Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Power Sources 154 (2006) 276–280

JOURNAL OF POWER SOURCES

www.elsevier.com/locate/jpowsour

Short communication

LiBOB-based gel electrolyte Li-ion battery for high temperature operation

S.S. Zhang*, K. Xu, T.R. Jow

U.S. Army Research Laboratory, Adelphi, MD 20783-1197, USA

Received 25 February 2005; accepted 20 March 2005
Available online 31 May 2005

Abstract

In this work, we evaluated the chemical compatibility of 1.0m (molality) lithium bis(oxalate)borate (LiBOB) 1:1 (w/w) propylene carbonate (PC)/ethylene carbonate (EC) liquid electrolyte with lithium metal and spinel $LiMn_2O_4$ cathode using storage and cycling tests at high temperatures. Impedance analyses show that LiBOB and lithium are very compatible due to the formation of a stable passivation layer on the surface of lithium. Cycling tests of Li/Cu and Li/$LiMn_2O_4$ cells, respectively, show that lithium can be plated and stripped in LiBOB-based electrolyte with more than 80% cycling efficiency, and that this electrolyte can support $LiMn_2O_4$ cycling reversibly up to 60 °C without visible capacity loss. Using LiBOB-based liquid electrolyte and porous Kynar® membrane, microporous gel electrolyte (MGE) Li-ion cells were assembled and evaluated. Results show that the MGE cell presents an improved cycling performance compared with a liquid cell, especially at elevated temperatures. It is confirmed that the LiBOB-based gel electrolyte Li-ion batteries can be operated at 60 °C with good capacity retention.

Keywords: Lithium bis(oxalate)borate; Microporous gel electrolyte; Gel polymer electrolyte; Polymer Li-ion battery; High temperature performance

1. Introduction

We recently introduced an easy and convenient method for the fabrication of polymer Li-ion batteries, in which microporous gel electrolyte (MGE) is formed in situ by swelling a porous polymer membrane with limited amount of liquid electrolyte [1–3]. The MGE so-formed is a multiphase structure consisting of liquid electrolyte, gel electrolyte and a polymer phase. Therefore, the MGE combines the advantages of liquid electrolytes (high ionic conductivity) and solid polymer electrolytes (good mechanical strength and good adhesion to the electrodes) although its phase structure is metastable and it finally may become a uniform gel phase. Our early work has shown that the MGE can withstand temperatures above 100 °C without significant loss in the mechanical strength, depending on the type of polymer and on the amount of liquid electrolyte [1–4]. Meanwhile, the MGE technique offers the advantage of allowing most procedures for battery fabrication to be conducted in a non-anhydrous environment except for the last electrolyte activation step.

In addition to the mechanical strength of the electrolyte membrane, thermal stability of the liquid electrolyte greatly affects cycling performance of the Li-ion batteries at high temperatures. It has been known that $LiPF_6$, being the salt most extensively used in the commercial Li-ion batteries, is thermally unstable. At elevated temperatures, it is easily decomposed into LiF and PF_5, and the decomposition is significantly accelerated in the presence of organic solvents [5,6]. In an effort to search for a replacement for $LiPF_6$, we found that lithium bis(oxalate)borate (LiBOB) has many unique properties [7–9], such as, (1) it is thermally stable up to 300 °C, (2) it passivates aluminum (the cathode current collector) very well at high potentials, (3) it participates in forming a very stable solid electrolyte interface (SEI) with a carbonaceous anode even in high PC-containing electrolytes, (4) its solution offers high ionic conductivity, (5) its synthesis is easy and of low cost and (6) its disposal using water does not release toxic materials. More recently, superior safety has been reported for the Li-ion batteries with a LiBOB-based electrolyte [10,11].

---

* Corresponding author. Tel.: +1 301 394 0981; fax: +1 301 394 0273.
E-mail address: szhang@arl.army.mil (S.S. Zhang).

0378-7753/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jpowsour.2005.03.196

Among the above advantages, we are in particular interested in the feature that LiBOB supports graphitic anodes being cycled in pure PC solution [8,9,12]. This property makes it possible to use PC-based electrolytes in the Li-ion batteries since PC not only has a very low freezing temperature but also is low cost [13]. In this work, we used LiBOB-PC based liquid electrolyte and porous Kynar® membrane to make MGE cells and studied the cycling performance of such cells at high temperatures. We here report the chemical compatibility of the LiBOB-based electrolyte with electrode materials and present cycling data of such cells at high temperatures.

2. Experimental

LiBOB was supplied by Chemmetal (Germany) and was used as received by drying it at 100 °C under vacuum for 8 h. Propylene carbonate (PC) and ethylene carbonate (EC), from Ferro Chemical, were dried doubly by using 3 Å molecular sieve and neutral alumina, respectively. In a glove-box having oxygen and moisture levels below 10 ppm, a 1.0m (molality) solution of LiBOB dissolved in 1:1 (w/w) PC/EC mixed solvent was prepared and used as the liquid electrolyte. Kynar Flex™ 2801, a poly(vinylidene fluoride-*co*-hexafluoropropylene) copolymer from Elf Atochem North America, was used as the polymer matrix of the MEG. The Microporous membrane was prepared by the phase inversion method using acetonitrile as the solvent and deionized water as the non-solvent. Detailed procedures for the preparation of the microporous membrane were described in our earlier papers [1,2]. The resulting membrane was dried at 90 °C under vacuum for 16 h before use.

A standard graphitic anode and a $LiNiO_2$-based cathode were provided by SAFT America. The electrode sheets were cut into discs of $1.27\,cm^2$ and $0.97\,cm^2$ for the anode and cathode, respectively, followed by drying at 120 °C under vacuum for 12 h. A Celgard® 3500 membrane was used as the separator in electrochemical cells for the evaluation of the liquid electrolyte. The MEG cells were assembled by the same procedure used for the liquid electrolyte cells, and activated with liquid electrolyte, followed by heating the cells at 80 °C for 20 min to promote formation of the MGE. As shown in previous work [1,2], the MGE such-formed generally has a thickness of 0.14 mm and contains $120 \pm 5\%$ of liquid electrolyte versus the weight of dried porous membrane.

A Tenney Environmental Oven Series 942 was used to control the temperature for the tests. Solartron SI 1287 Electrochemical Interface and SI 1260 Impedance/Gain-Phase Analyzer were employed to measure impedance. The impedance was measured potentiostatically by applying a dc bias (its value equals the open-circuit voltage of the cell) and an ac oscillation of 10 mV over the frequency range from 100 kHz to 0.01 Hz. Cycling test of the cells was performed on a Maccor Series 4000 tester. The cycling conditions are described either in the text or in the figure caption.

3. Results and discussion

3.1. Compatibility between LiBOB-based electrolyte and lithium metal

Chemical compatibility of LiBOB-based electrolyte and lithium metal was evaluated by monitoring the impedance change of a symmetric Li/Li cell in a 60 °C-storage test. Fig. 1a is a typical Nyquist plot of the cell, showing that the impedance spectrum consists of three over-lapping semicircles. An equivalent circuit for this type of spectra is shown in inset. R_b is the bulk resistance of the electrolyte, Z_p the impedance of the passivation layer formed on the surface of the lithium metal, which consists of the resistance (R_p) of the passivation layer and its related capacitance (C_p), and Z_f is the Faradaic impedance reflecting the impedances of

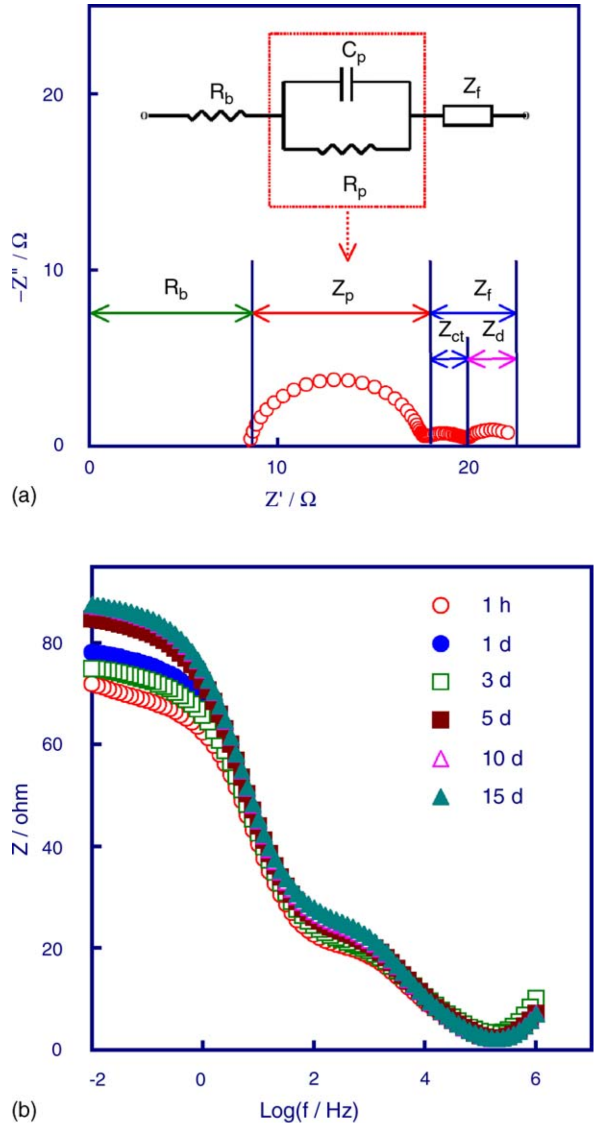

Fig. 1. (a) A typical Nyquist plot of the Li/Li symmetric cells and (b) Bode plots of a Li/Li cell using 1.0m LiBOB 1:1 PC/EC liquid electrolyte after different storage times at 60 °C.

charge-transfer (Z_{ct}) and ion diffusion (Z_d) at the lithium–electrolyte interface. These two semicircles, contributed by the charge-transfer and ion diffusion processes, may be merged with each other when the diffusion of Li^+ ions on the Li–electrolyte interface is fast. Fig. 1b compares Bode plots of the cell after different storage times. It is indicated that the impedances at frequencies above 10^0 Hz almost remained constant with storage time, while those at frequencies below 10^0 Hz slowly increased with the time. By comparing Fig. 1a and b, one sees that the impedances above 10^5 Hz correspond to R_b, those between 10^5 Hz and 10^2 Hz to Z_p, and those below 10^2 Hz to Z_f. Based on the analyses above, we conclude that the passivation layer formed on the surface of lithium is very stable, and that the LiBOB-based electrolyte is chemically compatible with lithium metal.

3.2. *Cyclability of lithium metal in LiBOB-based electrolyte*

Cyclability of lithium in a cell is affected by two aspects. One is morphology of the plated lithium, which relates to the formation of dendritic lithium. The other one is cycling efficiency, which relates to figure-of-merit (FOM) of lithium in the cell. To examine if the formation of dendritic lithium can be effectively suppressed in LiBOB-based electrolyte, we assembled a symmetric Li/Li cell using lithium foils (0.002 in. thick) as the electrodes and one piece of Celgard® 3500 membrane as the separator. Lithium was plated at a current density of 1.6 mA cm^{-2} until the cell was short-circuit by dendritic lithium or lithium had completely run out on the positive side. It was found that the plating process lasted for more than 14 h until the cell voltage sharply increased due to run-out of the lithium on the positive side. This fact suggests that the formation of dendritic lithium would be greatly hindered in the LiBOB-based electrolyte.

Fig. 2 shows the cycling efficiency of lithium metal on a Cu foil in the LiBOB-based electrolyte. In this experiment, a Li/Cu cell with one piece of Celgard® 3500 membrane as the separator was assembled and cycled at 1.6 mA cm^{-2}. To remain at constant capacity for all cycles, the plating process was fixed for 1 h, and the subsequent stripping process was controlled by the cell voltage that dramatically changed as the plated lithium was stripped out (see inset in Fig. 2). As shown in Fig. 2, lithium metal can be repeatedly cycled in the LiBOB-based electrolyte with the cycling efficiencies higher than 80%. The results described above indicate that cyclability of lithium metal in the LiBOB-based electrolyte is very good.

3.3. *Compatibility of LiBOB-based electrolyte with $LiMn_2O_4$ cathode*

Compatibility of the LiBOB-based electrolyte with the $LiMn_2O_4$ cathode was evaluated by a cycling test on a $Li/LiMn_2O_4$ cell at various temperatures and monitoring, the impedance change of the cell. For this purpose, an Al-doped $LiMn_2O_4$ cathode was coated using poly(acrylonitrile-methyl methacrylate) as the binder [14]. Using 1.0m LiBOB PC/EC electrolyte, a liquid electrolyte $Li/LiMn_2O_4$ was assembled and cycled at 0.5*C* between 3.5 V and 4.2 V at various temperatures. Fig. 3 plots charge and discharge capacities of $LiMn_2O_4$ cathode as a function of cycle number. It is shown that when cycling at room temperature and at 60 °C, the charge and discharge capacities are nearly identical and the $LiMn_2O_4$ remained at very stable capacity. It has been reported [15] that dissolution of Mn for $LiMn_2O_4$-based cathode materials can be substantially suppressed in the LiBOB-based electrolytes. Therefore, the excellent cycling performance observed above can be attributed to the reduced dissolution of Mn due to the presence of LiBOB. When the temperature was raised to 70 °C, however, both charge and discharge capacities started fading rapidly and the cycling efficiencies fell below 100%. Obviously, the fast capacity fading during cycling at 70 °C is associated with low cycling efficiencies.

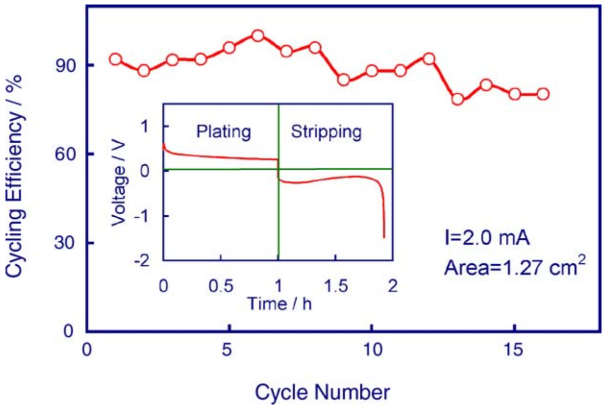

Fig. 2. Cycling efficiencies of plating and stripping of lithium metal on Cu foil in 1.0m LiBOB 1:1 PC/EC electrolyte. Inset is a plot showing voltage–time response of the cell recorded during the first cycle.

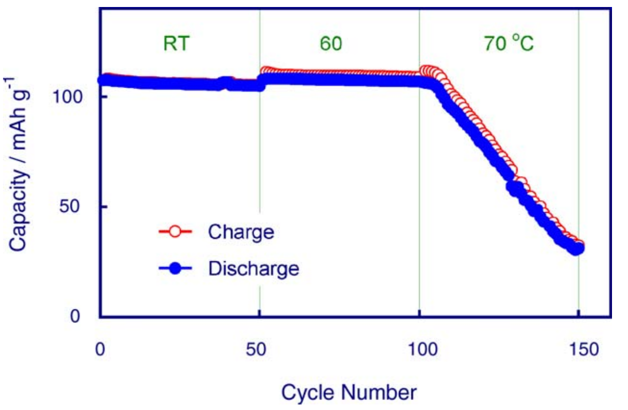

Fig. 3. Cycling performance of a liquid electrolyte $Li/LiMn_2O_4$ cell using 1.0m LiBOB 1:1 PC/EC electrolyte at different temperatures. The cell was cycled at a constant current rate of 0.5*C* between 3.5 V and 4.2 V.

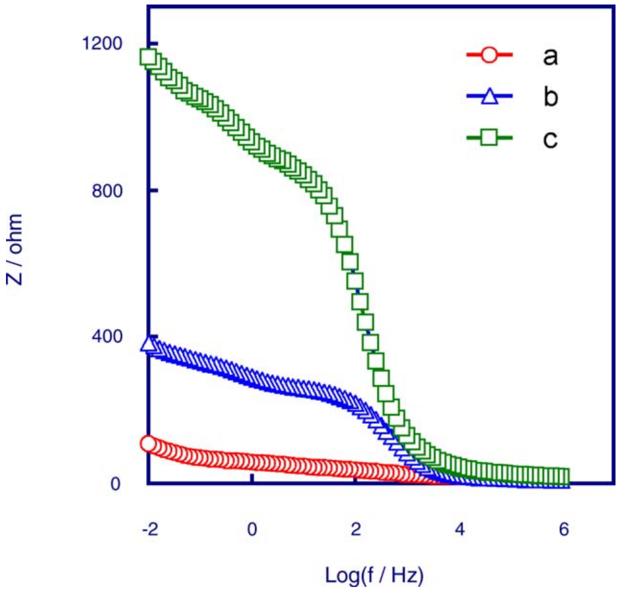

Fig. 4. Bode plots of the Li/LiMn$_2$O$_4$ cell after a progressive cycling at room temperature, 60 °C and 70 °C for 50 cycles, respectively.

To understand the phenomena observed above, we analyzed the cell impedance after the cell was cycled for 50 cycles at each temperature. In this experiment, the cell was cooled to 20 °C after every 50 cycles at each temperature, and then brought to the fully charged state by charging the cell at 0.5*C* to 4.2 V and then holding it at 4.2 V for 1 h. Fig. 4 displays Bode plots of the cell after 50 cycles at each temperature. It can be seen that the impedances below 10^3 Hz were significantly increased after the cell was cycled at 60 °C and 70 °C, respectively. In reference to the analyses on Fig. 1a and b, the impedances in these frequency regions correspond to the surface layer on the electrodes and Faradaic processes occurring at the electrode–electrolyte interface. We consider that the increased impedance of the surface layer in the Li/LiMn$_2$O$_4$ cell mainly resulted from the cathode since the impedance of the passivation layer on lithium surface remained constant during the storage at 60 °C (see Fig. 1b). Less than 100% cycling efficiency at 70 °C, as shown in Fig. 3, suggests that some side reactions must take place. These side reactions would be responsible for the increased impedance of the cell and subsequently for the fast capacity fading observed at 70 °C. On the basis of the above results, it is concluded that the LiBOB-based electrolyte is able to support LiMn$_2$O$_4$ cathode cycling up to 60 °C.

3.4. Cycling performance of LiBOB-based gel electrolyte Li-ion cell

Using porous Kynar® membrane and standard Li-ion electrodes of SAFT America, the LiBOB-based liquid electrolyte was assembled into a gel electrolyte Li-ion cells by means of MGE technique [1–3]. The weight ratio of liquid electrolyte to dried membrane in the gel electrolyte was about 1.25:1. After activation with the liquid electrolyte, the cell was formed at 0.1*C*, and then cycled at 0.5*C* between 2.7 V and 4.1 V. Voltage–capacity curves of the initial two forming cycles are displayed in Fig. 5, from which cycling efficiencies are estimated to be 82.5% and 98.3% for the first and second cycles, respectively. These values are very close to those observed with other electrolyte systems, such as LiPF$_6$-EC-EMC (ethyl methyl carbonate) [16], LiBF$_4$-EC-EMC [17], and LiBF$_4$-EC-GBL (γ-butyrolactone) [1]. High efficiency of the first cycle in the high PC-containing solution is attributed to the fact that the LiBOB participates into forming a stable SEI [8,9].

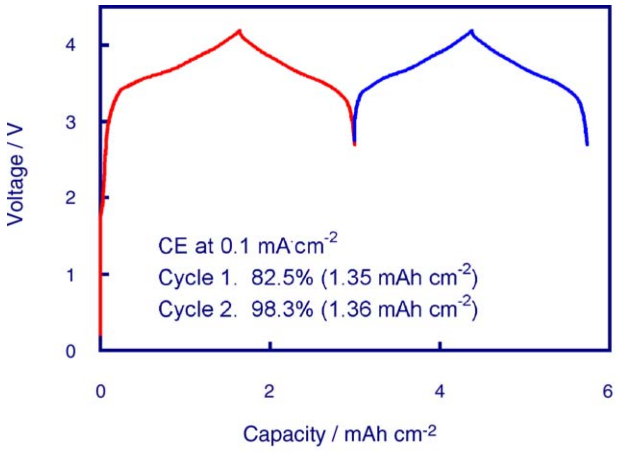

Fig. 5. Voltage–capacity curve of the initial two forming cycles of a Li-ion cell using LiBOB-based MGE, which was recorded at 0.1*C*.

Fig. 6 compares the cycling performance of the liquid electrolyte cell and gel electrolyte cell at different temperatures, in which the liquid electrolyte cell used one piece of Celgard® membrane as the separator. Generally, the gel electrolyte cell shows superior cycling performance, especially at high temperatures. Below 60 °C, both cells can be cycled with very stable capacity retention. However, capacity fading is significantly accelerated as the temperature was raised to above 70 °C. Fig. 7 compares Bode plots recorded from the

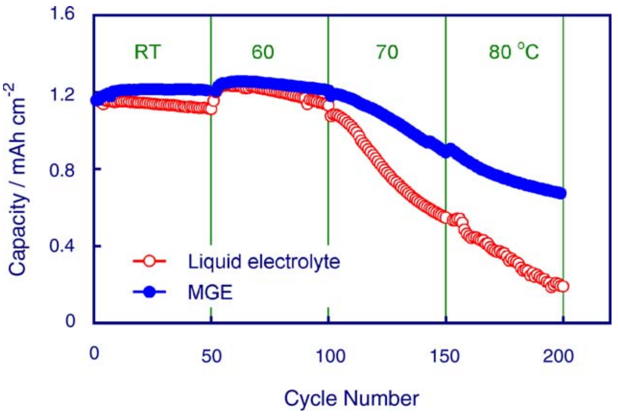

Fig. 6. Cycling performance of the Li-ion cells with LiBOB-based liquid electrolyte and MGE, respectively, at different temperatures. The cells were cycled at a constant current rate of 0.5*C* between 2.7 V and 4.1 V.

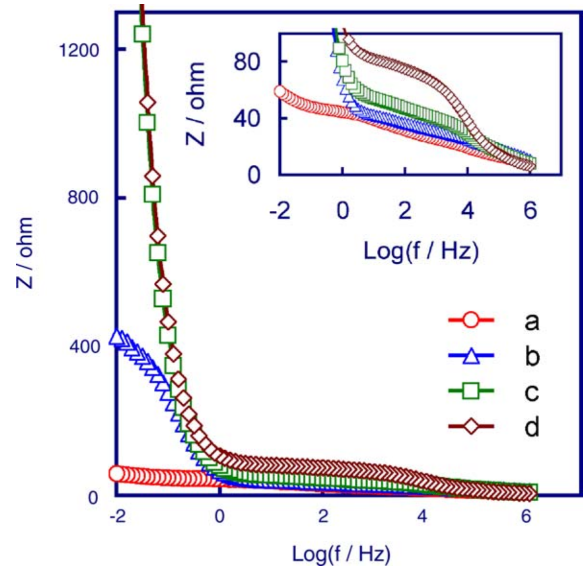

Fig. 7. Bode plots of the LiBOB-based MGE Li-ion cell after a progressive cycling at different temperatures.

gel electrolyte cell after 50 cycles at each temperature. It is shown that cell impedance was significantly increased after the cell was cycled at elevated temperatures. It is estimated from Fig. 7 that after 50 cycles at 60 °C, the total impedance of the cell at 0.01 Hz was increased by seven-fold (from 59 Ω to 430 Ω) although no significant loss in the capacity was observed. This may be because the current rate used (0.5*C*) is relatively low, which is not enough to reflect the change of cell impedance.

We are interested in the difference between Fig. 4 and Fig. 7. The data in these two figures were measured under nearly identical conditions. However, frequency regions for the significant change of the cell impedance are entirely different. For Li/$LiMn_2O_4$ cell (Fig. 4), the significant impedance increase starts at 10^3 Hz, and the increased impedance relates to both the surface layer and Faradaic process (see discussion in Section 3.3). For the Li-ion cell, however, the most significant increase of the cell impedance occurs below 10^0 Hz, which most likely corresponds to the Faradaic process. These observations reveal that capacity loss of the Li-ion cells at high temperatures mainly results from a slow-down of the electrode kinetics, rather than from the increased impedance of the surface layers. The slow-down of the electrode kinetics might be associated with degradation of the electrode structure.

4. Conclusions

Results of this work indicate that the LiBOB-based electrolyte is chemically compatible with lithium metal, and it is able to suppress the formation of dendritic lithium. For cathode materials, the LiBOB-based electrolyte can support $LiMn_2O_4$ cycling up to 60 °C without apparent capacity loss due to the substantially lower dissolution of Mn. In addition, LiBOB improves Li-ion cells even in the high PC-containing electrolytes because of its ability to participate in forming a very stable SEI with the graphitic anode. For the first forming cycle, the gel electrolyte Li-ion cell made of porous Kynar® membrane and 1.0m LiBOB 1:1 PC/EC liquid electrolyte has a high cycling efficiency (>80%) like other liquid/gel electrolyte cells, such as those using $LiPF_6$-EC-EMC, $LiBF_4$-EC-EMC, and $LiBF_4$-EC-GBL. The LiBOB-based gel electrolyte Li-ion cell can be cycled at 60 °C without visible capacity fading. However, the cell suffers from significant capacity fading as the temperature reaches or exceeds 70 °C, which is likely associated with the degradation of the electrode structure.

Acknowledgement

Receipt of electrode sheets from Saft America is gratefully acknowledged.

References

[1] S.S. Zhang, K. Xu, D.L. Foster, M.H. Ervin, T.R. Jow, J. Power Sources 125 (2004) 114.
[2] S.S. Zhang, M.H. Ervin, D.L. Foster, K. Xu, T.R. Jow, J. Solid State Electrochem. 9 (2005) 77.
[3] S.S. Zhang, M.H. Ervin, K. Xu, T.R. Jow, Electrochim. Acta 49 (2004) 3339.
[4] S.S. Zhang, K. Xu, T.R. Jow, Solid State Ionics 158 (2003) 375.
[5] S.E. Sloop, J.K. Pugh, S. Wang, J.B. Kerr, K. Kinoshita, Electrochem. Solid State Lett. 4 (2001) A42.
[6] K. Tasaki, K. Kand, S. Nakamura, M. Uec, J. Electrochem. Soc. 150 (2003) A1628.
[7] K. Xu, S.S. Zhang, T.R. Jow, W. Xu, C.A. Angell, Electrochem. Solid State Lett. 5 (2002) A26.
[8] K. Xu, S.S. Zhang, B.A. Poese, T.R. Jow, Electrochem. Solid State Lett. 5 (2002) A259.
[9] K. Xu, S.S. Zhang, T.R. Jow, Electrochem. Solid State Lett. 6 (2003) A117.
[10] J. Jiang, J.R. Dahn, Electrochem. Solid State Lett. 6 (2003) A180.
[11] J. Jiang, J.R. Dahn, Electrochem. Commun. 6 (2004) 39.
[12] H. Kaneko, K. Sekine, T. Takamura, The 12th International Meeting on Lithium Batteries, Nara, Japan, 27 June–2 July 2004 (abstract no. 65).
[13] S.S. Zhang, K. Xu, J.L. Allen, T.R. Jow, J. Power Sources 110 (2002) 216.
[14] S.S. Zhang, T.R. Jow, J. Power Sources 109 (2002) 422.
[15] K. Amine, J. Liu, S. Kang, I. Belharouak, Y. Hyung, D. Vissers, G. Henriksen, J. Power Sources 129 (2004) 14.
[16] S.S. Zhang, T.R. Jow, K. Amine, G.L. Henriksen, J. Power Sources 107 (2002) 18.
[17] S.S. Zhang, K. Xu, T.R. Jow, J. Electrochem. Soc. 149 (2002) A586.