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Deposition of Pt onto Pd thin films via Surface Limited Redox Replacements with Hydrogen

Ben Rawlings & Natasa Vasiljevic
School of Physics, University of Bristol, Bristol, BS8 1TL, UK,
e-mail: ben.rawlings@bristol.ac.uk

Our research has focused on the deposition of Pt using the Surface Limited Redox Replacement (SLRR) method. The SLRR method uses an underpotentially deposited layer (UPD) of Cu or Pb as a sacrificial layer which is replaced in a redox reaction by Pt [1]. A recent area of interest is the use of H as the mediator in place of the Cu or Pb. This method has shown the potential to also produce epitaxial Pt films and eliminate the incorporation of Cu and Pb from the final deposits. This talk will focus on a further extension of the method which introduces a Pd substrate for the Pt deposition.

In recent years the study of H adsorption on Pd surfaces has been made possible by the use of Pd thin films or so called limited volume electrodes [2]. Thin Pd films deposited on Au have shown a delayed onset of H absorption allowing the H adsorption to be observed during potential sweeps. For the SLRR depositions of Pt this control of H location is used to control the deposition of Pt upon Pd thin films.

Pseudomorphic Pd films electrodeposited [3] on Au films, with a pronounced (111) crystallographic orientation, have been used as substrates. The H electrosorption characteristics of Pd films of different thicknesses (2ML-10ML) have been determined in 0.1M sulphuric and perchloric acid solutions. These measurements were used to determine the SLRR replacement protocols for Pt deposition. The quality of the Pt films deposited using absorbed and adsorbed H on Pd films as determined by electrochemical techniques and scanning probe microscopy (AFM, STM) will be presented.

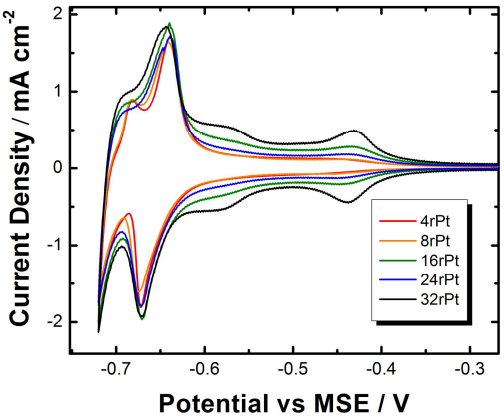

Fig 1 – Cyclic voltammetries (50mV/s) in 0.1M H_2SO_4 of 10ML Pd films following between 4 and 32 replacement cycles of H with Pt.

References:
[1] M Fayette et al, "From Au to Pt via Surface Limited Redox Replacement of Pb UPD in One-Cell Configuration" Langmur **27,** 5650- 5658 (2011);
[2] M Łukaszewski, A Czerwiński, "The method of limited volume electrodes as a tool for hydrogen electrosorption studies in palladium and its alloys" J Solid State Electrochem **15**, :2489–2522 (2011);
[3] L.A Kibler et al, "Initial stages of Pd deposition on Au(hkl) Part I: Pd on Au(111)" Surface Science **443**, 19-30 (1999);