In situ STM studies of Cd (0001) electrode in aqueous electrolyte solution

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The base boundary structure, adsorption properties and electrochemical kinetics of various interfacial charge transfer reactions at the solid surfaces depend significantly not only on the chemical composition but also on the morphology of the surface studied. According to our knowledge, there are no data for Cd (0001) plane obtained under the electrochemical in situ STM (scanning tunneling microscopy) conditions in the literature. Therefore, the main aim of these investigations was to develop the experimental conditions needed to obtain the atomic resolution STM data within the ideal polarization region of the Cd (0001) electrode ($-1.1\ V \geq E \leq -0{,}95\ V$ vs. Ag|AgCl in saturated KCl aqueous solution) [1].

Atomically resolved STM studies require the preparation of a flat surface with well-defined structure. Thus the Cd (0001) single crystal electrode was electrochemically polished in a heated 1:1 solution of concentrated phosphoric acid and Milli+ Q water [2, 3].

For the in situ STM studies tunnelling tips were prepared from tungsten wire (Ø = 0.25 mm) by electrochemical etching in 5 M KOH solution. The Molecular Imaging PicoSPM™ measurement system has been used.

The surface of the basal Cd (0001) plane has been submerged under polarisation (E = −1.1 V vs. Ag|AgCl in saturated KCl aqueous solution) into the 0,1 M Na_2SO_4 + $2\cdot10^{-6}$M H_2SO_4 aqueous solution, previously saturated with Ar (99.999%) inside the glove box (Ar 99.999% atmosphere). The self-made hermetic three-electrode cell with large Pt counter electrode and Ag|AgCl reference electrode, connected to the in situ STM cell through Luggin capillary, has been used.

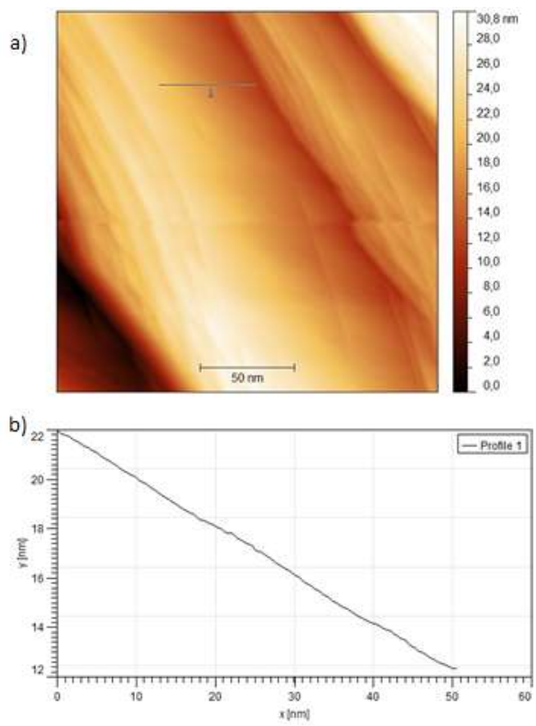

Fig.1. In situ STM image (a) and height profile (b) for Cd (0001) electrode in 0.1 M Na_2SO_4 + $2\cdot10^{-6}$M H_2SO_4 aqueous solution at E = −1.15 V.

During the measurements atomically flat areas have been seen on the in situ STM images of cadmium (0001) single crystal electrode surface (Fig. 1). The data in Fig. 2 show the atomic resolution picture (a) and the surface profile (b) for the electrochemically polished Cd (0001) electrode at E = −1.15 V vs Ag|AgCl in saturated KCl aqueous solution. According to these data, the quite regular atomic structure can be observed with interatomic distances d = 2.9 ± 0.1 Å, which are in good agreement with Cd (0001) crystallographic parameters.

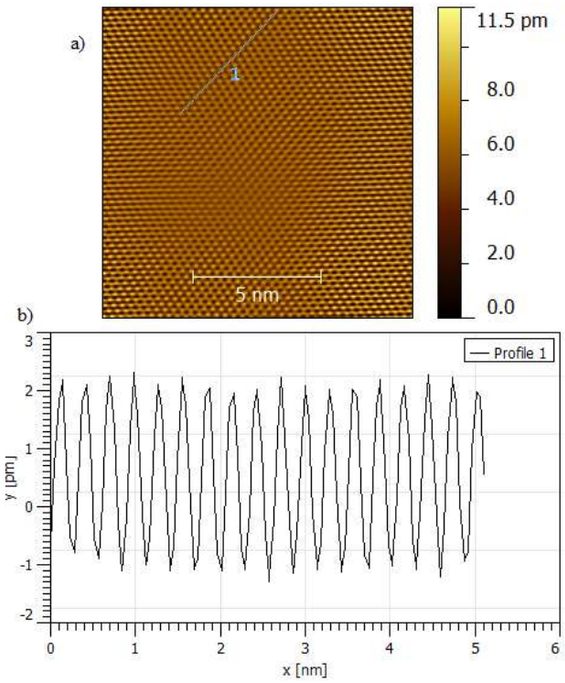

Fig.2. In situ atomic resolution STM image (a) and height profile (b) for Cd(0001) electrode in 0,1 M Na_2SO_4 + $2\cdot10^{-6}$M H_2SO_4 aqueous solution at E = −1.15 V.

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