

Influence of electrode potential on the interfacial structure of cleaved single crystal Bi(111) electrode | 1-butyl-4-methylpyridinium tetrafluoroborate interface

Erik Anderson, Vitali Grozovski, Liis Siinor, Carolin Siimenson, Vladislav Ivaništšev, Karmen Lust, Enn Lust*
University of Tartu, Ravila 14a, 50411 Tartu, Estonia. e-mail: erik.anderson@ut.ee

Interfacial structure at Bi(111) | 1-butyl-4-methylpyridinium tetrafluoroborate (BMPyBF₄) interface was studied applying *in situ* scanning tunneling microscopy (STM), cyclic voltammetry, electrochemical impedance spectroscopy (EIS) and computational chemistry methods. Influence of electrode potential and *in situ* STM scanning conditions on the dynamics of superstructure formation process were demonstrated. The region of ideal polarizability, series resistance and capacitance, limiting high-frequency and low-frequency capacitances, *etc* were obtained and compared with those established for 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄). Analysis of impedance data shows, that in case of Bi(111) | BuMePyBF₄, differently from Bi(111) | EMImBF₄ interface, noticeably more expressed influence of the mass transfer limited step on the electrical double layer formation kinetics is dominating. The multilayered superstructure formation of BMPyBF₄ at Bi(111) was verified by *in situ* STM, explaining impedance data results. The highest multilayered RTIL adsorption formations (more than four RTIL layers) at cleaved surface of Bi(111) single crystal electrode surface were observed, while scanning at positively charged tungsten STM tip conditions ($E_{tip} > E$). The potential E was varied from -1.2 V to -0.4 V (vs Ag/AgCl reference electrode). Note, that electrode cathodic currents ($i_{cathodic}$) are assumed to be negative.

Possible reasons of the lower values of the series capacitance for Bi(111) | BMPyBF₄, compared to Bi(111) | EMImBF₄ interface were examined on the basis of modern theoretical models.

In our electrochemical studies of Bi(111) | BMPyBF₄ system, there are similarities to Au(111) | RTIL interfaces, published by Kolb *et al* [2] and Drüschler *et al* [3]. Evidence of weak physical adsorption of BMPyBF₄ at Bi(111) took place from $E = -1.2$ V to $E = -0.6$ V (Figs. 1 and 2). The Bi(111) electrode potential step experiments from -0.8 V to -1.2 V and back from -1.2 V to -0.6 V indicate, that the multilayered adsorption of BMPyBF₄ onto Bi(111) and dissolution of cathodically formed multilayered structure (Fig. 2a) are very slow processes. Sometimes minutes are needed for restructuring of interfacial layer.

At STM tip potentials ($E_{tip} = -60$ mV vs $E_{tip} = +45$ mV (at $E = -1.2$ V)) and at higher image scanning rates, the superstructure was "brushed away" (Fig. 2a and 2b). Thus, a significant decrease of root mean square roughness (RMS) and STM image height value (Z-axis) were observed (Figs. 2a and 2b).

At higher STM scanning rates, after desorption/removal of weakly adsorbed RTIL superstructures, atomic resolution was repeatedly demonstrated (Fig. 3). The distances between atoms at Bi(111) basal plane are in a good agreement with the crystallographic data (of Bi(111) single crystal electrode and STM results of atomic resolution measured in aqueous electrolyte Na₂SO₄ + H₂SO₄), published by S. Kallip *et al* [3]. At $E \geq -0.4$ V, the tip induced surface roughening (*i.e* surface etching) of Bi(111) plane was observed (Fig 4a). Thus, the noticeable increase in surface roughness parameters was

demonstrated (Fig. 4a vs 4b).

The STM tip induced Bi(111) surface etching at different tip potentials under polarization needs further studies, while cathodic surface roughening processes at $E < -1.2$ V are of great interest.

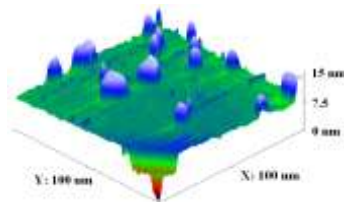


Fig. 1. Cleaved Bi(111) surface covered by RTIL adsorbates at $E = -1.2$ V (vs Ag/AgCl), $i = -0.07$ μ A, $i_{tunnel} = 1.2$ nA, $E_{tip} = +50$ mV (vs E), $v_{scan} = 0.25$ lines s⁻¹, RMS = 1.14 nm.

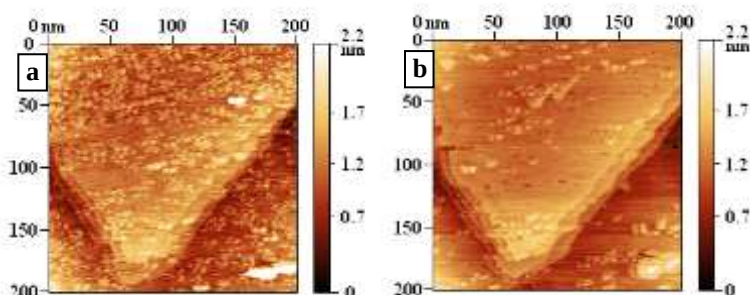


Fig. 2. Cleaved Bi(111) surface covered with RTIL multilayers (a) and the same area (b), where multilayers have been brushed away by the STM tip scan. $E = -1.2$ V (vs Ag/AgCl), $i = -0.07$ μ A, $i_{tunnel} = 1.8$ nA, $v_{scan} = 0.25$ lines s⁻¹.

(a) - $E_{tip} = -60$ mV (vs E), RMS = 0.345 nm.

(b) - $E_{tip} = +45$ mV (vs E), RMS = 0.254 nm.

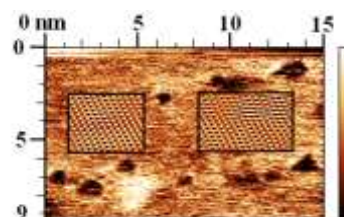


Fig. 3. Cleaved Bi(111) unfiltered atomic resolution image. $E = -1.2$ V (vs Ag/AgCl), $i = -0.09$ μ A, $v_{scan} = 2.2$ lines s⁻¹, $i_{tunnel} = 1.518$ nA, $E_{tip} = +20$ mV (vs E).

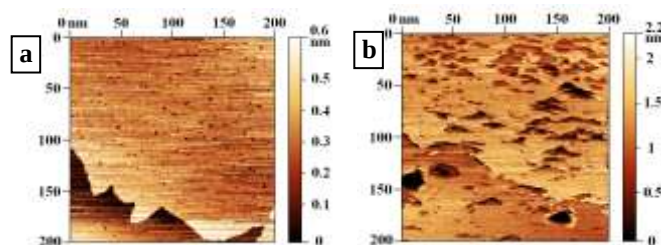


Fig. 4. Cleaved Bi(111) at different potentials, $v_{scan} = 0.5$ lines s⁻¹, $i_{tunnel} = 1$ nA = const.

(a) - $E = -0.6$ V (vs Ag/AgCl), $i = +0.28$ μ A, RMS = 0.105 nm.

(b) - $E = -0.4$ V (vs Ag/AgCl), $i = +0.08$ μ A, RMS = 0.499 nm.

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