

## ***In situ* STM Studies of Electrochemically Polished Cd(0001) Electrode in 1-ethyl-3-methylimidazolium tetrafluoroborate**

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The *in situ* scanning tunneling microscopy (STM) and electrochemical impedance spectroscopy studies of electrochemically polished Cd(0001) electrode have been performed in the 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF<sub>4</sub>) ionic liquid within electrode potential region from -1.6 V to -0.9 V (*vs.* Ag|AgCl|EMImBF<sub>4</sub>). The *in situ* STM data show that there are no quick surface reconstruction processes and the ideal surface structure of Cd(0001), very similar to that previously observed in aqueous electrolyte, has been established.

### **Introduction**

Room temperature ionic liquids (RTILs) are defined as molten salts and the poor coordination or interaction between the counterpart ions results in the liquid state of these ionic systems at room temperature (1,2). Due to RTILs high stability under applied electrode potential, low vapor pressure, excellent thermal stability, high ionic conductivity, non-flammability and tunable counterpart ions the RTIL|electrode interface attracts considerable attention determining the characteristics of various electrical power sources, including batteries, fuel cells, etc. (3-5). In particular, the wide electrochemical window and dual usability as solvent and electrolyte opened interesting possibilities in the field of fundamental and applied electrochemical studies. For instance, RTILs have been already used as electrolytes in supercapacitors and energy storage devices, as an environment for electrodeposition of metals and alloys, and for optimizing the heterogeneous reaction rate (2). It has been established that the performance of RTILs in the electrochemical applications depends on the strength of the physical and chemical interactions between RTIL ions and electrode surface. Hence, a detailed understanding of the RTIL|electrode interface structure, thermodynamics and formation kinetics is crucial for designing modern high energy density electrochemical devices.

In 1992, Wilkes and Zaworotko reported the first air and moisture stable ionic liquids based on 1-ethyl-3-methylimidazolium cation with either tetrafluoroborate or hexafluorophosphate anion (1). Nevertheless that the melting point of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF<sub>4</sub>) is too high (15°C) for many practical applications it is a widely used RTIL for analyzing the influence of the chemical nature and crystallographic structure of different metal electrodes on the RTIL|interface parameters (6-9).

According to our knowledge, no data can be found in the literature characterizing the Cd(0001)|EMImBF<sub>4</sub> interface under the *in situ* scanning tunneling microscopy (STM) electrochemical conditions. Therefore, the main aim of these investigations was to develop the experimental conditions needed to obtain the atomic resolution electrochemical *in situ* STM data for the Cd(0001) single crystal electrode in RTIL. A comparison of data with our previous results analyzing atomic resolution level structure

of the Cd(0001) electrode in aqueous surface inactive electrolyte solution (10) will be given.

## Experimental

The surface of the basal Cd(0001) plane has been prepared by electrochemical polishing in a hot ( $T=80^{\circ}\text{C}$ ) 1:1 solution of concentrated phosphoric acid and Milli Q+ water at current density  $j=1.48\text{ A cm}^{-2}$  and submerged under cathodic polarization ( $E=-1.1\text{ V vs. Ag|AgCl|EMImBF}_4$ ) into the EMImBF<sub>4</sub> (Fluka Analytical, for electrochemistry,  $\geq 99.0\%$ ,  $\text{H}_2\text{O}<200\text{ ppm}$ ), which was additionally dried inside of the glove box using dry Ar (99.999%). The self-made hermetic three-electrode cell with large Pt counter electrode and Ag|AgCl|EMImBF<sub>4</sub> reference electrode, connected to the *in situ* STM cell through Luggin capillary, has been used. All cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements (using Autolab PGSTAT 320 with FRA II) were performed inside a glove box ( $\text{H}_2\text{O}<1.0\text{ ppm}$ ,  $\text{O}_2<1.0\text{ ppm}$ ) in a three-electrode electrochemical cell. Potential cyclation rate was  $10\text{ mV s}^{-1}$  and EIS data were measured within the ac frequency range from 0.1 to  $1\cdot 10^4\text{ Hz}$ .

The Molecular Imaging PicoSPM<sup>TM</sup> measurement system applying the Apiezon<sup>TM</sup> coated tungsten STM tips, prepared in our laboratory, has been used. The STM tips and measurement system were tested and calibrated using the basal plane of highly orientated pyrolytic graphite C(0001)<sup>C</sup> (SPI<sup>TM</sup>). All STM images were recorded in constant current mode with tunneling currents from 0.5 to 10.0 nA. For image processing and surface roughness analysis the Gwyddion (11) free software program has been used.

## Results and Discussion

According to the *in situ* STM data given in Fig. 1a, the surface of the electrochemically polished Cd(0001) electrode consists of atomically smooth terraces which are separated by monoatomic steps of medium height  $5.6\pm 0.3\text{ \AA}$  (Fig. 1b)(or of multiple heights). The heights of the steps are in a good agreement with the data for Cd hexagonal close-packed crystallographic structure with cell parameters  $a=2.9793\text{ \AA}$  and  $c=5.6181\text{ \AA}$  (12).

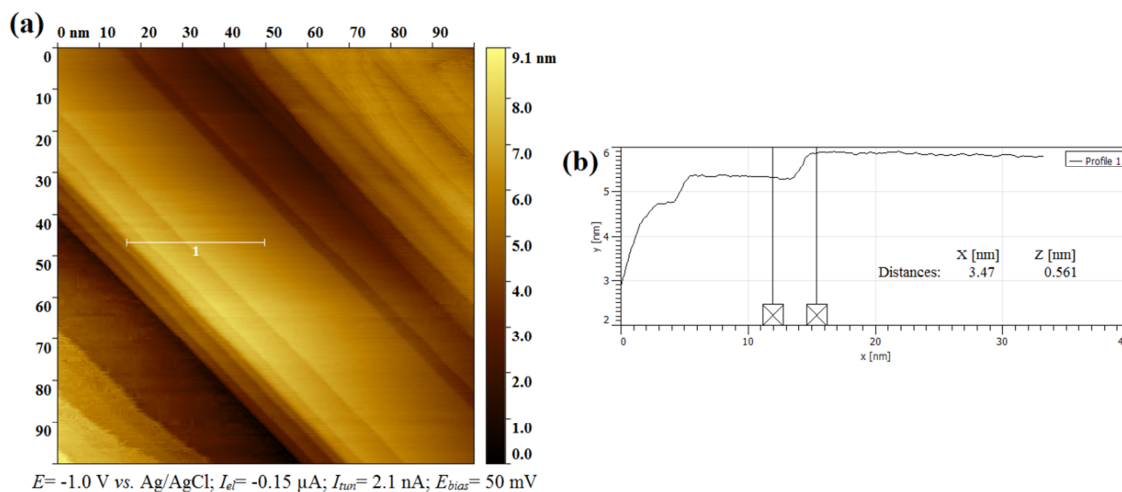


Figure 1. *In situ* STM image (a) and selected surface profile (b) for electrochemically polished Cd(0001) plane in EMImBF<sub>4</sub> at  $E = -1.0\text{ V}$ .

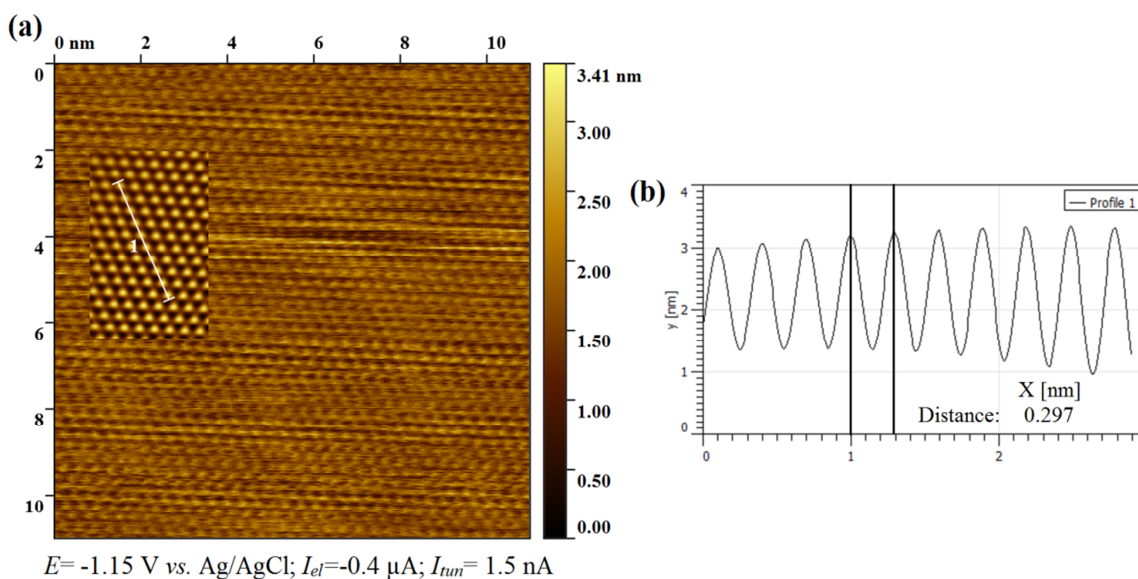


Figure 2. *In situ* STM atomic resolution image with a fast Fourier transform filtered image inset (a) and height profile (b) for Cd(0001) plane in EMImBF<sub>4</sub> at  $E = -1.15 \text{ V}$ .

The data given in Fig. 2 show the atomic resolution picture (a) with an inset of a fast Fourier transform (FFT) filtered image of the raw data (inset in 2a) and selected surface profile (b) for the Cd(0001) electrode at  $E = -1.15 \text{ V}$ . On these images the regular atomic structure of Cd(0001) can be seen with the interatomic distances measured from FFT analysis:  $2.9 \pm 0.3 \text{ \AA}$ , which also in conformity with the crystallographic data. Although in some regions small deviations of experimental data from the ideal crystallographic characteristics appear due to the thermal drift distortion, the height fluctuations within the region of  $100 \text{ nm}^2$  plateaus, exposed on Cd(0001) surface in EMImBF<sub>4</sub>, are very small, and in an agreement with the previously measured data for the Cd(0001) electrode in surface inactive aqueous electrolyte (10).

The structure of nanometric terraces separated by the steps, is very stable during few hours under the cathodic polarization from  $-1.6 \leq E \leq -0.9 \text{ V}$  (Fig. 3a-c). The root mean square roughness (*RMS*) vs. cathodic polarization dependence (Fig. 3d) has been analyzed to confirm this conclusion. The *RMS* values at fixed  $E$  have been calculated using Gwyddion software (11) according to the following relation:

$$RMS = \sqrt{\frac{1}{n} \sum_{i=1}^n |z_i|^2}, \quad [1]$$

where  $n$  is the number of data points and  $z_i$  is the height deviation of  $i$ -th point from the mean line, defined so that the arithmetic sum of all  $z_i$  is equal to zero. Therefore, as found for the surface of Cd(0001) in inactive aqueous electrolyte, it can be concluded that no quick surface reconstruction of the Cd(0001) surface layer is taking place at the electrode | ionic liquid interface as it has been established for Au(hkl) single crystal electrode [13-15].

At less negative potentials, no atomic level resolution has been achieved due to the surface oxidation and dissolution of the Cd(0001) surface.

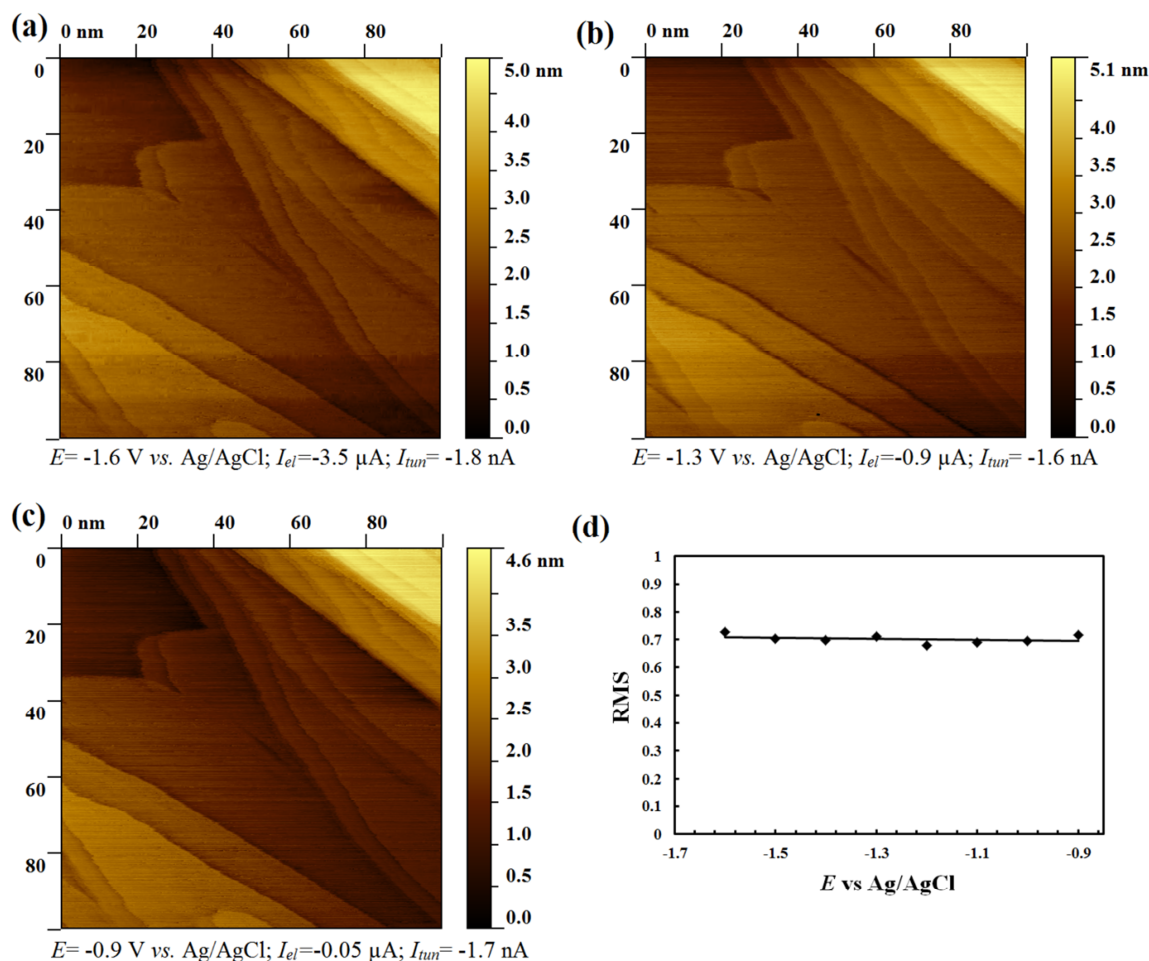


Figure 3. *In situ* STM images at various electrode potentials (a, b, c) and root mean roughness (RMS) vs. electrode potential dependence (d) for Cd(0001) electrode in EMImBF<sub>4</sub>.

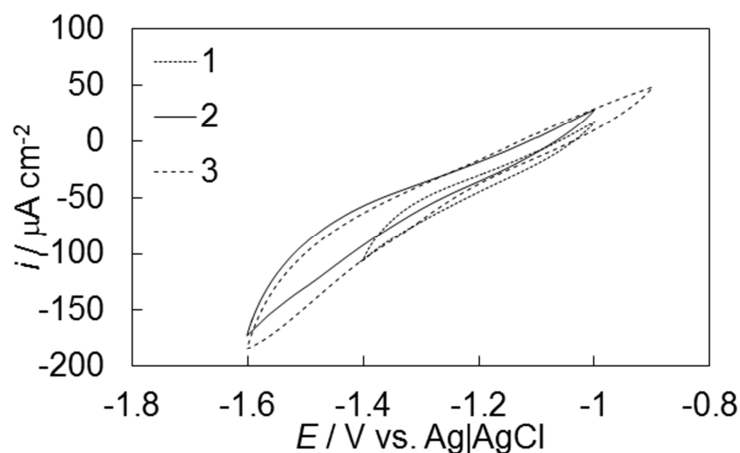


Figure 4. Cyclic voltammograms for Cd(0001) in EMImBF<sub>4</sub> at potential scan rate 10 mV s<sup>-1</sup>.

Current density ( $i$ ) vs. electrode potential ( $E$ ) dependencies (Fig. 4) were measured within a potential region from  $-1.6$  V to  $-0.9$  V (vs. Ag|AgCl|EMImBF<sub>4</sub>). Based on the data in Fig. 4, there are no surface oxidation or reduction peaks in the CVs, but the values of  $i$  are rather high due to relatively cathodic potentials for a sp-metal Cd(0001) electrode, where several decomposition processes might start.

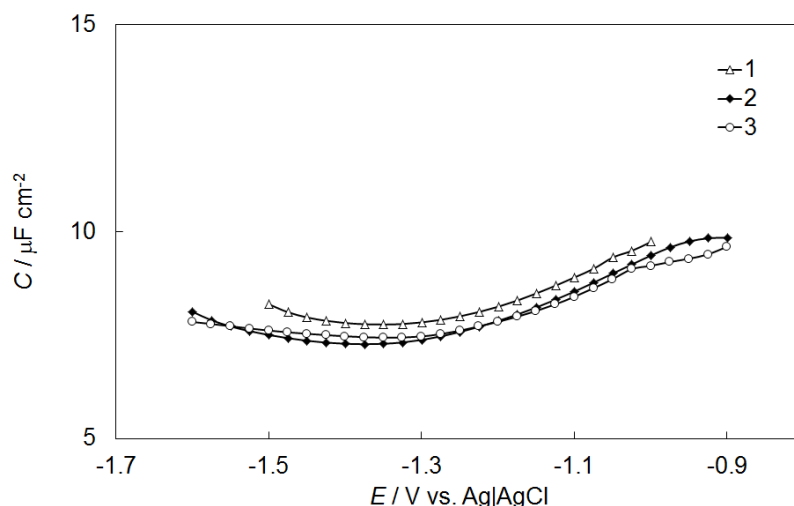


Figure 5. Differential capacitance ( $C$ ) vs. electrode potential ( $E$ ) dependences for Cd(0001) in EMImBF<sub>4</sub> at 210Hz.

According to the differential capacitance ( $C$ ) vs.  $E$  curves (Fig. 5), capacitance values increase at more positive and negative electrode potentials (measured at 210 Hz). The lowest values of  $C$  were measured at -1.35 V. The system is stable in time, as the time gap for curves 1 and 2 (Fig. 5) is approximately 24 h, but the capacitance values differ less than 5%. There is no hysteresis in the  $C$  and  $E$  curves in Fig.5, which are measured first forward positive (curve 2) and thereafter negative direction (curve 3). This indicates that the slow rate faradaic processes are nearly reversible.

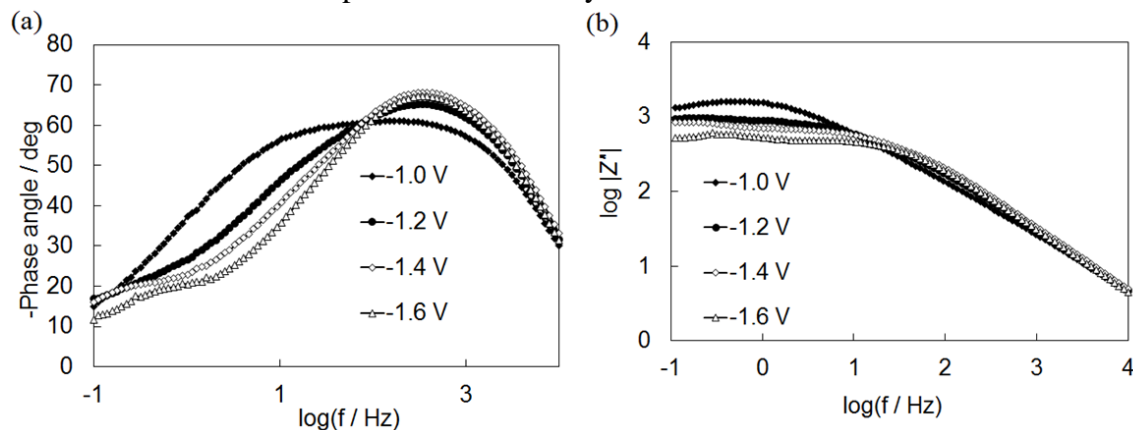


Figure 6. Phase angle (a) and  $\log |Z''|$  vs.  $\log$  frequency dependencies (b) for Cd(0001) in EMImBF<sub>4</sub> at several potentials, noted in figure.

All the measured EIS data (Fig. 5a,b), *i.e.* phase angle vs.  $\log$  frequency ( $f$ ) dependencies show a slow adsorption processes with the partial charge transfer processes at all potentials measured. This kind of behavior is different from data measured for bismuth single crystal electrode in EMImBF<sub>4</sub>, where there are no slow faradic or partial charge transfer processes at Bi(111)|EMImBF<sub>4</sub> interface within electrode potential region from -1.1 V to -0.2 V (*vs.* Ag|AgCl|EMImBF<sub>4</sub>) (16). Considering the shape of the phase angle vs.  $\log$  frequency plots (Fig. 5a) a deviation from an ideally polarizable interface can be seen at low and very low frequencies. At lower frequencies both adsorption and charge (including partial and faradic) transfer processes between the electrode surface and adsorbed species take place. Some traces of water and oxygen can be found in EMImBF<sub>4</sub> and they can be reduced at Cd(0001) surface. Due to the possible adsorption of water and



oxygen on the surface of Cd(0001) during the electrochemical polishing in an aqueous solution, as Cd is a highly hydrophilic metal (17). Based on the shape of the  $\log|Z''|$  vs.  $\log f$  (Fig. 5b) curves, we can conclude that at  $f > 50$  Hz the electrical double layer formation kinetics depends weakly on  $E$  applied, but at lower frequency range mixed kinetic processes occur. More detailed studies are in progress using *in situ* FTIR and other surface sensitive methods.

## Conclusions

The *in situ* STM studies of electrochemically polished Cd(0001) were performed under negative electrode potentials from  $-1.6$  V to  $-0.9$  V (vs. Ag|AgCl|EMImBF<sub>4</sub>) in EMImBF<sub>4</sub>. The atomic resolution images were obtained, indicating that there was no quick surface reconstruction process and the surface structure of Cd(0001) was stable within the potential region investigated. Electrochemical impedance data show, that only at very low ac frequency the partial or “true” faradaic processes prevail at the Cd(0001)|EMImBF<sub>4</sub> interface.

Therefore, it has been concluded that the Cd(0001) electrode can be used for future studies of the more complicated two-dimensional adsorption layer or superstructure formation processes of various RTILs and their mixtures [18-19].

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