

Electrochemical Performance of PEO₁₀LiX-Li₂TiO₃ Composite Polymer Electrolytes

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The conductivities of polyethylene oxide (PEO)-based polymer electrolytes (PE) can be improved by the addition of inorganic inert powder. The composite polymer electrolytes (CPE) PEO₁₀LiX (X = ClO₄⁻ or N(CF₃SO₂)₂⁻)-Li₂TiO₃ were prepared by solution casting with inorganic solid electrolyte Li₂TiO₃ powder as a filler. Results showed that the conductivities of PEO₁₀LiClO₄-3wt% Li₂TiO₃ and PEO₁₀LiN(CF₃SO₂)₂-10wt% Li₂TiO₃ at 30 °C were 8.6 × 10⁻⁶ and 5.6 × 10⁻⁵ S · cm⁻¹, respectively. The conductivities of CPE increased with the decrease of filler's particle size. The ionic conduction mechanism analysis showed that there may be three conduction routes in the CPE, *i.e.*, PEO bulk, polymer-filler interface and Li₂TiO₃ crystal.

Keywords rechargeable lithium batteries, polymer electrolyte, composite polymer electrolyte, conductivities, polyethylene oxide, Li₂TiO₃

Introduction

Recently, polymer electrolytes have attracted much attention for their potential use in replacing flammable organic solvent electrolytes currently used in lithium-ion batteries, thus improving the safety of rechargeable lithium batteries. Moreover, the batteries with PE can be made in any shape, which make fully use of the space of electronic devices. PEO is a linear polymer with helix structure, and its structure makes it have much higher dissolution ability for salt even though its dielectric constant is low (about 4.5). The low ambient conductivity is the main drawback for PEO-based PE, which is commonly explained by its high crystallinity. The studies of PEO-based PE have shown that the conductivity, mechanical strength and the stability of Li/electrolyte interface have been enhanced by the addition of nanosized inorganic inert fillers, such as TiO₂,¹ Al₂O₃,² C,³ BaTiO₃,⁴ SiO₂,⁵ to PEO-salt complex. The reason for the conductivity increment is that fast ion conduction can proceed in the surface of fillers, which can be explained by effective medium theory.⁶ Gray and Armand⁷ concluded that the trend is towards composites with reactive component, *e.g.*, LiAlO₂, which participates in the conduction process, rather than inert materials such as SiO₂. Inorganic solid electrolytes have high ambient conductivities but the processability is poor.⁸ Li₂TiO₃ is an inorganic solid electrolyte with ambient conductivity in the magnitude of 10⁻³ S · cm⁻¹, but it is difficult to be used in practice for its poor cathodic stability. This paper investigated the ionic conduction properties of PEO-based CPE prepared by solution casting with inorganic solid electrolyte Li₂TiO₃ powder as a filler, and discussed their electrochemical

stability window.

Experimental

The films of PEO-based CPE were prepared as follows. LiClO₄ or LiN(CF₃SO₂)₂ (Aldrich, used as received) and Li₂TiO₃ (Aldrich, 325 mesh, which means 90% or more of the material will pass through a 325 mesh sieve, the hole size of the sieve is about 45 μm, used as received) were added into acetonitrile. After the Li₂TiO₃ in the solution was uniformly dispersed by an ultrasonic bath, it was strongly stirred by magnetic force and at the same time, PEO (Aldrich, M_w = 4000000, used as received) powder was slowly added in the solution. The PEO/Li ratio was fixed to 10/1 and the content of Li₂TiO₃ was referred to the weight percent of Li₂TiO₃ to that of the amount of PEO and salt. The solutions were cast on a flat PTFE plate after stirring for 6 h. Then the solvent was evaporated completely, the films were dried at 100 °C under vacuum for 48 h to remove any trace of water and solvent. These procedures yielded homogeneous membranes with an average thickness of about 200 μm.

The films were sandwiched between two polished stainless steel (SS) blocking electrodes with an area of 1.1 cm² in a glove box filled with dry air atmosphere. The sealed symmetrical cell of SS/CPE/SS was carried out for impedance measurement with Solartron 1280 in a frequency region of 20 kHz—10 Hz at different temperatures, and the conductivities were obtained from the bulk impedance of the sample membrane.

The electrochemical stability window of the CPE films was estimated by subjecting a Li/CPE/SS cell to a

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linear sweep voltammetry at $10 \text{ mV} \cdot \text{s}^{-1}$ between 0 and 6 V with Solartron 1280, the SS electrode was the working electrode, the lithium electrode was the counter and reference electrode.

Results and discussion

Morphology of CPE

The SEM of $\text{PEO}_{10}\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{-10wt\% Li}_2\text{TiO}_3$ in Figure 1 showed that Li_2TiO_3 powder was uniformly dispersed in the polymer, and other CPE with different compositions had the similar morphology.

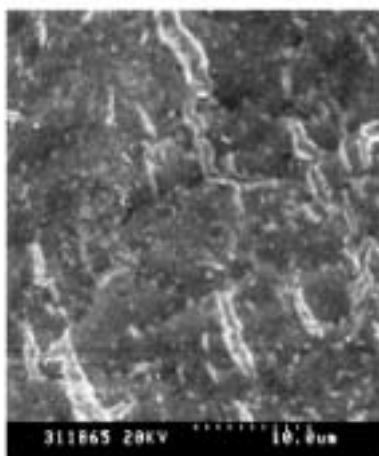


Figure 1 SEM of $\text{PEO}_{10}\text{LiN}(\text{CF}_3\text{SO}_2)_2\text{-10wt\% Li}_2\text{TiO}_3$ composite polymer electrolyte.

Conductivities of $\text{PEO}_{10}\text{LiClO}_4\text{-Li}_2\text{TiO}_3$

The ionic conductivity value, σ , of the CPE was determined by using the following equation:

$$\sigma = \frac{l}{A} \times \frac{1}{R} \quad (1)$$

where l and R represent the thickness and the ionic resistance of the sample membrane and A represents the area of the blocking electrode. The conductivities of $\text{PEO}_{10}\text{LiClO}_4\text{-Li}_2\text{TiO}_3$ as a function of temperature were shown in Figure 2. It showed that the conductivities of CPE increased with temperature.

Figure 3 was the conductivities of $\text{PEO}_{10}\text{LiClO}_4$ at 30°C with various contents of Li_2TiO_3 in CPE. It showed that the conductivity increased with the increase of the content of Li_2TiO_3 , then decreased with its increment. The maximum value $8.6 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ was obtained with 3wt% of Li_2TiO_3 . This value was one order of magnitude higher than the value for PEO-LiClO_4 film in the absence of Li_2TiO_3 powder. The higher value of σ was attributed to the presence of Li_2TiO_3 powder. The study of Wieczorek and co-workers⁹ on $\text{PEO}_{10}\text{NaI-}\text{Al}_2\text{O}_3$ showed that the conductivity of CPE did not increase when the particle size of inorganic filler was larger than $4 \mu\text{m}$. The filler added in this paper is 325 mesh, which is much larger than $4 \mu\text{m}$, thus

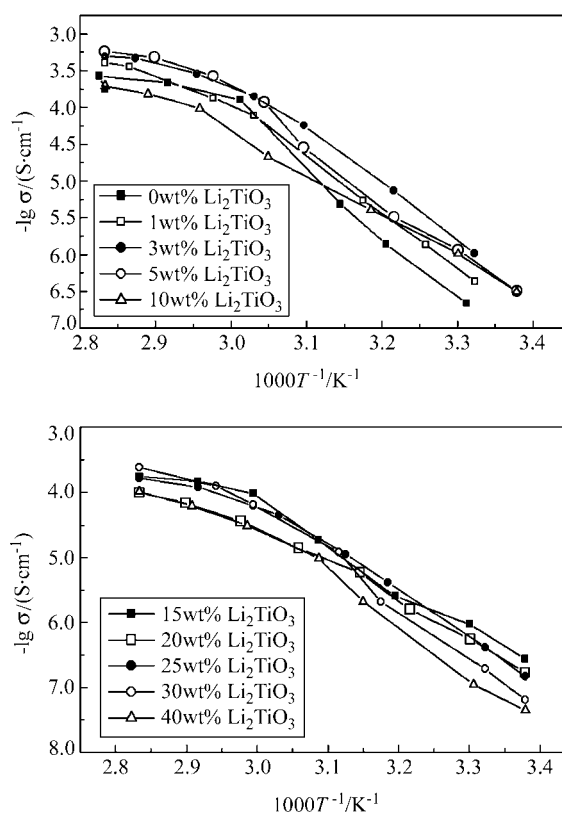


Figure 2 Temperature-dependent ionic conductivities of PEO-LiClO_4 composite polymer electrolytes.

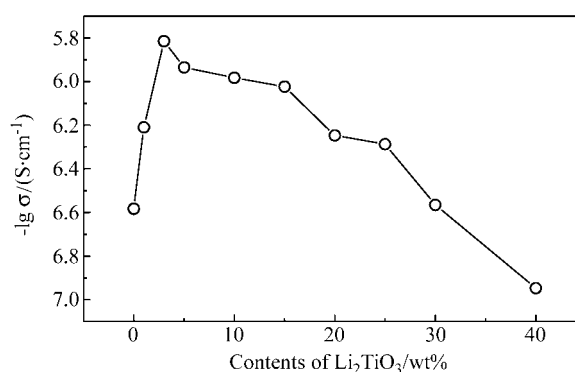


Figure 3 Ionic conductivities of $\text{PEO}_{10}\text{LiClO}_4$ with various Li_2TiO_3 contents at 30°C .

the conductivity of CPE should not increase if the filler is an inorganic inert material. Thus, the enhancement of ionic conductivities can only be connected with the Li_2TiO_3 crystal, which can transfer Li^+ ions by its crystal lattice. It should also be noted that there is an energy barrier between PEO -filler interface when the Li^+ ions transfer from one phase to another. Thus not all the particles in the electrolyte participate in the conduction process, only those with appropriate circumstance (that is, has lower energy barrier) can participate in the conduction.

In the PEO matrix, Li^+ ions are located in the helix of PEO chain and coordinate with the oxygen atoms of polymer chain.¹⁰ Under the influence of a potential gradient, the Li^+ ions keep changing to adjacent location due to the segmental motion of the PEO chain. Li^+ ions transferred by PEO helix are the main conduction manner for PEO-based PE.

It was shown in Figure 3 that the conductivities of CPE at 30 °C decreased with the increase of Li_2TiO_3 content when the content was higher than 3wt%. It was also shown in Figure 2 that the conductivities of CPE with higher content of Li_2TiO_3 were lower even at higher temperatures. The reason for the higher content of filler decreasing the conductivities may be related to the decrease of salt concentration by the addition of filler, which results in the decrease of the concentration of charge carriers.

As mentioned above, PEO-based CPE with large Li_2TiO_3 particle may have two ionic conduction routes, PEO bulk and Li_2TiO_3 crystal. But due to CPE is a three-phase system, the interactions among polymer, salt and filler make the analysis of ionic conduction mechanism much complex. As commented by Quartarone *et al.*,¹¹ the present overall knowledge of CPE is still quite unsatisfactory. More systematic experiments are still needed to investigate the influence of polymer, salt and filler on the conduction mechanism.

Effect of particle size on the conductivities of CPE

The conductivity of CPE was enhanced when the 'plasticized salt' with large anion $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ was added in the polymer (Figure 4). The Li_2TiO_3 powder was classified into two ranges by particle sizes, *i.e.*, between 320 and 360 mesh and below 360 mesh. Results showed that the conductivities of CPE with those fillers were 2.77×10^{-5} and $5.16 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$, respectively. Obviously, the conductivities increased with the decrease of the filler's size. The Li_2TiO_3 powder had a particle size distribution shown in Figure 5 after ball-milling for 40 h. It showed that about 70% of the powder had a particle size of 580 nm. The conductivity of CPE with this filler is $5.6 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ at 30 °C. From the above results, we may conclude that the conductivities can be further increased by the decrease of filler's particle size. The reason for the conductivity increasing with the decrease of particle size is that a new conduction route is formed in the polymer-filler interface. But for inorganic solid electrolyte, large particle is advantageous for ionic transfer. Thus, the contribution of ions transferred by Li_2TiO_3 crystal lattice to conductivities of CPE decreased with the decrease of particle size. Therefore, there may be three conduction routes in the CPE prepared in this paper, *i.e.*, PEO bulk, polymer-filler interface and Li_2TiO_3 crystal.

Electrochemical stability window

PEO-based polymer electrolytes are known to possess a wide voltage stability window. The potentiody-

namic measurement of $\text{PEO}_{10}\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -10wt% Li_2TiO_3 at 60 °C was shown in Figure 6. The magnitude of current was fairly low when the voltage below 5 V (vs. Li^+/Li), and current started increasing at potential beyond this value due to the decomposition of the electrolyte. But the electrochemical stability window of $\text{PEO}_{10}\text{LiClO}_4$ -20wt% Li_2TiO_3 was about 3.5 V (vs. Li^+/Li), which was related to the type of salt and the high content of Li_2TiO_3 .

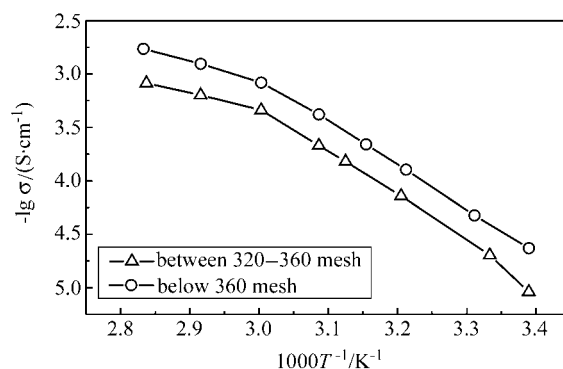


Figure 4 Temperature-dependent ionic conductivities of $\text{PEO}_{10}\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -10wt% Li_2TiO_3 .

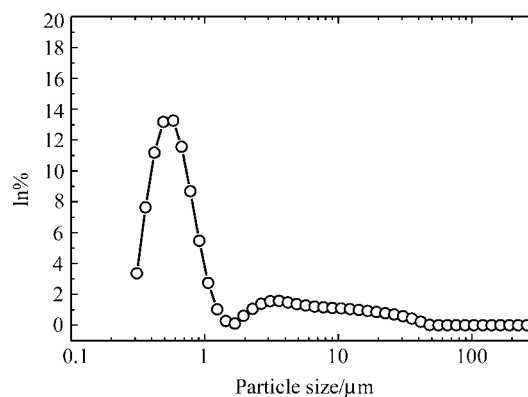


Figure 5 Particle size distribution of Li_2TiO_3 after ball-milling.

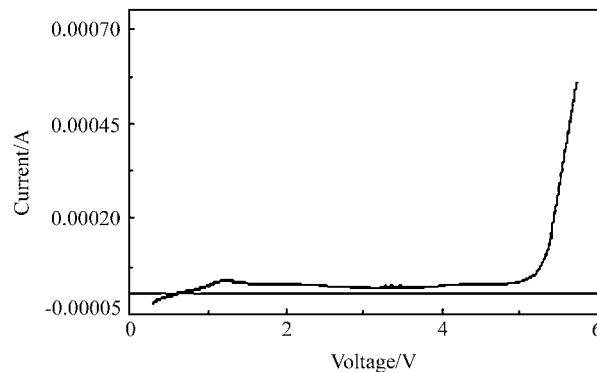


Figure 6 Linear sweep voltammetry of $\text{Li}/\text{PEO}_{10}\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -10wt% $\text{Li}_2\text{TiO}_3/\text{SS}$ cell at 60 °C.

Conclusion

Study on PEO-LiX-Li₂TiO₃ showed that the ambient conductivity of PE was effectively enhanced by the addition of Li₂TiO₃ powder. The maximum value of PEO-LiClO₄ complex was $8.6 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$ at 30 °C with a Li₂TiO₃ content of 3wt%. The conductivity of CPE with LiN(CF₃SO₂)₂ salt could reach $5.6 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$ at 30 °C. There may be three conduction routes in the CPE, *i.e.*, PEO bulk, polymer-filler interface and Li₂TiO₃ crystal. The conductivities of CPE increased with the decrease of filler's particle size. The electrochemical stability window of CPE can reach 5 V (vs. Li⁺/Li).

References

- 1 Croce, F.; Appetecchi, G. B.; Persi, L.; Scrosati, B. *Nature* **1998**, *394*, 456.
- 2 Croce, F.; Persi, L.; Scrosati, B.; Serraino-Fiory, F.; Plichta, E.; Hendrickson, M. A. *Electrochim. Acta* **2001**, *46*, 2457.
- 3 Appetecchi, G. B.; Passerini, S. *Electrochim. Acta* **2000**, *45*, 2139.
- 4 Sun, H. Y.; Sohn, H.-J.; Yamamoto, O.; Takeda, Y.; Imanishi, N. *J. Electrochem. Soc.* **1999**, *146*, 1672.
- 5 Capiglia, C.; Mustarelli, P.; Quartarone, E.; Tomasi, C.; Magistris, A. *Solid State Ionics* **1999**, *118*, 73.
- 6 Przulski, J.; Siekierski, M.; Wieczorek, W. *Electrochim. Acta* **1995**, *40*, 2101.
- 7 Gray, F.; Armand, M. In *Handbook of Battery Materials*, Ed.: Besenhard, J. O., Wiley-VCH, Weinheim, **1999**, Part III, Chapter 8.
- 8 Liu, H.-T.; Chen, R.-F.; Song, X.-Q. *Chin. J. Chem.* **2002**, *20*, 1536.
- 9 Wieczorek, W.; Florjanczyk, Z.; Stevens, J. R. *Electrochim. Acta* **1995**, *40*, 2251.
- 10 Andreev, Y. G.; Bruce, P. G. *Electrochim. Acta* **2000**, *45*, 1417.
- 11 Quartarone, E.; Mustarelli, P.; Magistris, A. *Solid State Ionics* **1998**, *110*, 1.

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