Short communication

Mixture of LiBF$_4$ and lithium difluoro(oxalato)borate for application as a new electrolyte for lithium-ion batteries

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ABSTRACT

An equimolar mixture of fluoroborate salts: LiBF$_4$ and lithium difluoro(oxalate)borate LiBF$_2$(C$_2$O$_4$) (MIX-LiFBs) was obtained from a simple one-step reaction of lithium oxalate and boron fluoride. Voltamperommetry shows that the salt obtained is stable in the potential range of 4.9 V. Impedance measurements of liquid electrolytes involving imidazolium ionic liquid and aliphatic carbonates have been carried out, which show the highest ionic conductivity of the order of 10^{-3} S cm^{-1} (and low activation energy of 0.14 eV) when using carbonates as the solvent. The mixture of fluoroborate salts MIX-LiFBs used as a component of solid polymer electrolytes provides much higher ionic conductivity values at high salt concentrations in "polymer-in-salt systems". The conductivity of solid polymer electrolytes was considerably increased by adding a low-molecular-weight organic plasticizer.

1. Introduction

Reversible lithium-ionic batteries are currently produced on a large scale mainly as equipment for powering portable electronic devices, but simultaneously intensive research is carried out on the development of large, high power batteries for powering hybrid electric vehicles (HEVs), plug-in HEVs and batteries for electric vehicles (EVs) [1–4]. One of the basic elements of batteries is the electrolyte, which must fulfill many strict requirements as high conductivity, low impedance of passivation layers, as well as chemical and electrochemical stability over a wide range of temperature. Lithium salt solutions in polar, aprotic organic solvents such as linear or cyclic aliphatic carbonates are most often used as the electrolyte, and LiPF$_6$ as the salt. However, many problems appear in such systems connected with the thermal and hydrolytic instability of the mentioned salt, the decomposition products of which cause deterioration of the electrode material [5–7]. The commonly used propylene carbonate (PC), which very well solvates anions, was noticed to undergo co-intercalation causing exfoliation of graphite electrodes that significantly shortens

the life of the battery [8]. In order to protect the electrode material, very good results were achieved when using lithium dioxalatoborate (LiBOB) as the salt, which provides a stable protection layer on the anode by forming a robust solid electrolyte interface (SEI) on the electrode surface. Furthermore, LiBOB is thermally stable and exhibits excellent overcharge tolerance [9–11].

Recent studies show that the properties of lithium difluoro(oxalato)borate (LiBF$_2$C$_2$O$_4$) exceed those of LiBOB, and also it is capable of stabilizing SEI on the surface of graphite anode, but resistance of this SEI layer is much smaller. Compared with LiBOB, it is better soluble in aliphatic carbonates giving less viscous solutions, and has been presented as the salt for improved electrolyte of a Li-ion battery [12–16]. In the range of low temperature it was found that electrolytes with LiBF$_4$ show better characteristics than that with LiPF$_6$, although the conductivity is significantly lower, which is attributed to the reduced charge-transfer resistance of LiBF$_4$ cells [17,18].

Our idea consists in the application of LiBF$_2$(C$_2$O$_4$) in a mixture with LiBF$_4$ (MIX-LiFBs) as an electrolyte for lithium-ion batteries. Such a mixture of equimolar composition is formed in the reaction of boron fluoride with lithium oxalate when at least a twofold molar excess of BF$_3$ is used. The reaction proceeds quantitatively, practically without the participation of side products, according to the following scheme:
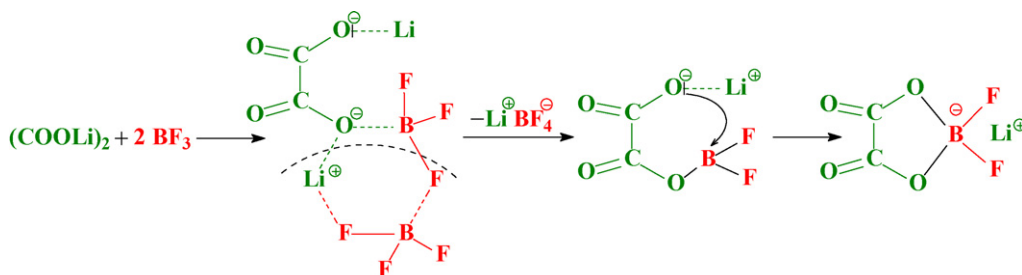
The proposed reaction mechanism results from our many years of studies on the reactions of carboxylate salts with boron fluoride. The obtained mixture of fluoroborate MIX-LiFBs was used as a component of liquid electrolytes involving various organic solvents as well as ionic liquids. Ionic liquids find now considerable interest as components of lithium electrolytes due to their special properties to which are included: high conductivity, non-volatile, incombustibility, as well as great thermal, chemical and electrochemical stability [19–22]. As the ionic liquid we used the proposed by us imidazolium salt with an oligooxyethylene substituent and BF_4^- anion as the counterion [23], of the chemical structure shown below:
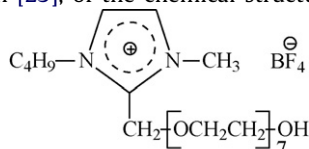
The impedance of solid polymeric electrolytes and polymeric systems plasticized with the addition of organic solvents is also discussed in this paper.

2. Experimental

The mixture of $LiBF_2(C_2O_4)$ with $LiBF_4$ (1:1) was obtained by the procedures described earlier, by subjecting lithium oxalate (Merck) with a 2.5-fold excess of BF_3 etherate (Aldrich) in anhydrous THF [24]. A clear solution resulted from the reaction, from which the MIX-LiFBs salt was isolated by distilling off the solvents and unreacted BF_3 etherate, and next purified by recrystallization from THF. The chemical structure of MIX-LiFBs was characterized by FTIR (Nicolet 6700) (pellet in KBr), ^{11}B NMR (referenced to pirazabol (2.6 ppm in C_6D_6) and ^{19}F NMR (referenced to CF_3COOH) in solutions in DMSO-d_6 (Varian 400 MHz). DSC was carried out on TA Q200 calorimeter in hermetically sealed pans for volatile samples under a nitrogen flow. The measurements were conducted from −100 to 300 °C with heating rate of 10 °C min^{-1}. The glass transition temperatures were determined from the modulated differential scanning calorimetry (MDSC) thermogram during heating cycle with heating rate of 20 °C min^{-1}.

The electrolytes were prepared by dissolving the MIX-LiFBs in anhydrous acetonitrile and adding an appropriate amount of ionic liquid (IL) and/or polymeric matrix: poly(ethylene oxide) (PEO) ($M_w = 5 \times 10^6$, Aldrich) or poly(acrylonitrile-co-butyl acrylate) [p(AN-BuA)]. Then, acetonitrile was removed under reduced pressure. In the case of electrolytes involving mixtures of anhydrous ethylene, propylene and dimethyl carbonate (EC, PC and DMC, respectively) at 1:1:3 ratio, acetonitrile was not used as a co-solvent. Ionic conductivity of the electrolytes was determined from the impedance measurements carried out in cells with stainless steel electrodes using VMP3 potentiostat/galvanostat (Bio-Logic, France) in the frequency range from 10 μHz to 500 kHz when the influence of temperature was studied in the range from 20 to 80 °C.

Cyclic voltammetry of the mixture of MIX-LiFBs in DMC solution was obtained using an Autolab potentiostat/galvanostat (Model PGSTAT128N). Platinum was employed as the working electrode
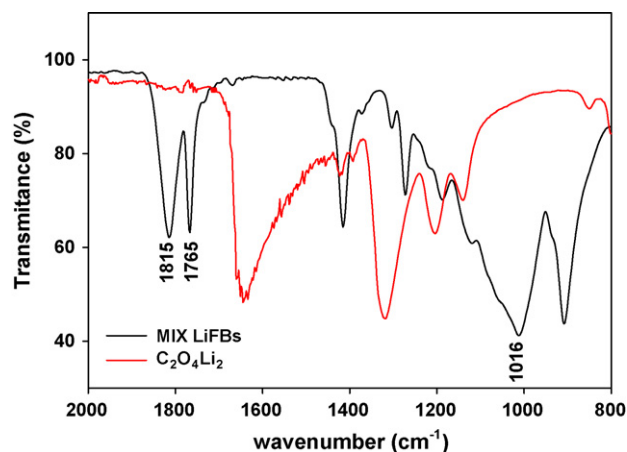
($d = 1.5$ mm) and counter electrode and Ag/0.1 M AgNO$_3$ (acetonitrile) as the reference. The scan rate was 50 mV s^{-1}. The true potential was established with butyl-ferrocene (Aldrich).

3. Results and discussion

In Fig. 1 is presented the FTIR spectrum of lithium oxalate and its product of reaction with BF_3 etherate in molar proportion 1:3. The absorption bands of carbonyl groups in the difluorooxalylborate anion $\nu_{C=O(sym)} = 1765$ cm^{-1} and $\nu_{C=O(asym)} = 1815$ cm^{-1}, and there is a new absorption band $\nu_{B-F} = 1014$ cm^{-1} present in both salts.

The NMR spectra confirm the course of reaction leading to the formation of an equimolar mixture of salts. Fig. 2a shows the ^{11}B NMR spectrum in which are present two signals of the same intensity, one signal at 3.22 ppm, which on the basis of analysis with the use of a standard was assigned to $LiBF_4$, and the second one at 7.53 ppm was assigned to $LiBF_2(C_2O_4)$. In the ^{19}F NMR spectrum (Fig. 2b) two signals, at 148.23 ppm and at 150.71 ppm in proportion 2:1 are observed.

DSC studies show that the obtained mixture of salts forms a complex, multiphase system, in which transformations connected with the glassy transition and melting of the crystalline phase are observed and thermal decomposition is visible. In Fig. 3 is presented a thermogram obtained for the first heating cycle from −100 to 300 °C in conventional DSC measurement. There we can see melting peaks at 31.1 °C with small enthalpy equal to 3.4 J g^{-1} and at 109.7 °C with $\Delta H = 49.7$ J g^{-1}, and at about 199 °C begins thermal decomposition with probable liberation of carbon dioxide formed during oxalate ring cleavage. In Fig. 3 is presented also a thermogram obtained from MDSC measurement where we can observe three glass transition temperatures, T_{g1} at −57.5 °C, T_{g2} at −43.3 °C and T_{g3} at −1.0 °C. An explanation of this type of transformations requires further studies involving a mixture of salts $LiBF_4$ and lithium difluoro(oxalate)borate of other than equimolar
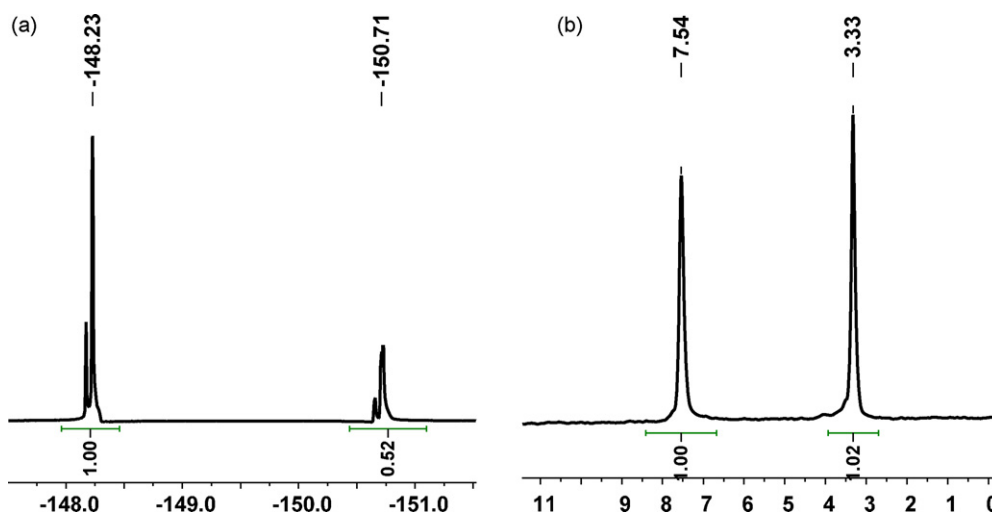
Fig. 2. ^{11}B (a) and ^{19}F (b) NMR spectra of the products of lithium oxalate with BF$_3$ etherate reaction in molar proportion 1:3 in DMSO-d_6.
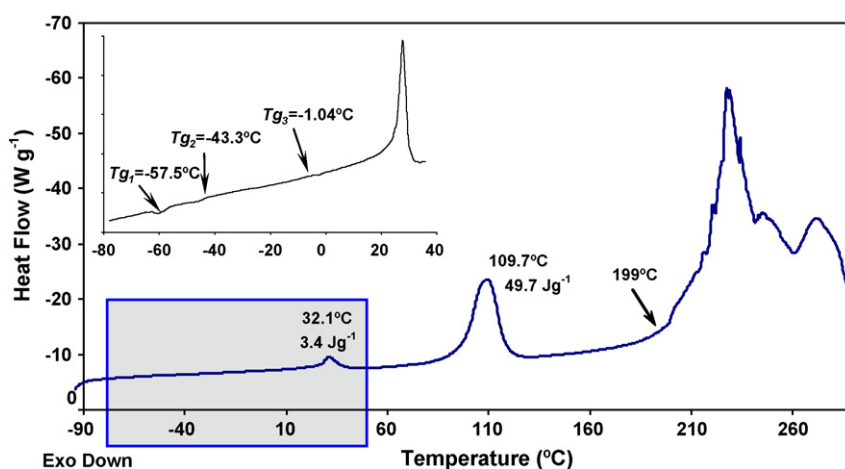

Fig. 3. Thermograms of the MIX-LiFBs mixture.

compositions. A very desirable situation, especially from the point of view of electrolytes of high salt concentration (polymer-in-salt ones), would be the obtaining of an eutectic mixture of low melting point. Generally, it can be assumed that the MIX-LiFBs mixture studied is thermally stable up to 200 °C, a temperature much above that of the battery operation.

The electrochemical stability of the mixture of MIX-LiFBs in DMC solution was determined by cyclic voltammetry (Fig. 4). The obtained electrochemical oxidation potential is *ca.* 4.9 V *vs.* Li$^+$/Li for the solution of MIX-LiFBs in 0.1 M DMC, this is a slightly greater potential window than that obtained for the LiBOB solution in PC of 4.5 V [9].

The overall ionic conductivity of the obtained mixture of MIX-LiFBs in the form of solutions of various concentration in the imidazolium ionic liquid containing an oligooxyethylene substituent (IL) and in a system of solvents typically used in lithium-ionic batteries—EC + PC + DMC (1:1:3) has been studied (Fig. 5). MIX-LiFBs in IL forms a viscous liquid, at 90 wt.% of salt the electrolyte is a solid of melting point $T_m = 71.8$ °C. The highest conductivity of electrolytes with IL is characterized by the system with small concentration of salt equal to 10 wt.%, at room temperature, the σ value is of the order of 10^{-5} S cm^{-1} and is slightly higher than that with neat LiBF$_4$. For higher concentration of 50 wt.% the conductivity is significantly reduced; probably due to high viscosity the mobility of ions is decreased,

which is illustrated by higher activation energy ($E_a = 0.82$ eV). For very high concentration of salt of 90 wt.%, the conductivity increases again, in this case the mechanism of ion transportation is changed and the ions are involved in hopping between the ionic clusters. Definitely the highest conductivity is characterized by the solution in the mixture of carbonates. Due to low
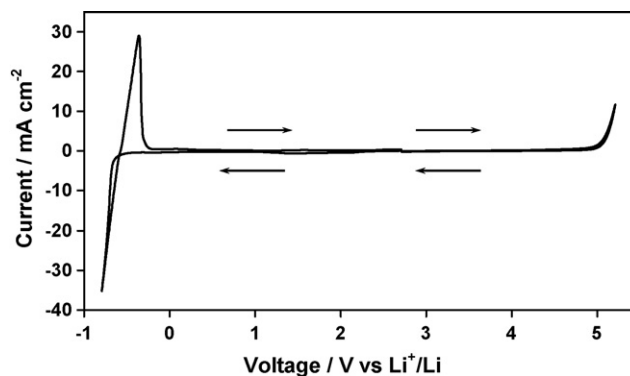

Fig. 4. Cyclic voltammogram for the mixture of MIX-LiFBs with the concentration 0.1 M in DMC solution on platinum as the working ($d = 1.5$ mm) and counter electrode and Ag/0.1 M AgNO$_3$ as the reference with a scan rate of 50 mV s^{-1} measured at room temperature.
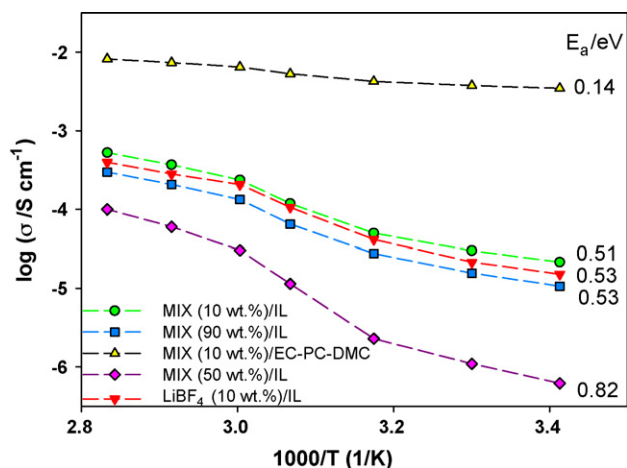
Fig. 5. Ionic conductivity of electrolytes in the form of solutions of MIX-LiFBs and LiBF$_4$ in IL and mixture EC + PC + DMC.

viscosity, at the 10 wt.% concentration it is of the order of 10^{-3} S cm^{-1} over the entire temperature range studied with low E_a equal to 0.14 eV.

Solid polymer electrolytes with MIX-LiFBs and PEO as polymeric matrix are characterized by low conductivity (Fig. 6), similarly as with neat LiBF$_4$. The conductivity significantly increases in systems with high salt concentration and for p(AN-BuA) it reaches values of 10^{-5} S cm^{-1} at room temperature and 10^{-4} S cm^{-1} at 50 °C. However, as seen, high conductivity is associated with the feature of MIX-LiFBs, because for other salts such high values were not obtained; the system with LiBF$_4$ shows conductivity lower by nearly three orders of magnitude.

Fig. 7 shows that the conductivity of the MIX-LiFBs polymer electrolytes increased after introducing IL by about three orders of magnitude at temperatures below T_m of PEO, affording values slightly higher than that of LiBF$_4$. The conductivity of these systems considerably increases after the addition to them of polar solvents such as the PC + EC mixture. At the content of these solvents of the order of 20–50 wt.%, the membranes are flexible solids. Their ambient temperature conductivity reaches values of the order of 10^{-3}–10^{-4} S cm^{-1} and slightly increases with a rise of temperature, which is typical for electrolytes in which charge transfer occurs in the liquid phase. Such transport is characterized also by lower activation energy (~0.4 eV) than that in solid PEO and lithium salt complexes.
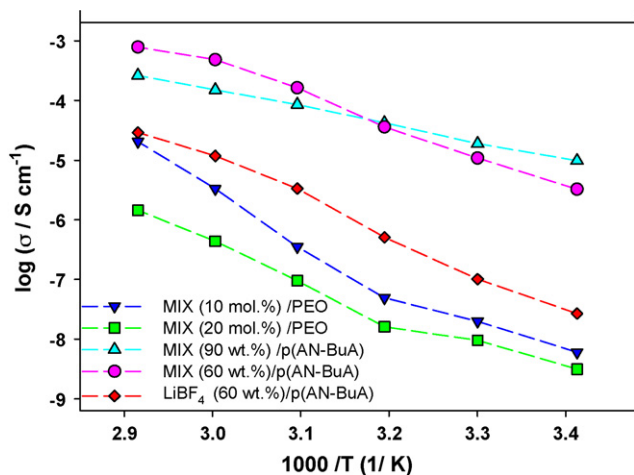

Fig. 6. Ionic conductivity of solid polymer electrolytes with MIX-LiFBs and PEO or p(AN-BuA) as polymer matrix.
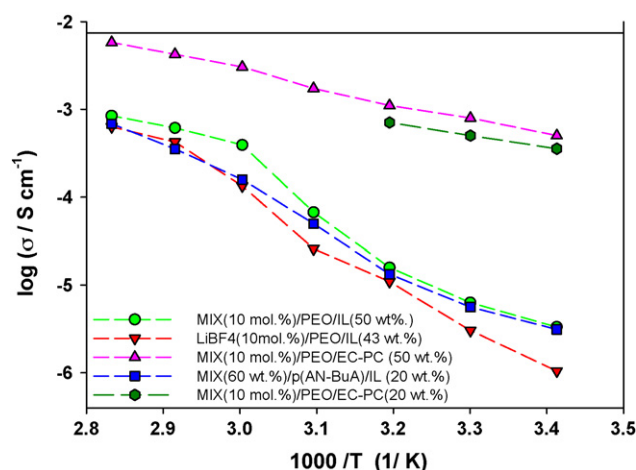

Fig. 7. Ionic conductivity of solid polymer electrolytes with MIX-LiFBs and PEO or p(AN-BuA) plasticized with IL or EC + PC mixture.

4. Conclusions

A salt in the form of an equimolar mixture of lithium difluoro(oxalate)borate [LiBF$_2$(C$_2$O$_4$)] and LiBF$_4$ was obtained in a very simple and economic method from lithium oxalate and boron trifluoride etherate. It was found that this mixture forms a multiphase system with several phase transitions of the vitrification and melting type. The obtained MIX-LiFBs is characterized by relatively high thermal stability up to about 200 °C and wide potential window of 4.9 V. The solutions of MIX-LiFBs in typical carbonate solvents used in lithium-ion batteries are highly conductive and electrochemically stable. The ionic conductivity of solutions in imidazolium ionic liquid with short oxyethylene substituent, due to high viscosity is significantly lower, in the order of 10^{-5} S cm^{-1} at room temperature. High conductive solid polymer electrolytes with MIX-LiFBs were obtained for systems of high salt concentration called "polymer-in-salt" systems, with the acrylonitrile and butyl acrylate copolymer as polymer matrix. Even a small amount of polar solvent added to solid polymeric electrolytes is an effective method of increasing ionic conductivity. Considering that LiBF$_2$(C$_2$O$_4$), as appears from the literature, gives a stable SEI layer of relatively low impedance, and that from the present studies it appears that in a mixture with LiBF$_4$ an electrolyte of high conductivity can be obtained, MIX-LiFBs is a promising electrolyte for application in lithium-ion batteries.

References

[1] M. Armand, J.-M. Tarascon, Nature 451 (2008) 652.
[2] T.R. Jow, K. Xu, M.S. Ding, S.S. Zhang, J.L. Allen, K. Amine, J. Electrochem. Soc. 151 (2004) A1702.
[3] A.N. Jansen, D.W. Dees, D.P. Abraham, K. Amine, G.L. Henriksen, J. Power Sources 174 (2007) 373.
[4] B. Scrosati, Chem. Rec. 5 (2005) 286.
[5] T. Yoshida, M. Takahashi, S. Morikawa, Ch. Ihara, H. Katsukawa, T. Shiratsuchi, J. Yamaki, J. Electrochem. Soc. 153 (2006) A576.
[6] K. Tasaki, K. Kanda, S. Nakamura, M. Ue, J. Electrochem. Soc. 150 (2003) A1628.
[7] H.F. Xiang, H. Wang, C.H. Chen, X.W. Ge, S. Guo, J.H. Sun, W.Q. Hu, J. Power Sources 191 (2009) 575.
[8] G.C. Chung, H.J. Kim, S.I. Yu, S.H. Jun, J.W. Choi, M.H. Kim, J. Electrochem. Soc. 147 (2000) 4391.
[9] K. Xu, S.S. Zhang, T.R. Jow, W. Xu, C.A. Angell, Electrochem. Solid-State Lett. 5 (2002) A26.

[10] K. Xu, U. Lee, S.S. Zhang, J.L. Allen, T.R. Jow, Electrochem. Solid-State Lett. 7 (2004) A273.
[11] K. Xu, U. Lee, S.S. Zhang, T.R. Jow, J. Electrochem. Soc. 151 (2004) A2106.
[12] S.S. Zhang, Electrochem. Commun. 8 (2006) 1423.
[13] S.S. Zhang, J. Power Sources 163 (2007) 713.
[14] J. Liu, Z. Chen, S. Busking, K. Amine, Electrochem. Commun. 9 (2007) 475.
[15] D.P. Abraham, M.M. Furczon, S.-H. Kang, D.W. Dees, A.N. Jansen, J. Power Sources 180 (2008) 612.
[16] Z. Chen, Y. Qin, K. Jun Liu, Amine, Electrochem. Solid-State Lett. 12 (2009) A69.
[17] S.S. Zhang, K. Xu, T.R. Jow, J. Solid State Electrochem. 7 (2003) 147.
[18] S.S. Zhang, K. Xu, T.R. Jow, Electrochem. Commun. 4 (2002) 928.
[19] M.M. Holzpfel, C. Jost, P. Novak, Chem. Commun. 4 (2004) 2098.
[20] Y. Wang, K. Zaghib, A. Guerfi, F.F.C. Bazito, R.M. Torresi, J.R. Dahn, Electrochim. Acta 52 (2007) 6346.
[21] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Nat. Mater. 8 (2009) 621.
[22] A. Martinelli, P. Matic, L. Jacobsson, A. Börjesson, B. Fernicola, Scrosati, J. Phys. Chem. B 113 (2009) 11247.
[23] T. Biedroń, P. Kubisa, J. Polym. Sci.: Part A 46 (2008) 6961.
[24] E. Zygadło-Monikowska, Z. Florjańczyk, N. Langwald, J. Ostrowska, A. Tomaszewska, PL patent application (P-385997).