

## Ion-conductive polymethylmethacrylate gel electrolytes for lithium batteries

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### Abstract

Polymer gel electrolytes based on PMMA were prepared by in situ polymerisation of methylmethacrylate, where solutions of inorganic and/or organic compounds in propylene carbonate can be used as an optional part incorporated in the gel. These elastic materials have suitable conductivity ca.  $10^{-3}$  to  $10^{-4}$  S cm<sup>-1</sup>, high optical transmittance and these properties are stable for weeks. Gels with lithium perchlorate and ferrocene–ferricinium redox couple were studied using impedance spectroscopy and cyclic voltammetry. The behaviour of glassy carbon in contact with the gels was studied by cyclic voltammetry and impedance spectroscopy.

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### 1. Introduction

The research of secondary lithium batteries is connected with a serious problem of irregular formation of metal lithium deposits on the negative electrode during electrodeposition of lithium. In consequence of reaction between metal lithium and the solvent poorly conducting compounds are produced. Metal lithium is therefore deposited in irregular dendrites, sponge and moss-like matter. These processes cause lower charging efficiency [1].

The solution of this problem is in the substitution of liquid electrolyte with polymer electrolyte. The first experiments were done with polyethyleneoxide (PEO) doped with lithium salts [2,3]. These first generation polymer electrolytes have very low conductivity at the room temperature [4]. As the second generation polymer electrolytes were therefore tested polymers based on PEO and similar compounds to which softeners (well known from the technology of polymers and plastics) were added with the aim to lower the tem-

perature at which the conductivity reached reasonable value [1,4].

Other point of view is in immobilisation of a solvent in the network of polymer and these materials are called third generation polymer electrolytes. Polymer electrolytes based on polymethylmethacrylate (PMMA) where prepared by in situ polymerisation, where anhydrous propylene carbonate (PC) serves as an embedded solvent [5]. The solvent can contain organic and/or inorganic compounds, which influence chemical, mechanical and optical properties of the gel. Gels containing solutions of various inorganic salts (perchlorates) [6] and ferrocene [7] were studied.

Chemical and mechanical properties of PMMA–PC system allows incorporation of many compounds and can be proton-conducting due to the presence of phosphoric acid [8] or electronically conducting containing composite materials [9]. Also incorporation of TiO<sub>2</sub> nanoparticles to improve mechanical properties [10] or combination with ionic liquids causing increase conductivity [11] was suggested.

Our recent work is based on electrochemical behaviour of transition metal complexes embedded in polymer electrolyte, particularly of ferrocene–ferricinium (Fc/Fc<sup>+</sup>) redox

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couple [12]. The aim is to find relationship between solvation changes of incorporated species and their electrochemical properties. This research is connected with application of  $I_3^-/I^-$  redox couple in hybrid electrochromic devices [13] and solid-state chemical sensors [14,15], where different process can appear in comparison with liquid systems.

In addition to the use of polymer electrolytes in lithium batteries and electrochromic devices, their application in electrochemical supercapacitors is also possible. These components use carbonaceous inert materials as electrodes. Therefore, we started to use glassy carbon planar electrode as a model of interface between the gel electrolyte and a solid inert electrode. The formation of a SEI layer in the range of stronger negative potentials is then probable.

## 2. Experimental

The principle of preparation is based on mixture of these components: methylmethacrylate monomer (99%; Sigma–Aldrich), polymeric PMMA resin containing polymerisation initiator dibenzoylperoxide (SUPERACRYL<sup>®</sup>, Spofa-Dental, Czech Republic) and an optional component. The optional component determines chemical properties of the gel and is realised as a solution of organic and/or inorganic compound in anhydrous propylene carbonate (99.7%; water content under 0.005%, Sigma–Aldrich). In the case of gel containing inorganic salt 0.25–1 M solution of anhydrous perchlorate in PC is used.

The mixture is kept for 5 days in a desiccator in the atmosphere of monomer and finally the gel is kept at 90 °C for 60 min in order to finish the polymerisation. This procedure guarantees the chemical and mechanical stability of the gel for weeks. The gel is elastic with thickness 0.5–0.7 mm, colourless and odourless. Elasticity and consistence is kept for months, required foils can be easily cut out. Gels can be stored on air without any decomposition and water absorption.

Inorganic perchlorates were dehydrated by vacuum heating at 110 °C overnight. Ferrocene and ferricinium tetrafluoroborate were purchased from Sigma–Aldrich and were used without further purification.

New cell for solid-state electrochemical measurements was developed [6] with glassy carbon as the working and auxiliary electrode (both  $\varnothing = 3$  mm) and PMMA–Cd–Cd<sup>2+</sup> solid-state pseudo-reference electrode [6,15,16]. All potentials are given versus this system.

Eco Autolab (Eco Chemie, The Netherlands) was used for the electrochemical investigation using two modules: potentiostat PGSTAT 10 for cyclic voltammetry measurements and the impedance unit FRA-2 was used to obtain impedance spectra. The spectra were analysed by the Autolab software and the equivalent circuit values were evaluated, especially value of the material ohmic resistance.

Temperature dependence of resistivity was measured in the range from –70 to 70 °C using thermostated bath. UV–vis

spectra of the gels were measured by two-beam spectrometer Perkin-Elmer Lambda 35.

## 3. Results and discussion

### 3.1. Conductivity measurements

First experiments were done with PMMA gels containing solution of anhydrous perchlorates (Li, Na, Mg, and Ca) in propylene carbonate to obtain values of ohmic resistivity. Thin sheet of the gel (of known thickness) was placed between two electrodes of stainless steel and the impedance spectrum was measured using the FRA-2 module with the frequency range from 10 kHz to 100 Hz. The ohmic resistance of the sample was then estimated from the analysis of the equivalent circuit consisting of a resistance  $R$  in the serial connection with the constant phase element  $Q$ . Fig. 1 presents the spectrum of the gel containing LiClO<sub>4</sub> with proposed equivalent circuit. Reproducible results are that the gel containing cation of higher radius has higher conductivity than the gel with smaller cation [7,15]. This effect is remarkable for the pair lithium–sodium, when the mobility of smaller lithium cation is strongly limited by the interaction with polymeric network. This theory was also confirmed by transference number measurement [5]. Table 1 presents specific resistivities of PMMA gels containing either pure propylene carbonate or solutions of inorganic perchlorates measured at the room temperature. For comparison, the resistivities of perchlorate solutions in PC are also introduced.

Conductivity of all PMMA gels is strongly temperature dependent. In Fig. 2, Arrhenius plot is indicated for the case of gel with lithium and sodium perchlorate. Gel containing other perchlorates would produce similar plot shifted to

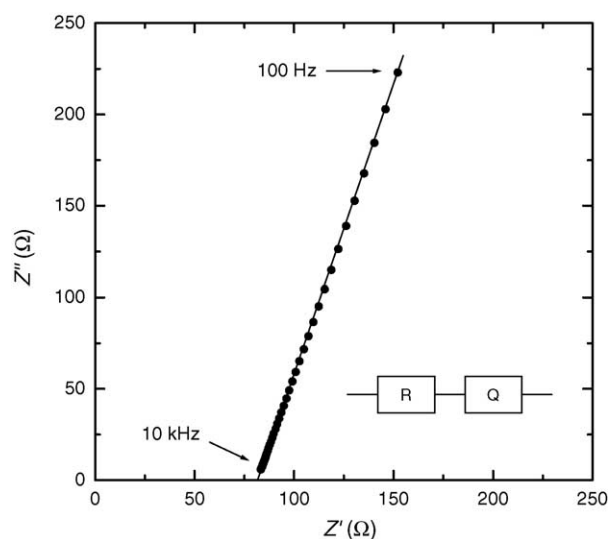


Fig. 1. Nyquist plot of PMMA gel containing 0.5 M LiClO<sub>4</sub> in PC with the equivalent circuit (frequency range from 10 kHz to 100 Hz, measurement temperature 20 °C).

Table 1

Specific resistivities of PMMA gels containing perchlorates and their solutions in propylene carbonate (temperature 20 °C, age of the gel 12 days, concentration of LiClO<sub>4</sub> and NaClO<sub>4</sub> solutions 0.5 M, concentration of Mg(ClO<sub>4</sub>)<sub>2</sub> and Ca(ClO<sub>4</sub>)<sub>2</sub> solutions 0.25 M)

Optional component	Specific resistivity (Ω cm)	
	PMMA gel	PC solution
PC only	$1.2 \times 10^6$	$8.21 \times 10^5$
PC–LiClO <sub>4</sub>	$7.8 \times 10^3$	$1.26 \times 10^2$
PC–NaClO <sub>4</sub>	$1.5 \times 10^3$	$1.24 \times 10^2$
PC–Mg(ClO <sub>4</sub> ) <sub>2</sub>	$4.2 \times 10^3$	$1.21 \times 10^2$
PC–Ca(ClO <sub>4</sub> ) <sub>2</sub>	$2.3 \times 10^3$	$1.24 \times 10^2$

higher or smaller values of resistivity. Conductivity of gel with NaClO<sub>4</sub> is higher in the whole range of temperatures. The plot presents the point of transformation at the temperature of ca. –25 °C (it corresponds to  $1000T^{-1} \approx 4.1$ ). At this point structural change of polymeric network occurs what leads to remarkable increase of resistivity. The resistivity of the gel rapidly increases under temperature –55 °C (equals to  $1000T^{-1} \approx 4.6$ ) what is caused by solidification of propylene carbonate. In this area of temperatures the material behaves like a dielectric with the value of resistivity similar to the gel with propylene carbonate only. These results allow application of PMMA gel electrolytes above temperature –25 °C.

### 3.2. Ageing of the gel

Structural changes of polymeric network, evaporation of monomer during polymerisation and evaporation of the solvent are the main contributions to the set of processes, which are called the ageing of material. These processes can influence chemical, optical and mechanical properties of the gel.

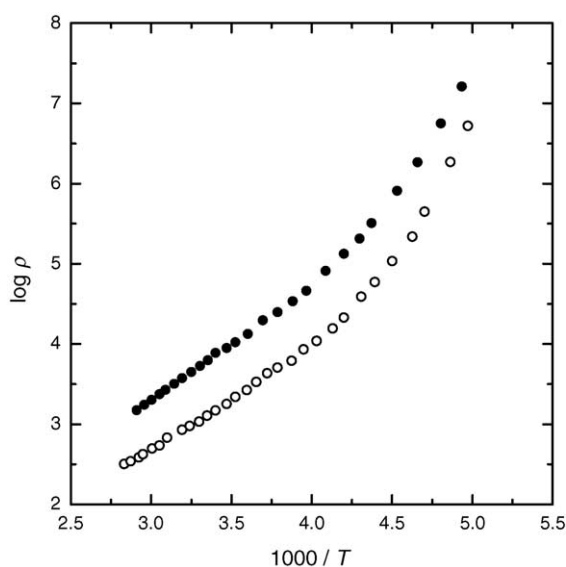


Fig. 2. Arrhenius plot for PMMA gels containing 0.5 M LiClO<sub>4</sub> (full dots) or 0.5 M NaClO<sub>4</sub> (empty dots) in PC (temperature range from –70 to 70 °C, decadic logarithm of specific resistivity vs. reciprocal temperature).

Suitable method for monitoring of structural changes is the measurement of resistivity and UV–vis spectroscopy.

The main contribution in the case of PMMA gel electrolytes prepared by described method is the incomplete polymerisation. Our method of preparation ensures that the process of polymerisation is terminated during the 60 min warming and the conductivity is stabilised after 5–10 days from preparation.

To prevent evaporation of monomer is the Petri dish with the initial mixture placed into a desiccator under MMA atmosphere. With regard to low vapour tension of propylene carbonate is the evaporation of the solvent insignificant for changes of conductivity.

Conductivity measurements in the case of PMMA gels containing sodium, lithium and calcium perchlorate show that no significant structural changes appear in the period of 3 months (see Fig. 3). The gels were placed on air at room temperature and the conductivity was measured every 2–4 days. In the case of PMMA gel with Mg(ClO<sub>4</sub>)<sub>2</sub> an increase of resistivity was observed after 2 months [15]. This change would not be an obstacle in further application.

Mechanical properties of studied materials are not changed within 12 months. Gels keep their reasonable elasticity and they do not disperse or disintegrate.

### 3.3. UV–vis spectra—optical properties

The monomer and the solutions of inorganic perchlorates in PC are colourless. The PMMA resin is dissolved in the gel during preparation without any residue. The polymer gel electrolyte has an excellent optical transparency therefore. This property is very important in one field of practical application—technology of electrochromics. The PMMA gel electrolytes are suitable for high ionic conductivity and transparency [17].

In the range of visible spectrum, the optical transmittance of gels is 90–93%. In the case of gels with inorganic

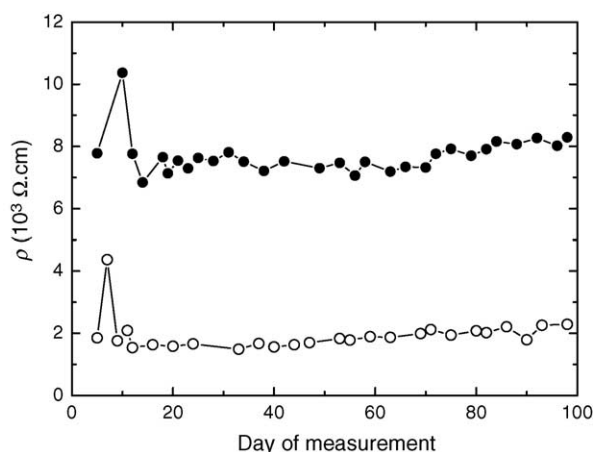


Fig. 3. Changes of the specific resistivity of PMMA gels containing lithium and sodium perchlorate for 100 days since preparation (measurement temperature 20 °C).

perchlorates is the high transparency kept for more than 3 months. In this experiment the gel samples were stored on air at the room temperature.

Transmittance rapidly decreases below 320 nm due to the strong absorption of polymer molecules. In the range from 320 to 360 nm is transmittance over 85%.

### 3.4. Behaviour of ferrocene–ferricinium redox couple in PMMA gel electrolyte

The gels containing lithium or sodium perchlorate exhibit a high ionic conductivity. The motion of ions is restricted due to the presence of polymer network, however the gel electrolyte contains remarkable amount of immobilised solvent. The lithium cation is more restricted in motion and the conductivity is five times lower than in the case of NaClO<sub>4</sub> gel. The conductivity is not influenced by co-immobilisation of metal complexes in used 0.05 M concentrations, when the ratio NaClO<sub>4</sub>:Fc:Fc<sup>+</sup> is 20:1:1. The comparison between liquid and gel system shows, that the formation of polymer network causes a decrease of the conductivity values by one order of magnitude (see Table 1).

Cyclic voltammetry of Fc/Fc<sup>+</sup> redox couple immobilised in the gel showed rapid decrease of the peak currents during the polymerisation. The diffusion coefficients for three systems (PC and PC–MMA liquids and PMMA–PC gel) were evaluated from the voltammetrical data using Randles–Sevcik equation [18,19]:

$$i_p = (2.69 \times 10^5)n^{3/2}AD_0^{1/2}v^{1/2}c, \quad (1)$$

where  $i_p$  is peak current (A),  $n$  number of transferred electrons,  $A$  area of the working electrode (cm<sup>2</sup>),  $D_0$  apparent diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $v$  scan rate (V s<sup>-1</sup>) and  $c$  concentration of the species (mol cm<sup>-3</sup>). The constant  $2.69 \times 10^5$  is calculated for 25 °C measurement temperature.

A couple of waves were found in the range of potentials from 0 to 1 V versus Cd–Cd<sup>2+</sup>. Due to the expected low diffusion coefficients low scan rate (10<sup>-4</sup> V s<sup>-1</sup>) was chosen. Fig. 4 presents the voltammogram of Fc/Fc<sup>+</sup> couple measured in the gel, where absence of convective diffusion known in liquid systems allows measurements with the low scan rate. Fc/Fc<sup>+</sup> couple exhibits almost reversible electrochemical reaction with peak separation value ( $\Delta E_p$ ) from 70 to 80 mV. The peak potentials for both cathodic and anodic reaction and diffusion coefficients for ferrocene and ferricinium cation are summarised in Table 2. The current ratio  $i_p(\text{Fc})/i_p(\text{Fc}^+)$  measured in PMMA gel is 0.92.

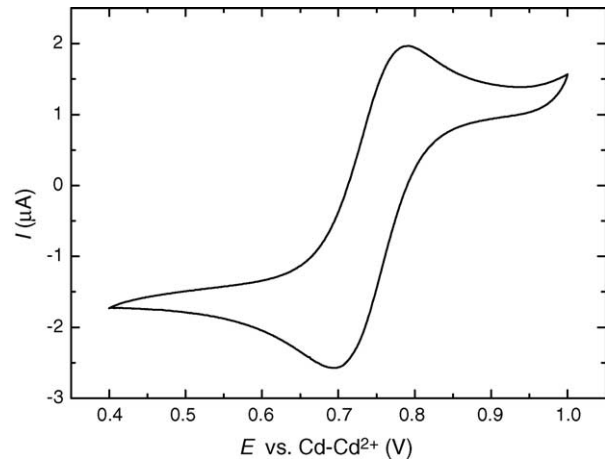


Fig. 4. Cyclic voltammogram of Fc/Fc<sup>+</sup> redox couple in PMMA gel electrolyte (0.05 M Fc/Fc<sup>+</sup>, 1 M LiClO<sub>4</sub> supporting electrolyte, 10<sup>-4</sup> V s<sup>-1</sup> scan rate).

Comparison of Fc/Fc<sup>+</sup> behaviour in the liquid systems (pure propylene carbonate and mixture PC–MMA 1:1 (vol)) and in the gel shows strong, almost 3-order decrease of diffusion coefficients for both, charged and uncharged forms (see Table 2).

### 3.5. Glassy carbon electrode in contact with PMMA gel electrolyte—impedance spectroscopy and cyclic voltammetry

The voltammetric curve of a glassy carbon in a gel containing LiClO<sub>4</sub> is depicted in Fig. 5. As we see, there is no electrode process at potential exceeding -0.2 V and lower than +1.5 V. This indicates the usable voltage range of a carbon-based supercapacitor to ±1.7 V. There is some electrode reaction below -0.2 V; it can be ascribed to well known SEI film formation on carbon electrode. The intercalation of lithium into glassy carbon does not seem probable.

An example of impedance spectrum is given in Fig. 6 for the potential of +0.7 V. The impedance spectrum was deciphered using the AUTOLAB software as a series resistance ca. 50 Ω, and two successive couples of a resistor and constant phase element. One of them is almost similar to a capacitor (with phase angle 75–80°) and it would be described as a double layer capacity of a solid-to-quasisolid interface; its magnitude corresponds to 20–40 µF cm<sup>-2</sup> as derived from the C.P.E. impedance at  $\omega = 1 \text{ rad s}^{-1}$ .

Table 2

Peak potentials and apparent diffusion coefficients for ferrocene and ferricinium cation (0.05 M Fc/Fc<sup>+</sup>, supporting electrolyte 1 M lithium perchlorate, age of the gel 12 days, scan rate  $5 \times 10^{-3} \text{ V s}^{-1}$  for the liquid and  $10^{-4} \text{ V s}^{-1}$  for gel medium)

Medium	$E_p(\text{Fc})$ (V)	$E_p(\text{Fc}^+)$ (V)	$D_0(\text{Fc})$ (cm <sup>2</sup> s <sup>-1</sup> )	$D_0(\text{Fc}^+)$ (cm <sup>2</sup> s <sup>-1</sup> )
PC	0.790	0.697	$6.5 \times 10^{-6}$	$5.8 \times 10^{-6}$
PC–MMA (1:1)	0.846	0.744	$12.9 \times 10^{-6}$	$12.7 \times 10^{-6}$
PC–PMMA gel	0.782	0.705	$2.2 \times 10^{-9}$	$2.6 \times 10^{-9}$

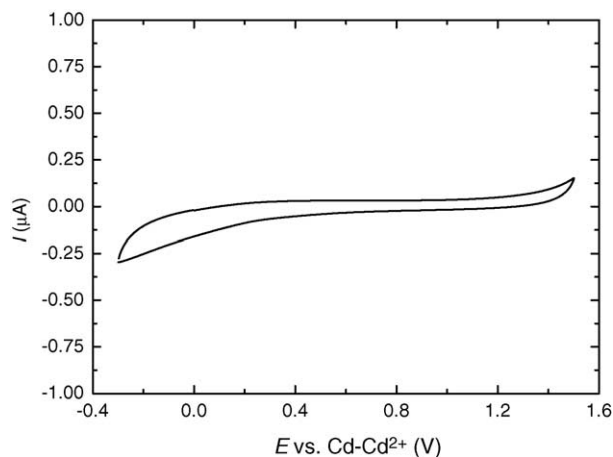


Fig. 5. Cyclic voltammogram of the gel containing 0.5 M LiClO<sub>4</sub> in PC (scan rate  $5 \times 10^{-3}$  V s<sup>-1</sup>) on the glassy carbon electrode ( $\emptyset$  5 mm).

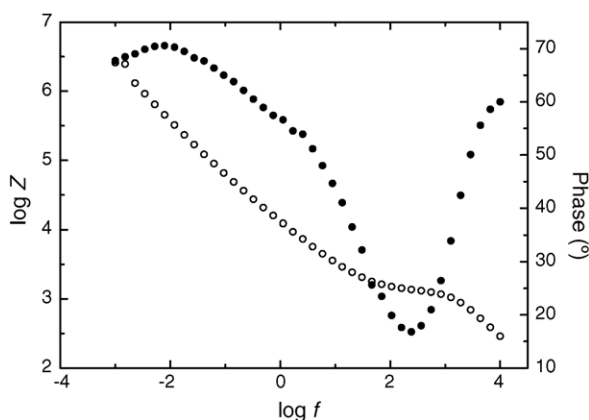


Fig. 6. Bode plot of the same electrode at the potential +0.7 V vs. Cd–Cd<sup>2+</sup>. Left scale—logarithm of module ( $\Omega$ ; empty dots), right scale—phase angle (full dots).

#### 4. Conclusions

Due to the low cost, long chemical and mechanical stability and reasonably high conductivity, the PMMA based electrolytes are suitable for various applications in the field of solid-state electrochemical devices such as lithium batteries, electrochromic elements and solid-state sensors. As optional part inorganic and/or organic compounds can be used, which determines chemical and optical properties of the gel. They are freeze resistant to  $-25$  °C. The UV initiated polymerisation yields in gels with lower conductivity than the chemically polymerised materials. Further, smaller cations are less mobile than larger ones.

Fc/Fc<sup>+</sup> redox couple immobilised in the gel is a suitable redox system for description of electrochemical changes during the polymerisation. The diffusion coefficients for ferrocene and ferricinium cation were estimated.

The properties of a glassy carbon electrode in contact of the gels are important for the usage of gels in electrochemical supercapacitors. The double layer capacity is quite within the expected values. The reaction below  $-0.2$  V will need more detailed investigation.

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#### References

- [1] M. Alamgir, K.M. Abraham, in: G. Pistoia (Ed.), *Lithium Batteries—New Materials, Developments and Perspectives*, vol. 5, Elsevier Science, Amsterdam, 1994, Chapter 3.
- [2] M.B. Armand, J.M. Chabagno, M. Duclot, 2nd International Meeting on Solid Electrolytes Extended Abstracts, St. Andrews Scotland, 20–22 August 1978.
- [3] M.B. Armand, *Solid State Ionics* 9–10 (1983) 745.
- [4] M.B. Armand, J.M. Chabagno, M.J. Duclot, in: P. Vashishita, J.N. Mundy, G.K. Shenoy (Eds.), *Fast Ion Transport in Solids*, Elsevier, New York, 1979.
- [5] J. Vondrák, M. Sedlářková, J. Reiter, T. Hodal, *Electrochim. Acta* 44 (1999) 3067–3073.
- [6] J. Vondrák, M. Sedlářková, J. Velická, B. Klápště, V. Novák, J. Reiter, *Electrochim. Acta* 48 (2003) 1001–1004.
- [7] J. Vondrák, J. Reiter, J. Velická, M. Sedlářková, *Solid State Ionics* 170 (2004) 79–82.
- [8] G.Z. Zukowska, V.J. Robertson, M.L. Marcinek, K.R. Jeffrey, J.R. Stevens, *J. Phys. Chem. B* 107 (2003) 5797–5805.
- [9] S. Šebková, T. Navrátil, M. Kopanica, *Anal. Lett.* 37 (2004) 603–628.
- [10] J. Adebahr, N. Byrne, M. Forsyth, D.R. MacFarlane, P. Jacobsson, *Electrochim. Acta* 48 (2003) 2099–2103.
- [11] A. Lewandowski, A. Świdarska, *Solid State Ionics* 169 (2004) 21–24.
- [12] J. Reiter, J. Vondrák, Z. Mička, The electrochemical redox processes in PMMA gel electrolytes—behaviour of transition metal complexes, *Electrochim. Acta*, in press.
- [13] B. Orel, A. Šurca Vuk, R. Ješe, P. Lianos, E. Stathatos, P. Judeinstein, Ph. Colomban, *Solid State Ionics* 165 (2003) 235–246.
- [14] F. Opekar, K. Štulík, *Crit. Rev. Anal. Chem.* 32 (2002) 253–259.
- [15] J. Reiter, M.Sc. Thesis, Charles University, Prague, 2003.
- [16] J. Reiter, J. Vondrák, F. Opekar, M. Sedlářková, J. Velická, B. Klápště, New reference electrode based on PMMA polymer electrolytes, 12th International Meeting on Lithium Batteries, Nara, Japan, June 27–July 2, 2004, Meeting Abstracts, abstract 237.
- [17] C.G. Granqvist, in: P.J. Gellings, H.J.M. Bouwmeester (Eds.), *The CRC Handbook of Solid State Electrochemistry*, CRC Press, Boca Raton, 1997, Chapter 16.
- [18] A.J. Bard, L.R. Faulkner, *Electrochemical Methods—Fundamental and Applications*, John Wiley & Sons, New York, 1980, Chapter 6.2.2.
- [19] K. Holub, R. Fuoco, *Annali di Chimica* 72 (1982) 531–546.