Gel-type polymer electrolytes with different types of ceramic fillers and lithium salts for lithium-ion polymer batteries

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Abstract

Gel-type polymer electrolytes are prepared using PVdF/PEGDA/PMMA, $LiPF_6$/$LiCF_3SO_3$ mixed lithium salts and ceramic fillers such as Al_2O_3, $BaTiO_3$ and TiO_2. The electrochemical properties of these electrolytes, such as electrochemical stability, ionic conductivity and compatibility with electrodes are investigated in addition to the physical properties. The charge–discharge performances of lithium-ion polymer batteries using these get-type polymer electrolytes are investigated. The gel-type polymer electrolytes containing a mixed lithium salt of $LiPF_6$/$LiCF_3SO_3$ (10/1, wt.%) exhibit more stable ionic conductivity and lower interfacial resistance than those containing only $LiPF_6$. In addition, an Al_2O_3 filler improves interfacial stability between the electrode and the polymer electrolyte. Stacking cells (MCMB 1028/$LiCoO_2$, 8 cm × 13 cm × 7 ea) composed of gel-type polymer electrolytes based on PVdF/PEGDA/PMMA, $LiPF_6$/$LiCF_3SO_3$ (10/1, wt.%) and Al_2O_3 filler maintain 95% of initial capacity after 100 cycles at a C/2 rate.
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1. Introduction

In order to solve the problems of irreversibility and stability of lithium metal in lithium batteries, attempts have been made to substitute the liquid electrolyte with polymer electrolyte. The aim is to inhibit dendritic growth of the lithium electrode without affecting the high capacity of the lithium metal. Conventional membranes for the liquid-electrolyte batteries have high porosity and the pores have a layered structure so that lithium is easily electrodeposited in a dendritic form. By contrast, gel-type polymer electrolytes (GTPEs) do not have pores. A GTPE forms a stable interface because it has less chemical reactivity with lithium metal in comparison with a liquid electrolyte. Lithium-ion polymer batteries have been studied actively since the 1980s. United States Advanced Battery Consortium (USABC), the Nippon Energy Development Organization (NEDO) in Japan, and many companies throughout the world are involved in the development of lithium-ion polymer batteries [1].

Polymer electrolytes have many advantages but there are also many technical problems to be solved. Low electrical conductivity is a particular disadvantage. Since viscosity of a polymer solution is much higher than that of a liquid type, the charge mobility of lithium-ions is correspondingly very low. The power density of lithium-ion polymer batteries is unsatisfactory at room temperature due to the low ionic conductivity and therefore their commercialization is very limited. Accordingly, the development of polymer electrolytes is focused on the enhancement of ionic conductivity. A GTPE is made by the impregnation of liquid electrolyte into the polymer matrix and its ionic conductivity is very close to the conductivity of liquid electrolyte at room temperature. Recently, a GTPE was developed by coating the

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polymer electrolyte on to a porous polyolefin (polyethylene or polypropylene) membrane. This material has good mechanical properties in the battery assembly plant and the increase of the internal resistance is controlled. This technique has been developed by Sony, Motorola and Mitsubishi [2–4], and it is claimed that commercialization is imminent.

In this study, polyvinylidene fluoride (PVdF), poly(methylmethacrylate) (PMMA) and poly[(ethylene glycol) diacrylate] (PEDGA) are blended to make an ultraviolet-cured polymer electrolyte [5,6]. PVdF has good mechanical properties and high ionic conductivity, PMMA has good affinity for the organic electrolyte and PEGDA is a cured oligomer. It is noted that Abraham et al. [7] have made a gel-coated electrolyte by coating and cross-linking an ultraviolet cured oligomer on the surface of a polyolefin membrane [7]. In the present study, the low molecular weight PEGDA oligomer penetrates the pores of the membrane, which are blocked by polymerization of the oligomer so that there is a decrease in ionic conductivity. When PEGDA is blended with PVdF and PMMA, the gel polymer layer is located on the surface of the membrane without penetrating into the pores. In order to form a uniform solid electrolyte interphase (SEI) and increase the mechanical strength of the polymer electrolyte, Al_2O_3, $BaTiO_3$ and TiO_2 ceramic fillers are dispersed in the bulk matrix. $LiPF_6$ and $LiCF_3SO_3$ mixed lithium salts are also used to investigate the interfacial phenomena between the electrode and the electrolyte.

2. Experimental

EDGA oligomer (Aldrich, $d = 1.12\,g\,cm^{-3}$, $M_w = 742$) was used in the liquid state at room temperature without pretreatment. 2-Chlorobenzophenone (Aldrich, F.W. $= 216.67$) was used as the photo-initiator of EGDA and triethylamine (TEA, Aldrich, $d = 0.73\,g\,cm^{-3}$, F.W. $= 101.19$) was employed as a curing accelerator without pretreatment. PVdF (Elf Atochem, Kynar 761), PMMA (Polyscience, $M_w = 350,000$), TiO_2 (Degussa, diameter $= 25\,nm$), $BaTiO_3$ (Aldrich, 50 nm) and γ-Al_2O_3 (Buchler, 30 nm) were used after drying under the vacuum at 80 °C for 24 h.

EGDA oligomer, PVdF and PMMA were mixed in a weight ratio of 2:1.5:1.5 and then 10 wt.% of ceramic filler was dispersed into the mixture. One molar $LiPF_6$/$LiCF_3SO_3$ was dissolved in a mixed solvent (1:1:1, vol.%) of ethylene carbonate (EC, Aldrich), dimethyl carbonate (DMC, Aldrich) and ethyl methyl carbonate (EMC, Aldrich). A 600 wt.% liquid electrolyte component was added to the polymer mixture that was then blended mechanically for 3 h at 300 rpm.

A total of 5 wt.% 2-chlorobenzophenone and 5 wt.% triethylamine (EGDA oligomer base) was added to the polymer mixture solution and mixed at 125 °C. The polymer solution was coated on a polypropylene (PP) membrane (Celgard® 2400, thickness: 20 μm, porosity: 38%) that was attached on the surface of Mylar film preheated at 60 °C. The thickness of the coating layer was 5 μm and PEGDA was cured by ultra-
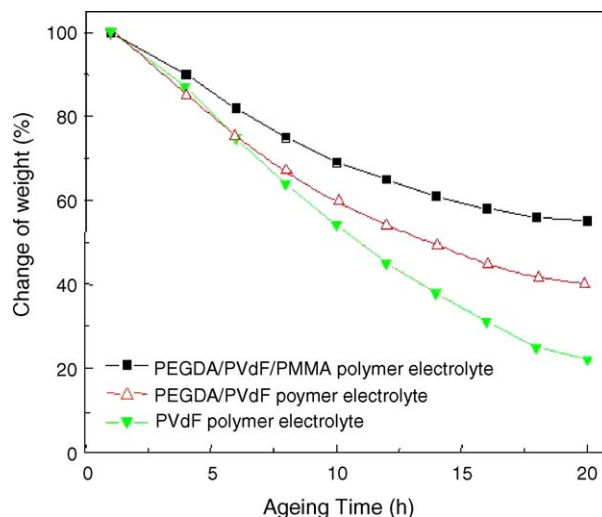

Fig. 1. Weight change of various GTPEs with ageing time at 80 °C.

violet irradiation. The ultraviolet lamp (Sanyo Denki GL20, λ = 325 nm) was rated at 100 W, and the distance between the lamp and the coating layer was about 10 cm. The procedure was performed in a dry room (dew point: −50 °C).

Scanning electro microscopy (Hitachi, S-4200) was used to analyze the cross-section of GTPE electrolyte and to observe the surface of the electrode both before and after the cycling tests.

The electrochemical stability window of GTPE matrix was examined with a potentiostat (EG&G Model 362). The ionic conductivity of the GTPE was measured by means of an ac impedance analyzer (Zahner IM6). The ac frequency range was 10 Hz to 1 MHz and the perturbation voltage was 5 mV.

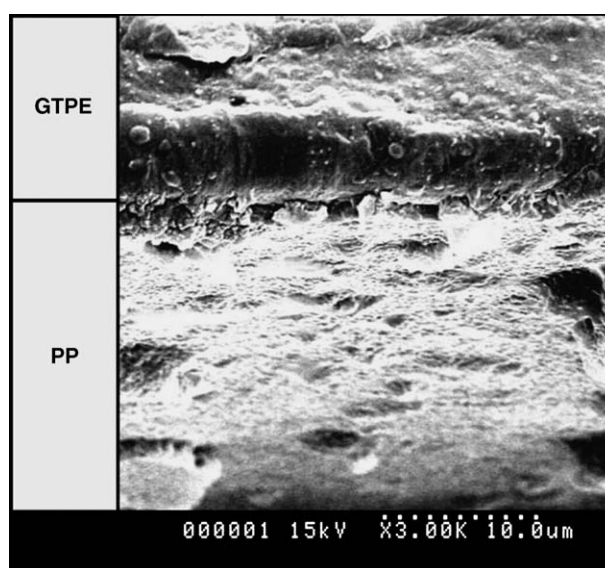The interfacial properties of the lithium electrode and the GTPE were examined with the ac impedance

Fig. 2. Scanning electron micrographs (cross-section) of GTPE film coated directly on the PP membrane.

method. A non-blocking cell with a configuration of Li/GTPE/Li was assembled and the impedance behavior was examined under open-circuit conditions at different temperatures.

Unit cells (8 cm × 13 cm) and stacked cells (8 cm × 13 cm × 7 ea) each composed of a MCMB 1028 carbon anode, a UV-curved GTPE and a $LiCoO_2$ cathode, were assembled. The cycle test was performed at constant cur-

rent over a voltage range of 3.0–4.2 V using a Maccor 4300 battery tester.

3. Results and discussion

The weight changes of various GTPEs with storage time after drying at 80 °C in the dry room are presented in Fig. 1.
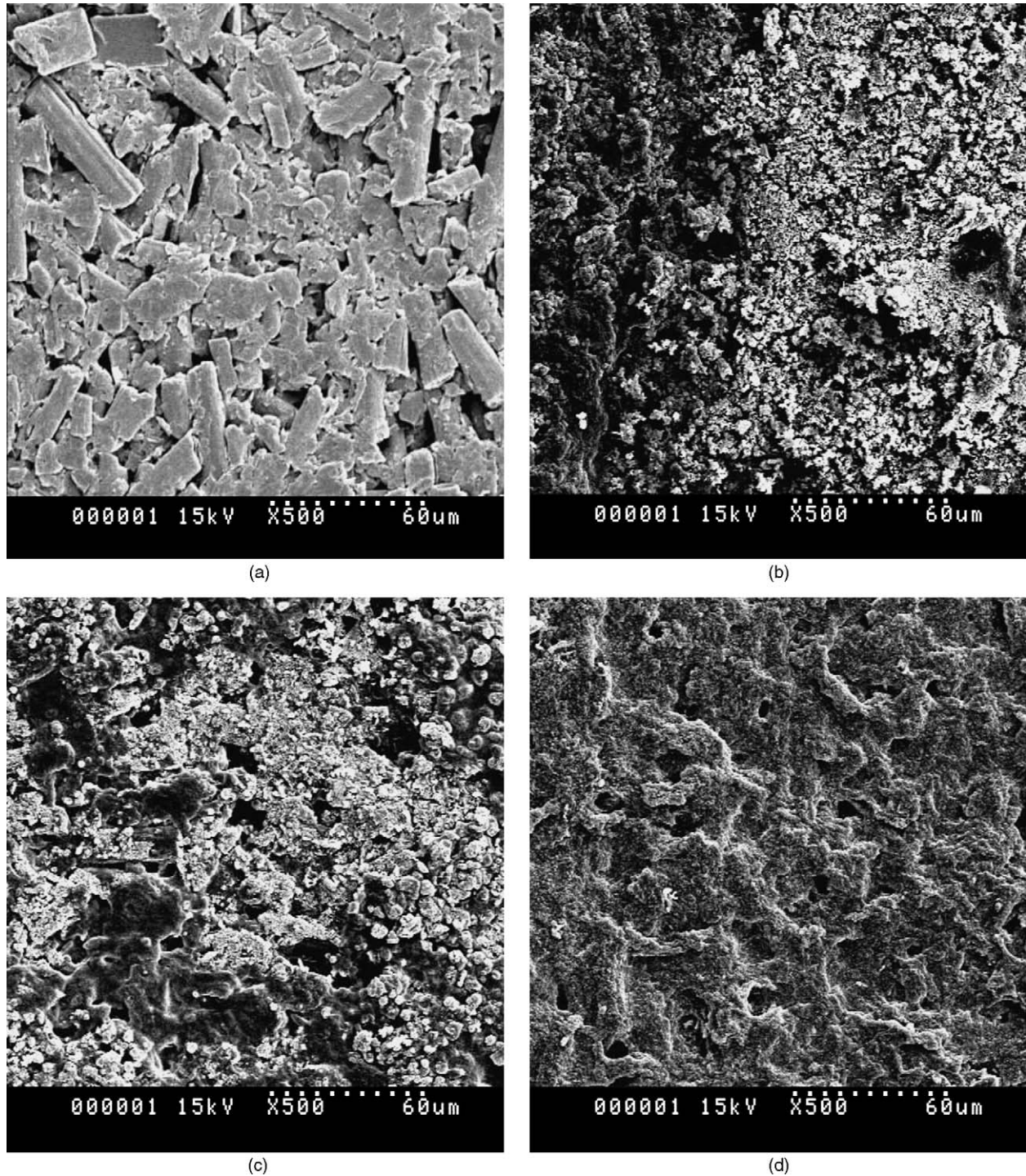

Fig. 3. Scanning electron micrographs of various graphite surfaces after 100 cycles: (a) bare; (b) $LiPF_6$:$LiCF_3SO_3$ (10:1, wt.%); (c) $LiCF_3SO_3$; (d) $LiPF_6$.

The PEGDA shows low electrolyte uptake of 300%, but the retention ability of the electrolyte is excellent because of the compact film structure. In the case of the polymer blend electrolyte, a porous structure is formed due to the addition of PVdF, and the electrolyte solvent evaporates rapidly. The PMMA has a good affinity for organic electrolyte. The addition of PMMA into the organic electrolyte prevents evap-

oration of organic electrolyte solvent, and thus reduces the decrease in ionic conductivity.

The cross-section of the GTPE coated directly on the PP membrane is shown in Fig. 2. The GTPE does not penetrate the pores of the PP membrane and form a different layer, as shown in Fig. 2. The adhesion between GTPE and PP membrane is excellent.
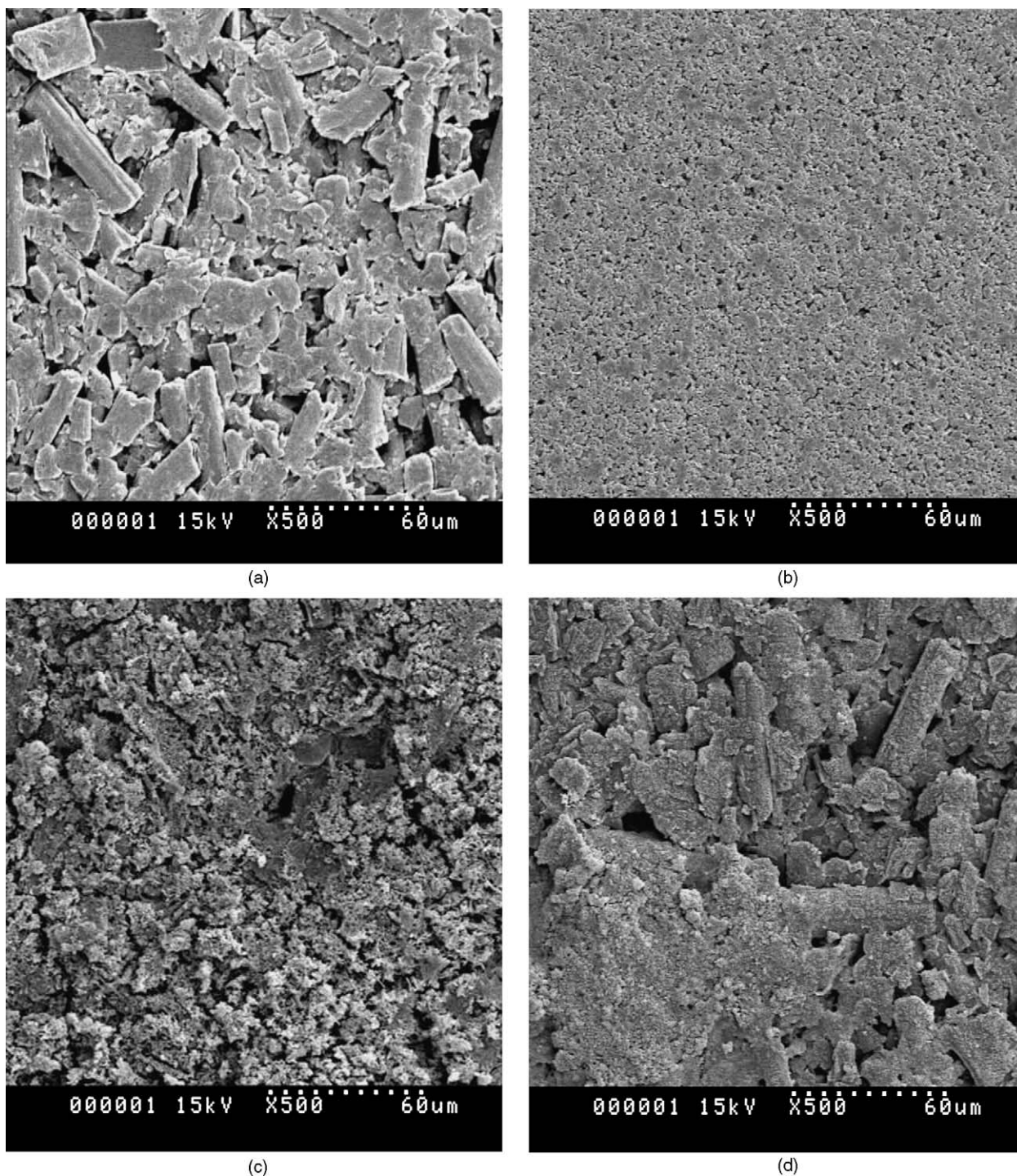

Fig. 4. Scanning electron micrographs of graphite surface after 100 cycles: (a) bare; (b) Al_2O_3; (c) $BaTiO_3$; (d) TiO_2.

Scanning electro micrographs of various graphite surfaces after 100 cycles are given in Fig. 3. The GTPE was used as the membrane. When only $LiPF_6$ is used as the lithium salt, PF_6 decomposes to form a LiF film, which has an inhomogeneous morphology. This film causes a decrease in the transfer path of the lithium-ions, so that the capacity of battery is decreased during charge–discharge cycles. By contrast, when $LiPF_6$ and $LiCF_3SO_3$ mixed lithium salts are used, a uniform SEI film is formed.

The surface structure of graphite anodes with different ceramic fillers that have been subjected to 100 cycles is shown in Fig. 4. With Al_2O_3 ceramic fillers, the surface of the graphite is smooth and has a uniform morphology. This effect may improve the cycle performance of cell because it prevents local current flow during the transfer of lithium-ions [8].

The electrochemical stability windows of GTPEs containing different lithium salts at room temperature are demonstrated in Fig. 5. Lithium rechargeable batteries generally operate between 3.0 and 4.5 V, but the local voltage can rise above 4.5 V. Thus, the electrochemical stability window must be greater than 4.5 V. $LiPF_6$, $LiCF_3SO_3$ and a mixture of the two lithium salts were examined. The currents are very stable up to 4.5 V, but increase rapidly above 4.5 V at which decomposition of the electrotype takes place. The GTPE is electrochemically stable within the working voltage irrespective of the type of lithium salt.

The ionic conductivity of GTPEs containing various lithium salts at different temperatures is shown in Fig. 6. $LiPF_6$ is known to have a high ionic conductivity but to have a poor thermal property. $LiCF_3SO_3$ has a good high-temperature property but a poor ionic conductivity. When only $LiPF_6$ salt is used, the ionic conductivity is excellent at room temperature but the slope of the ionic conductivity increment becomes smaller at high temperatures. The $LiCF_3SO_3$ and $LiPF_6$ mixed lithium salt has a slightly lower

Fig. 6. Ionic conductivity of GTPEs containing various lithium salts at different temperatures.

level ionic conductivity at room temperature, but maintains the behaviour of a GTPE with high ionic conductivity at high temperature. When the addition of $LiCF_3SO_3$ to $LiPF_6$ is increased, the ionic conductivity is decreased. Nevertheless, a proper ratio of mixing will show high ionic conductivity at both high and low temperatures.

The ionic conductivity of GTPEs with different fillers as a function of storage time is given in Fig. 7. When filter Al_2O_3, TiO_2 and $BaTiO_3$ are added to the mixed lithium salts, the ionic conductivities are higher than that of the electrolyte without fillers. This effect may be attributed to the fact that the ceramic fillers retain electrolyte and provide a route for ion transfer.

The interfacial resistance between a lithium electrode and a GTPE with various salts as a function of storage time is presented in Fig. 8. When only $LiPF_6$ is used, the interfacial
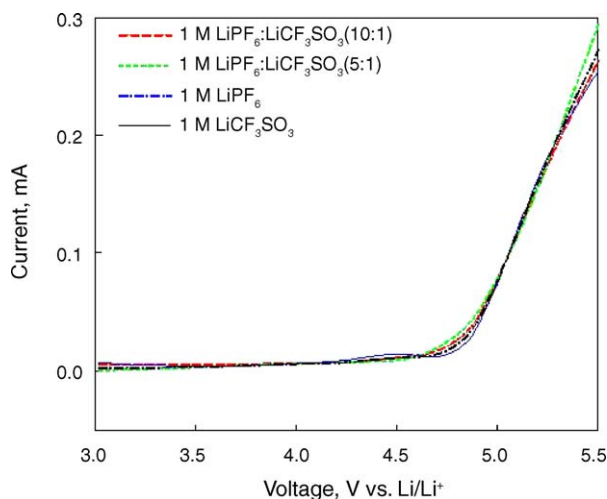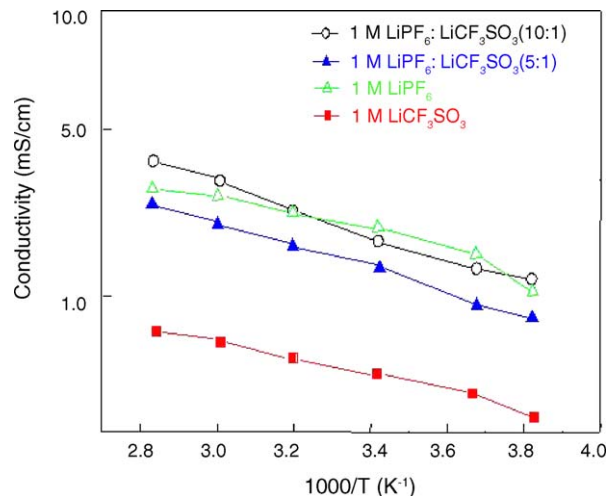

Fig. 5. Electrochemical stability window of GTPEs containing different lithium salts at room temperature.
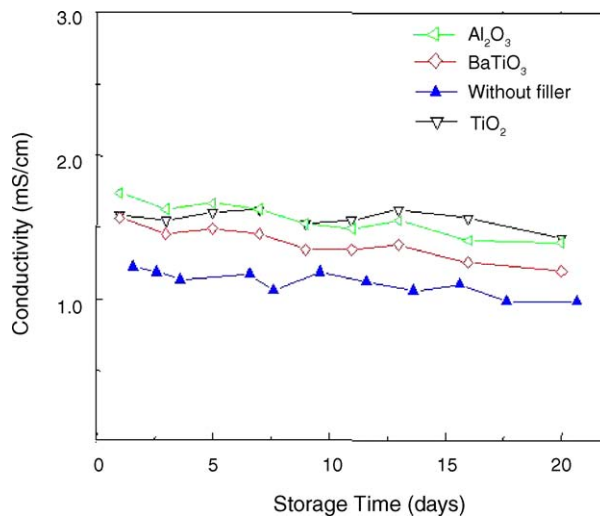

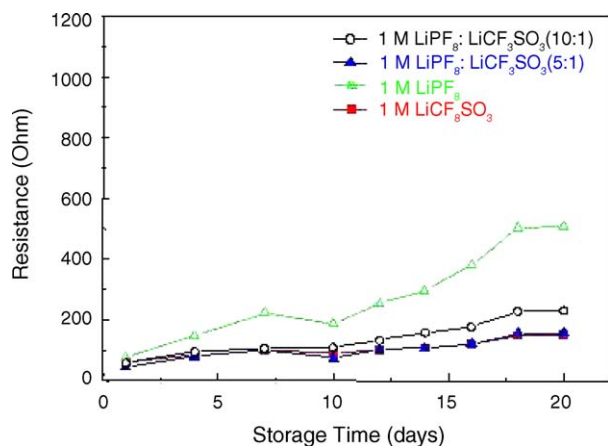Fig. 7. Ionic conductivity of GTPEs containing different ceramic fillers with storage time.

Fig. 8. Interfacial resistance of GTPEs with various lithium salts.

resistance is the highest with storage time. The difference in interfacial resistance is due to the reactivity between the GTPE and the lithium metal. The reactivity of $LiPF_6$ is slightly higher than that of $LiCF_3SO_3$, so a SEI film with high resistance is formed at the interface between the lithium metal and the GTPE. Therefore, proper addition of $LiCF_3SO_3$ decreases the interfacial resistance.

The interfacial resistances of GTPEs with ceramic fillers of Al_2O_3, TiO_2 and $BaTiO_3$ are displayed in Fig. 9 as a function of storage time. When Al_2O_3 is used as the filler, the interfacial resistance reports the lowest value of $190\,\Omega$ after 20 days. This nano-size ceramic filler with a high surface-area is evenly dispersed in the polymer matrix, so the chemical stability is enhanced. The filler can hold the solvent effectively due to the capillary force, and the reactivity between the solvent and the lithium metal is decreased. The increase in interfacial resistance also raises the internal resistance of the battery, and both the capacity and the lifetime of the battery are decreased. The optimum electrolyte is formu-
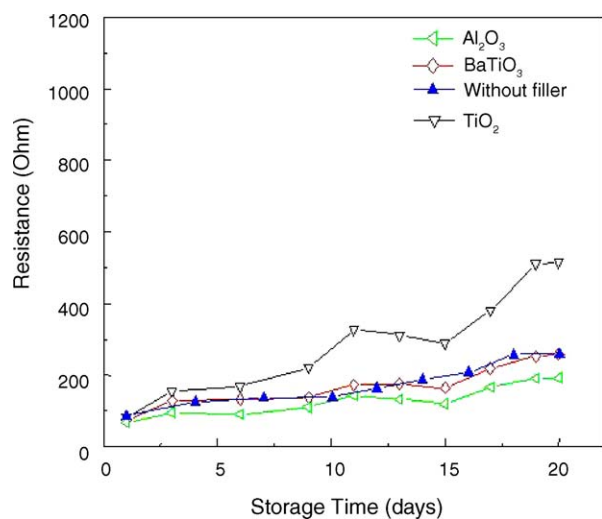

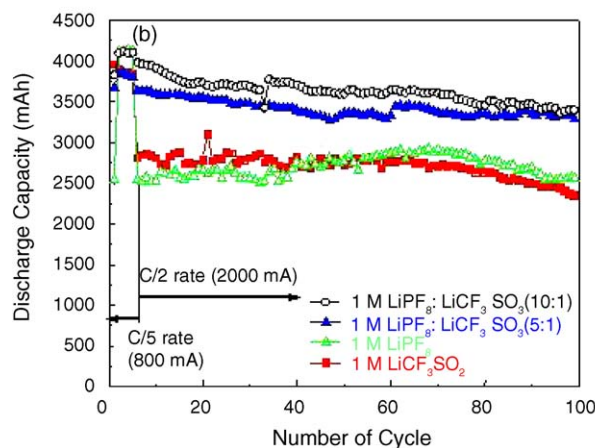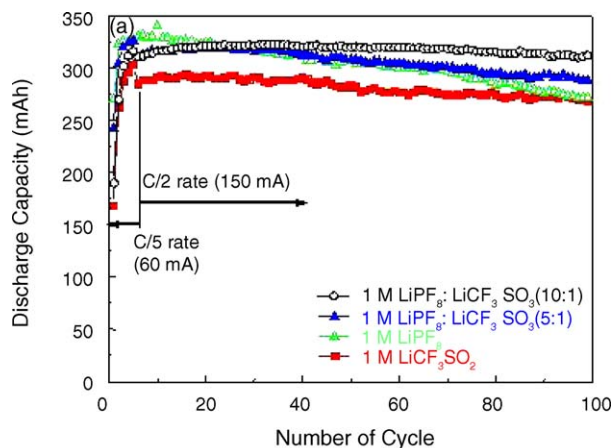Fig. 9. Interfacial resistance of GTPEs containing various ceramic fillers.

Fig. 10. Cycle performance of GTPEs with various lithium salts: (a) unit cell; (b) stacking cell.

lated by mixing $LiPF_6$ and $LiCF_3SO_3$ with Al_2O_3 ceramic filler.

The cycling performance of GTPEs with various lithium salts and ceramic fillers is shown in Fig. 10. The initial five cycles were conducted at the C/5 rate, and the remaining were at the C/2 rate. The results for a unit cell and a stacking cell are given in Fig. 10(a and b), respectively. When $LiPF_6$ and $LiCF_3SO_3$ mixed salts are used, the charge–discharge capacity is excellent. When the currents have relatively low values of 60 and 150 mA, the variation in discharge capacity of the unit cell with different lithium salts is small. For stacking cells, however, the difference in discharge capacity is large as the applied current is increased from 800 to 2000 mA. This effect may be attributed to the formation of a stable SEI film due to the reaction between the $LiPF_6$:$LiCF_3SO_3$ (10:1, wt.%) mixed salts and the electrodes.

The cycling performance of a cell containing $LiPF_6$: $LiCF_3SO_3$ (10:1, wt.%) mixed lithium salts and various fillers is given in Fig. 11. When ceramic fillers are added to the electrolyte, the discharge capacity exhibits a small change with discharge rate, except in the case of the TiO_2 filler, as shown in Fig. 11(a). When TiO_2 is used as filler, the photo-catalytic reaction between PVdF and TiO_2 generates H^+ which in turn,
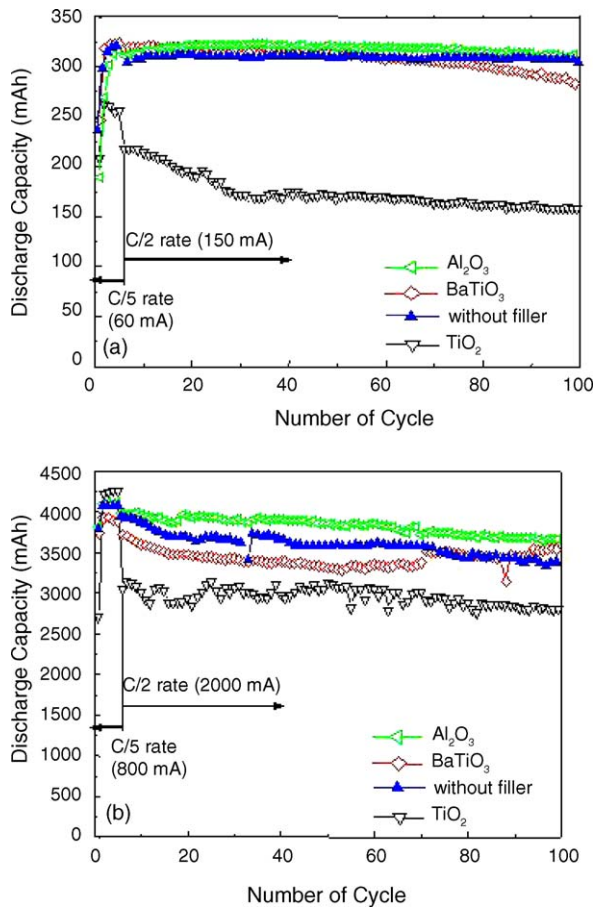
Fig. 11. Cycle performance of GTPEs with various ceramic fillers: (a) single cell; (b) stacking cell.

produces HF. Consequently, the HF etches the stable passive film and increases the interfacial resistance. For the stacking cell, the discharge capacity with an Al_2O_3 filler does not decrease even at a high rate as shown in Fig. 11(b). The adding of the ceramic fillers promotes a stable passive film between the electrode and the electrolyte and prevents local

current flow at a high discharge rates. Accordingly, cycling performance is improved.

4. Conclusions

UV-cured PEGDA, PVdF and PMMA have been blended to make a gel-type polymer electrolyte for a lithium-ion polymer battery. The GTPE was coated on a PP membrane and its electrochemical properties were investigated. The GTPE containing $LiPF_6$ and $LiCF_3SO_3$ mixed lithium salts (10:1, wt.%) has good ionic conductivity and a stable electrochemical window. The adding of Al_2O_3 filler minimizes interfacial resistance between the lithium electrode and GTPE. Finally, a lithium-ion polymer battery composed of MCMB 1028 anode with an optimized GTPE and $LiCoO_2$ cathode resulted in good cycling performance.

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