234 Chinese Chemical Letters Vol. 15, No. 2, pp 234 – 237, 2004
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Characterization of a Novel Polymer Electrolyte for Lithium-ion Battery

Yan Ping Liang,[1] Hong Zhu MA,[2] Bo WANG[2] *

[1]Xidian University, Xian 710071
[2]College of Chemistry and Materials Science, Shaanxi Normal University, Xian 710062

Abstract: A novel polymer electrolyte with the formula of $Li_2B_4O_7$-PVA for lithium-ion battery was synthesized and its ion conductivity and mechanical properties were also tested. It is found that the conductivity of the prepared polymer electrolytes is higher than that of $LiClO_4$/PEO or $LiClO_4$/EC-DMC by two or three orders in magnitude and a large delocalized bond formed in $Li_2B_4O_7$-PVA lead to transportation of Li ion easier, this electrolyte possesses high thermo-stability and can be used under 200°C.

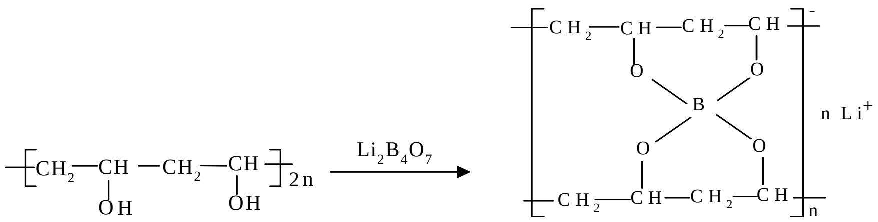
Keywords: Conductivity, lithium-ion battery, polymer electrolyte, $Li_2B_4O_7$-PVA.

Lithium ion conductive polymer electrolytes have attracted much attention because of their potential application in lithium-ion battery, particularly high energy density, reliability, safety and variable-shape geometry[1]. The solid electrolytes serve two chief roles: rechargeable lithium battery, as the medium for ionic transportation and separator for insulates the cathode from anode. Therefore, solid polymer electrolytes must exhibit high ionic conductivity of about 10^{-3} Scm^{-1} at ambient temperature and good mechanical strength. They should also possess wide electrochemical stability, typically between 0-4.5V for single cell and good compatibility with high voltage cathodes such as $LiCoO_2$, $LiNiO_2$, and low voltage anodes such as lithium, Li-graphic, Li-Sn. So far the most promising examples of solid polymer electrolytes are $LiClO_4$-PEO (polyethyl -eneoxy), $LiClO_4$-EC (ethylene carbonate), $LiClO_4$-PC (propylene carbonate), $LiClO_4$-DMC (dimethyl carbonate), $LiClO_4$-PVA (polyvinyl alcohol) and $LiClO_4$-lithium polyacrylicate [2-4]. However, $LiClO_4$ is a possible explosive compound in recharging, the main point in recent years concentrated on the replacement of $LiClO_4$ by $LiPF_4$, $LiAsF_4$, a small cation combined with a large anion [5,6], in which Li ion can be transported easily.

Here we report a new type of borate polymer electrolyte which has been prepared by the crossing-linking reaction of $Li_2B_4O_7$ with PVA, with the molecular weight from 2,000 to 18,000, as shown in **Scheme 1**.

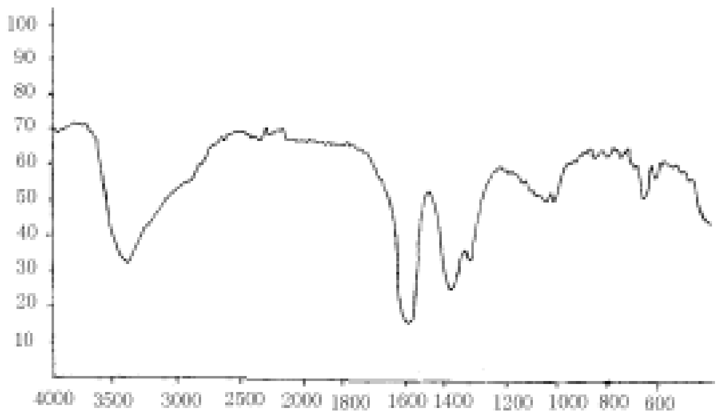
* E-mail: wangbo@snnu.edu.cn

Scheme 1



All of the polymer electrolytes obtained were colorless and its IR spectrum was shown in **Figure 1**, the thermal analysis diagram was shown in **Figure 2**. From the TG, DTG and DSC curse of the polymer electrolyte (molecular weight 6000), it is found that no mass loss is observed under 200°C, indicating that the polymer is high thermostability and can be used under 200°C, which is reported firstly so far in Li ion battery. The change in tensile strength σ_B with molecular weight is shown in **Figure 3**, with the increase of the molecular weight of the polymer electrolytes, the σ_B was increased and reached maximum at molecular weight *ca.*8000 and then decreased gradually. The behavior of shear modulus G with molecular weight of polymer electrolytes is similar to that for tensile strength, but show the maximum at molecular weight of *ca.*6000. **Figure 4** shows the change in elongation ε at break of the films prepared from the polymer electrolyte. With increasing molecular weight, the elongation increased. The tendency suggests that a homogeneous network structure is formed.

Figure 1 IR spectrum of the polymer electrolyte (molecular weight 6,000)



The ion conductivity of the polymer electrolytes were measured at the temperature range from –5 to 80°C. It is found that the conductivity of the polymer electrolytes independent on molecular weight and is higher than that of the solid $LiClO_4$/PEO or $LiClO_4$/EC-DMC for two or three orders of magnitude[6,7](**Figure 5**). Due to a large delocalization of the bond formed in $Li_2B_4O_7$-PVA, Li ion can transport easily.

Figure 2 Thermal analysis diagram of polymer electrolyte (molecular weight 6,000)

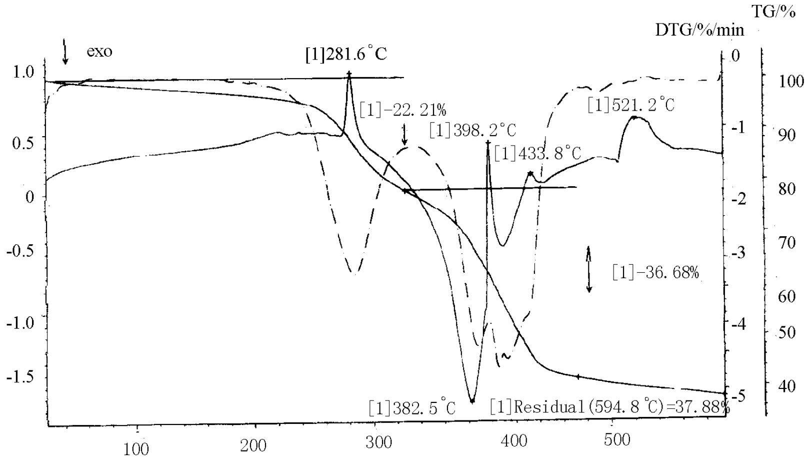


Figure 3 Tensile strength (σ_B) and shear modulus (G) of the polymer with molecular weight(×1000)

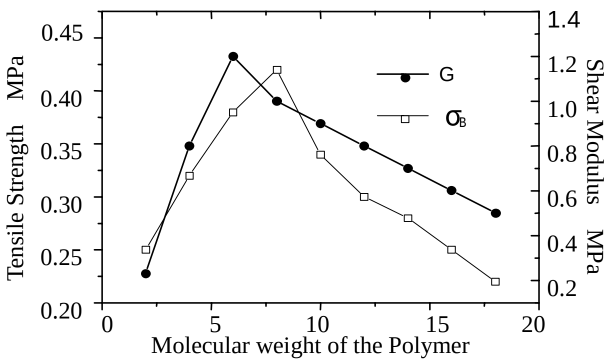


Figure 4 Elogation (ε) of the polymer with molecular weight(×1000)

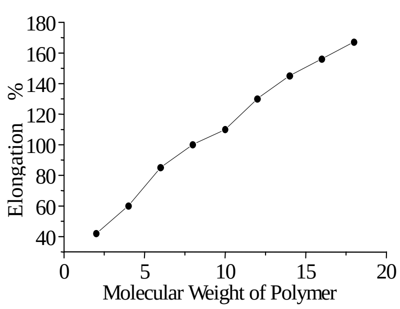
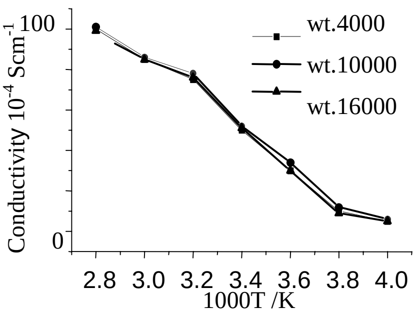


Figure 5 Conductivity of the polymer electrolytes



Experimental

Preparation of the electrolyte films

A stoichiometric ratio of $Li_2B_4O_7$ and PVA were dissolved in distilled water and heated at 50℃ for 2 h, then cooled, cast onto a quartz glass plate and dried till the water in the film was below 20 ppm and cut into 15 mm diameter disk with 500-510 μm thick.

General methods and materials

Stress-strain measurements and shear modulus measurements were performed to characterize the mechanical properties of the prepared polymer electrolyte according to the literature [8,9]. Ion conductivity and charge-transfer resistance measurements at Li electrolyte interface, electrolytes films (500-510 μm thick) were performed between Li metal disks of the same diameter. These films and electrodes were placed in moisture-tight polytetrafluoro-ethylene cells. Cyclic voltamograms of polymer electro -lytes were measured by using a potentiostat and a function generator. A disk sample of the polymer electrolytes was mounted on a stainless steel working electrode. Li was used as counter and electrodes.

Conclusion

The novel polymer electrolyte prepared by crossing-linking reaction of $Li_2B_4O_7$-PVA exhibited favorable mechanical properties and high ion conductivity. It is suitable for replacement of electrolyte $LiClO_4$/PEO or $LiClO_4$/EC-DMC, and can be used widely in Li-battery. The polymer electrolyte with the molecular weight 6000-8000 is the best candidate in terms of their mechanical properties.

References

1. M. Kono, E. Hayashi, M. Watanabe, *J. Electrochem. Soc.*, **1999**,*146*, 1626.
2. X.Wu, S. S. Kok, G. Zhiqiang, Y. L. Swee, *J. Electrochem. Soc.*, **1999**,*146*, 4410.
3. K. M. Abraham, M. Alamgir, *Chem. Mater.*, **1991,** *3*, 345.
4. J. Evans, C. A. Vincent, P. G. Bruce, *Polymer*, **1987,** *28*, 232.
5. Y. Matsuda, M. Morita, H. Tsutsumi, *J.Power Sources*, **1993**,*43*, 439.
6. C. Deimas and I. Saadoune, *Solid State Ions*, **1993,** *53*, 370.
7. G. B. Appetecchi, G. Dautzenberg, B. Scrosati, *Electrochim. Acta*, **1995**, *40*, 991.
8. D. J. Taylor and A. M. Kragh, *J. Phys. D: Appl. Phys.*, **1997,** *42*, 2667.
9. M. Kono, E. Hayashi, M. Watanabe, *J. Electrochem. Soc.*, **1998,** *145*, 1521.

Received 13 January, 2003