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The electrochemical redox processes in methacrylate-based polymer electrolytes II. – Study on microelectrodes

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ABSTRACT

The electrochemical behaviour of ferrocene was studied in different gel polymer electrolytes based on methyl, ethyl and 2-ethoxyethyl methacrylate and compared to the liquid aprotic solution (propylene carbonate). Voltammetric and chronoamperometric measurements on microelectrodes were conducted in order to describe the qualitative as well as quantitative behaviour of ferrocene in different conditions. Heterogeneous electron-transfer rate constants and diffusion coefficients of ferrocene in polymer electrolytes were estimated to be $1.1–7.8 \times 10^{-3}$ cm s^{-1} and $4–13 \times 10^{-8}$ cm^2 s^{-1} depending on the electrolyte composition. The influence of the polymer polarity, ferrocene concentration and level of polymer cross-linkage on the kinetics of ferrocene oxidation and its transport was discussed. The electrolytes with poly(2-ethoxyethyl methacrylate) exhibit the highest ionic conductivity ($2–4 \times 10^{-4}$ S cm^{-1}) as well as diffusion coefficient of ferrocene (1.3×10^{-7} cm^2 s^{-1}) in their structure.

1. Introduction

In the last three decades gel polymer electrolytes have been in the focus of intensive research since Iijima et al. [1], Bohnke [2,3], and Scrosati and co-workers [4] introduced poly(methyl methacrylate)-based systems with embedded salt solutions in various aprotic solvents. Beyond many others, acrylate and methacrylate-based polymers and copolymers play an important role due to their wide availability, low toxicity and a good electrochemical stability. Monomer and polymer structures can be modified and functionalised following various demands on the polymer functionality, system polarity or low polymerisation volume contraction [5–11]. Commonly studied gel polymer electrolytes are ternary systems consisting of a polymer, an aprotic solvent and a salt. Their high electrochemical stability allows their application as a part of the electrolyte in various electrochemical devices such as lithium-ion batteries, supercapacitors, chemical sensors and electrochromic devices [12–16].

For detailed description of the mass transport in the electrolyte and for the investigation of the electron-transfer kinetics at the polymer electrolyte|metal electrode interface, various metal complexes have been used: ferrocene or its derivatives [17,18], cobaltocene [19], cobalt(II) tris(bipyridine) [20], and ferro/ferricyanide [21]. Among them, ferrocene (Fc)–ferricinium (Fc^+) redox couple is mostly used for its excellent reversibility [22] and good solubility in many aprotic liquid and polymer electrolytes, where undergoes one-electron electrochemical reaction [23]:

$$[Fe(C_5H_5)_2] \leftrightarrow [Fe(C_5H_5)_2]^+ + e^-$$

Polymer electrolytes provide an unusual solvation shell, where molecules of the polymer and the solvent are competing and affect the rates of electron-transfer reactions. In our recent study we have used different electrochemical methods for the description of qualitative and quantitative behaviour of ferrocene in liquid electrolyte (propylene carbonate) and corresponding polymer electrolytes with poly(methyl methacrylate), poly(ethyl methacrylate) and poly(2-ethoxyethyl methacrylate) network. These electrolytes have been quite intensively studied in our laboratory in the last decade and also tested in various electrochemical applications [16,24–27]. Several parameters were changed and their influence on the ferrocene electrochemistry studied: polymer polarity, level of the polymer cross-linkage, and redox species (ferrocene) concentration. Our work wants to extend the knowledge of the charged and uncharged species motion and transport and their electrochemistry on the electrode–gel polymer electrolyte interface.

The electrochemical behaviour of ferrocene in the electrolytes was studied on a platinum disk microelectrode and a platinum

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disk macroelectrode under different conditions: steady-state cyclic voltammetry (CV) on the platinum rotating disk electrode (RDE), non-steady-state CV on the macroelectrode, and CV on the microelectrode under steady-state and non-steady-state (high scan rate) conditions. Also chronoamperometry (CA) on the microelectrode was performed. For obvious reasons, the measurement on the RDE was performed in liquid electrolyte only.

2. Experimental

2.1. Chemicals and preparation of the polymer electrolyte

All chemicals were purchased from Sigma–Aldrich. Monomers, methyl methacrylate (MMA), ethyl methacrylate (EMA), and 2-ethoxyethyl methacrylate (EOEMA) were distilled under reduced pressure. The cross-linking agents, ethyleneglycol dimethacrylate (EDMA) and 1,6-hexandiol dimethacrylate (HexadiMA) were used as received. The polymerisation initiator, 2,2′-azobis(isobutyronitrile) (AIBN) was recrystallised from chloroform and dried at 20 °C in vacuum. All monomers and the initiator were stored at 4 °C before use. Ferrocene (98%), lithium perchlorate (battery grade), and propylene carbonate (99.7%, water content under 0.005%) were used as received.

Polymer electrolytes were prepared using thermally initiated polymerisation following our previous experiments [16]. The initial mixture contains monomer, cross-linking agent, polymerisation initiator (1 mol.% of monomers) and ferrocene solution in 1 mol dm^{-3} lithium perchlorate in PC. After homogenisation, the mixture was bubbled with argon for 10 min as well as the cell for the sample preparation. The cell was filled with the initial mixture and placed into an oven for the period of 2 h at 80 °C. The design of the cell prevents electrolyte contamination by water or oxygen.

The electrolyte composition of the electrolyte (polymer–solvent–salt) is expressed in molar percentage, when the amount of cross-linking agent is involved in polymer content. The ferrocene molar concentration is calculated considering the volume contraction that does not exceeds 6 vol.%.

2.2. Apparatus, electrodes and cells

The electrochemical investigation of prepared polymer electrolytes was performed in a home-made PTFE cell with a three-electrode arrangement. The platinum macroelectrode (Eco-Chemie, 3 mm in diameter – used for the measurement on RDE in the liquid electrolytes; BASi, 1.6 mm in diameter – used for the measurements in the polymer electrolytes) or the microelectrode (EcoChemie, 20 μm in diameter) served as the working electrode; a glassy carbon rod served as the counter electrode. The surface of the working and the counter electrode was carefully polished with abrasives (0.3 alumina, Metroohm) and soft cloth after each measurement and the working electrode was sonicated in ethanol for 10 min before use.

A solid-state PMMA–Cd–Cd^{2+} system was used as the reference electrode and all potentials in the paper are related to this Cd/Cd^{2+} system, which was developed in our laboratory for the electrochemical investigation of liquid and polymer aprotic electrolytes with the potential of E(PMMA–Cd–Cd^{2+}) = 2.66 V vs. Li/Li^{+} in propylene carbonate [16,25].

The potentiogalvanostats PGSTAT 10 and 30 (Eco Chemie, The Netherlands) were used for the electrochemical measurements including the impedance measurements. Experiments with microelectrodes were performed in a Faraday cage.

3. Results and discussion

The prepared electrolytes are elastic and homogeneous membranes of a thickness from 0.8 to 1.0 mm depending on the thickness of the silicon spacer in the preparation cell. No phase-to-phase separation (neither solvent exudation nor salt crystallisation) was observed during storage either in an inert atmosphere or in air. Due to the presence of ferrocene, the samples are yellow or brownish coloured. For the electrochemical measurements, only freshly prepared samples were used.

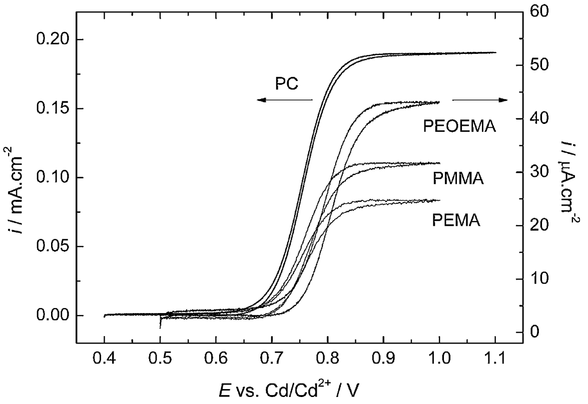

Fig. 1. Cyclic voltammograms (1st scan) of ferrocene on platinum 20 μm microelectrode in PC, PMMA–PC, PEMA–PC and PEOEMA–PC electrolytes at 1 mV s^{-1} scan rate (c(Fc) = 2.33 × 10^{-3} mol dm^{-3}; 22 °C temperature, reference PMMA–Cd–Cd^{2+}).

Following our previous investigation, we used the optimised polymer electrolyte composition to minimise the conductivity drop that is unavoidable during the change from liquid to polymer electrolyte. Usually, conductivity values from 2 to 7 × 10^{-4} S cm^{-1} were achieved at 20 °C.

Our previous experiments showed c. 5.1 V electrochemical window of methacrylate–PC–LiClO$_4$ polymer electrolytes [16]. Compared with the voltammetric measurements of liquid PC-based electrolytes conducted in an argon-filled glove box, we found that the electrochemical stability of the polymer electrolytes is limited by the properties of propylene carbonate. The electrochemical oxidation of ferrocene occurs at c. 0.7 V vs. Cd/Cd^{2+}, what is far from the potential window limits of the electrolyte [28].

3.1. A comparison of the electrochemical behaviour of ferrocene in a liquid and in a polymer electrolyte investigated by different electrochemical methods

The qualitative electrochemical behaviour of ferrocene can be characterised by the half-wave potential $E_{1/2}$ obtained, e.g. from the cyclic voltammograms measured on the platinum microelectrode at 1 mV s^{-1}. Fig. 1 shows the curves measured in four different electrolytes. The comparison of potentials obtained in liquid propylene carbonate and low-polar PMMA and PEMA-based polymer electrolyte showed no remarkable shift of potentials, which indicates only a minimum change of the solvation shell of ferrocene and ferricinium molecules and a minimum interaction between the redox species and the polymer network. This is caused by a higher content of propylene carbonate in the polymer structure as well as by elimination of the polymer resin Superacryl®, that was used in our previously studied PMMA-based polymer electrolytes [28]. In the presence of the more polar PEOEMA polymer, a *positive* shift of c. 40 mV of the oxidation wave was observed. The direction of the shift corresponds to a destabilisation of the ferricinium cation with respect to uncharged ferrocene, probably due to the interaction between the 2-ethoxyethyl side chain and ferrocene molecules.

In the case of a microelectrode (microdisk electrode), the spherical diffusion is dominant at scan rates:

$$v \ll \frac{RTD_R}{nFr^2} \qquad (1)$$