

ELECTROCHEMICAL REDOX PROCESSES IN PMMA GEL ELECTROLYTES – BEHAVIOUR OF FERROCENE-FERRICINIUM COUPLE

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Introduction

Polymer gel electrolytes, also called third generation polymer electrolytes, are suitable materials for electrochromics, lithium ion batteries, supercapacitors and chemical sensors [1]. They are formed by immobilisation of an aprotic solvent in the network of polymer. Polymethylmethacrylate (PMMA) and a solution of inorganic and/or organic compound in anhydrous propylene carbonate (PC) are used in our system. Good solubility of many compounds in propylene carbonate and long-term electrochemical and mechanical stability of prepared material allow their application in many areas.

Recent research is aimed at behaviour of transition metal complexes incorporated in polymer gel electrolytes. For the suitable electrochemical properties ferrocene (Fc) – ferricinium (Fc⁺) redox couple was chosen due to the one-electron reversible redox reaction [2]:



Electrochemical behaviour was studied by cyclic voltammetry in two arrangements: solid-state voltammetry was used in the case of formed thin layers of polymer gel electrolyte and *in-situ* measurement monitored the redox couple behaviour during polymerisation process.

Experimental

Preparation of polymer gel electrolytes was described in our previous papers [3, 4] and is based on mixture of these components: monomeric methylmethacrylate (MMA, Sigma-Aldrich), polymeric PMMA resin containing polymerisation initiator (dibenzoylperoxide, 1 wt. %) – commercially produced material Superacryl (Spofa-Dental Prague, Czech Republic) and an optional component – solution in propylene carbonate. 1M solution of anhydrous lithium perchlorate (Sigma-Aldrich) was used as a supporting electrolyte. In the case of electrochemical studies 0.05M solution of ferrocene and ferricinium tetrafluoroborate (both Sigma-Aldrich) was used. Potentiogalvanostat Eco Autolab (Eco Chemie, The Netherlands) was used for electrochemical measurements including FRA-2

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impedance module.

Three-electrode cell was developed for the solid state electrochemical measurements in the medium of polymer gel electrolytes [4]: glassy carbon was used as the working and counter electrode. The surface of working and counter electrode was cleaned by abrasives after each measurement.

For the *in-situ* measurements small glassy cell was used (5 ml volume). Glassy carbon electrode in PTFE rod (2.97 mm diameter of the active surface) served as a working electrode and platinum as an auxiliary electrode.

The PMMA-PC-Cd(ClO₄)₂-Cd system was used as a solid-state pseudo reference electrode described in our previous papers [5, 6] and all potentials are introduced versus this Cd-Cd²⁺ system.

Liquids (PC, MMA monomer) were stored under nitrogen and bubbled for 60 minutes before measurements. Cyclic voltammograms were measured with the scan rate 5 mV.s⁻¹ during the *in-situ* and 0.1 mV.s⁻¹ in the solid state measurements. First experiment was done with 2.00 ml of 1M LiClO₄ in propylene carbonate to find the available range of potentials. Than 3.00 ml of MMA monomer was added together with ferrocene and ferricinium tetrafluoroborate to form ca. 0.05M solution and after dissolution a new voltammogram was measured. Addition of 0.7 g of PMMA resin followed, the mixture was vigorously stirred and next set of cyclic voltammograms was measured every day for next several days.

Results and Discussion

Potential window in the PMMA-PC system is wide: from -1.5 to +1.3 V. In the presence of traces of water (over 5 ppm) in propylene carbonate small irreversible cathodic wave at ca. -0.3 V was confirmed [7], but this wave do not interfere with studied redox couple reaction.

First experiment was done with ferrocene and ferricinium tetrafluoroborate incorporated in the PMMA gel. A reversible couple of waves was found in the range of potentials mentioned above (see Table 1) and the experiment was repeated with narrower range of potentials (from 0 to 1 V). Due to the expected low diffusion coefficients very low scan rate was chosen – 0.1 mV.s⁻¹. Fig. 1 presents voltammogram measured in the gel 12 days old.

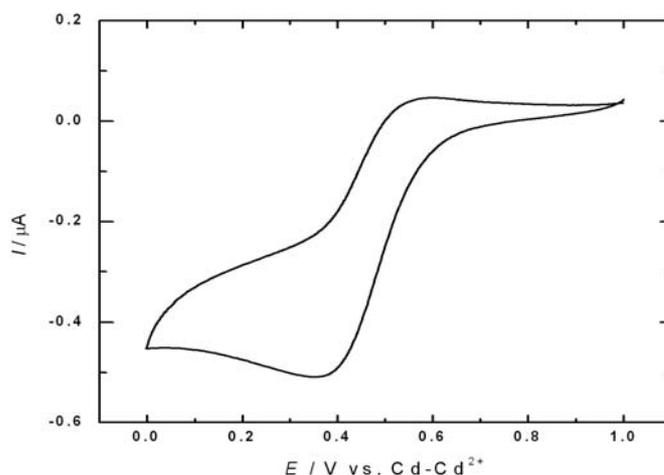


Fig. 1 The cyclic voltammogram of 0.05M ferrocene and 0.05M ferricinium tetrafluoroborate in formed PMMA gel electrolyte (supporting electrolyte 1M LiClO₄, scan rate 0.1 mV.s⁻¹, age of the gel 12 days)

The comparison of liquid and gel system showed, that remarkable shift of potentials of the redox process to the negative potentials after gelation appeared (see Table 1). Similar process was observed in similar inorganic silica sol-gel systems with embedded organic solvent [2].

Table 1 Peak potentials, apparent diffusion coefficients and their confidence intervals for liquid and gel polymer medium

| Medium | E_p (Fc) (V) | E_p (Fc ⁺) (V) | D_{APP} (Fc) (cm ² .s ⁻¹) | D_{APP} (Fc ⁺) (cm ² .s ⁻¹) |
|--------------|-------------------|---------------------------------|---|---|
| PC-MMA (1:1) | 0.842 | 0.676 | $(5.86 \pm 0.55) \times 10^{-6}$ | $(8.86 \pm 0.69) \times 10^{-6}$ |
| PC-PMMA gel | 0.543 | 0.386 | $(8.69 \pm 1.32) \times 10^{-10}$ | $(2.12 \pm 0.48) \times 10^{-9}$ |

Diffusion coefficients for both forms of ferrocene were calculated [8] using equation:

$$i_p = (2.69 \times 10^5) n^{3/2} A D_{APP}^{1/2} v^{1/2} c, \quad (2)$$

where i_p is peak current (A), n number of transferred electrons, A area of the working electrode (cm²), D_{APP} apparent diffusion coefficient (cm².s⁻¹), v scan rate (V.s⁻¹) and c concentration of the species (mol.cm⁻³). The constant 2.69×10^5 is calculated for 25°C measurement temperature. Diffusion coefficients for ferrocene and ferricinium cation were calculated for both phases – liquid and gel. The three-order decrease of the coefficients is caused by the restriction of motion in the polymer network and these values correspond with the conductivity measurements in liquid and gel system (see Table 2).

Table 2 Specific resistivities for liquid and gel systems at 20°C

| optional part | ρ (PMMA gel) ($\Omega \cdot \text{cm}$) | ρ (liquid) ($\Omega \cdot \text{cm}$) |
|------------------------------|---|---|
| PC | 1.2×10^6 | 8.21×10^5 |
| PC - 0.5M LiClO ₄ | 7.8×10^3 | 1.26×10^2 |

In-situ measurements show, that a remarkable decrease of the peak current and consequently of the diffusion coefficient appears during the polymerisation. Fig. 2 presents two curves: voltammogram in PC-MMA mixture before polymerisation (solid line) and after polymerisation in day 1 (dash line). During the further polymerisation the value of diffusion coefficients is approaching the values measured in the solid state arrangement.

ΔE_p value, the ratio representing reversibility of the process is increasing during polymerisation process. Both effects are caused by restriction of the species motion and probably by changed solvation.

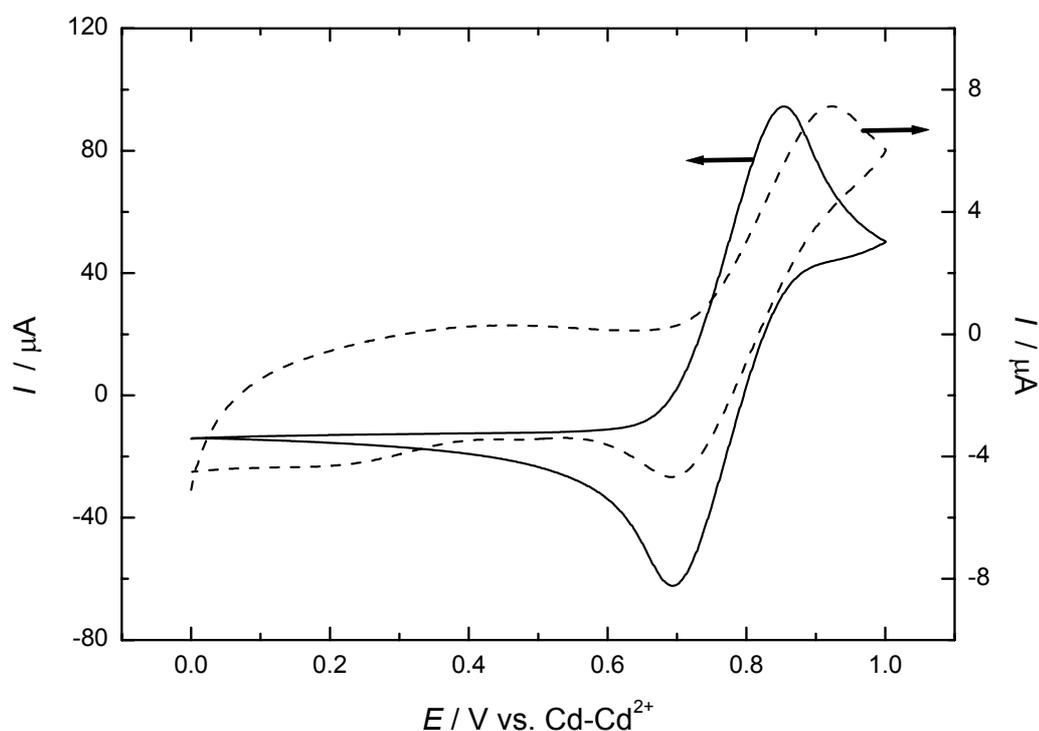


Fig. 2 *In-situ* voltammograms of Fc/Fc^+ in sol (liquid PC-MMA (solid line) and after polymerisation – day 1 (dash line; supporting electrolyte 1M LiClO₄, scan rate 5 $\text{mV} \cdot \text{s}^{-1}$):

Conclusions

Electrochemical behaviour of ferrocene-ferricinium redox couple was investigated in the medium of PMMA gel electrolytes and propylene carbonate-methylmethacrylate liquid. The diffusion coefficient values of both species were estimated for sol and gel systems, where immobilisation in the polymer network causes large decrease of the diffusion coefficients.

This change is corresponding to the decrease of ionic conductivity during the polymerisation.

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