Mixture of 1-Ethyl-3-methylimidazolium tetrafluoroborate and 1-Ethyl-3-methylimidazolium iodide: a new potential high capacitance electrolyte for EDLCs

Liis Siinor, Carolin Siimenson, Karmen Lust, Enn Lust Institute of Chemistry, University of Tartu 14A Ravila Street, 50411 Tartu, Estonia

The need for alternative high energy and power density energy sources has led scientists to study extensively the electrochemical energy conversion/storage devices such as electrochemical double layer capacitors (EDLC), batteries, fuel cells, etc. The values of power and energy densities of EDLC depend strongly on the properties of the electrode material and electrolyte used. EDLCs based on non-aqueous electrolytes or room temperature ionic liquids have a wider region of ideal polarizability (ΔE) compared to those based on traditional aqueous electrolytes ¹⁻⁶. The wider ΔE in turn improves the energy and power density values of EDLCs. The specific adsorption of halide ions at single crystal electrodes from aqueous and non-aqueous electrolyte solutions has been demonstrated before ⁷⁻⁹. However, the specific adsorption of ions is a complicated process and the kinetics of formation/rearrangement of electrical double layer between electrode and ionic liquid (IL) needs an extended examination.

The main aim of this work was to characterize the adsorption of iodide ions from the mixture of two ionic liquids based on the same electrochemically stable 1-ethyl-3-methylimidazolium cation.

Electrochemical impedance spectroscopy and cyclic voltammetry methods have been applied to study the electrochemical characteristics of the interface between pyrolytic graphite (PG) and mixture of 1-ethyl-3methylimidazolium tetrafluoroborate and 1-ethyl-3methylimidazolium iodide (1 wt%). All measurements were carried out in a 3-electrode electrochemical cell using a PG as a working, Pt net as a counter, and Ag wire coated with AgCl as a reference electrode.

Based on the cyclic voltammetry data (Fig. 1) the PG electrode is ideally polarizable within potential region ΔE = 2.4V, with clearly visible peaks of the reduction and oxidation processes of iodide ions.

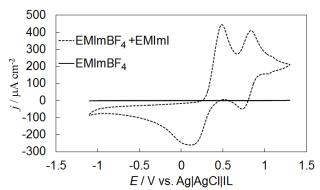


Fig.1. Cyclic voltammograms for PG in $EMImBF_4$ and in 1% mixture of EMImI in EMImBF4 at potential scan rate 10 mVs⁻¹.

The shape of the complex impedance plane, i.e. Nyquist plots (Fig. 2), total impedance and phase angle

vs. frequency dependences depend strongly on electrode potential.

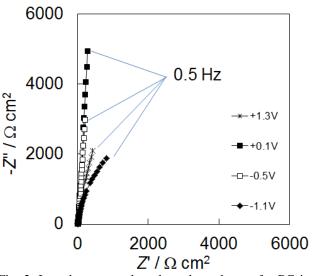


Fig. 2. Impedance complex plane dependences for PG in 1% mixture of EMImI in EMImBF₄ at electrode potentials marked in figure (vs. Ag|AgCl|mixture of ionic liquids).

The values of series differential capacitance (C_s) have been calculated from Nyquist dependencies at different fixed ac frequencies (C_s = $(Z''i2\pi f)^{-1}$; where $i = \sqrt{-1}$ and Z'' is the imaginary part of impedance). C_s depends strongly on ac frequency and electrode potential, increasing at lower ac frequencies and at anodic range of potentials (where is the peak in cyclic voltammograms in Fig. 1).

References

- L. Siinor, K. Lust and E. Lust, ECS Trans. 16 (49), 559 (2009).
- L. Siinor, K. Lust and E. Lust, J. Electrochem. Soc., 157, F83-F87 (2010).
- L. Siinor, K. Lust and E. Lust, Electrochem. Commun., 12, 1058-1061 (2010).
- 4. L. Siinor, C. Siimenson, K. Lust and E. Lust, J. Electroanal. Chem., **668**, 30 (2012).
- 5. H. Kurig, M. Vestli, A. Jänes, E. Lust, Electrochem. Solid State Lett., **14**, A120 (2011).
- R. Palm, H. Kurig, K. Tõnurist, A. Jänes, E. Lust, Electrochim. Acta, 85, 139 (2012).
- L. Siinor, K. Lust, E. Lust, J. Electroanal. Chem., 601, 39 (2007).
- K. Lust, M. Väärtnõu, E. Lust, J. Electroanal. Chem., 532, 303 (2002).
- M. Väärtnõu, E. Lust, J. Electroanal. Chem., 565, 211 (2004).

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