Ionic liquids offer a unique properties and a number of various energy technology related applications. RTIL properties are ideal for designing novel electrolytes for batteries, supercapacitors, dye sensitized solar cells, fuel cells, thermo-electrochemical cells, etc.1-3

First room temperature ionic liquid (RTIL) was synthesized at the beginning of XX century, but still there are many things to investigate and develop further.2 The main disadvantage of RTILs in practical aspect is the high cost of RTILs. Also purity issues, high viscosity and some specific properties (H2O and O2 sensibility) of pure RTIL and their mixtures are important to study.1

By mixing two or more ionic liquids with different properties (viscosity, dielectric permeability, polarity) it is possible to maximize the advantage of RTIL as an electrolyte.4-8

Our recent studies have shown that the addition of specifically adsorbed iodide ions strongly influences the electrochemical characteristics of RTILs systems increasing the specific capacitance and decreasing the series resistance values.8-12 For the further investigation of the specific adsorption of iodide ions from RTIL mixtures the 1-ethyl-3-methylimidazolium tetrafluoroborate and 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-ethyl-3-methylimidazolium iodide were characterized by using cyclic voltammetry and electrochemical impedance spectroscopy methods. The capacitance values of the system at potentials more positive than $-0.6$ V (vs. Ag/AgCl) mixture of RTIL strongly depend on the chemical nature of the anions in the mixture. Also the adsorption of $I^-$ at Bi(111) (well-known in aqueous and classical organic solvents) has been demonstrated in RTIL media. The capacitance values are noticeably higher for EMImOTF + EMImBF4 + 1 wt% EMImI than that for EMImOTF + 1 wt% EMImI.

The electrochemical behavior of RTIL mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-ethyl-3-methylimidazolium iodide were characterized by using cyclic voltammetry and impedance spectroscopy methods. The capacitance values of the system at potentials more positive than $-0.6$ V (vs. Ag/AgCl) mixture of RTIL strongly depend on the chemical nature of the anions in the mixture. Also the adsorption of $I^-$ at Bi(111) (well-known in aqueous and classical organic solvents) has been demonstrated in RTIL media. The capacitance values are noticeably higher for EMImOTF + EMImBF4 + 1 wt% EMImI than that for EMImOTF + 1 wt% EMImI.

The electrochemical behavior of RTIL mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-ethyl-3-methylimidazolium iodide were characterized by using cyclic voltammetry and electrochemical impedance spectroscopy methods. The capacitance values of the system at potentials more positive than $-0.6$ V (vs. Ag/AgCl) mixture of RTIL strongly depend on the chemical nature of the anions in the mixture. Also the adsorption of $I^-$ at Bi(111) (well-known in aqueous and classical organic solvents) has been demonstrated in RTIL media. The capacitance values are noticeably higher for EMImOTF + EMImBF4 + 1 wt% EMImI than that for EMImOTF + 1 wt% EMImI.

The electrochemical behavior of RTIL mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-ethyl-3-methylimidazolium iodide were characterized by using cyclic voltammetry and electrochemical impedance spectroscopy methods. The capacitance values of the system at potentials more positive than $-0.6$ V (vs. Ag/AgCl) mixture of RTIL strongly depend on the chemical nature of the anions in the mixture. Also the adsorption of $I^-$ at Bi(111) (well-known in aqueous and classical organic solvents) has been demonstrated in RTIL media. The capacitance values are noticeably higher for EMImOTF + EMImBF4 + 1 wt% EMImI than that for EMImOTF + 1 wt% EMImI.

The electrochemical behavior of RTIL mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-ethyl-3-methylimidazolium iodide were characterized by using cyclic voltammetry and electrochemical impedance spectroscopy methods. The capacitance values of the system at potentials more positive than $-0.6$ V (vs. Ag/AgCl) mixture of RTIL strongly depend on the chemical nature of the anions in the mixture. Also the adsorption of $I^-$ at Bi(111) (well-known in aqueous and classical organic solvents) has been demonstrated in RTIL media. The capacitance values are noticeably higher for EMImOTF + EMImBF4 + 1 wt% EMImI than that for EMImOTF + 1 wt% EMImI.

The electrochemical behavior of RTIL mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-ethyl-3-methylimidazolium iodide were characterized by using cyclic voltammetry and electrochemical impedance spectroscopy methods. The capacitance values of the system at potentials more positive than $-0.6$ V (vs. Ag/AgCl) mixture of RTIL strongly depend on the chemical nature of the anions in the mixture. Also the adsorption of $I^-$ at Bi(111) (well-known in aqueous and classical organic solvents) has been demonstrated in RTIL media. The capacitance values are noticeably higher for EMImOTF + EMImBF4 + 1 wt% EMImI than that for EMImOTF + 1 wt% EMImI.

The electrochemical behavior of RTIL mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate and 1-ethyl-3-methylimidazolium iodide were characterized by using cyclic voltammetry and electrochemical impedance spectroscopy methods. The capacitance values of the system at potentials more positive than $-0.6$ V (vs. Ag/AgCl) mixture of RTIL strongly depend on the chemical nature of the anions in the mixture. Also the adsorption of $I^-$ at Bi(111) (well-known in aqueous and classical organic solvents) has been demonstrated in RTIL media. The capacitance values are noticeably higher for EMImOTF + EMImBF4 + 1 wt% EMImI than that for EMImOTF + 1 wt% EMImI.
Figure 1. Cyclic voltammograms for EMImOTF + EMIml 1 wt%, EMImBF4 + EMIml 1 wt% and EMImOTF + EMImBF4 + EMIml 1 wt% at potential scan rate 10 mV/s (a). Experimental differential capacitance (C) vs. potential (E) curves at the fixed ac frequency (f = 210 Hz) for different RTIL mixtures noted in figure (b); inset in (b) C,E curves measured first toward positive (open marks) and thereafter negative (filled marks) potential scan directions (5 mV/s−1) at the fixed ac frequency (f = 210 Hz) for EMImBF4 + EMImOTF + EMIml 1 wt%.

According to the literature data and the producer information the dynamic viscosity of EMImOTF varies between 50 to 70 cP at room temperature due to the impurities and decreases noticeably with increasing temperature.23,24 The viscosity of EMImBF4 is 38 cP and the viscosity of EMImOTF + EMImBF4 + 1% EMIml mixture is 41 cP (measured with Anton Paar rheometer MCR101, at 22 °C).25–27 This is promising information and probably the three-component mixture can be used as an electrolyte in electrochemical devices.

The shape of the complex impedance plane, i.e. Nyquist plots (Fig. 2a) depends noticeably on the potential applied as well as on the composition of the mixture of RTILs (Z′′ is an imaginary component (Z′′ = −1/ωCs, were Cs is a series capacitance and ω = 2πf) and Z′ is a real component of the impedance equal to the series resistance). The phase angle vs. f plots for EMImBF4 + EMIml and EMImOTF + EMImBF4 + EMIml (Figs. 2b, 2c) measured within the potential region, where the specific adsorptions of I− anions takes place, show

Figure 2. Complex impedance plane (Z′, Z′) plots for RTIL mixtures (noted in figure) at electrode potential −0.3 V (a). Phase angle vs. log (frequency) dependencies for different RTIL mixtures (noted in figure) at electrode potentials −0.3 V (b) and for EMImOTF + EMImBF4 + EMIml 1 wt% at different electrode potentials (vs. Ag/AgCl mixture of ionic liquids).
only a weak deviation from adsorption limited process at lower frequencies \((1 < f < 1000\ \text{Hz})\). Both mixtures, containing \(\text{BF}_4^-\), have adsorption limited behavior also in the very low frequency area \(f < 1\ \text{Hz}\). Thus, there is a minor deviation from adsorption limited process at less negative \(E\) (from \(-0.7\) to \(-0.3\) V) for moderate and low frequency area. This could be explained by the strong specific adsorption of \(\Gamma^-\) ions. However, for \(\text{EMImOTF} + 1\%\ \text{EMIm} \) mixture, the mixed kinetic processes take place at low \(f \leq 10\ \text{Hz}\). Also, for less negative \(E\) (Fig. 2c) the maximum in phase angle vs. ac frequency is shifted toward lower frequencies because the slow adsorption of \(\Gamma^-\) with partial charges transfer is the main limiting process in this \(f\) region.

Form log \(|Z'|\) vs. \(f\) plots (Fig. 3) it can be seen that in a wide range of frequencies the graph is a straight line and only in very low and high frequency areas there is a small deviation from the ideal capacitive behavior.\(^{25-27}\)

The \(C_s\) values calculated from the values of \(Z'\) \((C_s(\omega) = -(Z'(\omega)2\pi f)^{-1})\), depend on \(f\) and \(E\) (Figs. 3b, 3c).\(^{22,28}\) \(C_s\) does not depend much on \(E\) at higher frequencies. \(C_s\) increases in both ends of ideal polarizability region and depends also on the chemical composition of RTILs mixtures studied. These phenomena could be explained by specific adsorption of the anions at less negative electrode potentials and by faradic processes with the redutive capacitive (desorption of \(\Gamma^-\)) behavior at more negative potentials.\(^9\) Surprisingly for \(\text{EMImOTF} + 1\%\ \text{EMIm} \) mixture, there is no increase in the capacitance at less negative electrode potentials (probably due to the blocking effect of \(\text{OTF}^-\) at the \(\text{Bi}(111) |\ \text{RTIL}\) interface). The \(\text{EMImBF}_4 + \text{EMImOTF} + 1\%\ \text{EMIm} \) mixture shows nearly similar behavior with \(\text{EMImBF}_4 + 1\%\ \text{EMIm} \) mixture used successfully in supercapacitor applications already. Capacitance values are comparable even at \(f = 0.2\ \text{Hz}\) (Fig. 3a).\(^{27}\)

The same phenomena are also seen in the complex power vs. log \(f\) plots, i.e. the normalized real part of complex power \((|P(\omega)|/|S(\omega)|))\) and imaginary part of complex power \((|Q(\omega)|/|S(\omega)|))\) vs. \(f\) plots (calculated from electrochemical impedance data) (Fig. 4). Equilibrium adsorption times are much longer for the \(\text{BF}_4^- + \Gamma^-\) containing systems. Thus, taking into account the very similar behavior of impedance data for the three-component RTIL mixture, this mixture could be used successfully in supercapacitor as well as in other electrochemical applications.

**Conclusions**

Cyclic voltammetry and electrochemical impedance spectroscopy have been used for characterization of the \(\text{Bi}(111) |\ \text{RTIL}\) interface. Analysis of the experimental and calculated parameters shows the noticeable dependence of the EDL structure on the chemical nature and geometric structure of the anions forming EDL. At less negative electrode potentials the capacitance for \(\text{EMImOTF} + \text{EMImBF}_4 + \text{EMIm} \) and \(\text{EMImBF}_4 + \text{EMIm} \) is much higher compared to that for \(\text{EMImOTF} + \text{EMIm} \) mixture. Good potential cyclability and reversibility of the capacitance vs. potential curves measured toward positive and negative scan directions have been demonstrated. It should be stressed that the cyclability and reversibility are the key parameters for the practical application of RTIL mixtures in supercapacitor. Thus, taking into account that the \(\text{EMImOTF}\) addition into the \(\text{EMImBF}_4 + \text{EMIm}\) mixture\(^{11,27}\) reduces the overall price of the
electrolyte, this three-component mixture can be tested as an electrolyte for supercapacitors.

Acknowledgments

This study was partially funded by the ESF grant 8786, Estonian Energy Technology Program (project 3.2.0501.10-0015), IUT20-13, PUT55 and Estonian Centers of Excellence in Science project TK117: High-technology Materials for Sustainable Development.

References

1. D. R. MacFarlane et al., Energy Environ. Sci., 7, 232 (2014).
2. M. Galinski, A. Lewandowski, and I. Stepniak, Electrochimica Acta, 51, 5567 (2006).
3. H. Okno, Electrochemical Aspects of Ionic Liquids, p. 505, John Wiley & Sons, (2011).
4. D. Song and J. Chen, J. Chem. Thermodyn., 77, 137 (2014).
5. M. Montanino et al., Electrochimica Acta, 60, 163 (2012).
6. R. Costa, C. M. Pereira, and A. Fernando Silva, Electrochim. Commun., 57, 10 (2015).
7. H. Srou et al., J. Solat. Chem., 44, 495 (2014).
8. V. Ivanishiev, K. Kirchner, T. Kirchner, and M. V. Fedorov, J. Phys. Condens. Matter, 27, 102101 (2015).
9. E. Anderson, V. Grozovski, L. Siinor, C. Siimenson, and E. Lust, Electrochem. Commun., 46, 18 (2014).
10. E. Anderson et al., J. Electroanal. Chem., 709, 46 (2013).
11. C. Siimenson, L. Siinor, K. Lust, and E. Lust, J. Electroanal. Chem., 730, 59 (2014).
12. L. Siinor, C. Siimenson, K. Lust, and E. Lust, Electrochem. Commun., 35, 5 (2013).
13. K. Sekiguchi, M. Atobe, and T. Fuchigami, Electrochem. Commun., 4, 881 (2002).
14. R. Hagiwara, Electrochemistry, 70, 130–136 (2002).
15. F. Endres and S. Z. El Abedin, Phys. Chem. Chem. Phys., 8, 2101 (2006).
16. P. Bonhote and A. P. Dias, (1997). http://www.google.com/patents/US5683832.
17. L. Siinor, K. Lust, and E. Lust, J. Electrochem. Soc., 157, F83 (2010).
18. M. György Inzelt, Andrezej Lewenstam, and Fritz Schöltz, Eds., Handbook of Reference Electrodes, Springer-Verlag Berlin Heidelberg, New York, (2013).
http://link.springer.com/content/pdf/10.1007/978-4-431-54472-2.pdf.
19. L. Siinor, J. Poom, K. Lust, and E. Lust, in Meeting Abstracts, p. 1425, The Electrochemical Society (2014). http://ma.ecsdl.org/content/MA2014-02/25/1425.short.
20. S. Kallip and E. Lust, Electrochem. Commun., 7, 863 (2005).
21. L. Siinor, K. Lust, and E. Lust, J. Electroanal. Chem., 601, 39 (2007).
22. B. E. Conway, Electrochemical supercapacitors: scientific fundamentals and technological applications, Springer, (1999).
23. N. V. Ignat’ev, P. Barthen, A. Kucheryna, H. Willner, and P. Sartori, Molecules, 17, 5319 (2012).
24. M. G. Freire et al., J. Chem. Eng. Data, 56, 4813 (2011).
25. H. Kurig, M. Vestli, A. Jaenes, and E. Lust, Electrochem. Solid State Lett., 14, A120 (2011).
26. H. Kurig, M. Vestli, K. Tõnurist, A. Jänis, and E. Lust, J. Electrochem. Soc., 159, A944 (2012).
27. T. Tooming et al., J. Electrochem. Soc., 161, A222 (2014).
28. F. Silva et al., J. Electroanal. Chem., 622, 153 (2008).