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Influence of anion composition and size on the double layer capacitance for Bi(111)|room temperature ionic liquid interface

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ABSTRACT

Cyclic voltammetry and electrochemical impedance spectroscopy have been applied for investigation of electrochemically polished Bi(111) electrode in 1-ethyl-3-methyl imidazolium tris(pentafluoroethyl) trifluorophosphate (EMImFAP), 1-ethyl-3-methyl imidazolium tetracyanoborate (EMImTCB) and 1-ethyl-3-methyl imidazolium tetrafluoroborate ($EMImBF_4$) ionic liquids. The region of ideal polarizability, series resistance and capacitance, limiting high-frequency and low-frequency capacitances have been calculated. The lower series capacitance values at electrode potential less negative than the potential of the minimum in the capacitance vs. voltage curve for Bi(111)|EMImFAP than that for $EMImBF_4$, and especially for EMImTCB, have been explained by the bigger diameter of FAP^-, higher cation and anion sizes symmetry, and less expressed surface activity (i.e. lower closest approach of the FAP^- mass centre to an electrode surface) compared with BF_4^- and TCB^- anions.

1. Introduction

The use of non-aqueous electrolytes and room temperature ionic liquids in electrochemical double layer capacitors (EDLCs) was initiated by the wider region of ideal polarizability (ΔE) of nanoporous carbon|electrolyte interface in comparison with aqueous electrolytes [1,2]. A wider ΔE in turn increases the energy and power densities of EDLCs and thus reduces the volume and mass of the device. Therefore, our recent work is focused on the use of the room temperature ionic liquids (RTILs) and non-aqueous solvent based electrolytes for high energy-power density EDLCs [3,4]. However, electrochemical measurements using nanoporous carbon electrodes are more complicated, time consuming and expensive, and thereof the measurements have been conducted on the electrochemically polished single crystal Bi(111) electrode to investigate the influence of the chemical composition, structure and possible dependence of the closest approach of ions, i.e. specific adsorption of the ionic liquid anions (well-known for halide, CN^- and SCN^- from the aqueous and non-aqueous electrolytes) on the electrical double layer capacitance [5–7]. The second aim was to analyse the electrical double layer (edl) formation/rearrangement, i.e. adsorption kinetics of RTIL on Bi(111) surface and to test the applicability limits of some modern models worked out to clarify the metal|RTIL interface structure [3,8–11]. The RTILs chosen are probably characterized by different packing parameter, γ, the ratio of the ionic density in the bulk to its maximum value in edl [9,10]. For densely packed RTILs with similar shape and size of ions it can be assumed that $\gamma \approx 1$ (like for EMImFAP or EMImTCB) and for RTIL with asymmetric structure (different ion molar volume) of ions $\gamma < 1$ (like for $EMImBF_4$). The values of relative static dielectric constant vary from 10 to 16 (12.8 for $EMImBF_4$) [12]. It has been demonstrated [11] that if $\gamma < 0.33$ and ions have the charged heads and neutral counterparts, the neutral "tails" of ions play the role of latent voids that can be replaced by charged groups via rotations and translations of ions. This provides extra degrees of freedom for the field-induced charge rearrangements in edl resulting in the peculiar double-hump capacitance profile [10] established for the glassy carbon electrode at high temperature [13]. Based on the molecular dynamic calculations, Fedorov et al. [11] demonstrated that the double hump in the differential capacitance (C) vs. potential (E) curves can be observed even in the case of dense ionic liquids (with $\gamma \approx 1$).

In the literature there are some controversial data for Hg and C electrodes in RTILs [13–15]. There is no edl formation kinetics data discussing the dependence of the high-frequency capacitance, C_{dl} (so-called "true edl capacitance"), and low-frequency equilibrium capacitance (adsorption capacitance, C_{ad}) [16,17] on the electrode potential, E. Usually only C,E curves at one or some different fixed frequencies f (for example, Au(001)|$EMImBF_4$ interface at $f = 18$ Hz [18]) have been given, except few papers [8,14,15]. However, edl formation kinetics data are inevitable to develop future the EDLCs with high power density [1–4].

2. Experimental

1-ethyl-3-methyl imidazolium tris(pentafluoroethyl)trifluorophosphate (EMImFAP), 1-ethyl-3-methyl imidazolium thiocyanate (EMImTCB) (both from Merck KGaA, assay 99.9%, $H_2O < 100$ ppm), and

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1-ethyl-3-methyl imidazolium tetrafluoroborate (EMImBF$_4$) (Fluka Analytical, for electronic purposes, electrochemical window from −2 to 4.4 V at glassy carbon, $H_2O < 200$ ppm, and conductivity ≥ 11.5 mS cm^{-1}) additionally dried for 48 h inside glove box (Labmaster, $H_2O \leq 1.0$ ppm, $O_2 \leq 1.0$ ppm) at 50 °C have been used as electrolytes at 23 °C. EMImFAP has been selected because FAP$^-$ is a non-coordinating anion. FAP$^-$ is one of the most hydrophobic and electrochemically stable anions (stabilizing the carbocations in RTIL) currently available. The specific surface activity of FAP$^-$ at the hydrophilic metal electrodes is believed to be nearly zero. TCB$^-$ containing the CN$^-$ groups probably possesses high specific Gibbs adsorption, i.e. strong interaction with Bi(111) surface [5–7].

RTIL was saturated for 24 h with clean Ar (99.9999) before submerging of the electrochemically polished Bi(111) electrode [5–8] into electrolyte. Electrochemically stable current density has been established after 1...1.5 h polarization of the Bi(111) electrode at −0.7 V (all potentials have been given vs. Ag|AgCl| in the same RTIL measured). All cyclic voltammetry and impedance measurements (using Autolab PGSTAT 20 with FRA II) have been performed inside glove box ($H_2O < 1.0$ ppm, $O_2 < 1.0$ ppm). Potential cyclation rate was varied from 0.5 to 50 mV s^{-1} and impedance data were measured within the ac frequency range from 0.1 to 1×10^4 Hz. 5 mV ac modulation was used [7,8]. At least 6 independent measurements were made for all RTILs studied, and the statistically treated series capacitance data have been analyzed. The parameters calculated from the impedance data have been statistically treated after fitting.

3. Results and discussion

Analysis of current density (j) vs. electrode potential (E) dependences (Fig. 1) shows that the Bi(111) electrode is ideally polarizable (current density lower than 10^{-6} A cm^{-2}) from −0.9 to 0.1 V in EMImFAP, and from −1.1 to 0.0 V in EMImBF$_4$ and EMImTCB. In comparison, the very wide region of ideal polarizability $\Delta E \geq 3.2$ V has been established (inside the same glowe box) for the interface between EMImBF$_4$ and microporous carbon electrode prepared from TiC by chlorination method [2]. Thus, the narrower region of ideal polarizability for Bi(111) electrode in comparison with Au(hkl) and carbon electrodes is mainly caused by the sp-metal character of bismuth. High adsorption activity for anions with the partial charge transfer step at positively charged Bi(hkl) and polycrystalline electrodes is well-known [2,5–8,12–15,19]. The increase of j outside these potential regions is caused by the faradic reduction and oxidation of residual water, oxygen and electrode surface. The width of the ideal polarizability region is in a good correlation with the impedance plane plots (Nyquist plots) [16,17,19] (Fig. 2a) — for Bi(111)|EMImBF$_4$ interface there are only weak deviations from the adsorption limited process mechanism within the region of $-0.9 < E < -0.2$ V. For Bi(111)|EMImTCB and Bi(111)|EMImFAP, the mixed kinetic processes take place (adsorption and diffusion both determine the rate) similarly to the Bi(111)|LiClO$_4$ aqueous solution interface [5,6,19]. Also the phase angle, δ ($|\delta| > 83°$ at $f < 10^2$ Hz) (Fig. 2b) and impedance modulus ($|Z|$) vs. frequency dependences for Bi(111)|EMImBF$_4$ confirm these conclusions. Only at very low ac frequency the small decrease in the negative values of δ has been established, which could be explained by occurring of the very slow first layer reorganization process of edl [9–11] or partial charge transfer from ions to the electrode surface [7,8,19]. Also the values of constant phase element exponent higher than 0.96 for Bi(111)|EMImBF$_4$, obtained from log(−Z''),log$f$ plots (Fig. 2b), demonstrate only very low deviation of the interface from the ideally polarizable (so-called "blocked," adsorption step limited) one [7,8,16,17].

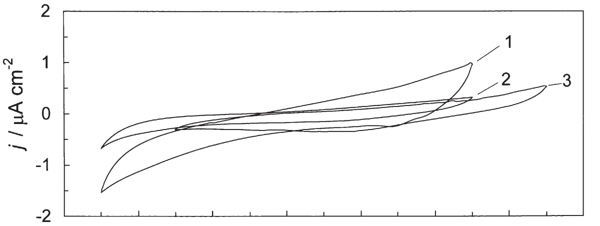

Fig. 1. Cyclic voltammograms for Bi(111) in EMImTCB (1); EMImBF$_4$ (2) and EMImFAP (3) at potential scan rate 10 mV s^{-1}.

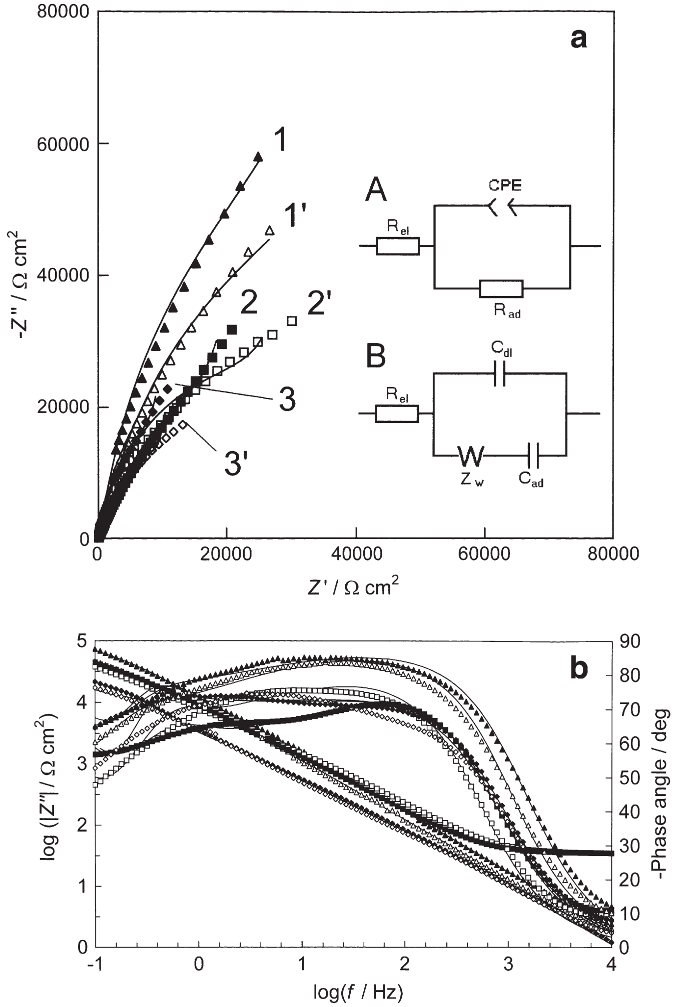

Fig. 2. Impedance complex plane (Z'',Z) plots (a), and log|Z''| and phase angle vs. log (frequency) plots (b) for Bi(111) in EMImBF$_4$ (triangles), EMImFAP (squares) and EMImTCB (rhombs) at −0.7 (filled marks) and −0.1 V (open marks) (vs. Ag|AgCl| EMImBF$_4$) (dots — exp. data, lines — fitting by Frumkin–Melik–Gaikazyan) electrical circuit with generalized finite length Warburg element (GFW) with a transmission boundary condition [16]. Insets in a: equivalent circuits used for fitting of the calculated curves to experimental data: EC with constant phase element (A) and Frumkin–Melik–Gaikazyan circuit (B), where R_{el} is high-frequency resistance, CPE is constant phase element, C_{dl} is double layer capacitance, C_{ad} is adsorption capacitance, R_{ad} is adsorption resistance, and Z_W is Warburg-like diffusion impedance.

The series differential capacitance C_s (Fig. 3a) has been calculated from Nyquist dependences ($C_s = (Z''j2\pi f)^{-1}; j = \sqrt{-1}$). The potential of the minimum in the C_s vs. E plots, E_{min}, being located at −0.7 V, has found to be independent of ac frequency. The values of C_s for EMImFAP at E_{min} are noticeably lower than those for EMImBF$_4$, and especially for EMImTCB, and C_s for EMImFAP at $E > E_{min}$ is somewhat lower than at $E < E_{min}$. Lower capacitance for EMImFAP can be explained by the larger molar volume (bigger diameter) for FAP$^-$ compared with BF$_4^-$ or TCB$^-$ (based on the application of the Helmholtz double layer capacitor model ($C_s = \varepsilon\varepsilon_0/l$, where ε is the absolute permittivity of vacuum, l and ε_0 are the effective thickness and relative permittivity of edl), applicable only to a very rough