Short communication

Electrochemical and physical properties of composite polymer electrolyte of poly(methyl methacrylate) and poly(ethylene glycol diacrylate)

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Abstract

The electrochemical and physical properties of composite polymer electrolytes based on a blend of poly(methyl methacrylate) (PMMA) and poly(ethylene glycol diacrylate) (PEGDA) are investigated. The addition of nanometre-size TiO_2 filler decreases the crystallinity of the polymer electrolytes and also improves the ionic conductivity and the interfacial resistance between the electrode and the electrolyte. In addition, this ceramic filler enhances the mechanical strength of the electrolytes. A prototype battery, which consists of a graphite anode, a $LiCoO_2$ cathode, and the composite polymer electrolyte coated on a poly(propylene) (PP) separator, shows good cycling performance at high rate.
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1. Introduction

The use of a composite polymer electrolyte is one of the most promising ways to improve the mechanical and electrochemical properties of polymer electrolytes in lithium battery [1–3]. This electrolyte is generally prepared by dispersing ceramic particles such as SiO_2, Al_2O_3 in a polymer matrix [4–6]. It has been shown that the addition of ceramic filler improves the conductivity of poly(ethylene oxide) (PEO)-based polymer electrolyte as well as the interfacial resistance in contact with a lithium metal electrode [7,8]. In general, SiO_2 is used as a ceramic filler in this type of electrolyte. This filler reduces the glass transition temperature and crystallinity of the polymer, and allows the amorphous polymer to provide specific liquid-like characteristics.

Other research groups have focused on a composite gel-type polymer electrolyte formed by liquid solutions entrapped in a polymer matrix [9,10]. A high conductivity of the order of $10^{-2}\,S\,cm^{-1}$ was obtained for a composite based on a poly(acrylonitrile) (PAN)–zeolite electrolyte. In all cases, the size and content of ceramic particles appear to be critical factors. As is well known, the ionic conductivity of a given composite polymer electrolyte increases when the ceramic particle size is changed from microns to nanometres. This effect is related to a new transport mechanism which develops due to interaction between the polymer and the ceramic phase. This interaction serves as a path for the conduction of lithium ions. Furthermore, the addition of ceramic filler improves the lithium–electrolyte interfacial stability as well as the mechanical properties to some extent in comparison with other conventional polymer electrolytes.

A polymer electrolyte must have sufficient mechanical strength to withstand the stress between the anode and the cathode. Gel-type polymer electrolytes do not meet this requirement. Therefore, new-concept electrolytes have been introduced by using a gel polymer electrolyte in combination with microporous membranes such as the poly(propylene) (PP) and the poly(ethylene) (PE) separators used in conventional lithium-ion batteries. The gel electrolyte acts as an adhesive bridge between the separator and the electrode. The resistance of these supported membranes must, however, be acceptably low and gel polymer electrolytes may solve the problem of high resistance by eliminating the possibility of electrolyte leakage and providing good adhesion to the electrodes.

In this work, nanometre-size TiO_2 is used as a ceramic filler in gel-type polymer electrolytes and its effect is characterized in terms of electrochemical and physical properties.

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With this gel-coated separator, lithium-ion polymer cells, each composed of a graphite anode and a $LiCoO_2$ cathode, are assembled. The cycling characteristics of these cells are presented and discussed.

2. Experimental

2.1. Preparation of polymer electrolyte

Poly(methyl methacrylate) (PMMA, Polyscience, M_w: 350,000) and TiO_2 ceramic fillers (P25, Degussa) were dried at $80\,^\circ C$ under vacuum for several days prior to use. Poly(ethylene glycol diacrylate) (PEGDA, Aldrich, M_w: 740) was used as received. Ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) were purchased from Mitsubishi Chemical Co. as battery-grade reagents. Lithium hexafluro phosphate ($LiPF_6$) was purchased from Hashimoto Ltd. and used without further purification. PMMA of 3.0 g and 0.5 g of ceramic filler were first dissolved in 1 M $LiPF_6$/EC:EMC:DMC (1:1:1) electrolyte. Some polymers were dissolved in the above solvents without lithium salt and TiO_2 filler. PEGDA of 2.0 g was added to the above solution and then mixed with 0.1 g of 2-chlorobenzophenone as an initiator and 0.1 g of triethylamine as a catalyst at $125\,^\circ C$ for 30 min. The viscous solution was then cast on a porous poly(propylene) separator (Celgard 2400; thickness, 20 μm; porosity, 38%) by the doctor-blade method. To cure the PEGDA, UV light (Osram, 100 W) was irradiated on the film for 3 h. This procedure produced homogenous and mechanically stable membranes with thickness of 30 μm. All the procedures mentioned above were conducted in a dry room (dew point: $-50\,^\circ C$).

2.2. Measurement of polymer electrolyte properties

The ionic conductivity of the electrolyte was measured by means of an impedance technique. The electrolyte was placed in an aluminum plastic bag and sandwiched between stainless-steel electrodes. The interfacial resistance between the lithium electrode and the polymer electrolyte was also investigated by using two lithium electrodes. Impedance data were collected with a Zahner IM6 impedance analyzer in the frequency range 1 MHz to 0.1 Hz. Cycling tests of cells (graphite/polymer electrolyte/PP/$LiCoO_2$) were performed under constant current using a Maccor cycle tester. These cells were also enveloped in aluminum plastic bags and sealed by vacuum sealer. The size and the crystal structure of the TiO_2 filler were examined by means of scanning electron microscopy (SEM; Hitachi, S-4200) and X-ray diffraction (XRD; Rint/Dmax-2500, Rigaku), respectively. The crystallinity of polymer electrolytes was also analyzed by XRD analysis. The mechanical properties of the polymer electrolytes were investigated with an Instron instrument (model; 5544).

3. Results and discussion

A scanning electron micrograph of the TiO_2 filler is shown in Fig. 1. The diameter of the filler is about 25 nm. These nano-sized particles are a typically spherical in shape and are mainly composed of an anatase structure, as shown in Fig. 2.

The tensile strength, the modulus and the elongation at break (%) of the electrolyte are given in Table 1. The polymer electrolyte without lithium salt has a much higher modulus
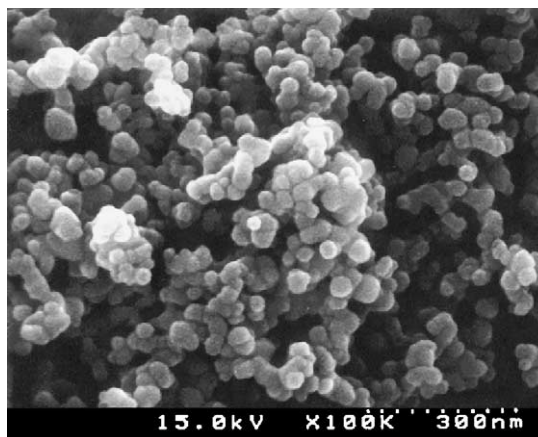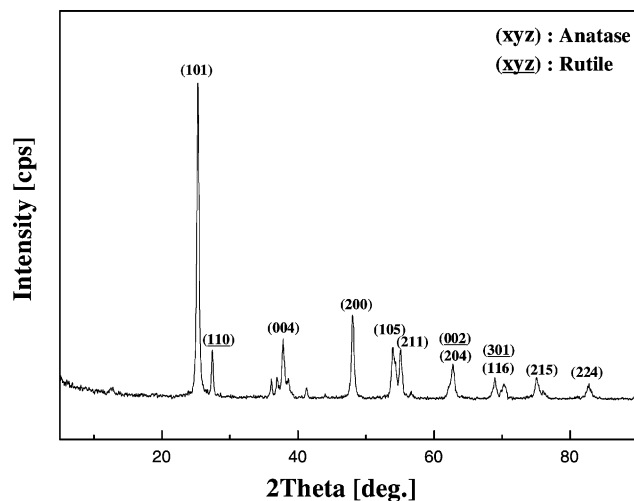

Fig. 1. Scanning electron micrograph of TiO_2 filler.

Fig. 2. X-ray diffraction pattern of TiO_2 filler.

Table 1
Physical properties of composite polymer electrolyte

	Displacement (mm)	Modulus (MPa)	Strain (%)	Strength (MPa)
Without salt	1.760	137.5	22.47	1.790
Without salt + TiO_2	1.980	316.6	7.816	5.467
With salt	48.540	6.546	80.94	0.0986
Salt + TiO_2 (5%)	68.710	10.1228	222.1	0.0262
Salt + TiO_2 (10%)	77.770	12.09	222.2	0.0294

Fig. 3. XRD patterns of polymer membrane without and with salt.

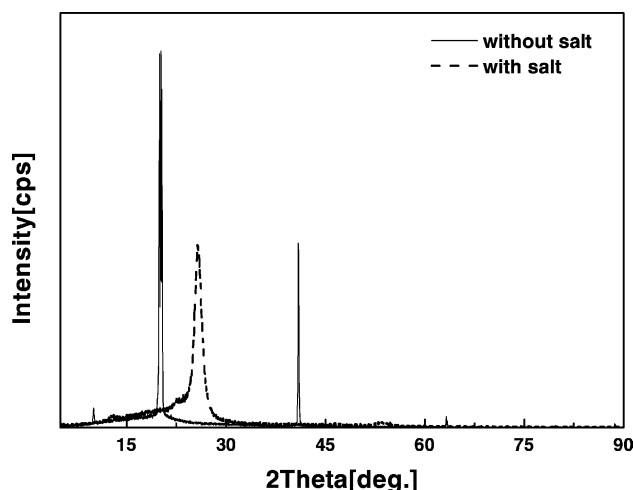Fig. 5. Ionic conductivity of composite polymer membrane without and with TiO$_2$ filler (10 wt.%).

than that with lithium salt. The maximum strain (%) of the polymer electrolyte with lithium salt increases with the ceramic filler. The tensile strength of the composite polymer electrolyte shows the highest value in the absence of lithium salt. These mechanical results are due to a decrease in the crystallinity of the polymer electrolyte on the addition of lithium salt, as shown in Fig. 3.

The intensity of the crystalline peaks also decreases on the addition of filler, refer Fig. 4. The effect of the ceramic filler on the crystallinity of the electrolyte is lower than that caused by lithium salt. This indicates that the amount of elastomeric phase (amorphous) increases to some extent as the salt concentration is increased. When oligomer EGDA containing initiator is irradiated with UV light, it is polymerized to form PEGDA. Moreover, the incorporation of lithium salt makes it possible to entangle the polymer chains during polymerization. Therefore, gel polymer electrolytes have a sufficient mechanical strength to assure easy battery fabrication.
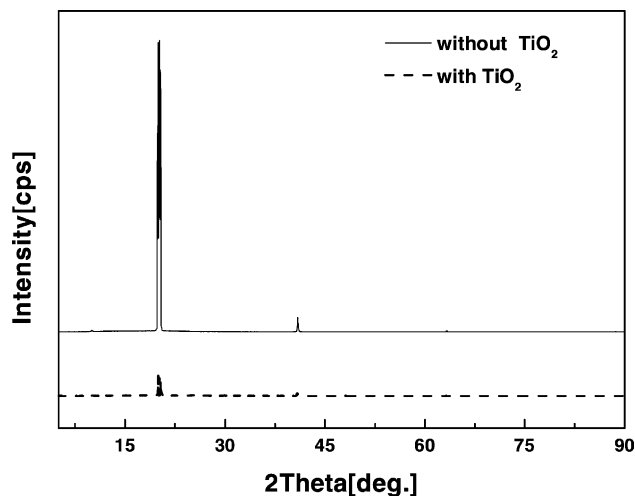
The ionic conductivities of the composite polymer electrolyte and the ceramic-free membrane at room temperature are compared in Fig. 5. The values are obtained from the intercept on the real-axis at high frequency. The ionic conductivity of the composite polymer electrolyte is higher than that of ceramic-free polymer electrolyte. This effect supports the idea that the addition of ceramic filler does not impede the mobility of lithium ions in the polymer matrix. The enhancement of ionic conductivity by adding filler is mainly due to a decrease in the crystalline phase of the polymer electrolyte. In addition, the high dielectric constant (170) of TiO$_2$ assists the dissociation of lithium salts in the polymer electrolyte. Therefore, the ionic polymer electrolyte can be improved by an increase in the carrier number of lithium ions. It has been reported [11–14] that ceramic filler may greatly influence the characteristics and the properties of polymer electrolytes. This effect depends on their nature and particle size. In the case of the gel-coated membrane
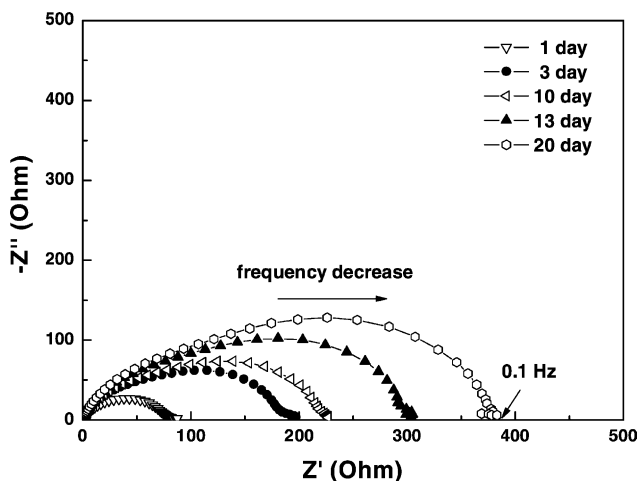

Fig. 4. XRD patterns of polymer membrane without and with TiO$_2$ filler (10 wt.%).

Fig. 6. Time dependence of impedance response of Li|PEGDA-PMMA, LiPF$_6$|Li cell.
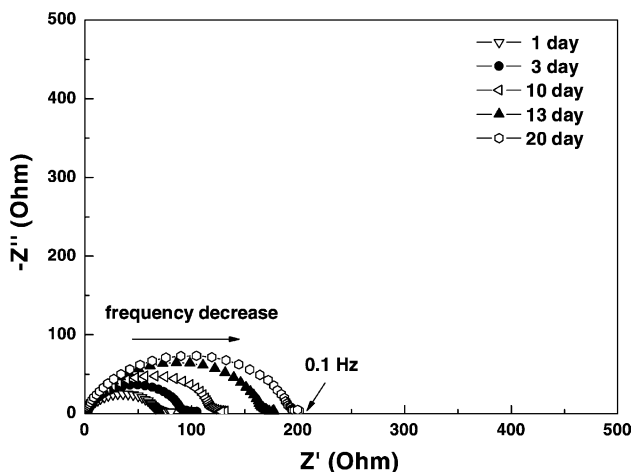
Fig. 7. Time dependence of impedance response of Li|PEGDA-PMMA, $LiPF_6$ + 10 wt.% TiO_2|Li cell.

examined here, it may help in holding the liquid electrolyte within the membrane structure.

Impedance spectra for a Li|gel polymer electrolyte|Li cell at open-circuit for different storage times are shown in Fig. 6. The interfacial resistance between the lithium and the polymer electrolyte can be calculated from the diameter of the semi-circle. It is found that the resistance of ceramic filler-free polymer electrolyte increases rapidly with storage time. The interfacial resistance of the composite polymer electrolyte is presented in Fig. 7. The interfacial resistance increases slightly with storage time compared with that of an electrolyte with no ceramic filler, i.e. the resistance is twice as high after 20 days. This phenomenon suggests that the ceramic filler increases the surface area in contact with the electrode and also the take-up of liquid electrolyte. A similar result is found for a membrane formed by combining linear poly(ethylene oxide) with a lithium salt and a nano-particle size SiO_2 filler [15]. The fast swelling rate leads to a 300 wt.% increase in
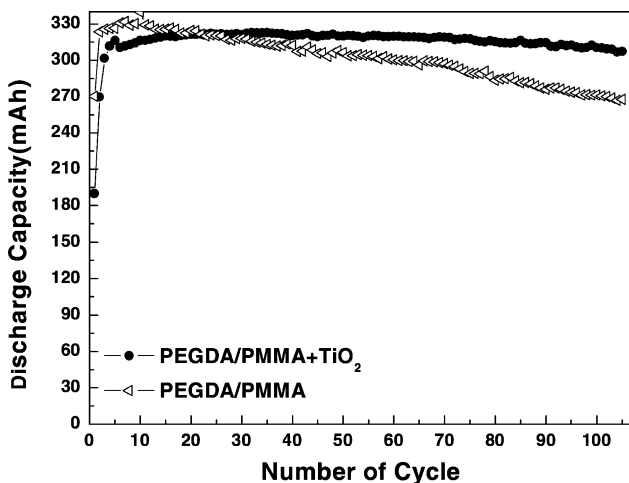
the membrane after only few minutes of dipping in the liquid.

The cycling performance of a graphite|polymer electrolyte|$LiCoO_2$ is given in Fig. 8. Such cells deliver about 320 mAh of discharge capacity at the $C/2$ rate during the initial cycle. This value is equivalent to a specific capacity of 132 mAh/g of $LiCoO_2$ active material in the cathode. The initial discharge capacity of the cell is higher for an electrolyte with no filler. On the other hand, the capacity declines faster during the cycling test compared with that for an electrolyte with the filler. In the latter case, the discharge capacity shows no decrease until 100 cycles. Thus, it appears that a composite polymer electrolyte containing TiO_2 filler is a promising electrolyte for lithium-ion polymer batteries.

4. Conclusions

An electrolyte made from a blend of PMMA and PEGDA has been investigated in terms of its physical and electrochemical properties. The addition of TiO_2 filler improves the ionic conductivity and lowers the interfacial resistance. Also, this electrolyte shows good mechanical properties on coating on to a poly(propylene) separator. A lithium-ion polymer cell composed of a graphite anode, the composite polymer electrolyte coated on a PP separator and a $LiCoO_2$ cathode shows a good cycling performance at a high rate.

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Fig. 8. Cycling performance of Li-ion polymer electrolyte cells.