Innovative conducting polymer materials and their application in all-solidstate Li batteries

Lithium-ion batteries are presently widely used power sources, especially in portable devices like laptops and cellular phones. These devices present definite advantages relative to other types of batteries – lead/acid, nickel metal hydride – like high specific energy and energy density [1,2]. However, an important drawback is the flammable nature of the commonly used liquid electrolytes which are a solution of a lithium salt in polar aprotic organic solvents, mostly carbonates mixtures (for example ethylene carbonate and dimethyl carbonate). These solvents not only restrict temperature range use (<55 °C) but also restrict life span due to their high reactivity towards electrodes [3].

Recently, the interest has turned to the "dry" polymer electrolytes, namely to polymeric ionic liquids or poly(ionic liquid)s (PILs) made out of ionic liquids (ILs), which are described as a novel class of materials combining of the properties of ILs mentioned and the specificities of polymers [4–9]. Since PILs offer great ability in the designing of cationic and anionic structures and their combinations, one can in principle manipulate their properties as desired and enhance their ionic conductivity to a high level $(10^{-11} \div 10^{-5} \text{ S/cm} \text{ at } 25^{\circ}\text{C}$ [5]).

Based on our recent joint investigations on PIL's structure-properties relationships [10-14] and success in the construction of first truly all-solid state electrochromic device based on PIL [15], for 2015 year it is planned to:

- synthesize two new ionic monomers with Li (MLi) and pyrrolidinium (MPyrr) counter ions (Fig 1);
- 2) study the homo polymerization of MLi and MPyrr;
- 3) investigate the copolymerization of **MLi** / **MPyrr** monomers with poly(ethylene glycol)methacrylate (PEGM);
- 4) examine the properties of the obtained polymers (molar mass, conductivity, thermal and electrochemical stability, etc.);
- 5) fabricate and test the all-solid-state Li batteries based on polymer composition with highest ionic conductivity.

Literature:

- [1] Tarascon J.M., Armand M. Nature, 2001, 414, 359-67.
- [2] Armand M., Tarascon J.M. Nature, 2008, 451, 652-57.
- [3] Xu K. Chemical Reviews, 2004, 104, 4303.
- [4] Ohno H, Yoshizawa M. Chapter 13 "Preparation and properties of polymerized ionic liquids as film electrolytes." Ionic Liquids IIIB: Fundamentals, Progress, Challenges, and Opportunities: Transformations and Processes, Washington, DC: American Chemical Society; 2005.
- [5] Shaplov AS, Lozinskaya EI, Vygodskii YS. Chapter 9 "Polymer Ionic Liquids: Synthesis, Design and Application in Electrochemistry as Ion Conducting Materials" in Electrochemical Properties and Applications of Ionic Liquids. In: Torriero AAJ, Shiddiky MJA, editors., New York: Novapublishers; 2010.



Fig. 1. Synthesis of novel ionic liquid like monomers: MLi and MPyrr.

- [6] Yuan J, Mecerreyes D, Antonietti M. Prog. Polym. Sci. 2013, 38(7), 1009–36.
- [7] Yuan J, Antonietti M. Polymer 2011, 52(7), 1469–82.
- [8] Green MD, Long TE. Polym. Rev. 2009, 49(4), 291–314.
- [9] Green O, Grubjesic S, Lee S, Firestone MA. Polym. Rev. 2009, 49(4), 339-60.
- [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, et. al. *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, et. al. *Macromol. Chem. Phys.*, **2012**, *213*, 1359-1369.
- [13] Shaplov AS, Ponkratov DO, Vlasov PS, Lozinskaya EI, Komarova LI, Malyshkina IA, F. Vidal, G. T. M. Nguyen, M. Armand, C. Wandrey, YaS. Vygodskii. *Polym. Sci. J., Ser B* 2013, 55(3-4), 122–38.
- [14] Shaplov A.S., Ponkratov D.O., Aubert P.-H., Lozinskaya E.I., Plesse C., Maziz A., Vlasov P.S., Vidal F., Vygodskii Y.S., *Polymer*, 2014, 55, 3385-96.
- [15] Shaplov AS, Ponkratov DO, Aubert P-H, Lozinskaya EI, Plesse C, Vidal F, Vygodskii YS, *Chem. Commun.* **2014**, *50*(24), 3191-3.