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Organic Electrolyte Improving the Performance of Ionic Liquid-PEO Polymer Electrolyte Based Lithium Ion Batteries

Lichun Xuan[1], *Yongxin An*[1, 2,*], *Wei Fang*[2], *Lixia Liao*[2], *Yulin Ma*[2], *Zhiyu Ren*[1], *GepingYin*[2,*]

[1] Chemistry and engineering department of Heilongjiang University, Harbin, 15001, China
[2] School of Chemical Engineering and Technology, Harbin Institute of Technology, No. 92, West Da-Zhi Street, Harbin 150001 China
[*]E-mail: Anyongxin2006@yahoo.com.cn; yingeping2006@yahoo.com.cn

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Ionic liquid (IL)- polymer composite electrolyte was prepared from $Pp_{13}TFSI$ and polyethylene oxide(PEO). Organic electrolyte -1 mol·L^{-1} $LiPF_6$ in EC: DEC (50:50, v/v) was added as the ameliorant to improve the interphase stability. The EIS, CV and XPS results showed that the well passive film forms between the IL-polymer electrolyte and $Li_4Ti_5O_{12}$ anode. The Li/$Li_4Ti_5O_{12}$ cell fabricated by the IL-polymer electrolyte also obtained the acceptable and reversible capacity by the addition of organic electrolyte.

Keywords: lithium ion battery; electrolyte; solid state polymer; ionic liquid, passive film

1. INTRODUCTION

Solid state polymer electrolytes (SPEs) have been widely investigated in lithium second battery for their particular properties such as no flaming, none-leakage, and fictile structure [1-5]. In the last decade, many works have been performed to develop the SPEs. Amongst them, the most popular polymer electrolyte is PEO.

However, the practical use of SPEs electrolyte in lithium ion battery is significantly hampered by the low conductivity of PEO and poor wetting ability of PEO with electrode. Up to now, much attention has been focused on improving ion conductivity, either decreasing the safety or improving conductivity value. So much works have been carried out to solve these problems [6-10]. But these efforts can improve the ion conductivity either decreasing the safety or improving conductivity value is not enough for use. Recently, J. Shin and others [11-13] have reported an approach that improves SPE's conductivity by the combination of PEO with ionic liquid $PYR_{14}TFSI$, and the excellent cycle performance was obtained in Li/$LiFePO_4$ batteries at 40 °C. They got the reasonable value of ion conductivity without reducing the safety of electrolyte.

It is noteworthy that the cycle performance of PEO electrolyte was measured only with cathode materials, due to the poor interphase contact between the PEO electrolyte and anode [14]. Therefore, to apply the ionic liquid-PEO polymer electrolyte (IL-PEO) in lithium battery, the optimal addition should be carefully selected, which facilitates the improvement of the interphase stability between the electrolyte and anode materials. In this paper, we used the 1M $LiPF_6$ in ethyl carbon (EC): Diethyl carbonate (DEC) (50:50, v/v) as addition to improve the interface stability between as-prepared PEO-based electrolyte and $Li_4Ti_5O_{12}$material.

2. EXPERIMENTAL PART

2.1. Preparation of IL-polymer electrolytes

The ionic liquid preparation is as our previous method [15], the PEO (purchased from Aldrich) average molecule amount is 3×10^6. Solvent-free IL-PEO electrolyte, $P(EO)_{20}LiTFSI+xPp_{1,3}TFSI$ (x is mole rate $Pp_{1,3}^+$ /Li^+, $x = 0, 0.5, 1$) electrolytes were prepared by a hot-press technique. In a typical synthesis, PEO and LiTFSI (EO/Li^+=20) were first mixed in a mortar and then $Pp_{1.3}TFSI$ was added to the mixture to achieve the selected mole ratio, then the polymer electrolytes were annealed under vacuum at 90 °C overnight.

A thin film was obtained by hot-pressing the polymer electrolytes at 115 °C for 2 min. the final, 1M $LiPF_6$ in EC:DEC(50:50, v/v) is added on IL-polymer electrolyte system(the mount is 10wt% of IL-polymer electrolyte).

2.2. Cell preparation and Electrochemical measurements

The electrode is consisted of 80 wt% $Li_4Ti_5O_{12}$, 10 wt% acetylene black, and 10 wt% polyvinylidene fluoride. The cells were assembled with 2025 coin cells in glove box, using lithium foil as counter electrode.

The electrochemical stability of electrolyte was measured by cyclic voltammetry (CV) from 2.5 V to 1 Vat scan rate of 0.5 $mV\cdot s^{-1}$. The electrochemical impedance spectroscopy impedance of cell was tested from 100 kHz to 0.01 Hz (CHI604B). The performance of the Li/$Li_4Ti_5O_{12}$ batteries was tested by battery test system (NewareTC51) from 2.5 V to 1 V at 0.1 C charge-discharge rate.

2.3. Materials Characterization

The morphology and the surface analysis of electrode were characterized by scanning electron microscopy (SEM, Hitachi S-4700) and X-ray photoelectron spectroscopy (XPS, PHI5800), respectively.

3. RESULTS AND DISCUSSION

The Nyquist plots of Li/P(EO)$_{20}$+Pp$_{13}$TFSI/Li$_4$Ti$_5$O$_{12}$ cell without or with organic electrolyte are shown in Fig.1.

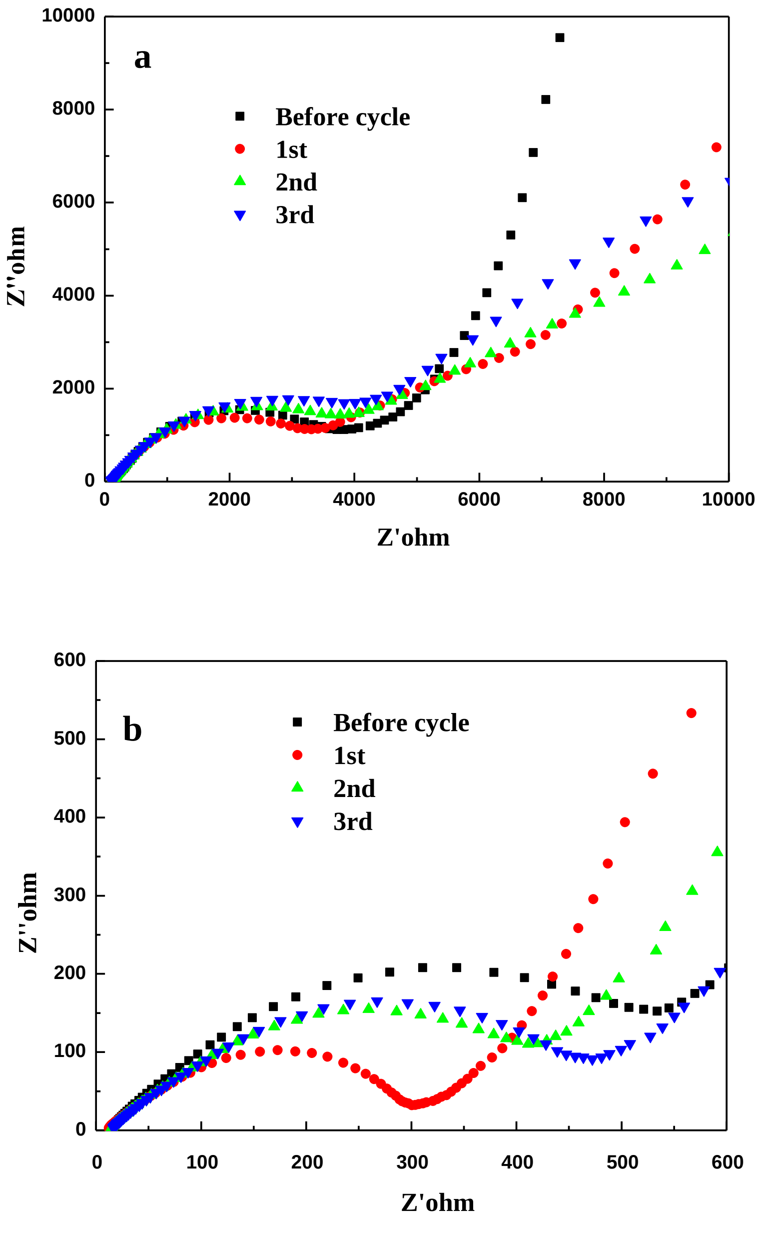


Figure 1. Nyquist plot of Li/Li$_4$Ti$_5$O$_{12}$ cell using IL-PEO electrolyte (a) without organic electrolyte (b) with organic electrolyte.

No obvious changes were found in the electrochemical properties of Li/P(EO)$_{20}$+Pp$_{13}$TFSI/Li$_4$Ti$_5$O$_{12}$ cell without organic electrolyte after cycling test. The interphase impendence is higher than 3500 Ω, The frequency of the semicircles after each cycling are 1.476×10^3 Hz, 1.758×10^3 Hz and 2.148×10^3 Hz, and the bulk impedance, usually that corresponding to interphase impendence, are 3594 Ω, 3644 Ω and 4156 Ω, respectively. On the contrary, with the cycles progressing, the frequency and the interphase impendence of the cell with organic electrolyte are also increasing. After three cycles, the frequency of Li/P(EO)$_{20}$+Pp$_{13}$TFSI/Li$_4$Ti$_5$O$_{12}$ cell with organic electrolyte is shifted from 9.668×10^3 Hz to 3.711×10^4 Hz. Meanwhile, the interphase impendence value is lower than 600 Ω. These changes are owing to organic electrolyte decomposition on the interphase between IL-PEO electrolyte and electrode, resulting in the formation of high ion conductivity and stability passive film.

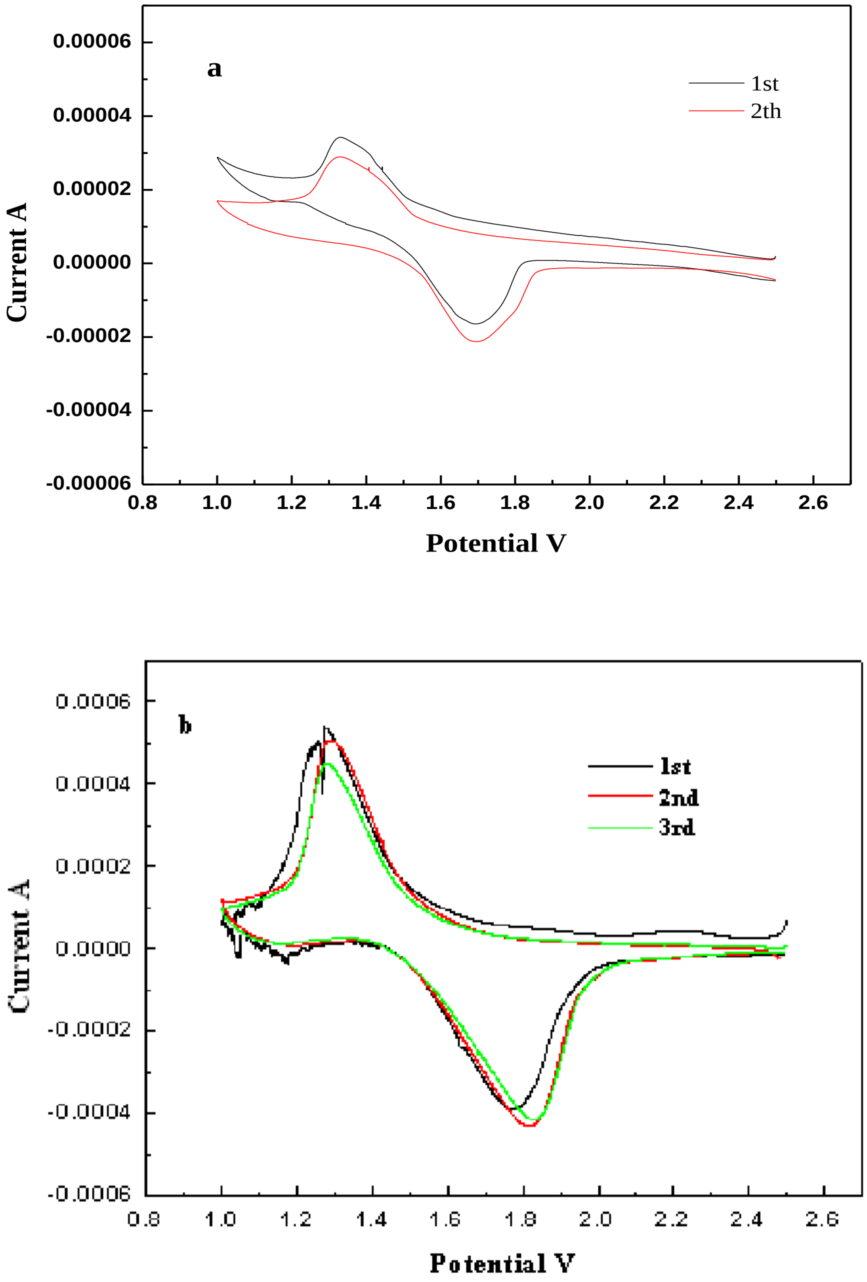
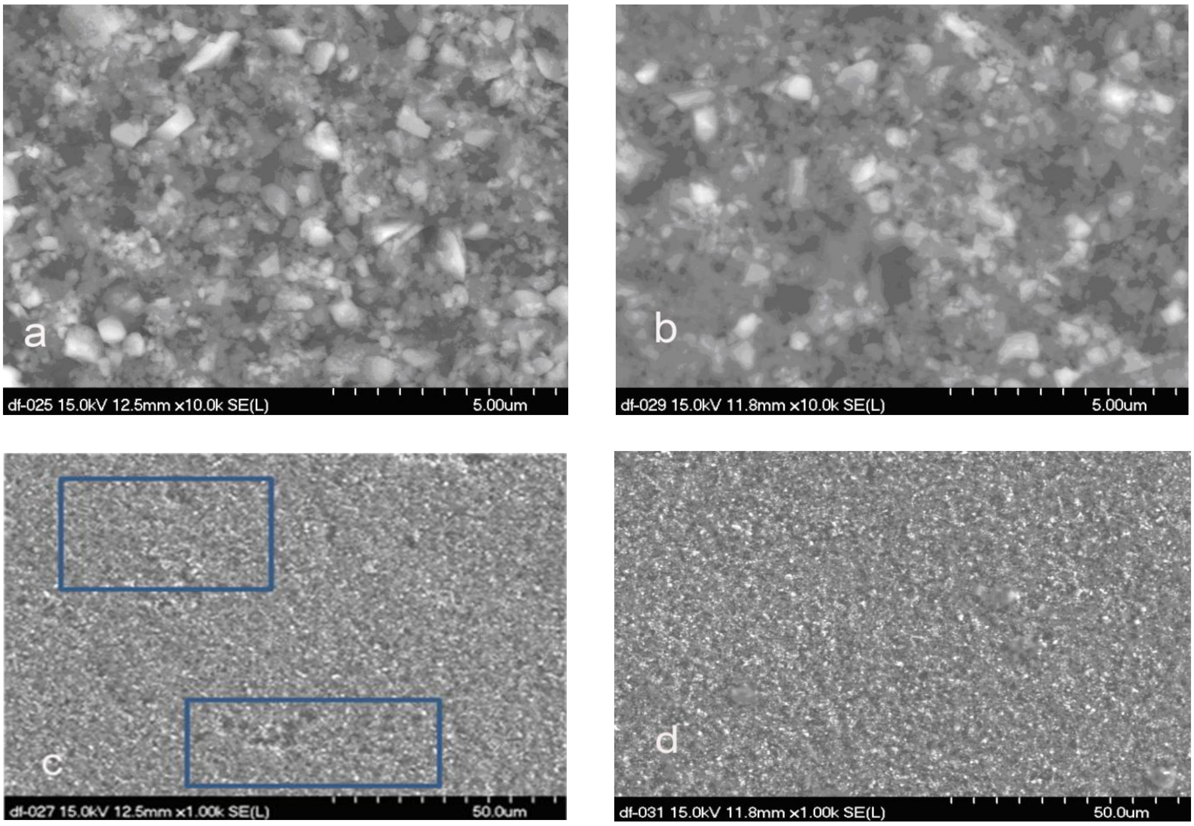


Figure 2. CV curves of the Li/Li4Ti5O12 cell using IL-PEO electrolyte (a) without organic electrolyte (b) with organic electrolyte

Fig. 2 show the cyclic voltammetry (CV) plots of Li/P(EO)$_{20}$+Pp$_{13}$TFSI/Li$_4$Ti$_5$O$_{12}$ cell with and without organic electrolyte for the first two cycles at a scan rate of 0.5 mV·s^{-1} in the potential window of 2.5 V-1 V(vs.Li/Li$^+$). In Fig. 2a, no apparent oxide peak and reduction peak can be found in the plots. This proves that the lithium ion can't effectively insert and extract from the Li$_4$Ti$_5$O$_{12}$ anode. On the other hand, the obvious oxide peak (at 1.2V) and reduction peak (at 1.8V) can be seen in the plots of cell using organic electrolyte addition. And the plots of first three cycles are well overlapped. Fig. 2b shows the well reversibility for the Li ion insertion and extraction in the cell using organic electrolyte addition. This is towing to the organic electrolyte addition decomposes and then forms the stable passive film on the Li$_4$Ti$_5$O$_{12}$ anode.

In order to examine the effect of organic electrolyte on the electrode, the micrograph of the electrode surface was presented in Fig.3. For the surface of electrode without using organic electrolyte addition, the big grain-like particles appear on the surface after ten charge/discharge cycles (as shown in Fig.3a). Moreover, the surface of the electrode using IL-polymer electrolyte without organic electrolyte addition became rough and some cavities appear on the electrode surface. It may come from the co-insertion of cation ion in ionic liquid and Li$^+$ into the electrode, which destroys the electrode (Fig.3c). However, the surface of electrode using organic electrolyte addition is kept smooth even after ten cycles (Fig. 3d); this is due to the protection of passive film formed by organic electrolyte. Significantly, the surface of electrode using organic electrolyte addition contains more oxygen and carbon contents by comparing the EDS of two electrodes after ten cycles (Fig.3e, f). The oxygen and carbon are the main components of passive film [16]. Also the more oxygen group is benefit to reduce the initial irreversible capacity and increase the performance of batteries.



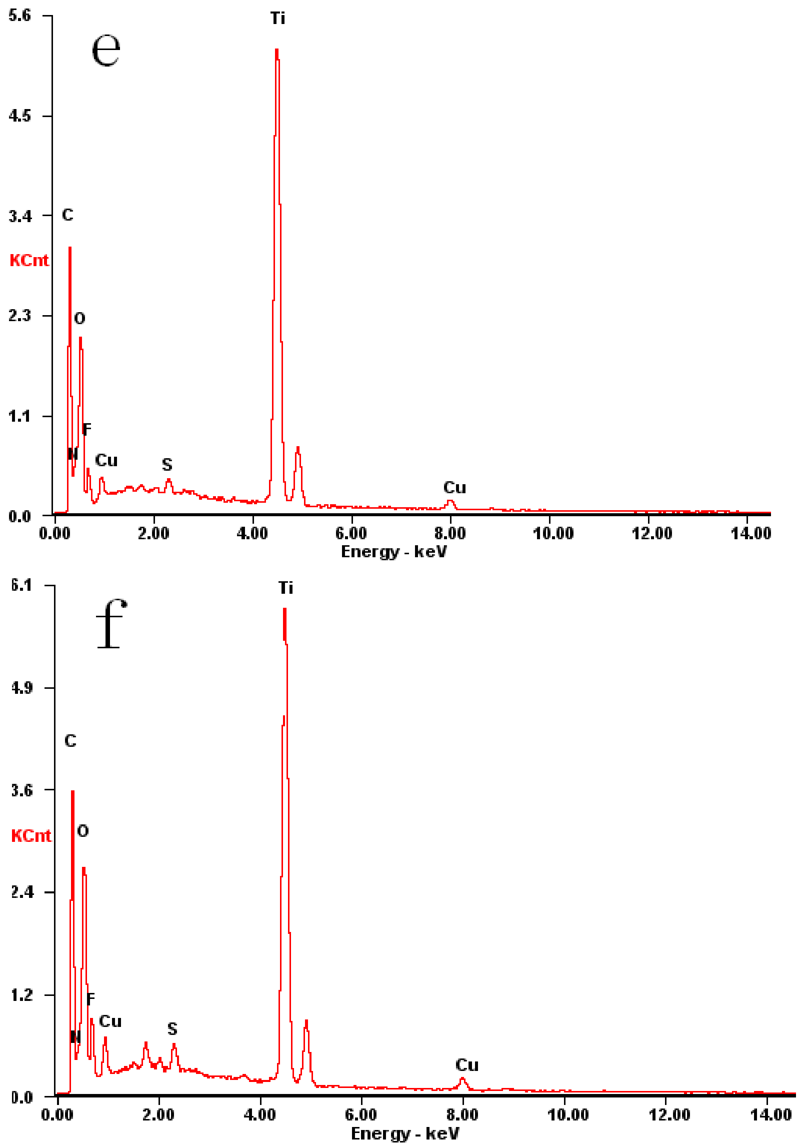


Figure 3. SEM and EDX analysis on the electrode .(a) and (c) are the electrode without organic electrolyte addition; (b) and (d) are electrode surface with organic electrolyte; (e) and (f) is the EDS of electrode without and with organic electrolyte, respectively.

In order to further validate the changes of the electrode, the surface elements of electrode after ten cycles were analyzed on XPS spectra (Fig. 4). In the C1s spectra of anode surface, the peak around 284.6 eV is attributable to C-C bond; the peak around 288-292 eV is corresponding to plays an active role in forming compact passive film layers (the main component of passive film is ROCOOLi), the obvious abundance of C-O bond appears in the electrode using organic electrolyte addition. Two peaks at 686 and 689 eV can be observed in the F1s spectra of electrode without the organic electrolyte. The peak at 686 eV is assigned to LiF, contributing to the decomposition of organic electrolyte. The peak at 689 eV is related to C-F bonding (which mainly comes from IL). Different from the F1s spectra of the electrode without using organic electrolyte addition, one strong peak at 689 eV was found for the electrode using organic electrolyte, which may be due to the formation of $LiPF_6$ in passive film layers.

The peak around 690eV corresponding to C-F show lower on the electrode using organic addition containing IL-PEO system, which due to the well stable passive film prevents the decomposition of IL(C-F component mainly comes from ionic liquid.

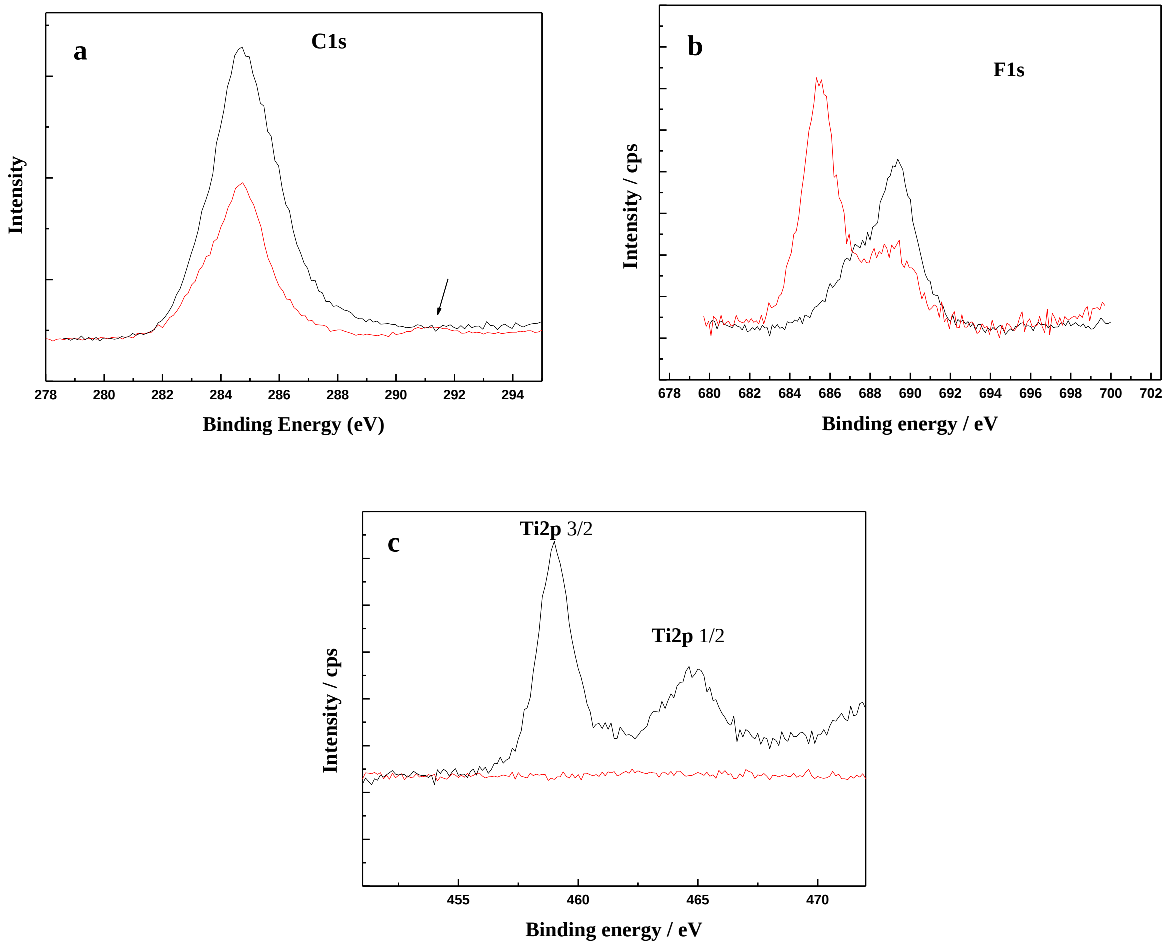


Figure 4. XPS of electrode surface after ten cycles (Black line is electrode without organic electrolyte; red line is electrode with organic electrolyte)

Peaks corresponding to Ti 2p 3/2 and Ti2p1/2 are observed at around 459 eV and 464eV on electrode without organic electrolyte. However, there is no clear Ti peaks in the Ti2p spectra of electrode with organic electrolyte addition indicated the formation of passive film on the surface of the electrode.Fig.5a shows the cycle performance of the Li/$Li_4Ti_5O_{12}$ cell using free organic electrolyte addition IL-polymer electrolyte. The first charge-discharge capacities of the cell are 60 mAh g^{-1} and 280 mAh g^{-1} respectively. The coulomb efficiency is lower than 20%. This may be higher viscosity of IL and the poorly wet ability of IL-PEO electrolyte with electrode, which leads to the obvious polarization of electrode. Starting from 2nd cycles, the charge-discharge capacity increases, and then steadily approaches the value about 140 mAh g^{-1}. But the Li/$Li_4Ti_5O_{12}$ cell using organic electrolyte addition IL-PEO electrolyte shows better cycle stability. The discharge voltage and charge voltage plats stay at 1.55 and 1.60 V even after 20 cycles. And the first charge-discharge capacities are 132 and 140 mAh g^{-1} respectively.

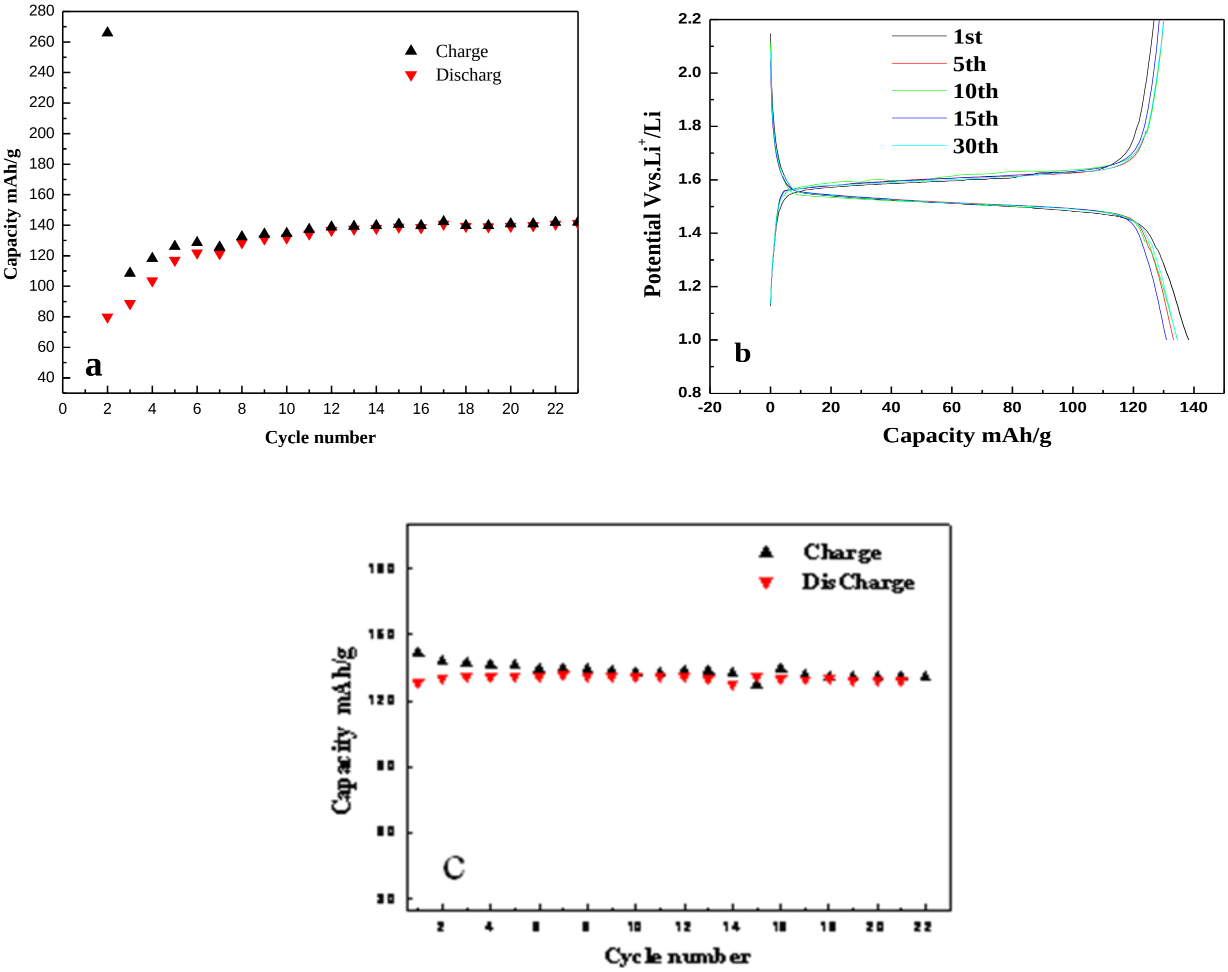


Figure 5. The cycle performance of the Li/$Li_4Ti_5O_{12}$ cells using containing (a) and free(c) organic electrolyte IL-polymer electrolyte at 0.1 C charge-discharge rate (b) The capacity vs. cycle number plots of cell using organic electrolyte addition

The 1^{st} cycle coulomb efficiency is higher than 90%. This is due to the organic electrolyte addition effectively formed passive film on Li4Ti5O12 electrode. Then it effectively improves the contact ability between the IL-PEO electrolytes with electrode. Moreover, the cell demonstrates the well cycle stability, even after the 20 cycles, and the charge-discharge capacities are higher than 130 mAh g^{-1}.

4. CONCLUSIONS

In the work, organic electrolyte was introduced into IL-PEO electrolyte system. It was shown from the CV, EIS, SEM and XPS measurement that the well stable passive film forms on the electrode, which effectively improves the interphase contact between the IL-PEO polymer electrolyte and $Li_4Ti_5O_{12}$ electrode. As a result, the performance of $Li/Li_4Ti_5O_{12}$ cell was improved: the reversible capacity of the cell is close to 132 mAh g^{-1} even after 20 cycles.

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References

1. J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
2. F. Yuan, H.Z. Chen, H.Y. Yang, H.Y. Li, M. Wang, *Mater. Chem. Phys*. 89 (2005) 390.
3. Y.X. An, P.J. Zuo, X. Q. Cheng, L.X. Liao, G.P. Yin, *Electrochim Acta*.56(2011)4841-4848.
4. C. Brissot, M. Rosso, J.-N. Chazalviel, S. Lascaud, *J. Power Sources* 81–82 (1999) 925.
5. M.D. Farrington. *J. Power Sources* 96 (2001) 260–265.
6. A.M. Stephan, S.G. Kumar, N.G. Renganathan, M.A. Kulandainathan, *Eur. Polym. J.* 41 (2005) 15.
7. S. Gopal, R. Ramchandran, S.A. Rashmi, Sol. Energy Mater. *Sol. Cells* 45 (1997) 17.
8. B. Scrosati, F. Croce, L. Persi, *J. Electrochem. Soc*. 147 (5) (2000) 1718.
9. F. Croce, B. Appetecchig, B. Scrosati, *Nature* 394 (1998) 456.
10. S. Ahmad, H.B. Bohidar, S. Ahmad, S.A. Agnihotry, *J. Power Sources* 47 (2006) 3583.
11. J.H. Shin, W.A. Henderson, S. Passerini, *Electrochemical and Solid-State Letters*, 8(2) (2005) A125-A127.
12. J.H. Shin, W.A. Henderson, S. Passerini, *Electrochem Commn*.5(12)(2003) 1016-1020
13. Y.X. An, X.Q. Cheng, P.J. Zuo, L.X. Liao, G.P. Yin, *Mater. Chem.Phys.*128(2011)250-255.
14. F.Coowar, D. Billaud, J.Ghanbaja, P.Baudry, *J.Power Sources* 62(2)(1996)179-186.
15. Y.X. An, P.J. Zuo, X.Q. Cheng, L.X. Liao, G.P. Yin, *Int. J. Electrochem. Sci.*, 6 (2011) 2398 - 2410
16. K. Xu, U. Lee, S.S. Zhang, *Electrochem. Solid-State Let.t*, 6 (2003) A144-A148