

Atomic-scale friction study: Underpotential deposition (UPD) of silver on I-modified Au(111) in aprotic electrolyte

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Friction in general is one of the main sources of energy loss, and therefore finding ways for better controlling friction is of uttermost importance. Atomic-scale friction is measured using electrochemical lateral force microscopy (EC-LFM) where the AFM tip slides on the surface of electrode under electrochemical control. It helps us to understand interfacial and tribological behavior on nanoscale. In ionic liquids (ILs) including solvate ILs, the friction as function of normal load has been studied on HOPG and Au(111), which shows that the structure of ions is a decisive factor for the friction behavior [1-4]. Our interest was focused on the adsorption of foreign metals, ranging from (sub)monolayer (underpotential deposition (UPD)) to multilayer (bulk) deposition and the adsorption of organic adsorbates, and its influence on friction as function of potential on single crystal electrodes in aqueous electrolyte[5-7].

The underpotential deposition (UPD) of silver had often been studied on gold in aqueous electrolyte since the lattice constants of silver and gold are fairly identical ($a_{Ag} = 4.09 \text{ \AA}$, $a_{Au} = 4.08 \text{ \AA}$) [8-12]. Previous results clearly show that the Ag UPD process is very sensitive to the presence of other adsorbates (e.g. SO_4^{2-} , ClO_4^-). Especially, the Ag UPD on iodine covered surface of Au(111) shows completely different atomic structures after the 1st, 2nd, and 3rd Ag UPD compared to the results on Au(111) [9, 13].

In this study, we investigate the interfacial properties on I-modified Au(111) during the Ag UPD in aprotic electrolyte. We observed two sets of Ag UPD peaks in cyclic voltammetry (CV). The charge density for these peaks is about $216 \mu\text{C}/\text{cm}^2$ close to the theoretical charge density for the monolayer ($222 \mu\text{C}/\text{cm}^2$). We observed the iodine structure at low normal load ($F_N < 20\text{nN}$), which shows that the iodine adlayer on Au(111) and Ag monolayer forms a $(\sqrt{3} \times \sqrt{3})R30^\circ$. It indicates that the iodine adlayer is stable during the Ag UPD. At high normal load, the AFM tip penetrates into iodine layer and reveals the structure of Au(111) or Ag monolayer depending on the potential. It is remarkable that there is no irreversible wear during the penetration of AFM tip meaning that the iodine structure appears again with decreasing normal loads. At high normal load where the tip penetrates into iodine layer and interacts with substrates (Au and Ag), the friction on Ag monolayer is higher than on Au(111). Interestingly, even though the cyclic voltammetry (CV) shows that the amount of water in the electrolyte has minor influence, the friction increases with an increase in water content on the I/Ag/Au(111).

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