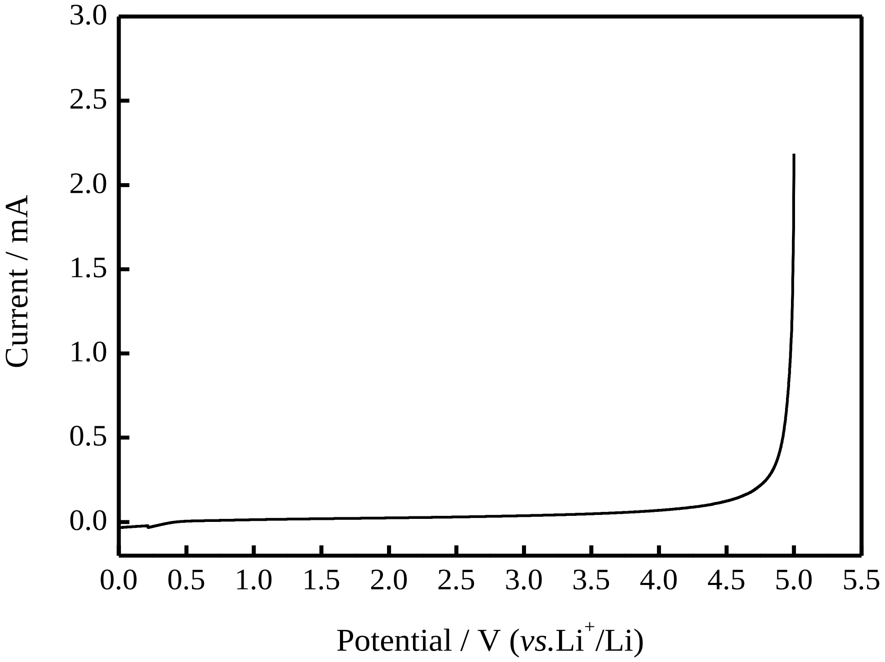

Figure 4. LVS diagrams of the composite polymer electrolyte

Fig.5(a) shows the initial voltage profiles of the Li/$LiFePO_4$ battery assembled with the composite polymer electrolyte. And the initial voltage profiles of the Li/$LiFePO_4$ battery assembled with the commercial PP/PE/PP film soaked with standard electrolyte (1 mol L^{-1} $LiPF_6$ (DMC:DEC:EC=1:1:1, w/w/w)) is present in Fig.5(b).

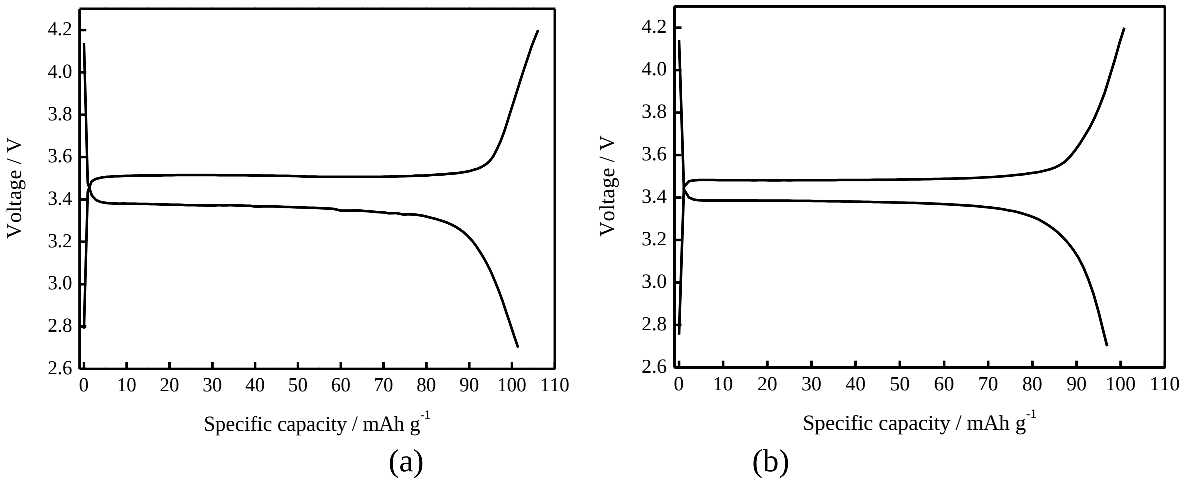

Figure 5. Initial voltage profile of the Li/$LiFePO_4$ cell. (a) PP/PE/PP film in 1 mol L^{-1} $LiPF_6$ (DMC:DEC:EC=1:1:1, w/w/w) used as the electrolyte, (b) composite polymer electrolyte used as the electrolyte

The parameters of Fig. 5 are summarized in Table 2. As is shown in Table 2, the initial charge capacity of the cell with the composite polymer electrolyte is 106.10 mAh g^{-1}, which is a little more than the cell with the PP/PE/PP film (soaked with the 1 mol L^{-1} $LiPF_6$ in DMC:DEC:EC=1:1:1, w/w/w) (the initial charge capacity is 100.83). The coulombic efficiency is 95.6 % and 96.1 % for the cells with the two kinds of the electrolytes, respectively. These indicate that the composite polymer electrolyte obtained by simply treating the commercial PP/PE/PP film does not have any adverse effect on either initial capacity or coulombic efficiency.

Table 2. Parameters of the initial voltage profiles of the Li/$LiFePO_4$ in different electrolyte

Electrolyte	Charge specific capacity / mAh g^{-1}	Discharge specific capacity / mAh g^{-1}	Coulombic efficiency / %
composite polymer electrolyte	106.10	101.41	95.6
PP/PE/PP film soaked with 1 mol L^{-1} $LiPF_6$ in DMC:DEC:EC=1:1:1, w/w/w	100.83	96.93	96.1

Because the battery applied in EV and HEV always needs to work at high temperature, the characterization of high temperature performance is of significance for electrolyte. Fig. 6 compares the variation of discharge specific capacity vs. cycle number obtained from Li/$LiFePO_4$ cells at 60℃. The cell with the commercial PP/PE/PP film displays around 17 % capacity loss at the 100th cycle, which is better than that reported newly in Ref. 11. The cell with composite polymer electrolyte displays only around 2 % capacity loss at the 100th cycle, which is preferable compared with open reports. These indicate that prepared composite polymer electrolyte could be treated as the possible electrolyte candidate for Li/$LiFePO_4$ batteries.

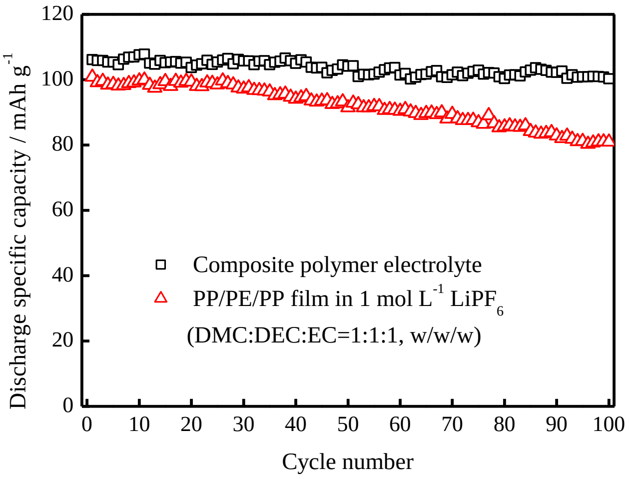

Figure 6. Cycle performance of the Li/$LiFePO_4$ cell. (a) PP/PE/PP film in 1 mol L^{-1} $LiPF_6$ (DMC:DEC:EC=1:1:1, w/w/w) used as the electrolyte, (b) composite polymer electrolyte used as the electrolyte

4. CONCLUSIONS

The composite polymer film was prepared by coating commercial PP/PE/PP film with PVDF-based polymer, SiO_2 and the composite polymer electrolyte was obtained by immersing the composite polymer film into the standard electrolyte (1 mol L^{-1} $LiPF_6$ (DMC:DEC:EC=1:1:1, w/w/w). The mechanical strength and the absorbing ability of the prepared composite polymer film is enhanced greatly by simple treated with the commercial PP/PE/PP film. And the treatment does not have any adverse effect on either ionic conductivity or initial capacity. Meanwhile, the Li/$LiFePO_4$ batteries with the obtained composite polymer electrolyte exhibit excellent capacity retention even after 100 cycles galvanostatically at 60 ℃. These demonstrate that the prepared composite polymer electrolyte could be a promising electrolyte candidate for Li/$LiFePO_4$ batteries used in electric vehicles and hybrid electric vehicles.

ACKNOWLEDGEMENTS
The work is supported by Project of National Nature Science Foundation of China (No. 21276057) and Natural Scientific Research Innovation Foundation in Harbin Institute of Technology (No. HIT. NSRIF. 2009121).

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