

New Insight into the Electro-Oxidation of the Irreversibly Chemisorbed Bismuth on Pt(111) through Temperature-Dependent Research

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Elements of the VB and VIB Groups of the Periodic Table of the Elements can spontaneously form a surface overlayer on Pt(hkl) surface upon immersion of the latter in aqueous solution of a respective water-soluble compound [1-4]. The spontaneous chemisorption can proceed via: (a) the oxidative pathway, (b) the disproportionation pathway of the chemisorbing species, or (c) chemisorption without any change of the oxidation state of the adsorbing species. Such formed an overlayer can be subsequently oxidized or reduced depending on the physico-chemical nature of the adsorbate. The process of spontaneous deposition can be used in preparation (synthesis) of semiconductor layers, hence its technological importance. On the other hand, such an atomically modified electrode surface can be used as a suitable electrode material.

An ultra-thin layer of Bi was formed by immersion of Pt(111) in aqueous solution of Bi^{3+} for 5 seconds followed by thorough rinsing in high-purity water. The Bi^{3+} solution was prepared by dissolution of Bi_2O_3 in 0.5 M aqueous H_2SO_4 . The formation of the respective overlayer was a spontaneous process. The Bi overlayer ($\theta_{\text{As}} \cong 0.30$) was electro-oxidized at different T in the 273-318 K range in 0.5 M aqueous H_2SO_4 [5].

The surface redox behavior of the overlayer of chemisorbed bismuth, Bi_{chem} on Pt(111) in 0.5 M aqueous H_2SO_4 manifests itself through sharp CV features that are not affected by the scan rate, s , variation (for $1 \leq s \leq 100 \text{ mV s}^{-1}$). The impact of T variation on the surface-oxidation behavior of Bi_{chem} was examined by T alteration in the 273 - 318 K range. The data show that the Bi_{chem} surface coverage is not affected upon T modification but the cyclic-voltammetry, CV, profiles undergo qualitative changes. The sharp anodic peak and the cathodic one shift towards less-positive potentials upon T increase. Despite some morphology changes in the CV profiles, the T variation does not affect the charge density distribution among the two anodic and two cathodic features. At q_{Bi} well below 0.30, say 0.20, the CV profiles representative of the Bi_{chem} oxidation reveal only one perfectly reversible peak. An analysis of the possible reaction pathways indicates that the Bi_{chem} surface oxidation proceeds in one step involving transfer of two electrons and addition of two OH groups. The standard enthalpy of the surface redox process is determined from the slope of the E/T versus $1/T$ plot, and then the standard enthalpy of formation of $\text{Bi}(\text{OH})_{2\text{chem}}$, $\Delta H_{\text{f}}^{\circ}(\text{Bi}(\text{OH})_{2\text{chem}})$, is elucidated, its value being -441 kJ mol^{-1} . It falls closely to 2/3 of the

standard enthalpy of formation of the bulk-type $\text{Bi}(\text{OH})_3$, thus pointing to the nature of the surface compound. The different electro-oxidation behavior of Bi_{chem} with respect to As_{chem} (it undergoes electro-oxidation to $\text{As}(\text{OH})_{3\text{chem}}$) is explained in terms of surface electronic effects [6].

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