

Lead Underpotential Deposition on Gold and its Application in Platinum Thin Film Growth

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Pb underpotential deposition (UPD) on Au(111) has been intensively studied for the last few decade. More recent surface stress measurements by a number of research groups raised questions regarding the role of surface alloying/dealloying transitions in the stress behaviour (Figure A). A quantitative analysis of alloying/dealloying during this UPD process has not been carried out yet.

In the present work we examined Pb UPD on Au(111) thin film electrodes. This system is characterized by large misfit of 21%. During Pb monolayer formation, the Pb/Au(111) system exhibits surface alloying/dealloying transition. The changes in the surface structures and the kinetics of surface alloying were examined by cyclic voltammetry and extended polarization measurements at different Pb coverages. The mechanisms of Pb monolayer formation at different stages of the growth have been studied by combination of in-situ techniques: laser beam reflection and scanning tunnelling microscopy (STM)

Pb underpotential (UPD) deposited layer can be used in Pt film growth on Au(111) via a method called Surface Limited Redox Replacement (SLRR). The growth was done in *one-cell configuration*, different from protocols previously reported in literature, which use either multiple immersions¹ or flow-cell setup². The SLRR method has two well decoupled steps: (1) formation of the epitaxial UPD layer under potential control and (2) surface-limited redox replacement of that UPD layer by a more noble metal at open circuit potential (OCP) i.e. electroless step. So far this method has been successfully applied in synthesis of functionalized Pt fuel cell catalysts and thin film growth³ using Cu UPD sacrificial metal.

In this work⁴ we explore deposition of Pt films obtained by SLRR of Pb UPD and compare the growth characteristics with the growth based on Cu UPD. We used OCP chronopotentiometry and electrochemical quartz crystal microbalance (EQCM) to follow displacement kinetics. The EQCM measurements show excess of Pt deposition that could be attributed to additional reduction power due to oxidative adsorption of OH_{ad} ⁵ taking place during Pt deposition or H-adsorption/ partial desorption⁶ expected to take place upon Pb UPD layer formation. This surprising result has motivated the present work where we examine the growth of Pt films based on SLRR of adsorbed H i.e. H-UPD layer.

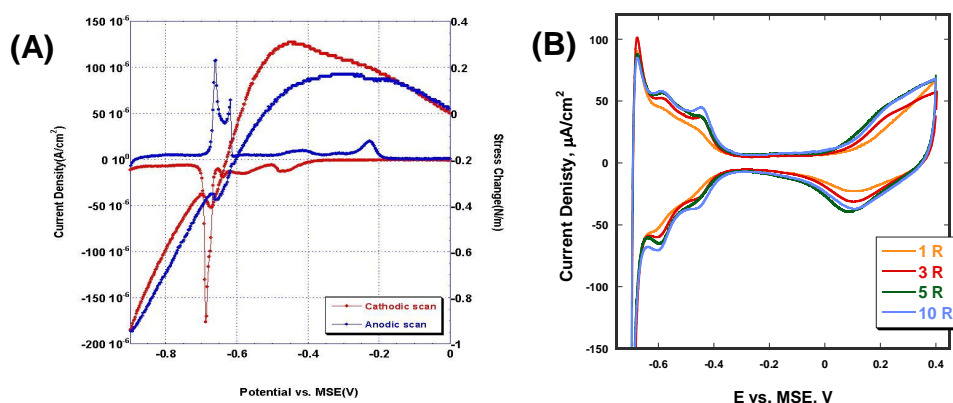


Figure (A) Cyclic voltammetry of Pb UPD and corresponding surface stress evolution in 10^{-3} M $\text{Pb}(\text{ClO}_4)_2 + 0.1$ M HClO_4 , scan rate 20mV/s. (B) Cyclic voltammetry in 0.1 M H_2SO_4 (50 mV/s) on Pt films deposited after different number of replacements using SLRR of Pb-UPD on Au-films

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