

Concentrational changes in PAN-based polymer gel electrolyte under current flow: in situ micro-Raman investigation

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Abstract

The processes occurring in the PAN-based gel polymer electrolyte have been in situ investigated by micro-Raman spectroscopy. It is found that in the polarized membrane a stable gradient of both Li cations and perchlorate anions appears: at the anode side of the assembly, the concentration of cations is essentially higher after polarization, while at the cathode side it is visibly lower; in the middle of the membrane concentration of charge carriers remains practically unchanged. While observed gradients are expected in a working electrolyte, an unexpected, and possibly more serious, depletion of the C≡N groups of the PAN matrix is observed at the anode side during polarization. The nature of this effect may be ascribed to the polymer mobility due to the strong polymer–electrolyte interaction and/or to the polymer degradation caused by internal heating under applied potential. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

During recent years, considerable efforts have been made to improve the performance of lithium and lithium ion polymer batteries. The present work mainly concerns the optimization of individual components (polymer electrolyte (PE), cathode, anode) and the strive for better compatibility between the PE and electrodes. At the same time, few investigations on the dynamical processes occurring inside PE membrane itself under current flow (or applied potential) can be found in literature [1–5]. Bruce and Vincent [1,2] have theoretically and experimentally shown that in the case of binary electrolytes (e.g. polymer–salt systems, inorganic solid electrolytes or liquid electrolytes immobilized in a polymer mesh), the cell demonstrates ideal (ohmic) behavior only at sufficiently low applied voltages (below 40 mV). At higher voltages, however, a stable gradient of charge carriers across the membrane appears, and different thermodynamical processes and coupling between ionic fluxes must be taken into account in order to describe the ion transport [2]. The situation becomes even more complicated in complex systems, such as polymer gel electrolytes, where a strong interaction between cations, anions, plasticizer and polymer matrix occurs [6,7]. In particular, coupling between the

mobile species and polymer matrix may lead to essential structural and compositional changes of the material when a potential is applied. Therefore, a knowledge of dynamical processes in the polymer electrolytes is extremely important for material optimization.

Micro-Raman spectroscopy appears to be a suitable and effective tool for in situ investigation of the state of PE membrane at battery operation. Since the diameter of the laser spot in micro-Raman experiments is significantly smaller than the typical thickness of investigated membrane (3–10 versus 100–500 μm), it becomes possible to determine the concentrational profiles of different components through the membrane cross-section. In addition, with a confocal technique, the probing can be done in the bulk of the membrane. In a pioneering work, Rey and co-workers [3,4] have applied confocal micro-Raman spectro-electrochemical technique for investigation of PEO_n–LiTFSI system under external potential. Recently, another optical method based on refractive index measurements (so-called Schlieren optical set-up) has been used to study the changes in ion concentration in a gel electrolyte [5], but the space resolution of this technique is essentially lower than in micro-Raman experiments.

In this work, we present the results of an in situ micro-Raman spectro-electrochemical investigation of typical polymer gel electrolyte under applied electric potential. A semi-cell of the type Li(s) (gel PE membrane) Ni(s) was

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polarized by dc potential of 2 V and then, when a steady-state regime was achieved, Raman spectra were recorded in different points between the electrodes in order to evaluate concentrational changes of the PE components and the presence of other chemical (electrochemical) processes.

2. Experimental

For in situ investigation of a battery assembly under polarization, we have designed a new optical cell (schematically shown in Fig. 1), which consists of teflon compartment (with possibility of purging) with an upper optical window (25 mm × 25 mm), and two Ni metal blocking electrodes attached to a built-in ceramic heater. Raman spectra were recorded with a Dilor-Labram Raman spectrometer equipped with a confocal microscope (Olympus BX40), 1800 lines/mm holographic grating, and Peltier cooled CCD detector. The 632.8 nm band of a He–Ne laser (about 10 mW power) was used as an excitation source; spectral resolution was about 2 cm⁻¹. To eliminate a possible influence of surface effects, Raman spectra were recorded at a depth of 30 μm under the membrane surface. Electrochemical control has been performed by EG&G potentiostat/galvanostat (model 263A).

Gel polymer electrolyte was prepared as previously described [8] by immobilizing of EC solution of lithium perchlorate (LiClO₄) in a poly(acrylonitrile) (PAN) matrix. The pieces of PE membrane (approx. 0.5 cm² surface) were sandwiched between a Li metal foil and a nickel plate and then pressed between the Ni blocking electrodes of the

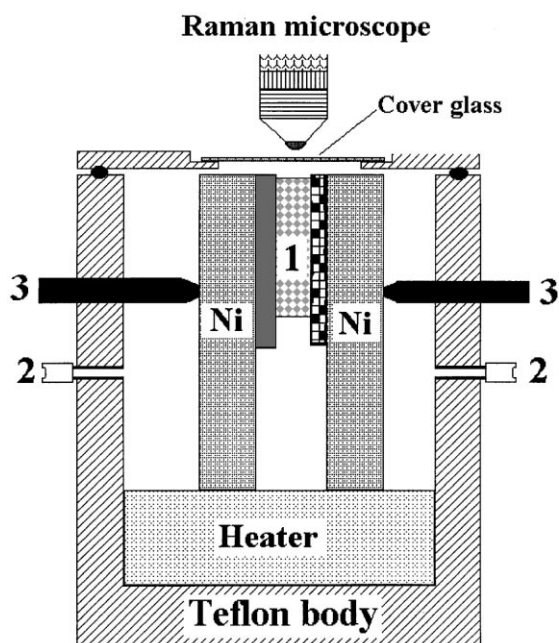


Fig. 1. Schematic representation of the spectro-electrochemical cell used in this work: (1) battery assembly; (2) purging inlets/outlets; (3) electrical contacts.

spectro-electrochemical cell (see Fig. 1). All materials and chemicals used were of high purity, and all preparation procedures were carried out inside a glove-box under dry argon gas atmosphere.

3. Results and discussion

Fig. 2 shows Raman spectra (in the spectral region of interest) of a LiClO₄–EC–PAN gel electrolyte in initial state and in steady state under dc polarization with a 2 V potential. In the spectrum of the unpolarized membrane, we note two bands of fundamental vibrations of the EC ring at 717 and 894 cm⁻¹, respectively (bending and breathing mode, marked with asterisks), symmetric vibration of the perchlorate anion, $\nu_1(\text{ClO}_4^-)$, at 934 cm⁻¹, characteristic band of a C=O stretching vibrations of EC (around 1800 cm⁻¹), and the peak of C≡N stretching vibrations of PAN (at 2245 cm⁻¹). Both EC fundamentals are accompanied by high-frequency satellite bands at 730 and 904 cm⁻¹, respectively (marked with crosses), which arise due to energy shift of the corresponding ring modes caused by cation–solvent interaction [6,9,10]. The intensity of the satellite bands was found to be proportional to the amount of cation–solvent

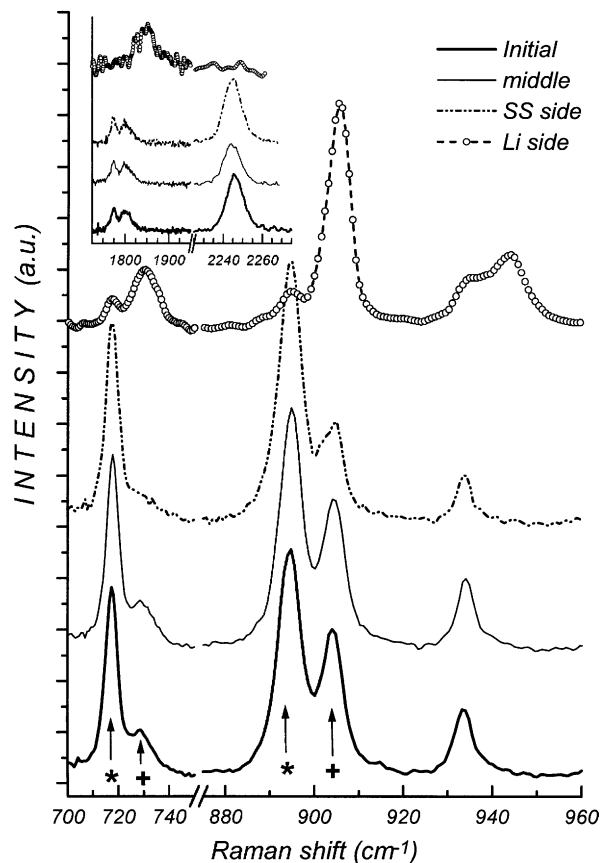


Fig. 2. Raman spectra of the LiClO₄–EC–PAN polymer gel electrolyte recorded before and after polarization by constant potential of 2 V. Asterisks mark the bands of EC molecule fundamental vibrations and crosses mark the corresponding satellite bands (see text).

complexes [9] and can, thus, be used as a measure of cation–solvent interaction.

We note that Raman spectra observed in different points of unpolarized membrane were practically identical, proving a high homogeneity of the initial material. The situation is changed, however, when the system is polarized with an external dc potential of 2 V. It is seen from Fig. 2 that the Raman spectrum recorded in the middle of the membrane is very close to the ‘initial’ one, showing no changes in the state of electrolyte. The concentration of cations and anions remains practically unchanged even under passing current, and the only noticeable difference is a small intensity decrease of the characteristic band of PAN (around 2245 cm^{-1} , see inset). In contrast, at the cathode side of assembly, the intensity of the EC satellite bands are significantly lower than in the initial state that can be attributed to the reduction of Li cation concentration. In addition, the band of $\nu_1(\text{ClO}_4^-)$ vibration at 934 cm^{-1} also shows a slight intensity decrease monitoring that the amount of anions is reduced at the cathode side as well.

The most striking changes in the gel electrolyte are, however, observed near the anode (Li metal) side of the cell. All spectral bands related to the ethylene carbonate are strongly affected here, such that intensity of peaks characteristic for free solvent molecules (at 717 and 984 cm^{-1}) decreases dramatically, whereas intensity of corresponding satellite bands (i.e. amount of cation–solvent complexes) grows enormously. Furthermore, the band of carbonyl stretching vibration around 1800 cm^{-1} , which is also sensitive to the state of the EC molecule [6], is shifted toward higher frequency and its spectral profile is seriously altered (see inset). The observed spectral transformations clearly suggest an intensive formation of cation–solvent complexes near the Li metal electrode. Strong complexation is also observed between Li cations and perchlorate anions. Indeed, instead of a single peak at 934 cm^{-1} , which was observed in all previous cases, the Raman spectrum recorded at the anode side of the polarized cell shows a broad multi-component profile. Thorough curve fitting reveals the presence of three spectral components centered at 934 , 938 and 944 cm^{-1} , which correspond, respectively, to free anions, ion pairs and ion aggregates [11]. Moreover, it is clearly seen that the center of gravity of the whole profile is shifted toward higher frequencies, proving that cation–anion complexes dominate. It is also important to stress that the total integral intensity of the anion related bands (i.e. free anions and anion–cation complexes) is visibly higher than in the initial material, suggesting that the concentration of anions is increased at the cathode side of the assembly.

The observed concentration gradients, i.e. increased concentration of cations and anions at the anode side and decreased at the cathode side, agrees, in general, with that theoretically predicted [1] and experimentally detected [2–4] for solid PE (PEO–salt systems). However, unlike all-solid PE, which may be considered as more or less ‘ideal’ electrolytes [1], the polymer gels are characterized by enhanced

anion mobility that results into strong coupling between cations and anions. Therefore, it is practically impossible to estimate numerically the concentration changes of cations and anions, especially near the Li metal anode.

In addition, near the lithium metal electrode dramatic changes related to the polymer matrix occur. The characteristic band of the $\text{C}\equiv\text{N}$ vibration disappears completely from the spectrum (see inset) during polarization, suggesting that no nitrile groups remain in the near-cathode layer. This effect may be explained in two ways. First, the strong interaction between CN groups of PAN and Li cations and/or solvent molecules [6,7] under conditions of cation excess and temperature increase due to internal heating, may cause an enhanced mobility of the polymer segments and, as a result, redistribution of the polymer across membrane cross-section. Another possible reason is the thermal degradation of poly(acrylonitrile) under battery operation. It is known that PAN tends to decompose at elevated temperature [12], in part due to breaking of the pendant nitrile groups.

The exact nature of this effect is, however, not yet clear and needs to be further investigated. In passing, we note, that degradation or/and redistribution of PAN matrix may be an important factor explaining the dramatic increase of the interfacial resistance of lithium metal electrode observed in the case of PAN-based gels electrolytes [10].

4. Conclusions

A micro-Raman spectro-electrochemical technique has been applied to investigate the compositional and structural changes occurring in a polymer gel electrolyte based on PAN under dc polarization. Our results infer that injection of Li cations from the Li metal electrode results in formation of an ‘over-saturated’ layer, where practically all solvent molecules and salt anions are complexed with Li^+ . In contrast, near the negative electrode, the concentration of both cations and anions is lower than in the initial state, while in the middle of the membrane their concentration remains practically unchanged.

The most interesting finding concerns the behavior of PAN matrix. Raman spectra show an essential variation of the polymer concentration across the membrane such that at the anode side there are no evidences of $\text{C}\equiv\text{N}$ groups, while at the cathode side their amount is slightly higher than in the initial material. The effect may be ascribed either to a ‘flow’ of PAN under applied potential due to strong interaction between the polymer and other components of the system and/or to thermal degradation of the polymer due to internal heating. This question will be investigated in our following articles.

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References

- [1] P.G. Bruce, C.A. Vincent, J. Electroanal. Chem. 225 (1987) 1.
- [2] P.G. Bruce, M.T. Hardgrave, C.A. Vincent, Electrochim. Acta 37 (1992) 1517.
- [3] I. Rey, J.L. Brunel, J. Grondin, L. Servant, J.-C. Lassegues, J. Electrochem. Soc. 145 (1998) 3034.
- [4] I. Rey, J.C. Lassegues, P. Baudry, H. Majastre, Electrochim. Acta 43 (1998) 1539.
- [5] R.A.M. Hikmet, Solid State Ionics 127 (2000) 199.
- [6] M. Alamgir, K.M. Abraham, in: G. Pistoia (Ed.), Lithium Batteries — New Materials, Developments and Perspectives, Elsevier, 1994, Chapter 3, p. 114.
- [7] D. Ostrovskii, A. Brodin, L.M. Torell, G.B. Appetecchi, B. Scrosati, J. Chem. Phys. 109 (1998) 7618.
- [8] G.B. Appetecchi, F. Croce, B. Scrosati, Electrochim. Acta 40 (1995) 991.
- [9] E. Cazzanelli, F. Croce, G.B. Appetecchi, F. Benevelli, P. Mustarelli, J. Chem. Phys. 107 (1997) 5740.
- [10] D. Ostrovskii, L.M. Torell, G.B. Appetecchi, B. Scrosati, Solid State Ionics 106 (1998) 19.
- [11] I.S. Perelygin, G.P. Mikhailov, Zh. Prikl. Spektrosk. 49 (1988) 65.
- [12] S.I. Stupp, S.H. Carr, J. Polym. Sci.: Poly. Phys. Ed. 15 (1977) 485.