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 tetrafluoroborate (EMImBF4) and 1-ethyl-3-methyl imidazolium tetrafluoroborate (EMImBF4) 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 EMImBF4, and especially for EMImTCP, 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 BF4− and TCB− anions.

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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 \(\Delta E\) of nanoporous carbon electrolyte interface in comparison with aqueous electrolytes [1,2]. A wider \(\Delta E\) 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 [8–11]. The RTILs chosen are probably characterized by different packing parameter, \(\gamma\), 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 EMImTCP) and for RTIL with asymmetric structure (different ion molar volume) of ions \(\gamma<1\) (like for EMImBF4). The values of relative static dielectic constant vary from 10 to 16 (12.8 for EMImBF4) [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)|EMImBF4 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 (EMImTCP) (both from Merck KGaA, assay 99.9%, H2O<100 ppm), and
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$_2$O $<$ 200 ppm, and conductivity $\geq 11.5$ mS cm$^{-1}$) additionally dried for $48$ h inside glovebox (Labmaster, H$_2$O $\leq 1.0$ ppm, O$_2$ $\leq 1.0$ ppm) at $50$ °C have been used as electrolyte 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 carboxations 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.

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 into electrolyte. Electrochemically stable current density has been additionally dried for $48$ h inside glovebox (Labmaster, H$_2$O ($3$ ppm) at potential scan rate $10$ mV s$^{-1}$).

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**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 glovebox) 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 the rate) similarly to the Bi(111)|LiClO$_4$ aqueous solution interface [5.6.19]. Also the phase angle, $\delta$ ($|\delta| > 83^\circ$ 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 $\delta$ 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($|Z|$) vs. 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].

The series differential capacitance $C_s$ (Fig. 3a) has been calculated from Nyquist dependences ($C_s = (Z''/2\pi f)^{-1}; j = \sqrt{-1}$). The potential of the minimum in the $C_s$ vs. $E$ plots, $E_{\text{min}}$ being located at $-0.7$ V, has found to be independent of ac frequency. The values of $C_s$ for EMImFAP at $E_{\text{min}}$ are noticeably lower than those for EMImBF$_4$, and especially for EMImTCB, and $C_s$ for EMImFAP at $E > E_{\text{min}}$ is somewhat lower than at $E < E_{\text{min}}$. 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 $\varepsilon$ is the absolute permittivity of vacuum, $l$ and $\varepsilon_0$ are the effective thickness and relative permittivity of edl), applicable only to a very rough

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**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($Z''$) vs. log($f$) and phase angle vs. log($f$) (frequency) plots (b) for Bi(111) in EMImBF$_4$ (triangles), EMImFAP (squares) and EMImTCB (rhombus) at $-0.7$ V (filled marks) and $-0.1$ V (open marks) (vs. Ag|AgCl|). EMImFAP (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 $R_s$ is high-frequency resistance, CPE is constant phase element, $C_{dl}$ is double layer capacitance, $C_{ads}$ is adsorption capacitance, $R_{ads}$ is adsorption resistance, and $Z_{W}$ is Warburg-like diffusion impedance.
approach of anions onto the Bi(111) surface on the anions chemical comparison with Bi(111)|EMImFAP, indicating the dependence of closest equilibrium adsorption capacitance, divided into experimental spectra can be obtained by modelling has been applied[7,8,16,17]. The non-linear least squares fitting shows that the more adequate approximation [8–10]. The product, \( le^{-1} \) (the reliable values of \( e \) in edl are not available) depends on the anion studied, but is nearly of the same order as for LiClO\(_4\) solutions in acetonitrile, methanol and ethanol [5,6]. The values of \( le^{-1} \) smaller than ion diameter, \( d \) (if we assume that \( e \approx 4...6 \), usually taken for aqueous solutions [5,6,20–23]), indicate that the potential drop inside surface layer of the metal electrode [20–23] has to be introduced into the modern edl theory to calculate the reasonable inner layer thickness values.

For calculation of high-frequency double layer capacitance, \( C_{dl} \), and equilibrium adsorption capacitance, \( C_{ad} \), the equivalent circuit (EC) modelling has been applied [7,8,16,17]. The non-linear least squares fitting shows that the more adequate fit of calculated with experimental spectra can be obtained by modified Frumkin–Melik–Galkazyan EC (EC B in Fig. 2a) where semi-infinite diffusion impedance has been replaced by the open circuit finite length Warburg impedance \( Z_{W(oC)} \) [2–8,16].

Thus, the values of \( C_{l} \) within the region of ideal polarizability can be divided into \( C_{l} \) and \( C_{ad} \) (Fig. 3b). \( C_{ad} \) weakly depends of RTIL studied, corresponding to the edl structure, if there is no specific adsorption of anions with partial charge transfer [19] between the negatively charged electrode surface and RTIL anion. However, in the all \( E \) region applied, \( C_{ad} \) is somewhat higher than \( C_{l} \), \( C_{ad} \) is higher for Bi(111)|EMImTCB compared with Bi(111)|EMImFAP, indicating the dependence of closest approach of anions onto the the Bi(111) surface on the anions chemical structure [13]. The diffusion-like process resistance \( R_0 \) depends on RTIL studied (Fig. 3c), being higher for EMImBF\(_4\). The values of fractional exponent of the Warburg-like diffusion impedance, \( \alpha_w \), are nearly 0.5 for EMImBF\(_4\), thus the semi-infinite diffusion-like edl reorganization process takes place similarly to the Bi(111)|KF+KI aqueous solution interface [7]. For EMImTCB, \( \alpha_w>0.5 \) indicates the formation of ordered layer of adsorbate at the electrode surface. Analysis of the fitting data for Au(111)|1-butyl-3-methyl imidazolium hexafluorophosphate [15] indicates that the mixed kinetics behaviour is valid within the all region of electrode potentials applied as the values of the contact phase element (CPE) exponent vary from 0.6 to 0.9 [2–4,7,8,16,17,19]. For Au (111) electrode, the CPE coefficient \( \alpha \) depends strongly on the potential applied, and the maximum value of \( Q \approx 25 \mu F cm^{-2} s^{-0.5}^{-1} \) at \( E = 0.2 \) V (Ag/AgCl) and \( n = 0.6 \) indicate the mainly diffusion limited step with small influence of the adsorption process \( (Q = \text{capacitance, if } n = 1; Q \text{ is equal to the Warburg semi-infinite diffusion impedance, if } n = 0.5) \) [16,17].

For Bi(111)|EMImBF\(_4\) (i.e. for RTIL with noticeable asymmetry of ions) the bell-shaped \( C_{dl} \) curve has been found, but for EMImFAP (higher symmetry of molar volumes of ions) there is only a wide and low maximum at \( E = E_{min} \). However, it seems that, in addition to the asymmetry of ions, the difference in surface activity, i.e. in the closest approach of anions to the electrode surface is also important obtaining mainly the asymmetric shape of the inner layer capacitance vs. potential curve for BF\(_4\) and particularly for TCB– containing RTILs. The surface activity for EMImTCB seems to be noticeably higher than for EMImFAP, explaining higher capacitance for EMImTCB within the all potential region applied (influence of second layer ions on \( C_{l} \) discussed by Kornyshev et al. [9–11]). The same shape of “hump” in the \( C_{l} \) curve has been found to be characteristic of Hg in LiBF\(_4\) of LiClO\(_4\) and Bi(hkl) in LiBF\(_4\), LiClO\(_4\) and LiSCN aqueous and non-aqueous solutions [5,6].

4. Conclusions

Cyclic voltammetry and impedance data show the strong dependence of electrical double layer capacitance, i.e. structure of Bi(111)|RTIL interface on the chemical composition, ion size asymmetry and surface activity, i.e. Gibbs adsorption of anions studied. The bell-shaped series differential capacitance vs. electrode curves have been observed for Bi(111)|EMImBF\(_4\) and Bi(111)|EMImTCB interfaces. The higher series capacitance and low-frequency adsorption capacitance values have been explained by stronger interaction, i.e. smaller distance of the closest approach of TCB– and BF\(_4\) anions onto the Bi(111) surface, compared with FAP–.

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