

L. X. Yuan · J. D. Piao · Y. L. Cao · H. X. Yang  
X. P. Ai

## Preparation and performance characterization of polymer Li-ion batteries using gel poly(diacrylate) electrolyte prepared by in situ thermal polymerization

Received: 26 February 2004 / Accepted: 16 April 2004 / Published online: 8 February 2005  
© Springer-Verlag 2005

**Abstract** A gel polymer electrolyte (GPE) was prepared by in-situ thermal polymerization of 1,3-butanediol diacrylate (BDDA) in a EC/EMC/DMC electrolyte solution at 100 °C. The GPE with 15 wt.% polymer content appears as apparently “dry” polymer with sufficient mechanical strength and shows a high ionic conductivity of  $3.2 \times 10^{-3} \text{ S cm}^{-1}$  at 20 °C. The MCMB–LiCoO<sub>2</sub> type polymer Li-ion batteries (PLIB) prepared using this in-situ internal polymerization method exhibit a very high initial charge–discharge efficiency of 92.1%, and can deliver 94.4% of its nominal capacity at 1.0 C rate and 70.7% of its room temperature capacity at –20 °C. Also, the PLIB cells show very good cycling ability with >85% capacity retention after 300 cycles. The excellent charge–discharge properties of the PLIB cells are attributed to the integrated structure in which the polymer matrix spreads over entire region of the cell acting as a strong binder and electrolyte carrier to produce a stabilized electrode–electrolyte interface. In addition, the fabricating process of the polymer cell is quite simple and convenient for practical applications.

**Keywords** Polymer lithium ion battery · Gel polymer electrolyte · In-situ polymerization · 1,3-Butanediol diacrylate

### Introduction

The polymer Li-ion battery (PLIB) is actively investigated because of its advantages of improved safety and flexible processability compared with the liquid electrolyte Li-ion battery. Successful development of PLIB requires that the polymer electrolytes not only have electrochemical stability and high ionic conductivity, but

also have good mechanical properties and structural compatibility with inserting electrodes. Thus, search for polymer electrolytes with all the required properties has become a crucial part in the development of a new generation of Li-ion batteries.

Earlier developments of lithium polymer electrolytes were mainly based on the polymer–salt complexes formed by dissolving lithium salt in suitable polymer matrixes such as PEO [1, 2, 3, 4, 5]. This type of solution-free electrolyte can be built into a thin film with required mechanical strength, but the ionic conductivity of these electrolytes is too low, typically in the range of  $10^{-5}$  to  $10^{-8} \text{ S cm}^{-1}$  at room temperature, for battery applications. In recent years, many approaches have been employed to enhance the ionic conductivity by use of so-called plasticized electrolytes or gel polymer electrolytes (GPE) in which liquid electrolyte is encapsulated in a polymeric matrix [3, 4, 5]. The matrix polymers frequently used include polymethylmethacrylate (PMMA) [6, 7], polyacrylonitrile (PAN) [8, 9], polyvinylidene fluoride (PVDF) [10, 11, 12], and some copolymers [13, 14, 15, 16, 17, 18]. This type of electrolyte is usually prepared by directly dissolving the polymer in the Li<sup>+</sup>-containing electrolyte and then solvent-casting the gelled solution into an electrolyte film. Although the GPE films can achieve very high ionic conductivities comparable to liquid electrolytes, their mechanical properties are usually inadequate for practical use.

Recently, there have been reports of in-situ synthesis of Li polymer electrolytes by radiation or thermal initiation of the polymerization of the electrolyte directly to form polymer Li-ion batteries [19, 20, 21, 22, 23]. This method seems to provide a simple solution to the preparation and electrochemical compatibility of the GPE films.

In this paper, we report a preparation method for preparing the GPE by in-situ polymerization of poly(diacrylate) in 1.0 M LiPF<sub>6</sub>/EC:EMC:DMC and describe the electrochemical characteristics of the polymer Li-ion batteries prepared using the in-situ synthesis method.

L. X. Yuan · J. D. Piao · Y. L. Cao · H. X. Yang · X. P. Ai (✉)  
Department of Chemistry, Wuhan University,  
430072 Wuhan, China  
E-mail: ece@whu.edu.cn  
Tel.: +86-27-87873526  
Fax: +86-27-87884476

## Experimental

### Preparation of GPE films

For experimental convenience, the conductivity of the GPE was characterized using the GPE films. The film was prepared by thermal polymerization of a precursor solution, which contained a liquid electrolyte solution, a diacrylate monomer and a thermal initiator. The electrolyte solution used in this work was 1.0 M LiPF<sub>6</sub>/EC:EMC:DMC (1:1:1, by vol., battery grade) purchased from Sumsang (Korea). The monomer and thermal initiator were 1,3-butanediol diacrylate (BDDA, 98% purity) and 2,2'-azo-bis-iso-butyronitrile (AIBN, 98% purity), respectively, purchased from Aldrich. All the reagents were used as received without further purification. In order to control the dimensions of the GPE films in the experiments, a piece of porous polypropylene membrane of 70 μm thickness was employed as a substrate. A typical procedure for preparing the GPE film was firstly to immerse the porous substrate into the precursor solution for 10 min, then to seal the impregnated membrane in a metallized plastic bag, and finally to place the bag in an oven for thermal-initiating polymerization at 100 °C for 1 h. Afterwards, the GPE film was taken out for experimental use. All procedures for preparing the precursor were carried out in a dry box filled with argon gas.

### Characterization of the GPE films

The electrochemical stability of the GPE film was calibrated with cyclic voltammetry (CV). The CV measurement was performed by a microelectrode method in a two-electrode configuration on a CHI660 electrochemical workstation (Shanghai, China). The working electrode was a Pt microelectrode of 80 μm diameter. A larger lithium sheet was used as both counter electrode and reference electrode. The CV curves were obtained by sweeping the potential between 0 V and 5.0 V at a scan rate of 5 mV s<sup>-1</sup>.

The conductive behaviors of the GPE films were measured by an ac impedance method. The cell for ac impedance measurements was a small piece of the GPE film (ca. 2.0 cm<sup>2</sup>) sandwiched between two stainless-steel electrodes. The ac impedance measurement was performed over the frequency range from 10 Hz to 1 MHz with amplitude of 10 mV, and was carried out on a CHI660 electrochemical workstation (Shanghai, China). In the measurements of the conductivity–temperature relationship of the GPE films, the test cell was kept at each temperature for 1 h before measurement in order to reach thermal equilibrium.

The thermal stability of GPE films was characterized by differential thermal spectroscopy (DTA) using a WCT-1A differential thermal analyser (China) with nitrogen purge of 20 mL min<sup>-1</sup>. The surface morpho-

logies of the GPE films were examined by scanning electron microscope (SEM) on an ISI-SE-40 machine (Japan).

### Preparation of the PLIB cells

The test PLIB cells were fabricated directly by the in-situ thermal polymerization method. This was done by inserting the uncased battery cores in metallized plastic pouches and then vacuum-sealing after filling with the precursor electrolyte solution. Finally, the assembled cells were kept at 100 °C for 1 h in an oven for internal thermal polymerization. The battery cores were prismatic C–LiCoO<sub>2</sub> battery cores with a nominal capacity of 780 mAh, provided by the Fenghua Lithium Battery Corp. (Guangdong, China). All the cell assembling processes were carried out in a dry box filled with argon gas.

The electrochemical performances of the pouched PLIB cells were evaluated galvanostatically by charge–discharge of the cells between the upper limit of 4.2 V and the lower limit of 2.75 V using a BTS-0518001 battery test system (Shenzhen, China).

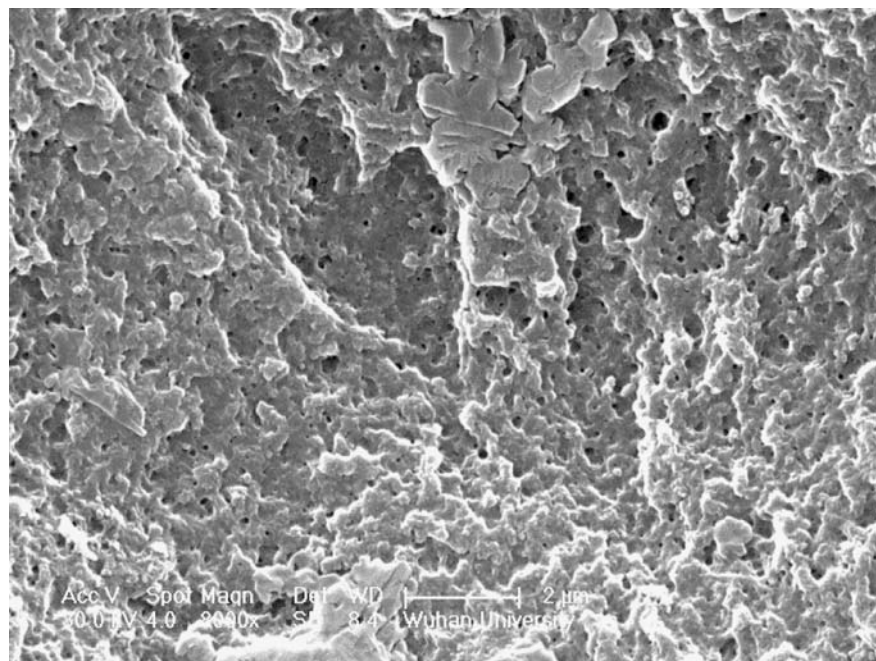
## Results and discussion

### Structural and electrochemical features of the GPE films

The structure of a GPE film is usually considered to consist of two phases: an insulating polymer matrix and a liquid electrolyte phase. The liquid electrolyte is trapped in the polymeric frameworks. In order to visualize the polymer matrix of the GPE film, we used SEM spectroscopy to characterize the structural features of the GPE films in-situ polymerized at various polymerization conditions. Figure 1 shows a typical SEM image of the framework structure of the GPE film rinsed with acetone. The polymer chains, produced in the thermal polymerization, are very well cross-linked to form a three-dimensional structure with an abundance of porosity. Thus it can be expected that this GPE structure has good mechanical strength and large ability to absorb liquid electrolyte.

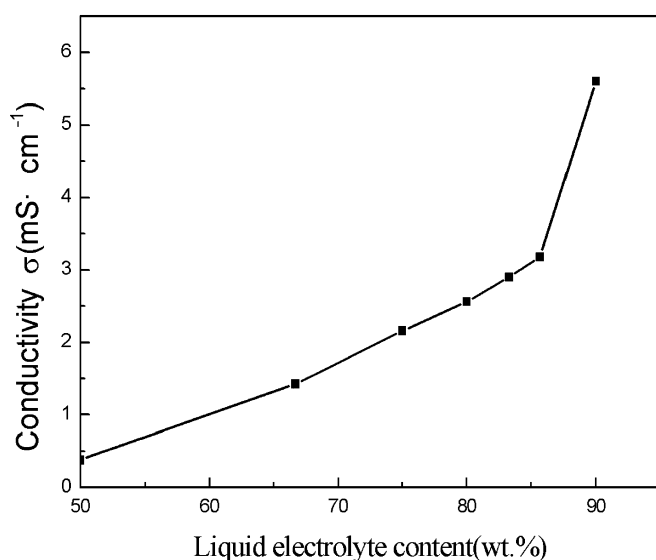
It is generally accepted that higher electrolyte content gives a higher ionic conductivity and, accordingly, higher polymer content leads to a higher mechanical strength of the GPE film. From the viewpoint of battery applications, it is of practical importance to obtain a sufficiently high conductivity with appropriate mechanical properties. In the thermal polymerization of poly(diacrylate) films, we compared the ionic conductivities and mechanical properties of the GPE films with various content of liquid electrolyte and found that all the films polymerized in-situ in the electrolyte had good mechanical properties as long as the polymer content was not less than 10 wt.%. Thus, of primary concern is the ionic

**Fig. 1** SEM image of the GPE film



conductivity in the optimization of chemical composition of the precursor electrolyte solution.

Figure 2 shows the ionic conductivities of the GPE films with liquid electrolyte content ranging from 50 wt.% to 90 wt.%, measured at ambient temperature. As expected, the ionic conductivity of the GPE films increases continuously with increasing content of the liquid electrolyte. When the film contains 90 wt.% liquid electrolyte, its ionic conductivity reaches a value of  $5.6 \times 10^{-3} \text{ S cm}^{-1}$ , which approaches the value of corresponding liquid solution ( $7.8 \times 10^{-3} \text{ S cm}^{-1}$ ). Except for this electrolyte content, all the conductivity data of the GPE films with lower electrolyte content are consider-



**Fig. 2** Ionic conductivity of the GPE film as a function of liquid electrolyte content at 20 °C

ably lower than the values expected from the amount of the electrolyte solution contained in the film. This phenomenon suggests that the liquid electrolyte is, at least, highly dispersed in (or may be coordinated with) the framework of polymer chains. Although this immobilization of the liquid electrolyte results in a reduction in the conductivity due to the frustrated ionic conduction, it is required from safety considerations of Li-ion batteries. Nevertheless, the conductivities of the GPE films all reach above  $10^{-3} \text{ S cm}^{-1}$  at an electrolyte content higher than 60 wt.%, which is sufficient for use in Li-ion batteries.

A significant drawback of polymer electrolytes is their poor conductivity at lower temperatures. To evaluate low temperature behaviors of the GPE film, we measured the ionic conductivities of the poly(diacrylate) films at wide temperature range of  $-40 \text{ }^\circ\text{C}$  to  $60 \text{ }^\circ\text{C}$ . Figure 3 shows the changes in the conductivity with temperature for a GPE film containing 85 wt.% liquid electrolyte. It can be seen from the figure that the ionic conductivity decreases appreciably, but not severely, with decreasing temperature. The ionic conductivity of the GPE film at  $60 \text{ }^\circ\text{C}$  is around  $5.0 \times 10^{-3} \text{ S cm}^{-1}$  and decreases to  $3.2 \times 10^{-3} \text{ S cm}^{-1}$  at  $20 \text{ }^\circ\text{C}$ . Even at  $-30 \text{ }^\circ\text{C}$ , the GPE film still has a considerable ionic conductivity of  $5.6 \times 10^{-4} \text{ S cm}^{-1}$ , which is comparable to the value of the liquid electrolyte at the same temperature. It can also be seen that the plot of logarithm  $\sigma$  versus  $T^{-1}$  for the GPE film shows a linear relationship in accordance with the Arrhenius equation, suggesting that ionic conduction in the GPE film proceeds with the same mechanism as in liquid electrolytes.

The electrochemical window of the GPE film can be visualized from the cyclic voltammogram of a Pt microelectrode in contact with the GPE film, as is shown in Fig. 4. The only noticeable feature in Fig. 4 is the

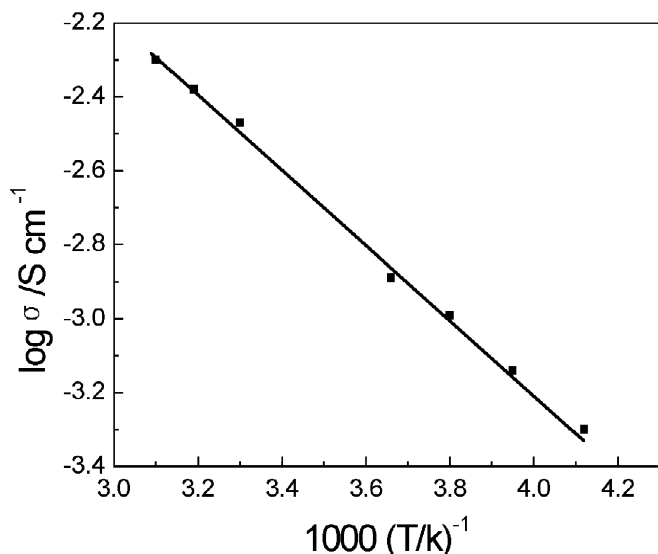


Fig. 3 Ionic conductivity of the GPE film containing 85 wt.% liquid electrolyte at various temperatures

appearance of strong oxidation current at an onset potential of +4.5 V. Since this current peak closely resembles the oxidation peak observed for anodic decomposition of the liquid electrolyte both in the potential position and peak shape, it is reasonable to attribute this peak to the oxidative decomposition of the liquid electrolyte contained in the GPE film. Except for this oxidation peak, no other CV features are observed in the potential region of 0–4.5 V, implying that the polymer structure of the GPE film is very stable in the operating potential region of Li-ion batteries.

Thermal stability of the GPE film is also an important consideration for its use in Li-ion batteries. Figure 5 compares DTA curves of the GPE film with those of the

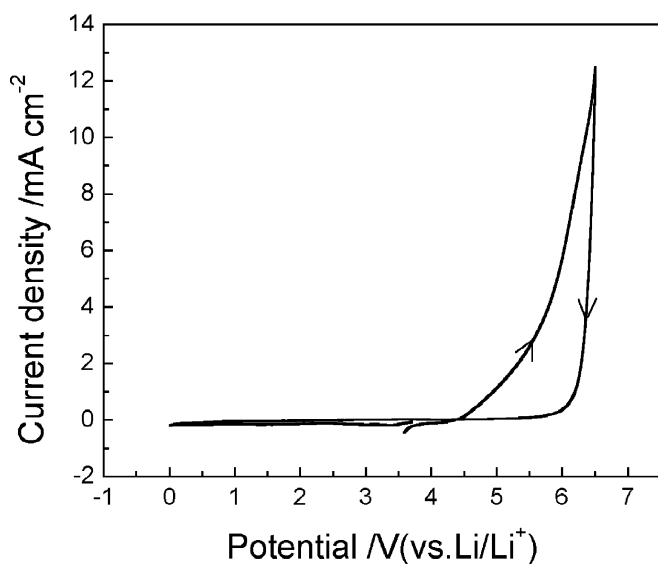


Fig. 4 Cyclic voltammograms of a Pt microelectrode on the GPE film at potential scan rate of 5 mV s<sup>-1</sup>

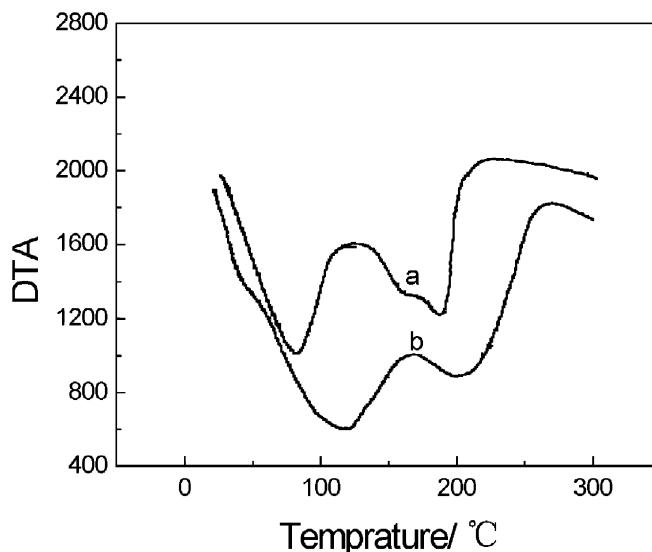


Fig. 5 Comparison of the DTA curves of a liquid electrolyte and b GPE

liquid electrolyte of 1.0 M LiPF<sub>6</sub>/EC+EMC+DMC. At the temperature below 300 °C, these two types of electrolytes have almost the same thermal properties, showing two similar endothermic bands at similar temperatures. For the liquid electrolyte, the two peaks appear at the temperatures of 85 °C and 200 °C, respectively, while the corresponding DTA bands for the GPE film appear at 110 °C and 210 °C. Considering that the boiling points of pure DMC, EMC, and EC are 90 °C, 109 °C, and 238 °C, respectively, the first endothermic peak is most likely to arise from the evaporation of DMC and EMC, and the second bands at ca.200 °C from EC evaporation. The slight shifts of the DTA bands to the higher temperatures observed for the GPE film suggest that there must exist a coordinating interaction between the polymer chains and the electrolyte molecules, which leads to the high solvent retention and low electrolyte fluidness in the GPE film. These data confirm that the GPE film has at least the same thermal stability as the liquid electrolyte already used in lithium ion batteries.

#### Performance characteristics of the PLIB cells

In order to evaluate the actual feasibility of the in-situ thermal polymerization method in practical lithium ion batteries, we adopted this method to fabricate the PLIB cells using the precursor electrolyte solution instead of the commonly used liquid electrolyte and thermally initiating polymerization of the pouched MCMB–LiCoO<sub>2</sub> cells at a constant temperature of 100 °C. After a large number of optimizing experiments, the chemical composition of the precursor electrolyte solution was selected to be a mixture of 5 wt.% BDDA monomer, 94.3 wt.% liquid electrolyte (1.0 M LiPF<sub>6</sub> in a mixture of EC+EMC+DMC) and 0.7 wt.% AIBN initiator.

Figure 6 shows the cross section image of a MCMB–LiCoO<sub>2</sub> type PLIB cell. It is clearly shown in the figure that the electrode–separator interface is not separated, and that the cathode, anode, and separator are all tightly bonded together and integrated into a whole after the in-situ polymerization. This is because the precursor solution contains only a very small amount of the monomer additives of 5 wt.% and have a very similar low viscosity as the pure liquid electrolyte, which could easily penetrate into every part of the cell to polymerize into an integrated three-dimensional network.

This network structure can provide not only a framework for immobilizing the liquid electrolyte, but can also act as a strong binder to bind the electrodes and separator together. In addition, this integrated structure provides the compact contact between the electrode and separator, and also between the electro-active particles. As a result, the interfacial resistance of the PLIB cells made by the in-situ polymerization would be effectively reduced and the operational stability is expected to be improved in comparison with the cells using the pre-manufactured GPE film as electrolyte.

Figure 7 shows the first charge–discharge curves of a pouched PLIB cell with dimensions of 3.6×34×58 mm (L×W×H) and nominal capacity of 780 mAh. It can be seen that the charge and discharge profiles show quite flat voltage plateaus with an average charging voltage of 3.9 V and average discharging voltage of 3.7 V, characteristic of the high voltage capability of a MCMB–LiCoO<sub>2</sub> lithium ion battery. The initial discharge capacity of the PLIB cell reaches about 780 mAh and the charge–discharge efficiency approaches 92.1%, demonstrating that the PLIB cells so prepared have almost the same electrochemical performance as the liquid electrolyte lithium ion batteries.

The rate capability of the PLIB cells is given in Fig. 8. Like liquid electrolyte Li-ion batteries, the discharge capacity of the PLIB cells decreases with increasing current rate. The discharge capacity of the PLIB cells is 785 mAh at 0.2 C, and decrease to 757 mAh

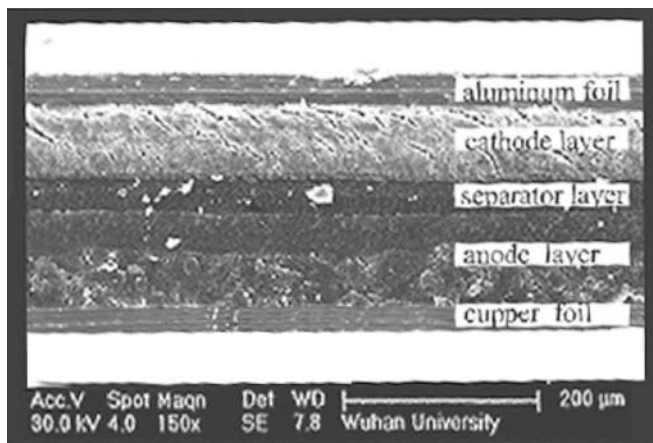


Fig. 6 SEM image of the cross section of the electrode/separators interface in the PLIB cells

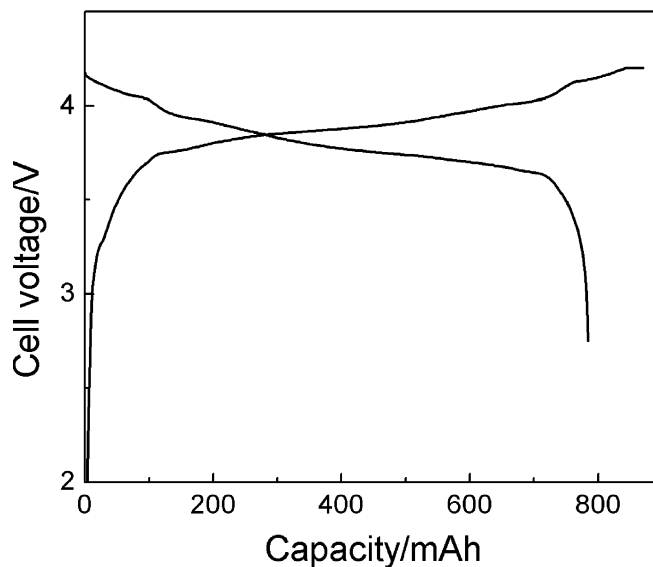


Fig. 7 Initial charge–discharge curves of the PLIB cells prepared by in-situ polymerization

and 742 mAh at 0.5 C and 1.0 C, corresponding to a capacity retention of 96.4% and 94.4% at 0.5 C and 1.0 C, respectively. Compared with the liquid electrolyte lithium ion batteries, the PLIB cells exhibit a slight reduction (ca. 6%) in the discharge capacity at high rate of 1.0 C. The reduced high rate capability is probably due to the lower diffusion rate of lithium ions in the gel electrolyte, which is the result of the frustrated ionic conduction mentioned above.

Figure 9 shows the discharge curves of the PLIB cells at various temperatures at constant current of 0.2 C. As shown, both the discharge voltage and capacity of the cells are decreased with lowering temperature. The discharge capacity at 0 °C is about 96% of the value

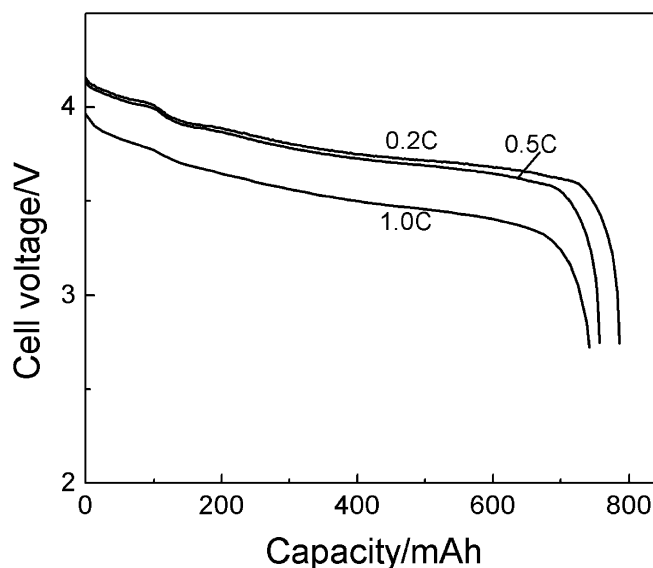


Fig. 8 Discharge curves of the PLIB cell at various discharge rates

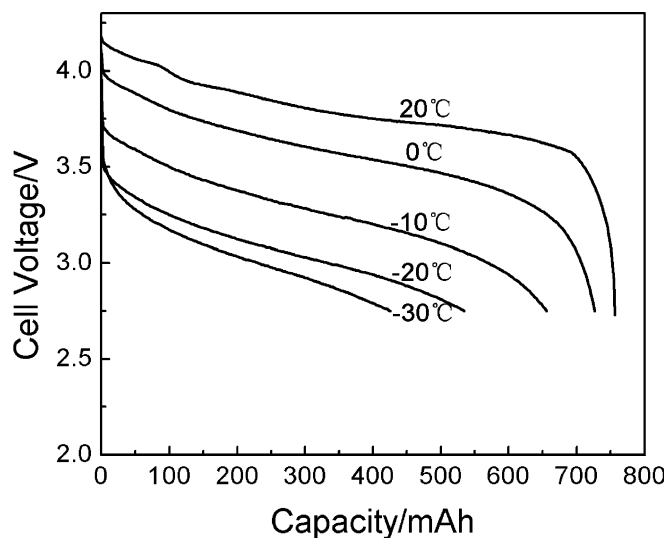


Fig. 9 Discharge curves of the PLIB cell at various temperatures

obtained at 20 °C, while at –20 °C the realized discharge capacity is only around 71% of the capacity delivered at 20 °C. At the temperature of –30 °C, the cells can still deliver 53% of ambient capacity. In fact, the reductions in the rate capabilities are acceptable and are still in the same magnitude as observed for liquid electrolyte lithium ion batteries [24, 25]. These results suggest that the PLIB cells prepared by the in-situ thermal polymerization may have improved low-temperature discharge ability over the cells using the pre-manufactured GPE films as electrolyte.

The structural stability and operational reliability of the PLIB cells can be seen from the cycling performances, as shown in Fig. 10. It can be seen that the capacity of the PLIB cell decreases very slowly with the cycling numbers. After 300 cycles at 100% depth of

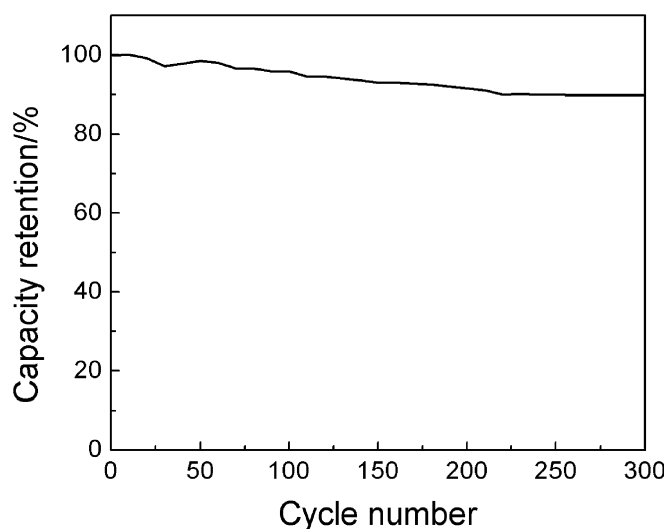


Fig. 10 Cycling performance of the PLIB at constant charging and discharging current of 0.5 C rate at ambient temperature

charge–discharge at 0.5 C rate, the capacity retention of the cell can still remain above 85% of its initial capacity, indicating that the electrode–electrolyte interface created by the in-situ polymerization has a very stable structure. Therefore, excellent cycling performances for the PLIB cells are expected.

## Conclusion

A gel polymer electrolyte (GPE) was prepared by in-situ polymerization of 1,3-butanediol diacrylate in an EC/EMC/DMC electrolyte solution. The GPEs thus prepared exhibit high room temperature conductivities (above  $3.0 \times 10^{-3} \text{ S cm}^{-1}$ ), wide electrochemical window ( $> 4.5 \text{ V}$ ) and sufficient mechanical strength with the polymer content  $\geq 10\%$ . This in-situ thermal polymerization method was developed to fabricate the PLIB cells simply by adding the curable monomer and initiator additives in the organic liquid electrolyte. The PLIB cells so prepared show almost the same electrochemical performances as liquid electrolyte lithium ion batteries. Since this in-situ polymerization method does not require the complicated film-making processes, it can be simply and conveniently used for manufacture of PLIB cells at an industrial scale.

**Acknowledgement** The authors gratefully acknowledge the financial support by the National 973 Program, China (Grant No. 2002CB211800) and the National 863 Program, China (Grant No. 2001AA323030).

## References

1. Wright PV (1998) *Electrochim Acta* 43:1137
2. Dias FB, Plomp L, Veldhuis JB (2000) *J Power Sources* 88:169
3. Murata K, Izuchi S, Yoshihisa Y (2000) *Electrochim Acta* 45:1501
4. Tarascon JM, Armand M (2001) *Nature* 414:359
5. Wakihara M (2001) *Mater Sci Eng R33*:109
6. Bohnke O, Frand G, Rezrazi M, Rousselot C, Truche C (1993) *Solid State Ionics* 66:97
7. Quartarone E, Tomasi C, Mustarelli P, Appetecchi GB, Croce F (1998) *Electrochim Acta* 43:1435
8. Jayathilaka PARD, Dissanayake MAKL, Albinsson I, Melander BE (2003) *Solid State Ionics* 156:179
9. Abraham KM, Alamgir M (1990) *J Electrochem Soc* 137:1657
10. Boudin F, Andrieu X, Jehoulet C, Olsen II (1999) *J Power Sources* 81–82:804
11. Sekhon SS, Singh HP (2002) *Solid State Ionics* 152–153:169
12. Jiang Z, Carroll B, Abraham KM (1997) *Electrochim Acta* 42:2667
13. Shi Q, Yu MX, Zhou X, Yan YS, Wan CR (2002) *J Power Sources* 103:286
14. Wang Y, Travas-Sejdic J, Steiner R (2002) *Solid State Ionics* 148:443
15. Travas-Sejdic J, Steiner R, Desilvestro J, Pickering P (2001) *Electrochim Acta* 46:1461
16. Kuo HH, Chen WC, Wen TC, Gopalan A (2002) *J Power Sources* 110:27
17. Kim HS, Shin JH, Moon SI, Kim SP (2003) *Electrochim Acta* 48:1573
18. Kang DW, Kim DW, Jo SI, Sohn HJ (2002) *J Power Sources* 112:1

19. Taniuchi, Masahiro, Inoue, Romohiro, Kabata et al. U.S.Pat No:6,013,393
20. Kim HS, Shin JH, Doh CH, Moon SI, Kim SP (2002) J Power Sources 112:469
21. Kim HS, Shin JH, Moon SI, Yun MS (2003) J Power Sources 119–121:482
22. Noda A, Watanable M (2000) Electrochim Acta 45:1265
23. Sun LY, Higaki K, McDonald R (1997) J Power Sources 68:352
24. Marsh RA, Vukson S, Surampudi S, Ratnakumar BV, Smart MC, Manzo M, Dalton PJ (2001) J Power Sources 97–98:25
25. Fellner JP, Loeber GJ, Sandhu SS (1999) J Power Sources 82–82:867