Novel polymers based on ionic liquid like monomers for use as solid electrolytes in electrochromic devices

Scientific and industrial research into the domain of electrochromic devices (ECDs) has gained a great deal of attention over the last decades, evidenced by numerous scientific papers, books and chapters in books as well as popular articles [1]. The typical ECD composition is a five-layer structure described as GS/TC/EC/IC/IS/TC/GS, where GS is a Glass Substrate, TC is a Transparent Conductor, EC is an Electrochromic Coating, IC is an Ion Conductor and IS is an Ion Storage coating [2]. This structure can be seen in Fig. (1).

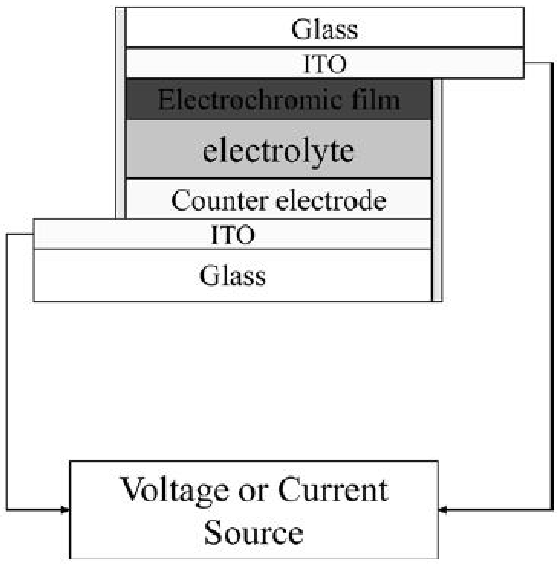

Fig. 1. Five-layer electrochromic device scheme composed of a glass-ITO substrate (GS-TC), electrochromic (EC) and counter electrode (IS) films and electrolyte (IC).

An important part of many ECDs is an electrolyte. Usually, the role of electrolyte is played by the solutions of various salts in organic solvents. However, upon the mechanical damage or depressurization of the device such liquid electrolytes undergo evaporation, which in its turn leads to the full loss of performance properties. To solve this problem polymeric electrolytes were intensively studied. Different polymer electrolytes have been proposed, most of them based on poly(ethylene oxide)/Li salts systems [3, 4], but also those with natural polymers have been recently published [5, 6]. However, the conductivity of polymer/Li salts materials is not sufficient for the fast change of the ECD’s color, due to slow migration rate of the ions in bulk polymer and the presence of the polar solvent is still needed.

As an alternative to PEO/Li salt/polar solvent systems in this project it is suggested to utilize “polymeric ionic liquids” (PILs) or polymeric analogues of ionic liquids, in which ionic species are covalently bonded with a polymer backbone [7-9]. PILs represent new class of polyelectrolytes that combine all beneficial properties of ionic liquids (high ion conductivity, wide electrochemical window, chemical and thermal stability, non-flammability, and nearly absence of vapor pressure) with the macromolecular architecture. PILs offer a great opportunity for the regulation of their properties, for example, by means of simple design of cationic and anionic structures, the quantity of ions per one monomer unit, the length and the nature of the spacer connecting the polymer chain and the bonded ion. [9].

Based on our recent investigations on PIL's structure-properties relationships [10-12] along with the literature analysis [9] for 2014 year it is planned to synthesize four new ionic monomers (Fig. 2) that will produce PILs with high ionic conductivity, low glass transition temperature and good adhesive properties.

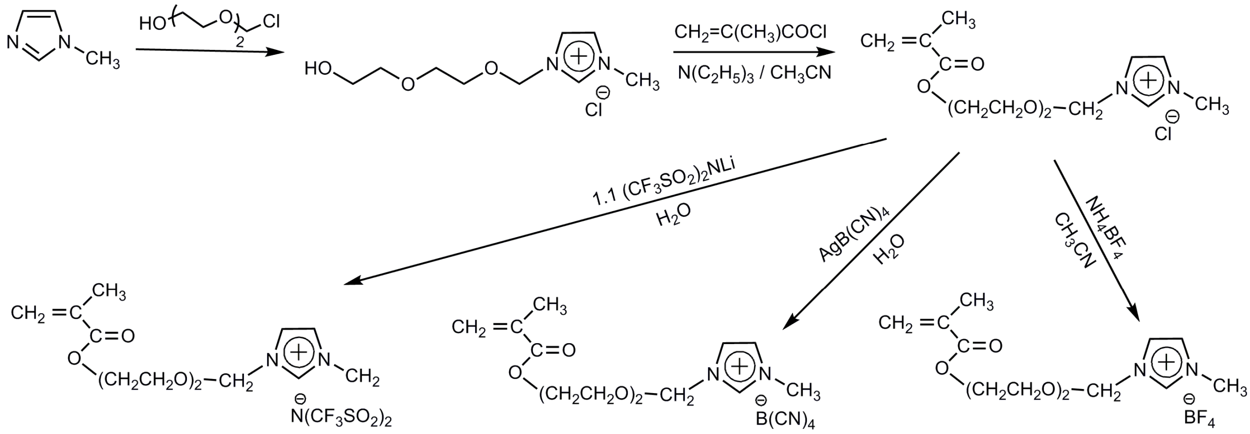

Fig. 2. Structures of the new ionic monomers.

Besides synthesis of linear PILs based on the ionic monomers mentioned above, it is proposed to elaborate the optimal conditions for their copolymerization with cross linking agents in order to obtain conductive films with good mechanical properties. Finally, all the prepared polymer electrolytes will be tested in all-solid-state ECDs, including "smart" windows and artificial muscles.

[1] A. Pawlicka, *Recent Patents on Nanotechnology*, **2009**, *3*, 177-181.
[2] Granqvist CG. Handbook of inorganic electrochromic materials. Elsevier: Amsterdam 1995.
[3] MacCallum JR, Vincent CA. Polymer Electrolyte Reviews-1 and 2.1987 and 1988.
[4] Gray FM. Solid polymer electrolytes, fundamentals and technological applications 1991.
[5] Vieira DF, Avellaneda CO, Pawlicka A. *Electrochim. Acta* **2007**, *53*, 1404-1408.
[6] Leite ER, Pawlicka A, Aegerter MA, et al. *Electrochim. Acta* **2007**, *53*, 1648-1654.
[7] Ohno, H. *Macromol. Symp.* **2007**, *249-250*, 551–556.
[8] Ohno, H.; Ito, K. *Chem. Lett.* **1998**, *27*, 751–752.
[9] Shaplov, A. S.; Lozinskaya, E. I.; Vygodskii, Y. S. *Chapter 9 «Polymer Ionic Liquids: Synthesis, Design and Application in Electrochemistry as Ion Conducting Materials» in Electrochemical Properties and Applications of Ionic Liquids*; Torriero, A. A. J.; Shiddiky, M. J. A., Ed.; Novapublishers: New York, 2010.
[10] Shaplov, A. S.; Vlasov, P. S.; Lozinskaya, E. I.; Ponkratov, D. O.; Malyshkina, I. A.; Vidal, F.; Okatova, O. V.; Pavlov, G. M.; Wandrey, C.; Bhide, A.; Schönhoff, M.; Vygodskii, Y. S. *Macromolecules* **2011**, *44*, 9792-9803.
[11] A.S. Shaplov, P.S. Vlasov, M. Armand, E.I. Lozinskaya, D.O. Ponkratov, I.A. Malyshkina, F. Vidal, O.V. Okatova, G.M. Pavlov, C. Wandrey, I.A. Godovikov, Ya.S. Vygodskii, *Polymer Chem.*, **2011**, *2*, 2609–2618.
[12] A.S. Shaplov, P.S. Vlasov, E.I. Lozinskaya, O.A. Shishkan, D.O. Ponkratov, I.A. Malyshkina, F. Vidal, C. Wandrey, I.A. Godovikov, Y.S. Vygodskii, *Macromol. Chem. Phys.*, **2012**, *213*, 1359-1369.