Short communication

Partially fluorinated solvent as a co-solvent for the non-aqueous electrolyte of Li/air battery

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ABSTRACT

In this work we study methyl nonafluorobutyl ether (MFE) and tris(2,2,2-trifluoroethyl) phosphite (TTFP), respectively, as a co-solvent for the non-aqueous electrolyte of Li–air battery. Results show that in certain solvent ratios, both solvents are able to increase the specific capacity of carbon in Li/O_2 and Li/air cells. More interestingly, the improvement in discharge performance of the Li/air cells increases with discharge current density. These results cannot be explained by the ionic conductivity and viscosity data of the electrolytes since the participation of fluorinated co-solvents hardly changes viscosity of the solvent blends while reversely reduces ionic conductivity of the electrolyte. In particular, we find that a 30 wt.% (vs. solvent) addition of TTFP into a 0.2 m (molality) $LiSO_3CF_3$ PC electrolyte can significantly improve the discharge performance of Li/air cells, and that the resultant electrolyte is able to support long-term operation of Li/air cells in dry ambient environments due to its low volatility. We believe that the observed performance improvement is associated with the increased dissolution kinetics and solubility of oxygen in fluorinated solvent containing electrolyte.

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1. Introduction

Non-aqueous electrolyte Li/air battery has recently received extensive research interest due to its high theoretical energy density and the potential to be operated as a rechargeable battery [1–26]. Theoretically, the operation of a Li/air battery can last as long as the supply of oxygen from environmental air and metal Li can remain. However, the operation of a practical Li–air battery is often halted by the insoluble oxygen reduction products (Li_2O_2 and Li_2O) that deposit and accumulate on the surface of carbon and eventually clog the porous channels for diffusion of gaseous oxygen. Therefore, the specific capacity of Li/air batteries is generally expressed against the weight of carbon, instead of the weight of metal Li [1–26]. In order to maximize the specific capacity of Li/air battery, many publications have devoted to developing novel non-aqueous electrolytes that are able to facilitate the diffusion of dissolved oxygen in liquid electrolyte [2,3,5,11,13] and to increase the solubility of oxygen reduction products in organic liquid electrolyte [12,19,26].

Catalytic reduction of oxygen in Li/air battery can be divided into three steps: (1) dissolution of gaseous oxygen into liquid electrolyte, (2) diffusion of dissolved oxygen into catalytic sites of the carbon surface, and (3) catalytic reduction of oxygen into Li_2O_2 or Li_2O. Many papers have discussed the role of Step 2 and Step 3 in the discharge performance of Li–air battery in terms of the electrolyte viscosity [3,5,11,12] and battery polarization [1,7,8,14,16,20,21]. Independent works by Read et al. [3,5] and Xu et al. [12], respectively, have shown that the solubility of oxygen in liquid electrolyte will no longer affect the specific capacity of carbon as long as the solubility reaches a certain value. To our knowledge, however, there are no publications addressing the role of Step 1 in Li/air battery except for few ones discussing the effect of oxygen partial pressure on the specific capacity of carbon [3,15,16].

Perfluoro solvents have been long studied as the liquid media for oxygen respiration of mammals due to fast dissolution kinetics and high solubility of oxygen in these compounds [27,28]. It has been reported that mice and cats could survive for several weeks with breathing oxygen dissolved in fluorocarbon solvents [27]. Due to their low polarity, perfluoro solvents neither dissolve lithium salt nor are miscible with polar electrolyte solvents. Therefore, perfluoro solvent itself cannot be used as the co-solvent for the non-aqueous electrolyte of Li–air battery. Assuming that fluoro-solvents increase the dissolution kinetics of oxygen into liquid electrolyte, we in this work study the effect of partially fluorinated solvents on the discharge performance of Li–air battery. For this purpose, we here select methyl nonafluorobutyl ether (MFE) and tris(2,2,2-trifluoroethyl) phosphite (TTFP), respectively, as the co-solvent since they have been well established as the co-solvent for the non-flammable electrolyte of Li-ion batteries [29–31].

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2. Experimental

Lithium triflate (LiSO$_3$CF$_3$, 96%) was purchased from Aldrich and dried at 100 °C under vacuum for 8 h. Electrolyte grade propylene carbonate (PC) and 1,2-dimethoxyethane (DME) were purchased from Ferro and used as received. Methyl nonafluorobutyl ether (MFE, >99%) and tris(2,2,2-trifluoroethyl) phosphite (TTFP, 99%) were purchased from Aldrich and dried over activated aluminum oxide for a week prior to use. Electrolytes with different compositions were prepared in a glove-box and expressed as a molality (m) for the concentration of lithium salt and a weight ratio for the composition of solvent blends. Ionic conductivity of the electrolytes was determined from the impedance of solution measured by using a two-platinum-electrode cell. Kinematic viscosity of the solvents and solvent blends was measured in a 25 °C constant temperature bath by using a Ubbelohde viscometer (Cannon Instrument Company).

Carbon air cathode with a composition of 90 wt.% Super P carbon and 10 wt.% polytetrafluoroethylene (PTFE) was prepared by mixing calculated amounts of Super P and PTFE emulsion (Teflon®, solid content = 61.5%, DuPont Co.) and rolling the mixed paste into a free-standing cathode sheet. The resultant air cathode sheet was punched into small disks with an area of 0.97 cm^2 and dried at 100 °C under vacuum for at least 8 h. Typically, the air cathode has a thickness of 0.5–0.6 mm and a porosity of 2.9–3.2 cm^3 g^{-1} (vs. Super P).

In a dry-room having a dew point of below −90 °C, Li/air cells with an air window of 0.97 cm^2 were assembled by stacking a Li foil, a Celgard® 3500 membrane, a carbon air cathode, a Ni mesh as the current collector, and an air window in sequence into a coin cell cap. To activate the cell, 200 μL of liquid electrolyte was added through the air-window, followed by applying a vacuum for 20 s to ensure complete wetting. Extra liquid electrolyte was removed by gently swiping a filter paper on the top of Ni mesh. The electrolyte-activated cell was clamped on a cell holder as a Li/air cell or sealing the cell in an O$_2$-filled plastic bag as a Li/O$_2$ cell. Detailed procedures for the assembly of Li/O$_2$ and Li/air cells are referred to our previous papers [17–19]. Before discharging, the cells were rested for 2 h to reach the equilibrium of oxygen concentration between the air cathode and O$_2$ in the cell. In dry room the cells were discharged on an Arbin BT-2000 cycler with a 1.5 V cutoff voltage. Specific capacity of the cell was referred to the weight of Super P carbon in the air cathode, and all discharging tests were carried out at room temperature (22 °C).

3. Results and discussion

3.1. MFE and TTFP as the co-solvent of Li/O$_2$ battery electrolyte

First, we randomly select a 20 wt.% of MFE and TTFP, respectively, as the co-solvent of electrolyte and examine its effect on the discharge performance of Li/O$_2$ cells. For this purpose, we employ a 0.2 m LiSO$_3$CF$_3$ 3:7 PC/DME electrolyte as the baseline since MFE is immiscible with highly polar organic solvents, including PC, ethylene carbon and γ-butyrolactone while very miscible with low polar DME [29]. By replacing 20% DME with fluorinated solvent, we get two electrolytes with a composition of 0.2 m LiSO$_3$CF$_3$ 1:3:1 PC/DME/MFE and 0.2 m LiSO$_3$CF$_3$ 1:3:1 PC/DME/TTFP, respectively. Both electrolytes are homogeneous in a wide temperature range. The discharge voltage profiles of Li/O$_2$ cells with these electrolytes, respectively, are plotted in Fig. 1. It is clear that the presence of both MFE and TTFP increases specific capacity of carbon. Interestingly, more significant improvement is observed from more viscous TTFP (9.8 × 10^{-7} m^2 s^{-1} at 25 °C), instead of less viscous MFE (3.8 × 10^{-7} m^2 s^{-1} at 25 °C). This observation suggests
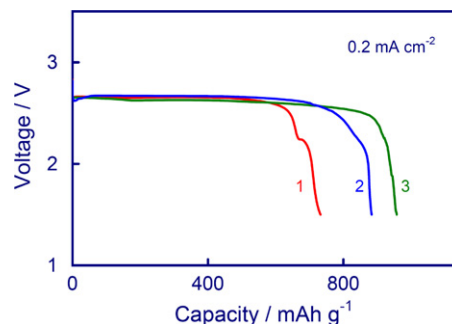

Fig. 1. Discharge profiles of Li/O$_2$ cells with different electrolytes. (1) 0.2 m LiSO$_3$CF$_3$ 1:3 PC/DME, (2) 0.2 m LiSO$_3$CF$_3$ 1:3:1 PC/DME/MFE, and (3) 0.2 m LiSO$_3$CF$_3$ 1:3:1 PC/DME/TTFP.

that in the present electrolyte system, the viscosity of electrolyte would not be the main factor to determine discharge capacity of the Li/O$_2$ cells. Therefore, our further efforts are focused on PC/TTFP electrolytes due to their high boiling points (PC = 240 °C and TTFP = 130–131 °C at 743 mm Hg), which make it possible to develop a non-aqueous electrolyte for the operation of Li/air batteries in dry ambient environments.

3.2. PC/TTFP electrolyte for Li/O$_2$ battery

A series of electrolytes with a general composition of 0.2 m LiSO$_3$CF$_3$ (1 − x):x PC/TTFP (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5, respectively) were prepared, and the discharge performances of Li/O$_2$ cells using these electrolytes are plotted in Fig. 2. It is shown that the lower discharge voltage plateau at 2.1–2.2 V, which corresponds to Li$_2$O$_2$ + 2Li → 2Li$_2$O [17,18], is only present in PC-electrolyte cell (curve-1). For better comparison of the impacts of TTFP, the specific capacity of carbon is plotted together with the isothermal ionic conductivity (at 22 °C) of electrolytes as a function of the electrolyte composition in Fig. 3. It can be seen from Fig. 3 that the specific capacity of carbon presents a maximum value at x = 0.3, while the ionic conductivity nearly linearly decreases with the content of TTFP. The decrease of ionic conductivity with TTFP content is due to the reduced polarity of the solvent blend as a result of the addition of low polar TTFP. Based on the results of Fig. 3, we conclude that the specific capacity of Li/O$_2$ cells does not follow the ionic conductivity of electrolyte.

Composition dependences of the specific capacity and solvent viscosity are indicated in Fig. 4, respectively. In the range of TTFP content from x = 0 to x = 0.4, the viscosity of PC/TTFP solvent blends remains almost unchanged, and it starts to decrease slowly with the content of TTFP only when x exceeds 0.5. Again, there are no clear links in the composition dependences between the specific capacity of Li/O$_2$ cells and the viscosity of solvent blends. Results of
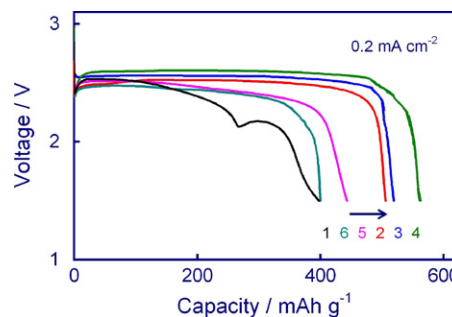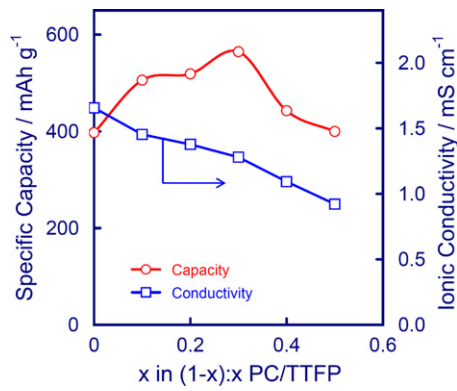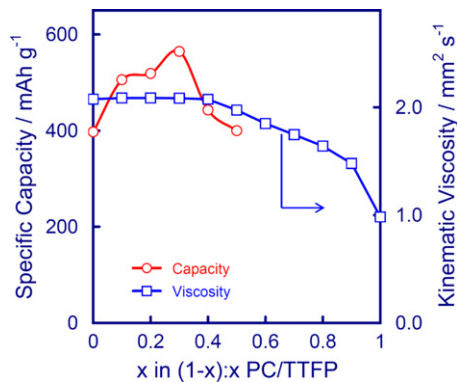

Fig. 2. Discharge performance of Li/O$_2$ cells with electrolytes in a composition of 0.2 m LiSO$_3$CF$_3$ (1 − x):x PC/TTFP. (1) x = 0, (2) x = 0.1, (3) x = 0.2, (4) x = 0.3, (5) x = 0.4, and (6) x = 0.5.

Fig. 3. The effect of solvent ratio on electrolyte conductivity and cell capacity for a 0.2 m LiSO$_3$CF$_3$ $(1-x)$:x PC/TTFP electrolyte and its resultant Li/O$_2$ cells, where both were measured at room temperature (22 °C).

Fig. 4. The effect of solvent ratio on Kinematic viscosity and cell capacity for a $(1-x)$:x PC/TTFP solvent blend and its resultant Li/O$_2$ cells, where the viscosity was measured at 25 °C while the capacity was measured at room temperature (22 °C).

Figs. 3 and 4 indicate that the performance improvement of Li/O$_2$ cells by TTFP cannot be explained either by the ionic conductivity of liquid electrolytes or by the viscosity of solvent blends. A very possible reason, we believe, for the performance improvement of
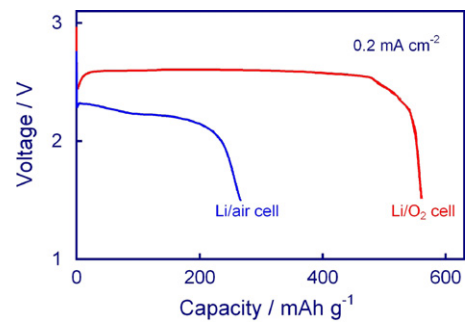

Fig. 5. Comparison of the discharge curves for a Li/O$_2$ cell and a Li/air cell, in which both cells used a 0.2 m LiSO$_3$CF$_3$ 7:3 PC/TTFP electrolyte and were discharged at 0.2 mA cm^{-2}.

Li/O$_2$ cells by TTFP is due to the interaction of these two inverse effects: (1) the participation of TTFP as a co-solvent increases dissolution kinetics and solubility of oxygen in liquid electrolyte and (2) the addition of TTFP reduces ionic conductivity of the liquid electrolyte due to low polarity of TTFP. As a result of the interaction of these two inverse factors, the Li/O$_2$ cell presents highest capacity at $x = 0.3$.

### 3.3. PC/TTFP electrolyte for Li/air battery

Due to low volatility of PC and TTFP, it is possible to use PC/TTFP electrolyte in a Li/air cell for the operation in dry ambient environments. Fig. 5 compares the discharge profiles of a Li/O$_2$ cell and a Li/air cell at 0.2 mA cm^{-2}. Since Li/O$_2$ cell has higher partial pressure of oxygen, it shows significantly higher discharge voltages and higher specific capacity than the Li/air cell. This is because high partial pressure of oxygen not only enhances dissolution kinetics but also increases solubility of oxygen in liquid electrolyte [3,15,16]. After discharging and leaving the cell in dry room for a week without closing the air window, we found that the air electrode and separator of Li–air cell still remained electrolyte-wetting.

The discharge performances of Li/air cells with PC and PC/TTFP electrolyte, respectively, at different discharge current densities are compared in Fig. 6a–d. One sees that at low current density
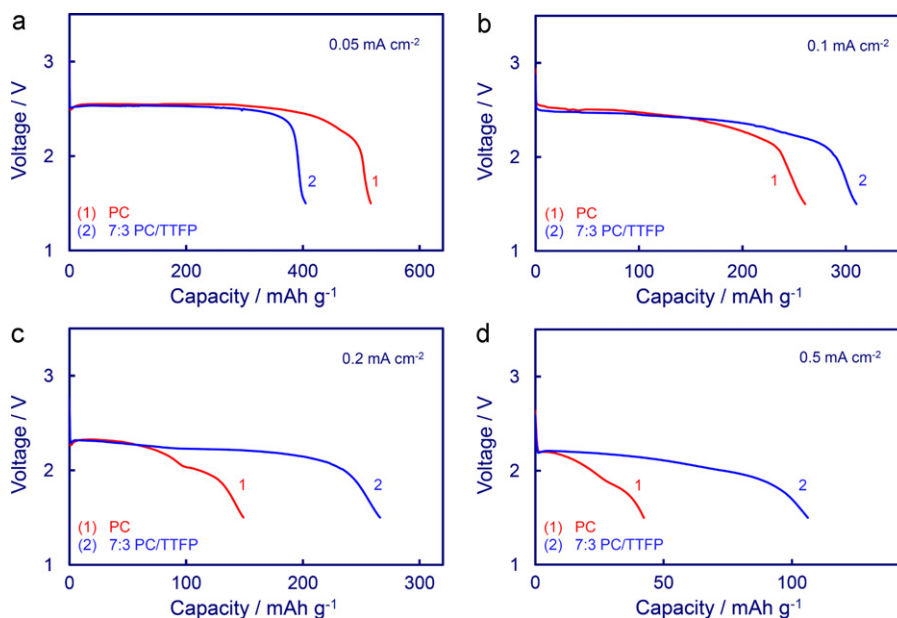
Fig. 6. Comparison of discharge curves of a Li/air cell using a 0.2 m LiSO$_3$CF$_3$ PC electrolyte and a 0.2 m LiSO$_3$CF$_3$ 7:3 PC/TTFP electrolyte, respectively. (a) 0.05 mA cm^{-2}, (b) 0.1 mA cm^{-2}, (c) 0.2 mA cm^{-2}, and (d) 0.5 mA cm^{-2}.
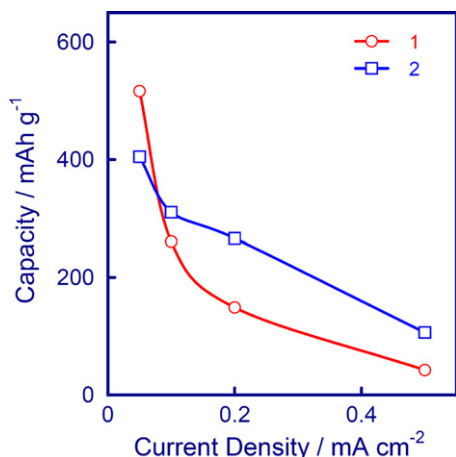
Fig. 7. The effect of discharge current density on specific capacity of Li/air cells with a 0.2 m $LiSO_3CF_3$ PC electrolyte and a 0.2 m $LiSO_3CF_3$ 7:3 PC/TTFP electrolyte, respectively.

(0.05 mA cm^{-2}, Fig. 6a), PC electrolyte cell has higher capacity than PC/TTFP electrolyte cell in spite of higher viscosity of PC than the 7:3 (wt.) PC/TTFP blend. This is because at low current density, the dissolved oxygen has sufficient time to diffuse into the catalytic sites of carbon surface. In this case, the ionic conductivity of electrolyte may play more important role than the viscosity of electrolyte in determining the discharge capacity of Li/air cell. As the discharge current density increases to 0.1 mA cm^{-2} or higher, however, the PC/TTFP electrolyte cell significantly outperforms PC–electrolyte cell (see Fig. 6b–d). Furthermore, the improvement seems to become more significant when the discharge current density is increased.

The effects of TTFP co-solvent on the rate capability of Li/air cells are summarized in Fig. 7, which shows that PC/TTFP electrolyte outperforms PC electrolyte in the rate capability of Li/air cells although it has lower ionic conductivity and similar viscosity as compared with the PC baseline electrolyte. This fact from another point of view verifies that the use of partially fluorinated solvent, TTFP, benefits dissolution kinetics and solubility of oxygen in liquid electrolyte.

4. Conclusions

The results of this work show significant effect of partially fluorinated solvents, MFE and TTFP, on the discharge performance of Li/air batteries. Although the use of partially fluorinated solvents reduces ionic conductivity of the liquid electrolyte, it really enhances discharge performance of Li/air cells, including both specific capacity and rate capability of the Li/air cells. This result can neither be supported by the ionic conductivity of electrolyte nor be explained by the viscosity of electrolyte solvent blend. We attribute the obtained performance improvement to the nature of partially fluorinated solvents in enhancing dissolution kinetics and solubility of oxygen in the liquid electrolyte. In addition, it is possible to develop a non-aqueous electrolyte for the operation of Li/air batteries in dry ambient environments by selecting low volatile fluorinated compound as a co-solvent.

References

[1] K.M. Abraham, Z. Jiang, J. Electrochem. Soc. 143 (1996) 1.
[2] J. Read, J. Electrochem. Soc. 149 (2002) A1190.
[3] J. Read, K. Mutolo, M. Ervin, W. Behl, J. Wolfenstine, A. Driedger, D. Foster, J. Electrochem. Soc. 150 (2003) A1351.
[4] T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, J. Power Sources 146 (2005) 766.
[5] J. Read, J. Electrochem. Soc. 153 (2006) A96.
[6] S.S. Sandhu, J.P. Fellner, G.W. Bructchen, J. Power Sources 164 (2007) 365.
[7] T. Ogasawara, A. Debart, M. Holzapfel, P. Novak, P.G. Bruce, J. Am. Chem. Soc. 128 (2006) 1390.
[8] A. Debart, J. Bao, G. Armstrong, P.G. Bruce, J. Power Sources 174 (2007) 1177.
[9] J.P. Zheng, J. Electrochem. Soc. 155 (2008) A432.
[10] S.D. Beattie, D.M. Manolescu, S.L. Blair, J. Electrochem. Soc. 156 (2009) A44.
[11] W. Xu, J. Xiao, J. Zhang, D. Wang, J.G. Zhang, J. Electrochem. Soc. 156 (2009) A773.
[12] W. Xu, J. Xiao, D. Wang, J. Zhang, J.G. Zhang, J. Electrochem. Soc. 157 (2010) A219.
[13] W. Xu, J. Xiao, D.Y. Wang, J. Zhang, J.G. Zhang, Electrochem. Solid-State Lett. 13 (2010) A48.
[14] X.H. Yang, P. He, Y.Y. Xia, Electrochem. Commun. 11 (2009) 1127.
[15] X.H. Yang, Y.Y. Xia, J. Solid State Electrochem. 14 (2010) 109.
[16] C. Tran, X.Q. Yang, D. Qu, J. Power Sources 195 (2010) 2057.
[17] S.S. Zhang, D. Foster, J. Read, J. Power Sources 195 (2010) 1235.
[18] S.S. Zhang, D. Foster, J. Read, J. Power Sources 195 (2010) 3684.
[19] S.S. Zhang, D. Foster, J. Read, Electrochim. Acta (2011), doi:10.1016/j.electacta.2010.10.052.
[20] Y.C. Lu, H.A. Gasteiger, M.C. Parent, V. Chiloyan, S.H. Yang, Electrochem. Solid-State Lett. 13 (2010) A69.
[21] H. Cheng, K. Scott, J. Power Sources 195 (2010) 1370.
[22] O. Crowther, B. Meyer, M. Morgan, M. Salomon, J. Power Sources 196 (2011) 1498.
[23] F. Mizuno, S. Nakanishi, Y. Lotani, S. Yokoishi, H. Iba, Electrochemistry 78 (2010) 403.
[24] J.S. Hummelshoj, J. Blomqvist, S. Datta, T. Vegge, J. Rossmeisl, K.S. Thygesen, A.C. Luntz, K.W. Jacobsen, J.K. Norskov, J. Chem. Phys. 132 (2010) 071101.
[25] G. Girishkumar, B. McCloskey, A.C. Luntz, S. Swanson, W. Wilcke, J. Phys. Chem. Lett. 1 (2010) 2193.
[26] D.L. Foster, J.A. Read, W.K. Behl, Proceedings of the 44th Power Sources Conference, Las Vegas, NV, June 14–17, 2010, pp. 47–50.
[27] L.C. Clark, F. Gollan, Science 152 (1966) 1755.
[28] J.L. Bull, S. Tredici, E. Komori, D.O. Brant, J.B. Grotberg, R.B. Hirschi, J. Appl. Physiol. 96 (2004) 1633.
[29] J. Arai, in: S.S. Zhang (Ed.), Advanced materials and methods for lithium-ion batteries, Transworld Research Network, Kerala, India, 2007, pp. 279–294.
[30] S.S. Zhang, K. Xu, T.R. Jow, Electrochem. Solid-State Lett. 5 (2002) A206.
[31] S.S. Zhang, K. Xu, T.R. Jow, J. Power Sources 113 (2003) 166.