

## 1. Introduction

Electrochemical and mechanical properties of polymer gel electrolytes have been intensively investigated since the introduction of the 1<sup>st</sup> generation of solid polymer electrolytes by M. Armand [1]. Their electrochemical application includes secondary lithium batteries, supercapacitors, chemical sensors and electrochromic devices. Wide application of the gel polymer electrolytes is allowed due to the higher ionic conductivity compared with solid polymer electrolytes and due to the higher safety properties in comparison with common liquid electrolytes.

Organic methacrylate-based polymers are perspective materials for their low toxicity both of monomer and polymer form, when methyl methacrylate (MMA) is widely used in the dental praxis. Poly(methyl methacrylate) PMMA was used in electrochemistry for the first time by Iijima [2] and than either pure or in different polymer modifications including various copolymers [3, 4]. Aprotic solvents like sulpholane, organic carbonates, N,N-dimethylformamide, and formamide are usually incorporated in the polymer structure to form ternary electrolyte polymer-solvent-salt. PMMA polymer gel electrolytes with embedded particles of nanosized TiO<sub>2</sub> [5], carbon [6] or proton-conductive membranes with different organic acids [7] or orthophosphoric acid [8] were reported.

Recent polymer gel electrolytes are prepared by immobilisation of an aprotic solvent in the polymer network. Many organic and/or inorganic compounds can be dissolved in the solvent and then uniformly located in the polymer gel medium. There are two general methods of the gel polymer electrolyte preparation. The first method - solvent casting is based on mixture

of polymer, salt and aprotic solvent in a volatile co-solvent followed by partial or complete removal of the co-solvent. The other method is in using direct polymerisation of monomers mixed with the aprotic solvent. In this case, thermal or UV polymerisation is used. This method brings the possibility of using cross-linking agent, precise preparation of the gel electrolyte and uniform distribution of compounds previously dissolved in the solvent.

Generally the research is aimed at several important tasks: increase of the ionic conductivity, improvement of the electrochemical stability, elimination of environmentally hazardous compounds, and improvement of the safety properties.

## **2. Objectives of the Thesis**

Presented work is aimed at development and investigation of new electrolytes for electrochemical applications. New polymer gel electrolytes were prepared combining aprotic solvents and/or ionic liquids with various methacrylates. Developed materials exhibit excellent electrochemical and material properties and are considered to be promising materials for modern electrochemical applications.

New method of direct, UV or thermally initiated polymerisation was developed to ensure homogenous structure and reproducible properties of the sample. Prepared polymer membranes were investigated using electrochemical, optical and thermogravimetric methods. Elastic and non-volatile materials exhibit high ionic conductivity (up to 1 mS/cm), broad

accessible potential window (4.2 - 4.6 V) and reasonable thermal stability up to 150 °C.

For detailed description of the species motion in the structure of the polymer electrolyte, extensive impedance measurements were performed resulting in the determination of the conductivity activation energy. Also the kinetics of the electrochemical redox reaction of ferrocene and other transition metal complexes was studied together with the estimation of the apparent diffusion coefficients. This part of research is important also for the investigation of the transport processes in the membranes of fuel cells.

For the specific conditions of the electrochemical measurements, a new solid-state Cd-Cd<sup>2+</sup> reference electrode was developed and successfully tested in aprotic liquid as well as polymer gel electrolytes. The electrode potential was found to be stable and reproducible and the design flexibility and defined preparation allow its application also for the electrochemical gas sensors.