THE INVESTIGATION OF POLYMER GEL ELECTROLYTES BASED ON ACRYLATES IN CZECHIA

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Introduction

Gel polymer electrolytes were introduced into the electrochemistry of lithium secondary cells approximately 20 to 15 years ago [1]. They offered some advantages in comparison to liquid ones. Therefore, an intensive research started and it has proceeded until now. Besides lithium batteries, another application appeared when electrochemical windows and mirrors reached application level. Finally, another possible application of them has arisen recently as the electrolytes for electrochemical supercapacitors. We have proposed a new preparation of them and have opened a program of systematic research of this new family of electrolytes.

Review of our results

Fundamental idea

The main idea was the preparation of gel electrolytes by polymerization of PMMA from monomer MMA and industrial polymerization agent SUPERACRYL (SPOFA Inc., Czechia) used regularly in dentistry and other fields. A solution of aprotic salt in propylene carbonate was added to the monomer MMA before polymerization [2, 3]
Their properties were compared with gels prepared by a photochemically induced polymerization of methyl, ethyl and 2-ethoxyethyl methacrylate by UV irradiation [4].

Family of prepared gels

We have prepared gels containing perchlorates, triflates, iodides and tetrafluoroborates of Li, Na, K, Mg, Ca, Zn, Cd, and tetraalkylammonium [2, 5].

Conductivity and material ageing

The gels are in general reasonably conductive (up to 0.2 $mS.cm^{-1}$ for gel prepared from 0.5 M solution of salt) [5]. The nature of conductivity was retained for temperature going down to ca. -25 [5, 6]. After several days, it reached constant value that remained stable for a period of many months provided that the gel had been sealed hermetically [6, 7]
In general, smaller ions (Li^+, Mg^{2+}) exhibited markedly lower mobility than their larger analogs (Na^+, Ca^{2+}) [3]. The explanation of this phenomenon by NMR is in progress.

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Experimental methods

A pseudoreference electrode based on Cd-Cd^{2+} couple was developed and carefully tested [6, 8]. It has been used successfully in a three-electrode arrangement and all potentials are now related to it as a reference value [9, 10].

Electrodeposition of metals

The main problem of lithium secondary cells - irregular formation of metal during charging of negative electrode - was modeled using cadmium electrodeposition. In fact, the deposition of Cd from gels is much more regular than from liquid solution [3]. This confirms the observation reached with lithium.

Redox processes

Redox processes such as the reaction of ferrocene - ferricinium redox couple were studied by voltammetry in the liquid and polymer gel phase [10]. It was possible to monitor the process of polymerization by *in-situ* measurements. The named system exhibited behavior corresponding to the theory. Due to the absence of convective mass transport, it was possible to use sweep rate 0.1 mV/s or less without distortion of peak shape.
Another investigated system was the iodine - iodide couple used in hybrid electrochromic devices [11].

Electrochemical lithiation of WO_3

The electrochemical coloration and/or discoloration of thin WO_3 films was tested and electrochromic elements were designed. Their counter electrodes were either V_2O_5 or Pt - iodide redox couple [2, 11].

Double layer capacity

With respect to proposed usage in electrochemical supercapacitors, the capacity of glassy carbon electrode was investigated in PMMA-PC gels of various composition. In general, the behavior of the electrode in the range of negative potential range is influenced by impurities and it is not quite clear now. In the positive potential range the capacity reaches 10 - 50 $\mu F.cm^{-2}$ with a well developed minimum at +0.2 V vs. Cd-Cd^{2+}. Experiments with carbon samples possessing high physical surface area are in progress.

Electrochemical sensors using PMMA gels

The PMMA gels were used in two sensors for detection of gaseous HF. The sensor itself contained a film of gel electrolyte to which aliphatic amine was added. The traces of HF were captured by the film under formation of corresponding fluoride. The change of electrochemical properties of the film served for detection of hydrogen fluoride [6, 12, 13].

Electrochemistry without convectional mass transport

Under circumstances, a theory of electrochemical reactions in an immobile electrolyte is under investigation. The concentration changes in such an environment are rather

permanent and in the case of binary electrolyte they yield in interesting phenomena. This problem is just under explanation of experimental results and will be treated mathematically.

The participation of students on the research

At present, 6 PhD students and corresponding number of pregraduate students are directly attached to our scientific program.

Future development

- Investigation of other polymer electrolytes than PMMA-PC system is expected.
- Deeper knowledge of electrochemical reactions in binary electrolytes without natural convection has to be obtained.
- Explanation of binding forces and hindrances of ionic movements will be performed by NMR and UV-VIS spectroscopy.
- The usage of gel electrolytes in the lithium-ion batteries, electrochromic devices and supercapacitors will be developed.

Cooperating institutions

- Institute of Macromolecular Chemistry, Academy of Sciences, Prague
- Institute of Scientific Instruments, Academy of Sciences, Prague
- BOCHEMIE Inc., Bohumín, Czech Republic
- National Chemical Institute Ljubljana, Slovenia
- Department of Electrochemistry, University of Southampton, United Kingdom
- University Le Mans, France
- Central Laboratory of Power Sources and Batteries, Poznań, Poland

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