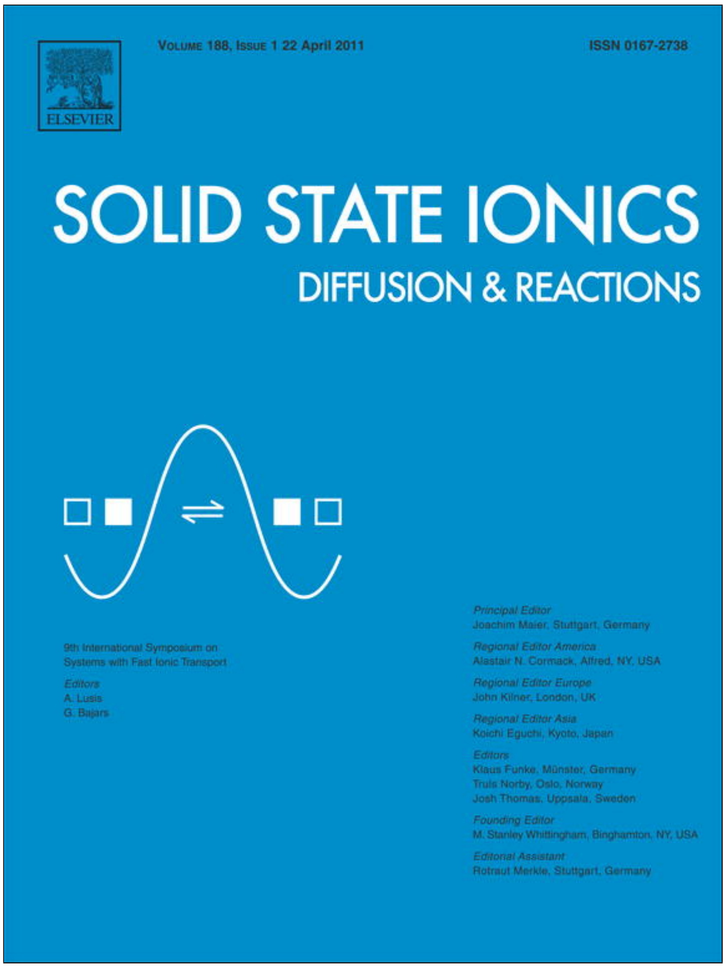
Volume 188, Issue 1 22 April 2011
ISSN 0167-2738
ELSEVIER
SOLID STATE IONICS
DIFFUSION & REACTIONS
9th International Symposium on
Systems with Fast Ionic Transport
Editors
A. Lusis
G. Bajars
Principal Editor
Joachim Maier, Stuttgart, Germany
Regional Editor America
Alastair N. Cormack, Alfred, NY, USA
Regional Editor Europe
John Kilner, London, UK
Regional Editor Asia
Koichi Eguchi, Kyoto, Japan
Editors
Klaus Funke, Münster, Germany
Truls Norby, Oslo, Norway
Josh Thomas, Uppsala, Sweden
Founding Editor
M. Stanley Whittingham, Binghamton, NY, USA
Editorial Assistant
Rotraut Merkle, Stuttgart, Germany

Solid State Ionics 188 (2011) 114–117

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Electrical impedance spectroscopy of ionic liquid 1-ethyl-3-methylimidazolium methanesulfonate (ECOENG™ 110)

J. Katkevics, A. Viksna *, A. Zicmanis, G. Vaivars

Faculty of Chemistry, University of Latvia, Kr. Valdemara Str. 48, LV-1013, Latvia

ARTICLE INFO

Article history:
Received 17 October 2010
Received in revised form 4 November 2010
Accepted 8 November 2010
Available online 4 December 2010

Keywords:
Ionic liquids
Impedance spectroscopy
Pt
Cu
Mo
Carbon electrodes

ABSTRACT

Ionic liquid "ECOENG™ 110", a promising electrolyte for electrochemical devices, was investigated by impedance spectroscopy. Metallic electrodes (Pt, Cu, Ag, and Mo) as well as carbon were used for the electrochemical characterization. The dependences of the real and imaginary impedance, polarization resistance and electrochemical capacity of the double layer on the electrode potential were investigated using electrical equivalent circuits of $R_1(QR_2)$ and $R_1[Q(R_2W)]$ types.

1. Introduction

Ionic liquids (IL) are gaining interest as a new reaction media for organic transformations. They can be used as solvents for a wide range of organic and inorganic reactions and their unique properties make them important candidates for the so-called "green chemistry". Their negligible vapor pressure and relatively high thermal stability make it possible to use high vacuum conditions and high temperatures to drive chemical reactions. It is also possible to recover products by simple washing the ILs or by distillation [1]. The electrical conductivity of ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (ECOENG™ 110) was evaluated by means of an AC impedance technique using only the platinum electrode and R_1 (QR_2) type equivalent circuit [2]. Nowadays there is an interest to use ILs as electrolytes for electrochemical syntheses of nanorodes and nanowires [3].

The objective of the present work is to investigate the electrochemical behavior of ionic liquid "ECOENG™ 110" using different metal and carbon electrodes and their potential usability in electrochemical applications.

2. Experimental

The ionic liquid "ECOENG™ 110" is a commercial substance with the structural formula presented in Fig. 1. It was kept under argon to prevent chemical oxidation. Metallic electrodes (Pt, Cu, Ag, and Mo) as well as carbon were used for the electrochemical characterization of ionic liquid "ECOENG™ 110" by impedance spectroscopy. The dependence of the real (Z_r) and imaginary ($-Z_j$) impedance, polarization resistance (R_2) and electrochemical capacity of the double layer (Cs) from the electrochemical cell potential was investigated. A computer controlled frequency response analyzer FRA with module (Autolab PGSTA–30 for Windows version 4.9) in impedance measurements. The impedance spectra were measured in a frequency range from 0.01 Hz to 35 kHz with AC potential amplitude of 10 mV at 20 °C. Impedance spectra were measured at following polarization potentials: −0.04; −0.1; −0.35; −0.50; −0.60 and −0.85 V. Dry instrumental argon gas was used to avoid oxygen and humidity influence on measurements. Laboratory made electrochemical cell was used in all electrochemical experiments. Cell parameters are the following: volume — 12 mL, electrode area — 1.0 × 1.0 cm, and distance between anode (Pt plate) and cathode (Pt, Cu, Ag, and Mo plates) — 1.0 cm. Pt wire was used as a reference electrode. According to Ohm's law, the resistance R for the above circuit is given by $R = \rho \cdot \ell / A$, where ρ is the resistivity (also called specific electrical resistance) of the solution (in Ω cm), ℓ — distance between electrode (in cm) and A — the cross-sections area of electrodes (in cm^2). The electrodes were used without additional polishing. The active area of each electrode was determined with a 0.1 M NaCl solution before impedance measurements and experimental results were normalized taking in account the surface roughness of electrodes.

Impedance data of ionic liquid was analyzed using the complex plane Nyquist plot and a quality of measured results was validated by the Kramers–Kronig test. After successful validation of experimental

* Corresponding author. Tel.: +371 26400965.
E-mail address: arturs.viksna@lu.lv (A. Viksna).

0167-2738/$ – see front matter
doi:10.1016/j.ssi.2010.11.013

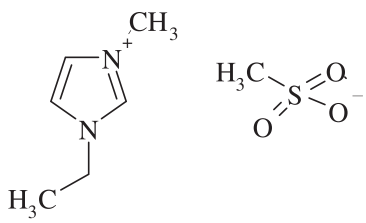

Fig. 1. Ionic liquid: 1-Ethyl-3-methylimidazolium methanesulfonate — "ECOENG™ 110".

results, the Bode plot diagram was used to evaluate the number of elements in Randle's equivalent circuit. Parameter fitting for equivalent circuit elements at used electrodes in ionic liquid was done by fitting and simulation program "RCNTRANS and EQUIVCRT", which is based on non-linear least squares method [4]. Impedance ($|Z|_{(E)}$ and $|Z|_{(\text{Bode plot})}$) [5,6] and double layer capacity $|Cs|_{dl}$ values were calculated also by Autolab software.

3. Results and discussion

In our measurements, the resistivity (specific electrical resistance) of ionic liquid (R_e) for carbon, Pt, Mo and Cu electrodes is 365 ± 10 Ω cm (Table 1) and it is stable in all polarization potential range (−0.04 to −0.85 V). It is in a good agreement with IL producer technical specification.

The electrochemical impedance spectra and parameters of equivalent circuits of ionic liquid "ECOENG™ 110" measured with Pt, Cu, Mo and carbon electrodes are presented in Fig. 2 and Table 1. The impedance spectra are represented in the complex-impedance-plane or Nyquist plot [6]. The spectra, which were taken by using the Pt, Mo, and Cu electrodes are similar by shape, but strongly depend on polarization potential in a range from −0.1 V to −0.85 V (Fig. 3). At the same time, the impedance spectra measured with carbon electrode are independent of potential in a range from −0.1 V to −0.85 V.

The Bode plot (Fig. 4) demonstrated that the electrochemical cell with ionic liquid and Pt, Mo and Cu electrodes could be represented by a three-element electrical equivalent circuit "$R_1(QR_2)$", including ionic liquid resistance (R_1), constant phase element (CPE) and charge transfer or polarization resistance (R_2). The resistance R_2 (Table 1) decreases by 1–2 orders for electrochemical cell with metallic electrodes by increasing polarization potential from −0.04 V to −0.85 V. For example, in the case of Pt electrode, the resistance R_2 decreases from 191 to 3 kΩ cm^2. At the same time, the parameter Q of CPE for Pt electrode varies slightly (9–11 μF cm^{-2}). The parameter Q for Mo and Cu electrodes depends on applied polarization potential. The parameter Q increases with the applied polarization potential from 6 to 29 μF cm^{-2} and decreases from 26 to 13 μF cm^{-2} for Mo and Cu electrode, respectively.

The values of the double layer capacitance $|Cs|_{dl}$ measured using the Autolab software as $[(1/wZ_r)^2+(1/-wZ_j)^2]^{-2}$ change from 8 to 6 μF cm^{-2} for the Pt electrode, and from 32 to 12 μF cm^{-2} for the Cu electrode, when the applied polarization potential increases from −0.04 V to −0.60 V (Table 1, Fig. 5). In the case of the Mo electrode this parameter varies from 32 to 19 μF cm^{-2}. The Autolab software calculates $|Cs|_{dl}$ taking in account that the impedance spectra might be evaluated using "$R_1(QR_2)$" equivalent circuit. In a potential range from −0.04 V to −0.60 V the capacitance values calculated using both approaches are practically the same. It suggests that the above mentioned equivalent circuit might be applied. At high negative potentials $E_p \leq -0.85$ V, the obtained values strongly differ from theoretical ones and additional parameters should be included.

The R_2 values were also obtained by extrapolation from Bode plots and denoted as $|Z|_{(\text{Bode plot})}$. As it is shown in Table 1 at higher negative potentials (−0.60 and −0.85 V) the extrapolation gives the same values as obtained from the equivalent circuit method. At the same time, at lower potentials the values differ and it is not correct to use the simple extrapolation method.

The behavior of the carbon electrode in ionic liquid was different from the used metallic electrodes. Firstly, the impedance spectra are independent of applied polarization potential (Fig. 2). Secondly, the impedance spectra might be fitted to different electrical equivalent

Table 1
Fitting parameters of the equivalent circuit $R_1(QR_2)$ used for the description of the electrode impedance data for different electrodes in the ionic liquid "ECOENG™ 110".

Elements	Units	Polarization potential, V				
		−0.04	−0.10	−0.35	−0.60	−0.85
			Pt electrode			
R_e	Ω cm	346 ± 20	366 ± 20	357 ± 20	346 ± 20	343 ± 20
R_2	kΩ cm^2	162 ± 5	191 ± 7	35 ± 4	7 ± 2	3 ± 1
Q	μF cm^{-2}	10 ± 1	9 ± 1	9 ± 1	10 ± 2	11 ± 3
n		0.91 ± 0.01	0.94 ± 0.01	0.90 ± 0.01	0.89 ± 0.01	0.79 ± 0.02
$\|Cs\|_{dl}$	μF cm^{-2}	8 ± 1	8 ± 1	8 ± 1	6 ± 1	70 ± 2
$\|Z\|_{(\text{Bode plot})}$	kΩ cm^2	161 ± 7	147 ± 5	126 ± 5	8 ± 2	6 ± 1
			Cu electrode			
R_e	Ω cm	–	358 ± 20	369 ± 20	370 ± 20	369 ± 20
R_2	kΩ cm^2	–	580 ± 7	654 ± 8	121 ± 3	3 ± 1
Q	μF cm^{-2}	–	26 ± 8	10 ± 2	9 ± 1	13 ± 2
n		–	0.65 ± 0.01	0.88 ± 0.01	0.91 ± 0.01	0.88 ± 0.01
$\|Cs\|_{dl}$	μF cm^{-2}	–	32 ± 2	14 ± 1	12 ± 1	216 ± 5
$\|Z\|_{(\text{Bode plot})}$	kΩ cm^2	–	–	360 ± 9	122 ± 6	3 ± 1
			Mo electrode			
R_e	Ω cm	377 ± 5	376 ± 4	377 ± 3	375 ± 3	375 ± 6
R_2	kΩ cm^2	895 ± 13	856 ± 22	598 ± 11	167 ± 7	69 ± 8
Q	μF cm^{-2}	6 ± 2	7 ± 1	13 ± 3	16 ± 2	29 ± 2
n		0.89 ± 0.01	0.89 ± 0.02	0.83 ± 0.01	0.81 ± 0.01	0.70 ± 0.01
$\|Cs\|_{dl}$	μF cm^{-2}	19 ± 2	20 ± 2	23 ± 3	32 ± 2	45 ± 3
$\|Z\|_{(\text{Bode plot})}$	kΩ cm^2	–	–	301 ± 3	150 ± 3	87 ± 3

R_1, R_2, Q, and n — parameters of electric equivalent circuit $R_1(QR_2)$, see text.
$|Cs|_{dl}$ — complex (double layer) capacitance calculated by using Autolab software [6].
$|Z|_{(\text{Bode plot})}$ — R_2 values as obtained by extrapolation from Bode plots [6].

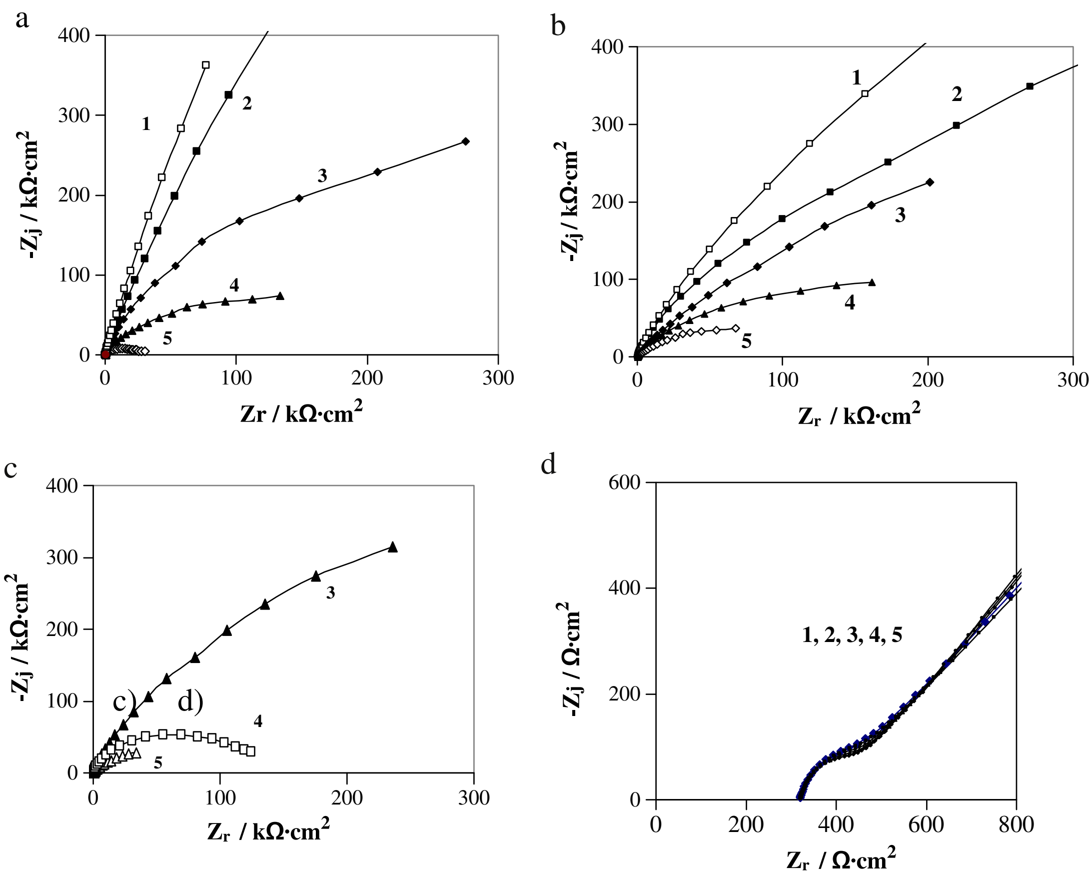

Fig. 2. Nyquist diagrams for Pt (a), Mo (b), Cu (c), and carbon (d) electrodes using ionic liquid as the electrolyte. Applied polarization potentials in the impedance measurements: 1) −0.04 V; 2) −0.10 V; 3) −0.35 V; 4) −0.60 V; and 5) −0.85 V.

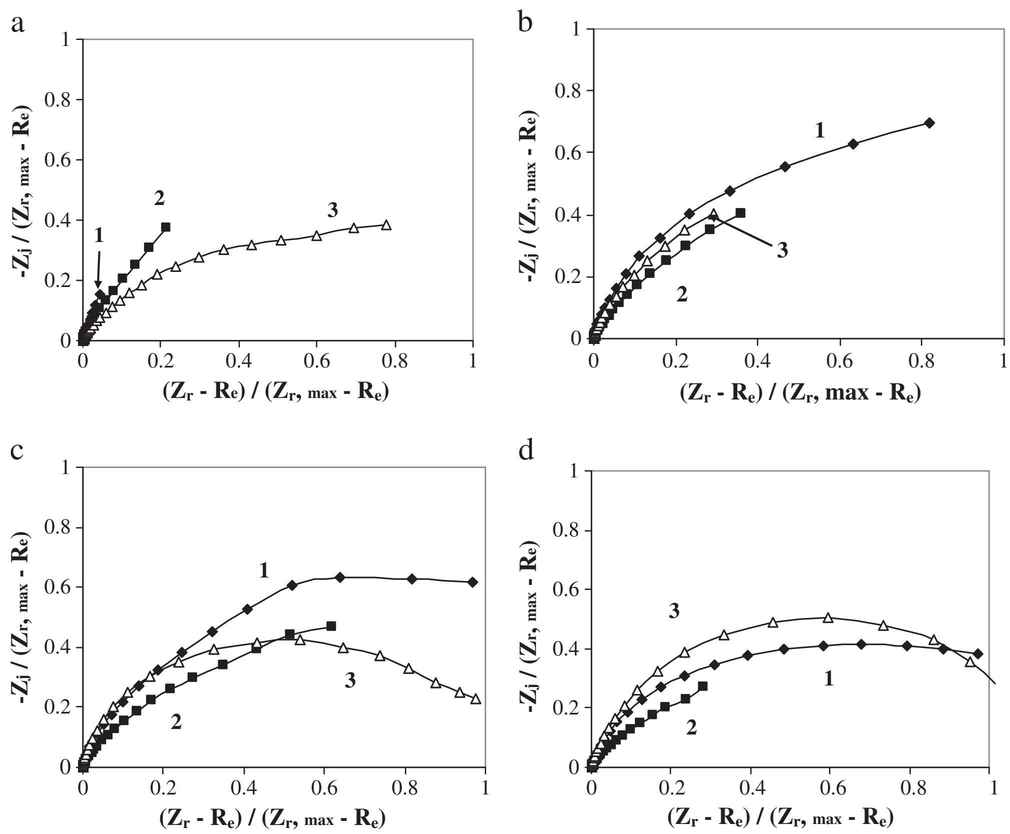

Fig. 3. Impedance spectra represented in normalized scale, where $Z_{r,\ max}$ is a maximum impedance modulus value. Applied polarization potentials in the impedance measurements: a — −0.10 V; b — −0.35 V; c — −0.60 V; d — −0.85 V; 1 — Pt electrode; 2 — Mo electrode; and 3 — Cu electrode.

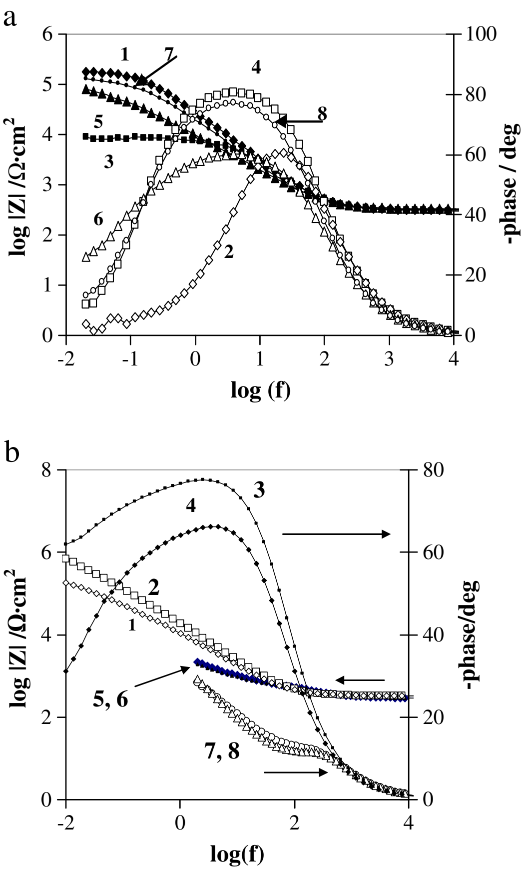

Fig. 4. Bode plot diagrams: a) for Pt (1–4) and Cu (5–8) electrodes, b) Mo (1–4) and carbon (5–8) electrode. Applied polarization potentials in the impedance measurements: −0.10 V (a — 1; 2; 5; 6 and b — 2; 3; 5; 7), −0.60 V (a — 3; 4; 7; 8 and b — 1; 4; 6; 8).

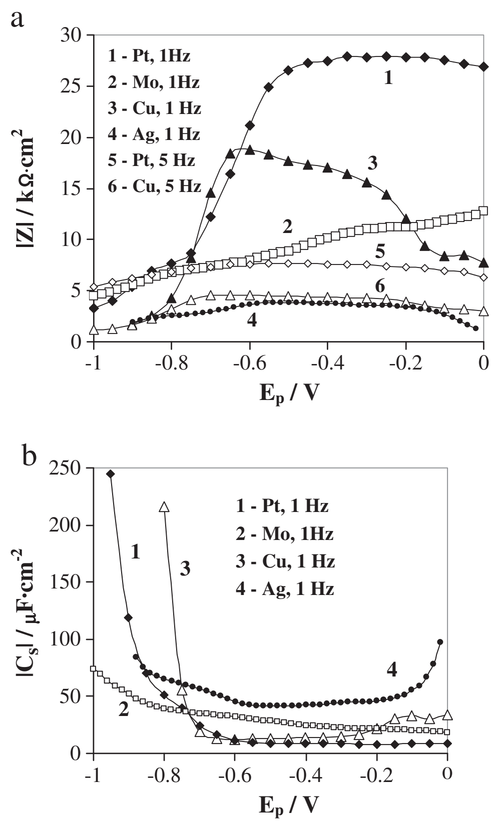

Fig. 5. Modulus values of complex impedance $|Z_E|$ (a) and modulus values of double layer capacitance $|C_S|$ (b) for metallic electrodes at different polarization potential (E_p) and frequencies in ionic liquid: 1, 5 — Pt electrode; 2 — Mo electrode; 3, 6 — Cu electrode; and 4 — Ag electrode.

circuit, which consists of four elements ($R_1(Q[R_2W])$. Similar equivalent circuit was used to describe the behavior of carbon nanotube and black carbon mixture electrode in the $LiClO_4$ electrolyte [7]. In our case, the electrode process is limited by the non-faradic diffusion process, which is most probably caused by water impurities and water sorption on the porous carbon electrode.

4. Conclusions

The electrode impedance spectra of the cells with the ionic liquid “ECOENG™ 110” were interpreted in terms of equivalent circuits denoted as $R_1(QR_2)$ and $R_1[Q(R_2W)]$ for metallic electrodes and carbon electrodes, respectively. The specific electrical resistance (R_e) for 1-ethyl-3-methylimidazolium trifluoromethanesulfonate is equal to $365 \pm 10\ \Omega$ cm and it is stable in the polarization potential range from −0.04 V to −0.85 V. At the same time, some changes in the interface ionic liquid/metallic electrode were observed at potentials higher than −0.6 V as it was concluded from equivalent circuit analysis. It might be related to the faradic process caused by water impurities. The impact of the water impurities will be further investigated.

References

[1] S.S. Moganty, R.E. Baltus, D. Roy, Chemical Physics Letters 483 (2009) 90.
[2] Yuria Saito, A. Manuel Stephan, Hiroshi Kataoka, Solid State Ionics 160 (2003) 149.
[3] Yong Wang, Hong Yang, Chemical Engineering Journal 147 (2009) 71.
[4] B.A. Boukamp, Electrochemical Impedance Spectroscopy., Nano-Electrocatalysis, U. Leiden, 24-28 Nov., 2008, EIS, 99 pp.
[5] A. Lasia, Electrochemical Impedance Spectroscopy and its applications, in: B.E. Conway, J. Bockris, R.E. White (Eds.), Modern aspects of electrochemistry, 32, 1999, p. 143, New York.
[6] Orazem M.E., Tribollet B., Electrochemical Impedance Spectroscopy, Wiley, 2008, 433 pp.
[7] Zhan-hong Yang, Wu. Hao-qing, Chemical Physics Letters 343 (2001) 235.