All solid-state lithium-polymer battery using poly(urethane acrylate)/nano-SiO$_2$ composite electrolytes

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Abstract

New composite polymer electrolytes composed of polyurethane acrylate (PUA), nano-size SiO$_2$ as a ceramic filler, and LiN(CF$_3$SO$_2$)$_2$ as a lithium salt were examined in an all-solid-state lithium-polymer battery (Li/PUA-SiO$_2$/Li$_{0.33}$MnO$_2$). The addition of hydrophobic SiO$_2$ could increase the ionic conductivity of polymer electrolyte about one-fold. The dynamic modulus of polymer electrolyte increased 50 and 150% by adding 9.1% hydrophobic and hydrophilic SiO$_2$, respectively. The addition of nano-size SiO$_2$ powders enhanced greatly the interfacial stability between polymer electrolytes and lithium electrode. The capacity fading of the cell could be improved by the addition of nano-size SiO$_2$ powders. The cycling performance of the cell reached about 75 and 45% of initial capacity (192 mAh g^{-1}) after 100, and 500 cycles, respectively, with an efficiency of charge–discharge of about 100% at 60 °C.
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1. Introduction

Solid polymer electrolytes have attracted a great deal of interest for the last 20 years. The major motivation for this interest is a technological application: rechargeable and high energy density power sources. The research and development efforts are mainly focused on ambient temperature conductivity, the cationic transport number, and electrode–electrolyte interfacial reactions [1–9]. However, despite more than two decades of scientific and industrial research, all solid-state lithium polymer electrolyte battery system is still not available commercially. The main problems include: (a) low ionic conductivity at ambient temperature, (b) certain reactivity with the lithium metal electrode, and (c) low mechanical strength for use as an electrolyte separator. Large research efforts have been made to optimize the properties of poly-mer electrolytes to satisfy the need of all solid-state lithium-polymer electrolyte battery. Among the studies, introduction of ceramic fillers is one of the most successful ways. Croce et al. [10,11] demonstrated that the addition of ceramic fillers (such as SiO$_2$, TiO$_2$, Al$_2$O$_3$, γ-LiAlO$_2$) for the PEO-based electrolyte results in an enhancement of the ionic conductivity, an increase of cation transference numbers, and an improvement of the interfacial stability between the polymer electrolytes and the lithium metal electrode.

Recently, we have developed a new solvent-free polymer electrolyte based on poly(urethane acrylate) (PUA) [12,13]. We have found that the polymer electrolyte can be directly membranous in the absence of any solvent, and can be cast directly on a lithium foil or a composite cathode. However, there are still some drawbacks for the polymer electrolyte: (1) a lower ionic conductivity (about 1.1×10^{-4} S cm^{-1} at 60 °C); (2) lower mechanical strength, when used as an electrolyte separator; (3) a faster capacity fading in the Li/Li$_{0.33}$MnO$_2$ system.

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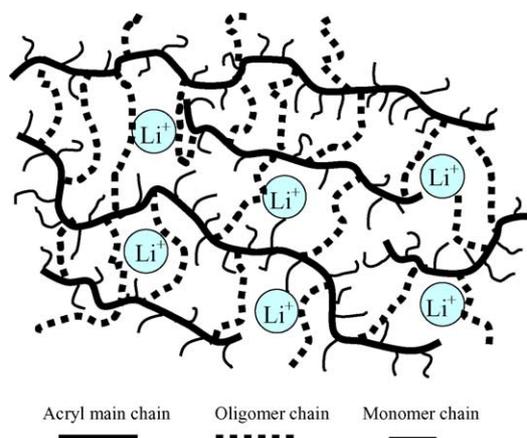 *E-mail address:* sakai-tetsuo@aist.go.jp (T. Sakai).

Fig. 1. Schematic structure of urethane acrylate polymer electrolyte.

In this paper, we plan to use different surface modified nano-size SiO_2 powders to improve the properties of the polymer electrolyte based on polyurethane acrylate (PUA). We not only investigate the effects of different surface modified nano-size SiO_2 powders on ionic conductivity and mechanical strength of the polymer electrolyte, but also study the charge–discharge properties in detail.

2. Experimental

Polymer electrolyte films used here were prepared by a solvent-free casting technique in dry air. Urethane acrylate (UA) was synthesized from 2-hydroxyethyl acrylate (Osaka Organic Chemical Industry), isophorone diisocyanate (IPDI) (Degussa, Japan) and polyoxyethylene polyoxypropylene glycol (P(EO/PO), Asahi Denka). The detailed synthesis condition of the poly(urethane acrylate) (PUA) was reported elsewhere [13,14]. Schematic structure of the polymer electrolyte film is shown in Fig. 1.

Methoxypolyethylene glycol monoacrylate (Nof Corporation) as a monomer, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (Kishida Chemical) and 1-hydroxy cyclohexyl phenyl ketone (Ciba Specialty Chemicals) as a photoinitiator were dissolved into UA, and stirred to form a homogenous mixture. The mixture then was irradiated by an UV light to yield homogenous and mechanically stable membranes of average thickness $100 \,\mu m$. Nano-composite polymer electrolytes were prepared by mixing nano-size SiO_2 powders (Nippon Aerosil) to the above polymer electrolyte in a dry procedure before the UV radiation. All of the ce-

ramic powders were dried at $160\,^{\circ}C$ under vacuum for 48 h before use. Some properties of those ceramic powders were summarized in Table 1.

The active material, $Li_{0.33}MnO_2$, was prepared by preheating a mixture of $LiNO_3$ and MnO_2 at $260\,^{\circ}C$ for 5 h, followed by heating at $320\,^{\circ}C$ for 12 h in air [15]. The composite cathode was prepared by mixing proper amounts of $Li_{0.33}MnO_2$ with polyethyleneglycol dimethylether (Aldrich Chemical), LiTFSI and carbon (Ketjen black). The mixture was strongly stirred before casting on an aluminum substrate. After the cathode composite material was dried at $80\,^{\circ}C$ under vacuum for 48 h, it was pressed into a thin film of about $50\,\mu m$ in thickness. The typical weight ratio of active material, carbon, and PEG-LiTFSI in the cathode mixture was 65, 5 and 30 wt.%, respectively.

The electrical conductivity of the polymer electrolyte films and the interfacial resistance between the polymer electrolyte and the electrodes (Li metal anode and composite cathode) were measured by an ac impedance method using a Solartron 1260 frequency analyzer. Stainless steel blocking electrode cells were used for conductivity measurements, and symmetrical non-blocking lithium electrode (or the composite cathode) cells were used to investigate the interfacial phenomena. The ac oscillation amplitude was 10 mV, and the impedance spectra were collected by recording 10 points per decade over a frequency range from 10 kHz to 0.1 Hz in conductivity measurements, and from 100 kHz to 0.1 Hz in interfacial resistance measurements.

Dynamic modulus of polymer electrolyte films was measured at a frequency of 10 Hz with a heating rate of $2.5\,^{\circ}C\,min^{-1}$.

Test cells for cycling performance were assembled by sandwiching the polymer electrolyte film between a lithium foil and the composite cathode. The charge–discharge tests were performed galvanostatically at a current rate of $C/4$ ($0.05\,mA\,cm^{-2}$, $50\,mA\,g^{-1}$) and at a regulated cut-off voltage between 2.0 and 3.5 V at $60\,^{\circ}C$.

3. Results and discussion

3.1. Electrochemical stability window of new polymer electrolytes

Although high lithium ion conductivity and low interfacial resistance are necessary to obtain high performance poly-

Table 1
Properties of SiO_2 ceramic additives

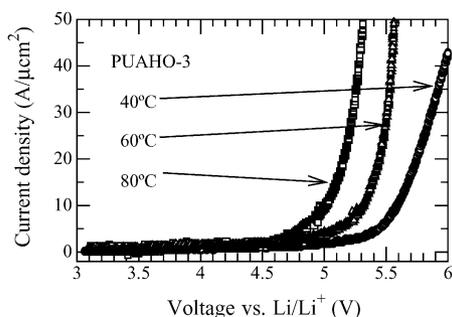| Sample	Amount (wt.%)	Size (nm)	Surface area ($m^2\,g^{-1}$)	Surface groups	Type of surface
PUA	0				
PUAHI-3	2.9	12	200	Si—OH	Hydrophilic, weakly acidic
PUAHI-5	4.8	12	200	Si—OH	Hydrophilic, weakly acidic
PUAHI-9	9.1	12	200	Si—OH	Hydrophilic, weakly acidic
PUAHO-3	2.9	12	140	Si—$(CH_3)_3$	Hydrophobic, neutral
PUAHO-5	4.8	12	140	Si—$(CH_3)_3$	Hydrophobic, neutral
PUAHO-9	9.1	12	140	Si—$(CH_3)_3$	Hydrophobic, neutral

Fig. 2. Linear sweep voltammogram of Li/PUA-SiO$_2$/SS (stainless steel blocking electrode) cell at a scan rate of 0.1 mV s^{-1} at 40, 60, and 80 °C.

mer lithium batteries, a high polymer electrolyte decomposition voltage is also very important for high performance secondary lithium polymer batteries. Decomposition of polymer electrolytes can cause a drastic decrease of the cathode capacity upon cycling. An important parameter in the characterization of a given polymer electrolyte is electrochemical stability window. Ordinarily, the electrochemical stability window is evaluated by linear sweep voltammetry using a two-electrode cell with a stainless steel working electrode and a lithium metal counter electrode. Fig. 2 shows typical voltammetry results of the PUA + 2.9% SiO$_2$ (PUAHO-3) system at various temperatures. We notice that the sweep could be extended to over 4.50 V at 60 °C versus Li/Li$^+$ in the anodic region before observing appreciable current, when the sweep rate was 0.1 mV s^{-1}. However, the electrochemical stability window will become lower than the above value in a real cell due to the reaction between polymer and cathode active materials. Here, we have also examined the dependence of the cut-off voltage on the cycling performance of the Li/PUAHO-3/Li$_{0.33}$MnO$_2$ cell. Fig. 3 shows the cut-off voltage dependence on the discharge capacity versus cycling time curves at 60 °C, where the capacity was calculated from the amount of Li$_{0.33}$MnO$_2$ in the cathode mixture. As the charge voltage rose to 4.4 V, the cell capacity decreased rapidly with the cycling time. However, no significant capacity fade was observed, when the charge voltage was below 4.2 V. From these results, we can conclude that the stable voltage (versus Li/Li$^+$) of the nano-composite polymer electrolytes in the Li/Li$_{0.33}$MnO$_2$ system is below 4.2 V at 60 °C.
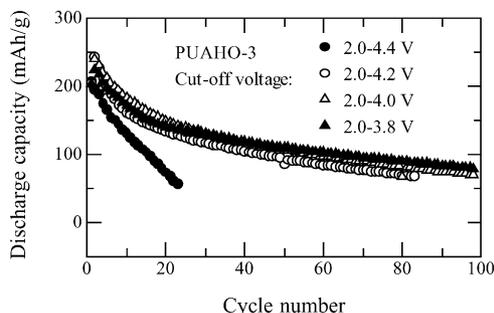

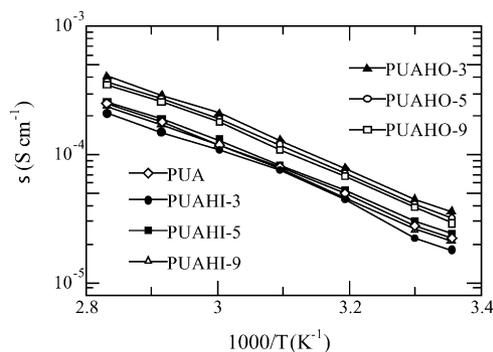Fig. 3. Cut-off voltage dependence of discharge capacity on cycles at 60 °C.

Fig. 4. Ionic conductivities of composite polymer electrolytes with either hydrophilic or hydrophobic SiO$_2$ powders.

3.2. Ionic conductivity and dynamic modulus of composite polymer electrolytes

We investigated the effects of hydrophilic and hydrophobic SiO$_2$ powders on the ionic conductivity of the PUA system. Fig. 4 shows the ionic conductivity of the PUA-SiO$_2$ system taken on the heating run. According to these observations, the addition of hydrophilic SiO$_2$ powders has not obviously improved the ionic conductivity of polymer electrolyte. However, the conductivity of the composite polymer electrolyte with hydrophobic SiO$_2$ powders does increase by about one-fold at all temperatures. The detailed reason for the increasing conductivity is still not clear.

Fig. 5 shows the dynamic moduli of composite polymer electrolyte films with hydrophilic and hydrophobic silica. The results show that the tensile dynamic modulus of composite polymer electrolyte films increased 50 and 150% by adding 9.1% hydrophobic and hydrophilic SiO$_2$ powders, respectively. Especially, above 150 °C, the polymer electrolyte with hydrophilic SiO$_2$ showed the better mechanical property.

3.3. Interfacial stability between composite polymer electrolytes and electrodes

The interfacial resistances between the electrodes and the polymer electrolytes are shown in Figs. 6 and 7, respectively,
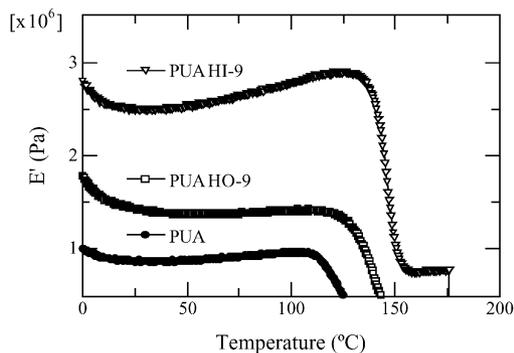

Fig. 5. Dynamic moduli of polymer electrolyte films with either hydrophilic or hydrophobic SiO$_2$ powders.
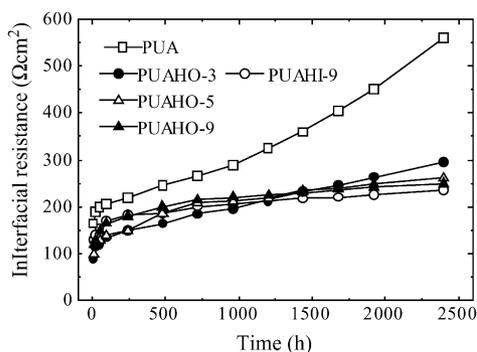
Fig. 6. Time dependence of interfacial resistances of the Li/PUA-SiO$_2$/Li cell stored in OCV conditions at 60 °C.

where the resistances were measured for the cell, Li (or composite cathode)/PUA-SiO$_2$/Li (or composite cathode), kept under open-circuit conditions at 60 °C. The composite cathode consists of Li$_{0.33}$MnO$_2$–polymer electrolyte–carbon (65:30:5 weight ratio). From Fig. 6, the lithium interfacial resistance with the ceramic-free polymer film increased consistently with time. Contrast to this, the lithium interfacial resistance with the nano-size SiO$_2$ polymer films was almost independent on time. This shows that the addition of nano-size SiO$_2$ powders would improve the interfacial stability between the polymer electrolyte and the lithium metal electrode, especially for the hydrophilic nano-SiO$_2$ powder. However, as shown in Fig. 7, the interfacial resistances between the composite cathode and the polymer electrolyte increased consistently upon time, even though the addition of nano-size SiO$_2$ powders slightly slowed the ascent. The significant increase of the interfacial resistance between the cathode and the polymer electrolyte could be the main reason for the capacity fading of the cell.

Another method to characterize the interfacial stability between lithium electrode and the polymer electrolyte is to monitor the overvoltage during lithium plating/stripping cycles. The voltage change during cycling is directly linked to the reversibility of the lithium plating/stripping which affects the battery cyclability. A typical experiment is performed by applying a constant current (0.1 mA cm^{-2}) to the cell for 3600 s in each direction. Fig. 8 shows the overvoltage changes of the
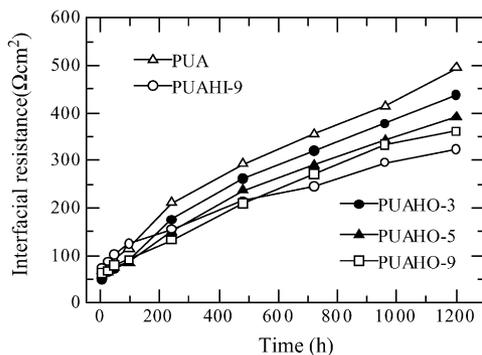

Fig. 7. Time dependence of interfacial resistances in a symmetric Li$_{0.33}$MnO$_2$/PAU-SiO$_2$/Li$_{0.33}$MnO$_2$ cell stored in OCV conditions at 60 °C.
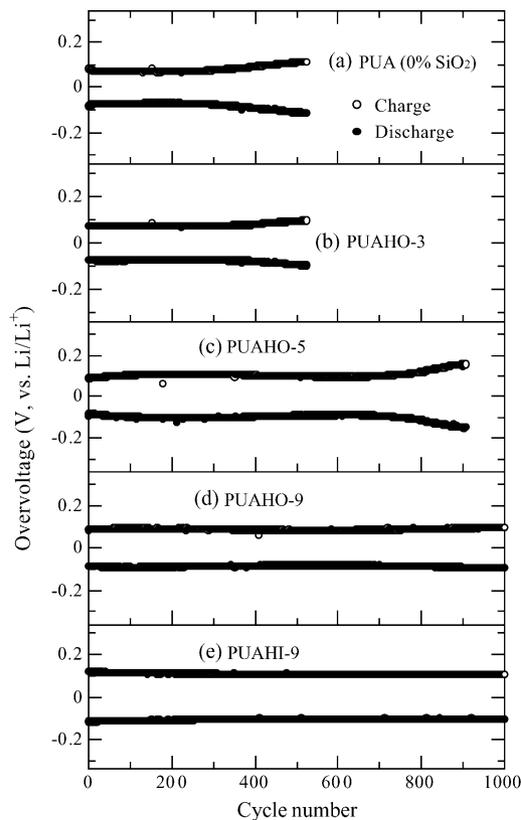

Fig. 8. Change in overvoltage upon cycling at a current density of 0.1 mA cm^{-2} for 1 h for symmetric Li/PAU-SiO$_2$/Li cells containing various electrolyte films at 60 °C.

symmetric Li/PUA-SiO$_2$/Li cells containing the ceramic-free and various amounts of SiO$_2$ additive polymer electrolyte films at 60 °C. It is evident from the results in Fig. 8 that the cell containing 9.1 wt.% nano-size SiO$_2$ additive polymer electrolyte (see Fig. 8(d) and (e)) shows a very stable voltage above 1000 cycles, indicative of a high stability with metal lithium. However, other cells show a voltage increase upon cycling time for the ceramic-free electrolyte after 300 cycles (see Fig. 8(a)) for 2.9 wt.% SiO$_2$ additive electrolyte after 400 cycles (see Fig. 8(b)), and for 4.8 wt.% SiO$_2$ additive electrolyte after 700 cycles (see Fig. 8(c)). We would conclude that the addition of surface modified nano-size SiO$_2$ improves greatly the lithium interface stability; moreover, the amount of SiO$_2$ powders should be more than 9.1 wt.%.

3.4. Cyclic performance of the Li/PUA-SiO$_2$/Li$_{0.33}$MnO$_2$ cell

The layered phase Li$_{0.33}$MnO$_2$ is an attractive cathode material for rechargeable lithium batteries, because of its high specific capacity and low cost compared to LiCoO$_2$. The cyclic performance of the cells with a lithium metal anode and Li$_{0.33}$MnO$_2$ composite cathode using the PUA electrolyte films of various thicknesses (50–150 μm) at 60 °C is shown in Fig. 9. The Li$_{0.33}$MnO$_2$ cathode showed a high initial capacity of about 200 mAh g^{-1}, and a fast capacity
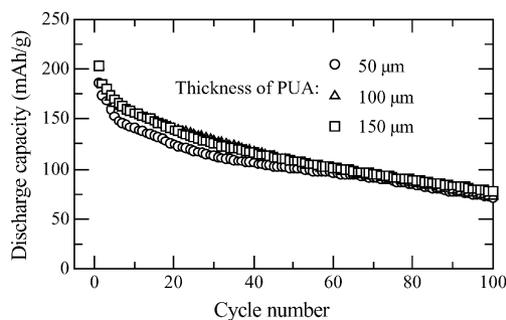
Fig. 9. Cyclic performance of Li/PUA/Li$_{0.33}$MnO$_2$ cells with various thicknesses of polymer electrolyte films at 60 °C.

Fig. 11. Cyclic performance of composite polymer electrolytes with various amounts of hydrophobic SiO$_2$ powders.

Fig. 12. Cyclic performance of the Li/PUAHI-9/Li$_{0.33}$MnO$_2$ cell at 60 °C.

fading appeared with cycling time. We have also found that charge–discharge properties were not obviously influenced by the thickness of PUA films from 50 to 150 μm. The fast capacity fading may be due to the fast increase of interfacial resistances between the lithium metal anode and the polymer electrolyte, or between the composite cathode and the polymer electrolyte (see Figs. 6 and 7).

Fig. 10 shows the effects of hydrophilic SiO$_2$ powders on the cyclic performance of the cells in the PUA-SiO$_2$ system. The fading rates of the cathode capacity upon cycling at 60 °C were different from the electrolyte films with different amounts of SiO$_2$ powders. The fading rate depended on the properties of polymer electrolyte films. The addition of hydrophilic SiO$_2$ to the polymer electrolyte could improve the cyclic performance of the cells (compared with PUA sample). The lowest fading rate was observed at the PUAHI-9 sample with 9.1 wt.% hydrophilic nano-SiO$_2$ powders. The better charge–discharge properties should be attributed to the improvement of the lithium interface stability after the addition of suitable amount of SiO$_2$.

Fig. 11 shows the effects of hydrophobic SiO$_2$ powders on the cyclic performance of the cells in the PUA-SiO$_2$ system at 60 °C. Like the hydrophilic silica, the hydrophobic SiO$_2$ powders also improved the cyclic performance of cells. With the increase of silica amount, the cycling property of the cells was getting better (PUAHO-9 > PUAHO-5 > PUAHO-3 > PUA).
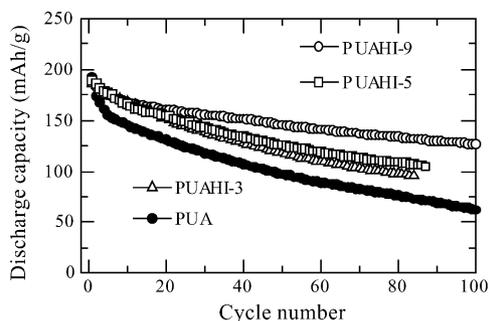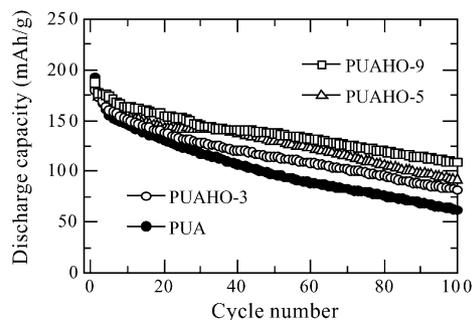
Fig. 12 shows the long cycling test for the PUAHI-9 sample with 9 wt.% hydrophilic SiO$_2$ powders. The charge–discharge efficiency of the cell was about 100%. The cell also showed a good cycle life and retention of 75, 55 and 45% of the initial capacity (192 mAh g^{-1}) after 100, 300 and 500 cycles at 60 °C, respectively. To our knowledge, the cyclic performance of the cell is so far the best in the all-solid-state lithium-polymer electrolyte battery for the Li$_{0.33}$MnO$_2$ cathode.

4. Conclusions

1. Composite polymer electrolytes composed of urethane acrylate, nano-size SiO$_2$ as a ceramic filler, and LiN(CF$_3$SO$_2$)$_2$ as a lithium salt showed a high decomposition voltage of around 4.2 V (versus Li/Li$^+$) at 60 °C.
2. The addition of hydrophobic SiO$_2$ could increase the ionic conductivity of polymer electrolyte about one-fold. The tensile modulus of polymer electrolyte films increased 50 and 150% by adding 9.1% hydrophobic and hydrophilic SiO$_2$, respectively.
3. Only the addition of more than 9.1 wt.% nano-size SiO$_2$ powders could improve significantly the interfacial stability between the polymer electrolyte and lithium electrode.
4. The all-solid-state lithium polymer cell (Li/PUA/Li$_{0.33}$MnO$_2$) showed a high initial capacity of about 192 mAh g^{-1}, and a faster capacity fading. However, the capacity fading could be improved by the

Fig. 10. Cyclic performance of composite polymer electrolytes with various amounts of hydrophilic SiO$_2$ powders.

addition of hydrophilic nano-size SiO_2 powders. The long cycling performance of the cells reached about 75, 55 and 45% of initial capacity after 100, 300 and 500 cycles, respectively, with an efficiency of charge–discharge of about 100% at 60 °C.

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