Formation of UPD and metallic adlayers on well-defined single crystal surfaces.

Javier Gutiérrez de Dios, Roberto Gómez, Juan M. Feliu
Dpto. Química Física, Universidad de Alicante,
Apdo. 99, E-03080 Alicante, Spain

Electrochemical properties of different adatom (sub)monolayers have interest as they constitute the first stage of metal deposition processes and have a distinct reactivity. In Electrochemistry, a traditional way to prepare these adlayers is by means of underpotential deposition (UPD). This type of processes has been the subject of a considerable amount of work. These studies deal with deposition of monovalent or divalent cations. However, UPD of trivalent cations, namely from IIIA elements, has not been reported as fas as we know. Deposition of trivalent species from the group VA has been reported, but they are mainly involved in irreversible adsorption processes in which OH adsorption plays a role in the electrochemical reaction.

In fact, UPD of elements such as Ga or In can take place on Pt(111) electrodes provided that mild acidic solutions are used. In these cases it should be considered the existence of solution equilibrium reactions such as:

$$Ga^{3+} + H_2O \Leftrightarrow GaOH^{2+} + H^+ \qquad (1)$$

$$GaOH^{2+} \Leftrightarrow GaO^+ + H^+ \qquad (2)$$

in which $pK_1 = 2.6$, and $pK_2 = 3.3$. For sake of simplicity, hydration water molecules are not considered. These hydrolysis-type equilibrium reactions lead to cationic species with lower positive charge as final product. It appears that these low charged species undergo UPD processes more easily.

Figure 1 reports the voltammetric positive-going sweep corresponding to the desorption of underpotentially deposited Ga on Pt(111), from perchloric acid solutions of different pH. It can be seen that the charge under the oxidation peak increases with pH, thus suggesting that the relevant species involved in the UPD process from the solution side involve partially hydrolyzed cations. It is also noteworthy that the most acidic solutions would correspond to real UPD processes, because the oxidation step is accompanied by the dissolution of the adlayer. Thus, the characteristic butterfly process of Pt(111) in perchloric acid is observed as in the clean Pt(111) substrate. At higher pH, however, the oxidation of the adlayer would not imply total adatom dissolution and similar responses as those observed in irreversibly adsorbed systems are recorded. In this way the UPD modified electrodes may be transferred to a solution free of the dissolved cation and the adlayer remains reasonably stable upon oxidation. This would agree with the final formation of a stable gallium oxide on the Pt(111) surface. At higher pH values Ga is no longer present in solution due to precipitation of the corresponding hydroxide.

Similar processes can be considered in the case of In UPD on Pt(111). In this case the deposition takes place within the butterfly region and the OH adsorption on the platinum surface contributes to the deposition of the metal (figure 2).

Another interesting group of adlayers is that of noble metals on noble metals. A promising system is that of Pt on well-defined Rh substrates, which can be used as a potential electrocatalyst. Results have been obtained by electrodeposition of Pt on Rh single crystals as well as by chemical displacement of UPD Cu previously deposited on the Rh substrate. It is remarkable that the voltammogram of Pt deposited on Rh(100) resembles that of Pt(100) after some cycles in the oxygen adsorption/desorption region. In the limit at which the Rh(100) substrate becomes fully blocked a wide distribution of platinum adsorption states appears at lower potentials than those corresponding to well ordered Pt(100) electrodes.

Financial support of E.U. through contract No. G5RD-CT-2001-00463 is greatly acknowledged.

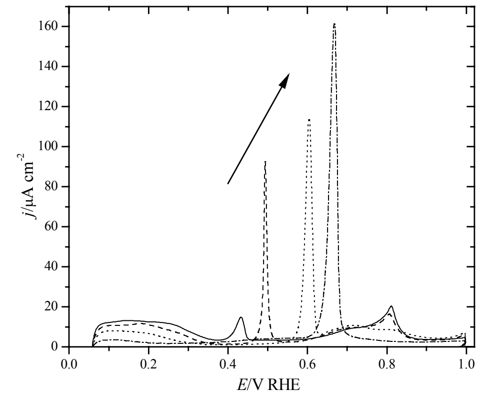

Figure 1. Ga UPD on Pt(111) in 10^{-3} M $Ga(ClO_4)_3$ versus pH. Variation of pH from left to right: 0.08 (___), 1.1 (----), 2 (....) and 3.1 (-.-.-). Positive sweep. v=20 mV/s.

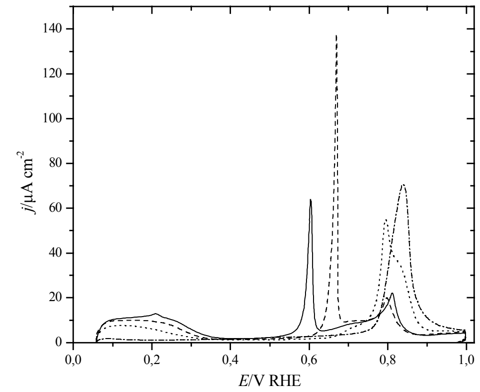

Figure 2. In UPD on Pt(111) in 10^{-3} M $In(ClO_4)_3$ versus pH. Variation of pH from left to right: 0.08 (___), 1.1 (----), 1.56 (....) and 3.5 (-.-.-). Positive sweep. v=20 mV/s.

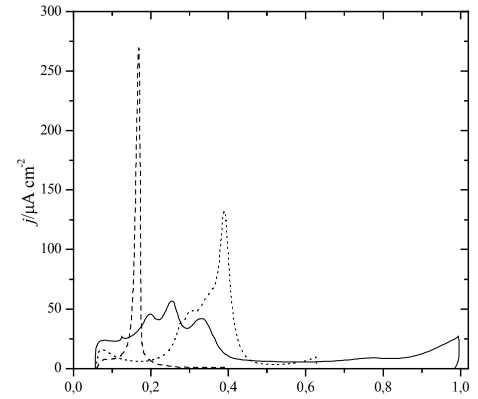

Figure 3. Rh(100) (---), Pt(100) (...) and Pt/Rh(100) (___) deposited electrochemically in 0.1 M H_2SO_4. Positive sweep. v=50 mV/s.