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Journal of Power Sources 97–98 (2001) 632–636

JOURNAL OF  
POWER  
SOURCES

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# Studies of the interface between lithium electrodes and polymeric electrolyte systems using in situ FTIR spectroscopy

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Received 20 June 2000; accepted 28 December 2000

## Abstract

This paper describes studies of the interface between lithium electrodes and solid electrolyte systems using in situ FTIR spectroscopy in a single internal reflectance mode. In this method, the masking effect of the electrolyte matrix components is largely avoided. We studied gel electrolytes based on polyvinylidene difluoride-hexafluoropropylene with cyclic alkyl carbonates as plasticizers, suitable for ambient temperatures, and a solvent free polymer, derivatives of polyethylene oxide (PEO) with a branched structure: poly[ethyleneoxide-2-(2-methoxyethoxy)ethyl glycidyl ether] at elevated temperatures. We found that the surface chemistry of Li electrodes in contact with the gel matrixes is dominated by alkyl carbonate solvent reduction to  $\text{ROCO}_2\text{Li}$  surface species. In the case of the PEO-based polymer, the surface reactions of Li electrodes are dominated by salt and trace water reduction. The polymer itself seems to be stable with lithium even at 60°C.

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**Keywords:** Li electrodes; Gel electrolytes; Combed-branched PEO-based polymers; In situ FTIR spectroscopy; SIR mode

## 1. Introduction

Special interest is currently being focused on the use of polymeric electrolytes in lithium battery systems. The main advantage in their use is a considerable gain in safety and performance in terms of stability, shelf life and cycle life. The main problem of these solid electrolytes in Li batteries is their low conductivity at room temperature compared with liquid electrolyte solutions. One of the solutions to this problem is the addition of plasticizers to form gel type membranes [1]. These types of membranes have a sufficient ionic conductivity at room temperature. Another approach for solving this problem is R&D of new-branched polymers, usually based on substituted polyethyleneoxide (PEO), which can solvate a variety of Li salts and enable ion transport mechanisms, which lead to an improved Li ions conductivity at low temperatures [2].

A great deal of efforts has been invested in the synthesis of solid electrolyte systems for Li batteries and their application in practical rechargeable batteries. However, fewer efforts were invested in the interfacial studies of Li and

Li-carbon electrodes in contact with solid electrolyte systems. The structure of the interface between lithium electrodes and polymeric electrolyte systems in terms of chemical composition was hardly explored. This should be attributed to the lack of spectroscopic tools for a proper study of Li electrodes in contact (or after contact) with solid electrolyte systems.

Using spectroscopic measurements that provide information on the surface chemistry that is developed in the interface between lithium and solid electrolytes is very important for the understanding of the electrochemical behavior of these systems. In situ techniques must be used for these studies because polymer matrixes cannot usually be removed properly from lithium electrodes for the performance of ex situ analysis, as is the case for studying active metal electrodes in liquid solutions. One of the best techniques for studying the surface chemistry of reactive electrodes such as Li in contact with solid electrolytes may be in situ FTIR spectroscopy. In this report, we demonstrate the application of the single internal reflectance (SIR) mode [3] in order to investigate lithium–polymer electrolyte interfaces. In this mode, the W.E is a thin layer of metal deposited on an optical window, which is transparent to infrared radiation. The IR beam hits the optical window from the back and is reflected from the internal interface between the

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window and a thin metal layer. The beam has some penetration depth beyond the reflective surface, and hence, can be partially absorbed by species at the metal-electrolyte side. Optical windows inert to lithium and solution species such as KBr, NaCl, etc. can be used. The usefulness of this technique for the study of Li electrodes in liquid electrolyte solutions was previously demonstrated [3].

## 2. Experimental

The experimental set-up included a spectroelectrochemical cell in which the working electrode is a thin layer of gold (100 Å) deposited on a KBr window using a special evaporation system (in high vacuum) made by VST Inc. (Israel). The counter and the reference electrodes are lithium disks. The polymeric matrix is positioned between the two electrodes, forming a thin layer cell. The cell configuration is illustrated in Fig. 1. The spectroscopic measurements were carried out in the single internal reflectance mode [3]. A Nicolet Model Magna 860 FTIR spectrometer operated in a glove box under H<sub>2</sub>O and CO<sub>2</sub> free atmosphere, equipped with a grazing angle reflectance accessory (Spectratech) was used.

Each experiment started with a measurement of a spectrum at open circuit voltage (OCV) before the electrochemical process. Galvanostatic steps (lithium deposition and dissolution) were then applied, followed by measurements of spectra after each step and subtraction of the OCV spectrum from each spectrum.

Two types of polymers were studied. One is a polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) gel type polymer [1] with ethylene carbonate (EC) and propylene carbonate (PC) as plasticizers, and LiClO<sub>4</sub> as the salt. The concentration of EC/PC LiClO<sub>4</sub> 1 M solution in the matrix was 20% by weight. This electrolyte system could be used at room temperature. The second polymeric system was poly[ethylene oxide-2-(2-methoxyethoxy)ethyl glycidyl ether] (P(EO/MEEGE)) [2] with several salts. The following salts were used: LiClO<sub>4</sub> (Tomiyama Inc.), LiAsF<sub>6</sub> (FMC Inc.),

The configuration of the cell for *in situ* FTIR spectroscopy

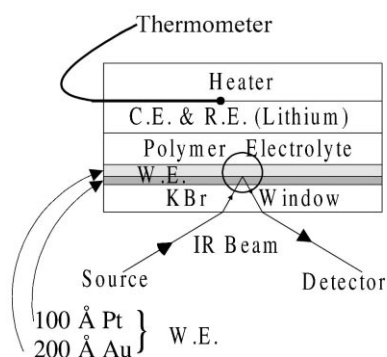


Fig. 1. A scheme of the spectroelectrochemical cell used for the *in situ* FTIR measurements in the single reflectance mode.

LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> and LiN(SO<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (3M Inc.). The [Li]/[O] ratio was 0.08. These polymeric systems were measured at elevated temperatures (>50°C).

## 3. Results and discussion

Fig. 2 shows FTIR spectra obtained *in situ* from a thin gold electrode (on a KBr window) in contact with a PVdF-HFP/EC/PC/LiClO<sub>4</sub> gel type electrolyte membrane at room temperature. Spectrum 2a was measured at OCV and contains mainly superimposed IR peaks of EC and PC (the plasticizers). Spectrum 2b was obtained by subtracting the OCV spectrum from a spectrum that was measured after Lithium deposition on gold (1 C/cm<sup>2</sup>). In spectrum 1b, the original features, belonging to the electrolyte system, are absent due to a correct subtraction, and new peaks are present around 1620–1550, 1300, 1200–1100 and 830 cm<sup>-1</sup>.

Such a combination of peaks is an indication of the formation of lithium alkyl carbonates in the lithium-gel interface. These compounds are known to be formed by the reduction of EC and PC by lithium [3]. Hence, the formation of ROCO<sub>2</sub>Li compounds at the Li-gel interface is expected, and was indeed confirmed by the *in situ* FTIR measurements. The pronounced peak around 1100 cm<sup>-1</sup> in spectrum 2b may relate to reduction of ClO<sub>4</sub><sup>-</sup> to LiClO<sub>3</sub> species. From the spectroscopic results, there is no evidence that the PVdF-HFP polymer itself undergoes a reduction process on lithium under these conditions. It is quite possible that the dominance of the PC/EC reduction on the active surface suppresses possible reduction of the polymer.

Fig. 3 represents typical first cyclic voltammograms obtained with the P(EO/MEEGE)/LiClO<sub>4</sub> electrolyte system at 60°C with Ni and Au electrodes. The background cathodic currents in the cyclic voltammograms of Fig. 3 are attributed to a continuous reduction of trace water (40 ppm in the polymer matrices) and possible reduction of the salt anion. Fig. 3a shows a cyclic voltammogram that was measured with a Ni electrode. The cathodic peak around -0.05 V relates to a lithium deposition process and the anodic peak around 0.05 V relates to consecutive lithium dissolution. Fig. 3b shows a cyclic voltammogram obtained with an Au electrode. The reduction peaks around 0.25 and 0.05 V are attributed to lithium under potential deposition (Li-UPD) on gold. The reduction peak around -0.3 V relates to lithium bulk deposition. The oxidation peak around 0.3 V is attributed to lithium bulk dissolution and the anodic peak around 0.5 V can be attributed to dissolution of the ad-layer of lithium on gold which was formed by the Li UPD. Hence, this peak belongs to the cathodic peaks around 0.25 and 0.05 V (Li/Li<sup>+</sup>).

A similar voltammetric picture was obtained with the other polymeric systems containing LiAsF<sub>6</sub>, LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> and LiN(SO<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> as the salts. However, the fine structure of these voltammograms in terms of the peak resolution and shape depended on the salt used. This picture qualitatively

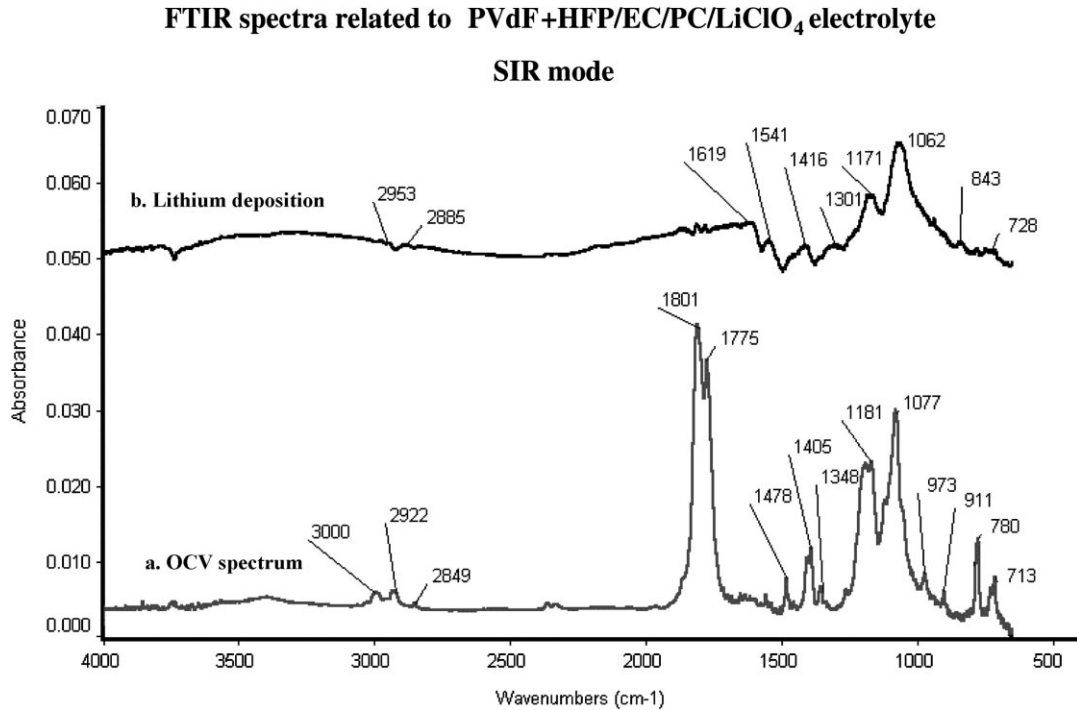


Fig. 2. FTIR spectra obtained in situ from thin film gold electrode on a NaCl window (single internal reflectance mode) in contact with a PVdF-HFP/EC-PC/LiClO<sub>4</sub> gel electrolytic matrix at room temperature. (a) A spectrum measured at open circuit voltage ( $\approx 3$  V versus Li/Li<sup>+</sup>), dominated mostly by EC and PC peaks. (b) A spectrum measured after galvanostatic Li deposition (1 C/cm<sup>2</sup>) on the thin Au film. The OCV spectrum (2a) was subtracted from the actual spectrum measured in situ.

resembles the behavior of gold electrodes in Li salt non-aqueous solutions that were previously explored at 25°C [4]. However, with liquid electrolyte solutions at 25°C, the CV peaks related to Li UPD appear at potentials which are

about 0.5 V more positive compared with the peaks in Fig. 3b. The lack of Li UPD peaks with Ni electrodes is also in line with the previous work with Li salt solutions at room temperature [4].

### Cyclic voltammograms related to the P(EO/MEEGE)/LiClO<sub>4</sub> electrolyte, T= 60°C

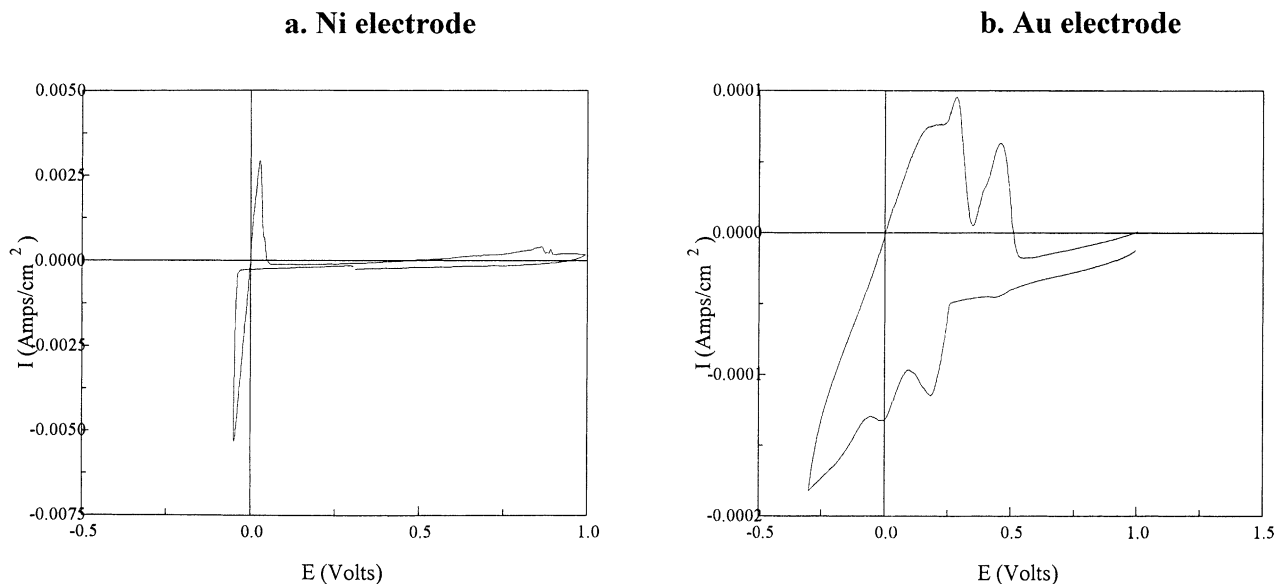


Fig. 3. Cyclic voltammograms of the P(EO/MEEGE)/LiClO<sub>4</sub> electrolytic matrix at 60°C. The potential scan rate was 5 mV/s. (a) Nickel electrode: the CV reflects mostly Li deposition–dissolution processes. (b) Gold electrode: the CV reflects both Li bulk and UPD deposition and dissolution processes.

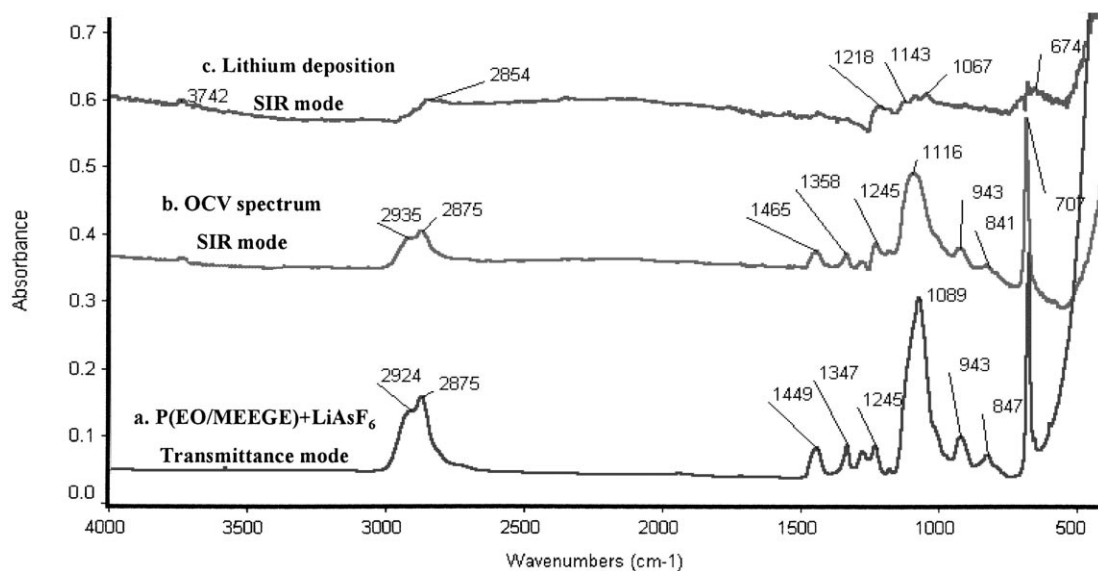
FTIR spectra related to the P(EO/MEEGE)/LiAsF<sub>6</sub> electrolyte

Fig. 4. FTIR spectra obtained in situ from a thin film gold electrode deposited on NaCl, using the SIR mode at 60°C, with P(EO/MEEGE)/LiAsF<sub>6</sub> solid electrolytic matrix. (a) A FTIR spectrum of the polymeric matrix in transmittance mode. (b) A spectrum measured from the thin gold electrode in contact with the polymeric electrolyte at OCV ( $\approx 3$  V versus Li/Li<sup>+</sup>) in the SIR mode, almost identical to that of the polymer in transmittance mode. (c) A spectrum measured in situ after galvanostatic Li deposition on gold (1 C/cm<sup>2</sup>), followed by subtraction of the OCV spectrum (4b).

Fig. 4 shows in situ FTIR spectra obtained from a thin gold electrode (on KBr) in contact with the P(EO/MEEGE)/LiAsF<sub>6</sub> electrolytic matrix. Fig. 5 shows FTIR spectra obtained from a similar experiment with the P(EO/

MEEGE)/LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolyte system. Figs. 4a and 5a show spectra of the solid electrolytes obtained in transmittance mode. Figs. 4b and 5b show spectra of the solid electrolytes obtained in the SIR mode at open circuit (OCV).

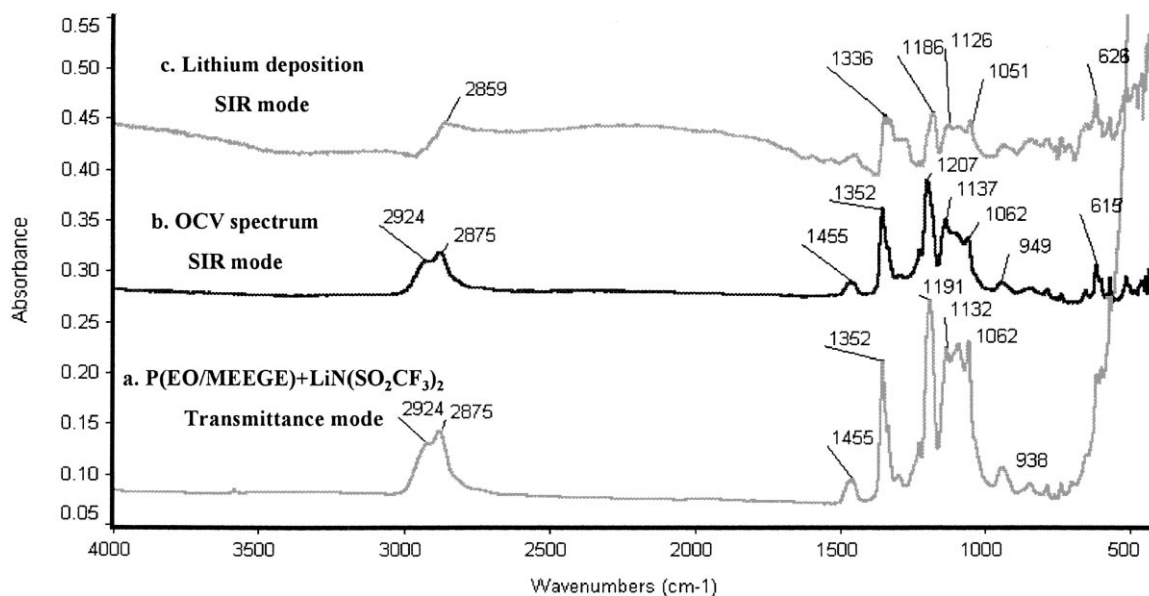
FTIR spectra related to the P(EO/MEEGE)/LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolyte

Fig. 5. FTIR spectra obtained in situ from a thin film gold electrode deposited on NaCl, using the SIR mode at 60°C with P(EO/MEEGE)/LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> solid electrolytic matrix. (a) A transmittance mode TIR spectrum of the polymeric matrix in transmittance mode. (b) A spectrum measured from the thin gold electrode in contact with the polymeric electrolyte at OCV ( $\approx 3$  V versus Li/Li<sup>+</sup>), SIR mode. (c) A spectrum measured in situ (SIR mode) after galvanostatic Li deposition on gold (1 C/cm<sup>2</sup>), followed by subtraction of the OCV spectrum (5b).

It can be seen that the spectra obtained in these two modes of measurements are very similar. This proves that in the SIR mode, the IR beam indeed penetrates beyond the interface between the KBr and the gold layer, thus, interacting with the thin polymeric layer at the interface between the electrode and the electrolyte system.

The spectrum in Fig. 4c was obtained by subtracting the OCV spectrum from the spectrum measured after lithium deposition on gold from the P(EO/MEEGE)/LiAsF<sub>6</sub> electrolyte system. This spectrum is nearly featureless. The small peaks appearing in this spectrum look like artifacts resulting from subtraction of the OCV spectrum, rather than as real peaks of new surface species. Similar results were obtained with polymeric matrixes containing LiClO<sub>4</sub> and LiN(SO<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>. These results obviously reflect relatively high stability of these solid electrolyte systems towards lithium. These results are different from previous results obtained from studies of lithium electrodes in contact with liquid polyethers of the “Glyme” family [5]. In this previous work, it was shown that in the case of liquid polyethers, they are reactive with lithium metal and the etheric C–O bond is cleaved by the reactions with lithium to form ROLi surface species. The IR spectra measured from lithium electrodes after being in contact with these solvents, provides clear evidence for the formation of surface films composed of lithium alkoxides [5].

Fig. 5c was obtained after lithium deposition (and subtraction of the OCV spectrum) from a P(EO/MEEGE)/LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> electrolyte. The spectrum shown in Fig. 5c contains features that can be attributed to salt reduction products. Based on a previous work [6], the peaks around 620, 1050, 1180, 1230 and 1330 cm<sup>-1</sup> may relate to reduction products such as Li<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, Li<sub>2</sub>NSO<sub>2</sub>CF<sub>3</sub>, etc. [6]. This seems to be in line with the expectation that this salt is more reactive than the other salts [6].

#### 4. Conclusion

This paper demonstrates the application of in situ spectroscopy for the study of the surface chemistry developed on lithium in contact with solid electrolyte systems. The results obtained with the two types of solid electrolyte that were explored seem to show that the single internal reflectance (SIR) mode is a suitable technique for the study of the complicated interfaces between lithium and the polymeric matrices. It was found that the surface chemistry of Li in gel electrolytes with alkyl carbonates of the plasticizers is dominated, as expected, by solvent reduction to ROCO<sub>2</sub>Li species and possible salt anion reduction.

Polymeric matrices based on P(EO/MEEGE) designed by Watanabe et al. [2] seem to be stable with lithium, even at 60°C. The interfacial reactions with lithium are probably dominated by salt anion and trace water reduction.

#### Acknowledgements

This work was supported by the New Energy Development Organization (NEDO), Japan.

#### References

- [1] T. Osaka, S. Komaba, X. Liu, in: D. Aurbach (Ed.), *Nonaqueous Electrochemistry*, Marcel Dekker, New York, 1999 (Chapter 7).
- [2] A. Nishimoto, M. Watanabe, Y. Ikeda, S. Kohjiya, *Electrochim. Acta* 43 (1988) 1177.
- [3] E. Goren, O. Chusid, D. Aurbach, *J. Electrochem. Soc.* 138 (1991) L6.
- [4] D. Aurbach, M.L. Daroux, P. Faguy, E.B. Yeager, *J. Electroanal. Chem.* 297 (1991) 225.
- [5] D. Aurbach, E. Granot, *Electrochim. Acta* 42 (1997) 697.
- [6] D. Aurbach, I. Weissman, A. Zaban, O. Chusid, *Electrochim. Acta* 39 (1994) 51.