Supplementary Information for:

Electrodeposition of Zn and Au-Zn alloys at low temperature in an ionic liquid

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We investigated the electrochemical deposition of Zn on Au surface by in-situ surface x-ray diffraction, in order to understand the processes occurring at the Zn/metal electrochemical interface. A Au single crystal with a polished (111) surface (MaTecK, Germany) was used as substrate for the experiment. For the in-situ diffraction studies, we used a portable electrochemical setup (TRECXI) with an addition of a heating stage which allowed to heat the ionic liquid in UHV conditions. With this heating stage, it is also possible to perform electrodeposition at elevated temperatures around 130 °C. The electrochemical cell (EC) is encapsulated in a concentric capillary system, where the reference electrode (Pt wire) is inserted in the inner capillary, while the counter electrode (Pt wire) is wound around the inner capillary (Fig. 1c). With this setup, the electrolyte contact with the sample surface can be attained in the controlled gas atmosphere. Prior to the experiment, the Au (111) surface was prepared by few sputter-anneal cycles in UHV. The surface quality of the sample was examined by Auger spectroscopy and LEED. The electrolyte comprises of ZnCl₂ and 1-butyl-3-methylimidazolium chloride (BMIC) in 60:40 mol%. This ionic electrolyte is hygroscopic in nature and requires heating prior to the experiment to remove the absorbed water. Ionic liquid was heated in the portable chamber using a PCTFE container (Fig. 1a) for 12 hours in UHV (1×10⁻⁸ mbar) up to 100°C. The chamber was then filled with inert gas at ambient pressure and the electrochemical (capillary) cell was inserted by opening a UHV valve. The ionic liquid was pumped into the capillaries by using two syringes. The electrochemical cell was then separated from the rest of the chamber and was evacuated to allow the sample transfer.* Corresponding author. Tel: +49 (0)211 6792 473 Fax: +49 (0)211 6792 218 E-mail: d.borissov@gmx.de

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Figure 1: Picture of the electrochemical setup used at the ESRF. a) The container half-filled with the ionic liquid during heating. b) The portable EC cell-UHV chamber with the six-circle diffractometer. c) Schematic of the EC-cell explaining the experimental arrangement.
(Au (111) crystal) from the UHV system. After the sample transfer, the portable chamber (TRECXI) was transported to the diffractometer. During the measurements, the portable chamber was again filled with the inert gas at ambient pressure to introduce the EC cell and a droplet of electrolyte at the end of the capillary was then brought into contact with the sample surface. Figure 1c shows a schematic of the electrochemical setup. This setup allows tracking the interface changes by in-situ x-ray diffraction without exposing the ionic liquid electrolyte and sample surface to ambient air. The in-situ X-ray diffraction experiments were performed at the undulator beamline ID32 at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France, using a wavelength ($\lambda$) of 0.539062 Å. The incident angle was chosen to 0.2°. The scattering vector $q$ is defined as $q = k_f - k_i$, where $k_i$ and $k_f$ are the incoming and diffracted wave vectors, respectively. Au crystal possess a FCC unit cell (lattice parameters $a_0 = 4.08$ Å, $\alpha = \beta = \gamma = 90°$), which can be transformed to a surface unit cell for Au (111) surface ($a_1 = a_2 = \sqrt{2} \times a_0 = 5.767$ Å, $a_3 = \sqrt{3} \times a_0 = 7.064$ Å, $\alpha = \beta = 90°, \gamma = 120°$). This unit cell leads to a hexagonal reciprocal unit cell with lattice parameters $a_1^* = a_2^* = 1.258$ Å, $a_3^* = 0.8895$ Å, $\alpha = \beta = 90°, \gamma = 60°$. To describe the scattering vector $q$ and the reciprocal space of Au (111), we used the above mentioned reciprocal unit cell. The in-plane miller indices are then denoted by H & K, while L is the out-of-plane index.