Abstract #2348, 224th ECS Meeting, © 2013 The Electrochemical Society

Exploiting the H-sorption properties of Pd for the epitaxial deposition of Pt

Ben Rawlings and Natasa Vasiljevic
School of Physics, University of Bristol
H.H. Wills Physics Laboratory, Bristol BS8 1TL, UK
ben.rawlings@bristol.ac.uk

The formation of new, low cost Pt catalysts with much higher activity and stability than those currently used is very active area of research, essential for the development of future fuel cell technology. Thin film Pt overlayers and Pt clusters on different noble metal surfaces as well as Pt-X nano-alloys, present three general types of bimetallic systems currently attracting a lot of attention. These bimetallic systems have the advantage of a low Pt content and benefit from a combination of nanoscale structure effects and electronic modifications to the Pt structure caused by the second metal.

Highly active strained Pt-monolayer catalysts[1] are one example and their development is based on a recently introduced deposition method called Surface Limited Redox Replacement (SLRR).[2] The SLRR method is based on a surface limited redox (galvanic) replacement of a sacrificial underpotentially deposited (UPD) metal monolayer by a more noble metal such as Pt.[2] Several research groups pursued and demonstrated successful deposition of epitaxial Pt monolayes as well as 2D films using Cu UPD and Pb UPD.[3-6] Moreover our group recently extended SLRR approach to grow Pt films using a H UPD layer adsorbed on Pt.[7]

In this work we used a similar approach to demonstrate the deposition of Pt on Pd thin films using electrosorbed H as the sacrificial "layer" in the galvanic replacement protocol. Ultra thin Pd films (2-10 ML) were electrodeposited on Au(111) films from the 10^{-1} M H_2SO_4 + 10^{-4} M H_2PdCl_4 solution at constant potential of 0.27V vs SCE.[8] The thickness of deposited Pd was charge controlled taking in consideration that a monolayer of Pd on Au(111) has an equivalent charge of 440 $\mu C/cm^2$. The quality of the deposited epitaxial Pd films was confirmed by cyclic voltammetry (CV) in 10^{-1} M H_2SO_4 solution that showed characteristic potentially separated process of H adsorption and H-absorption on films of thicknesses above 2ML. The amount of H absorbed and adsorbed is determined and can be controlled by the thickness of Pd film.

Pt deposition was conducted via galvanic replacement of H in 10^{-1} $NaClO_4$ + 10^{-3} M $HClO_4$ + 5×10^{-4} M K_2PtCl_4 solution. Elementary steps of H-sorption, by potential impulse for 1s at the potential of -0. 75V vs MSE, were followed by the redox replacement of H by Pt at OCP until the potential reached -0.2V (H-free surface). The deposited Pt films of different thicknesses were characterized electrochemically using cyclic voltammetry in 10^{-1} M H_2SO_4. As shown in Figure 1A and 1B, Pt films grown by different number of replacement cycles on Pd films of 2ML and 10 ML thickness show distinctly different behavior. Films grown on 2ML Pd have all the characteristics of typical Pt behavior. In contrast, Pt films on 10 ML Pd exhibit H- sorption behavior with features of both adsorbed and absorbed H similar to Pd. Moreover the H-absorption peaks are more reversible yet have a charge similar to that of the underlying Pd film. The results are intriguing as the surface composition analysis carried out by X-ray Photoelectron Spectroscopy (XPS) suggests a Pt-covered surface layer.

An Electrochemical Quartz Crystal Microbalance (EQCM) was used to determine the Pt deposition yield in each replacement step, Figure 1 insets; this showed the expected stoichiometric Pt(II)-H exchange ratio (1:2). Furthermore, Pt films morphology and roughness evolution was investigated electrochemically and through Scanning Tunneling Microscopy. Finally, catalytic activity in formic acid oxidation of Pt-Pd films was examined and compared to recent work on highly active Pt decorated Pd nanoparticles.[9]

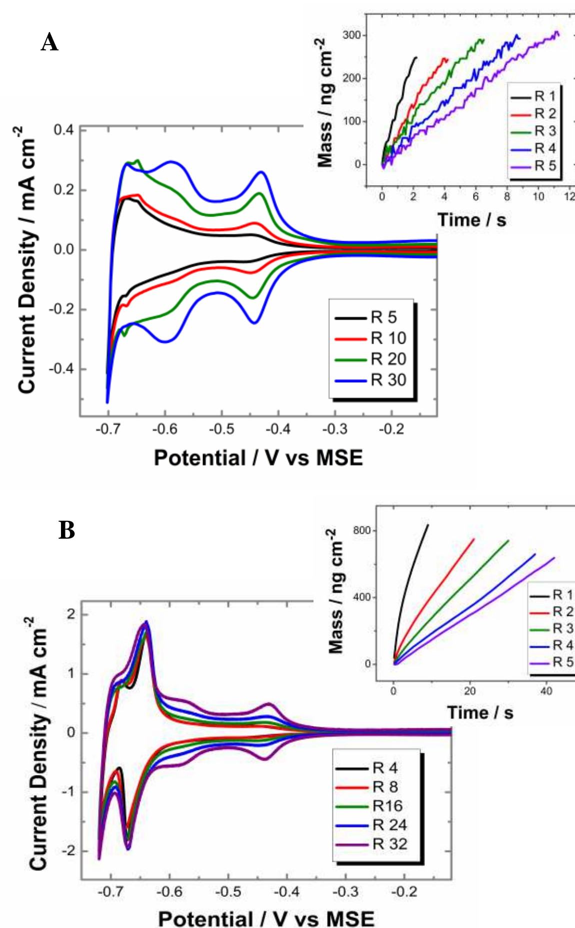

Figure 1. Cyclic voltammetry of Pt films deposited using H-absorbed on (A) 2ML and (B) 10 ML Pd films on Au in 10^{-1} M H_2SO_4. Scan rate 50 mV/s. Inset shows EQCM results for the increase of mass due to the galvanic replacement of H during 5 successive replacement events.

Reference

1.R.R. Adzic, J. Zhang, K. Sasaki, M.B. Vukmirovic, M. Shao, J.X. Wang, A.U. Nilekar, M. Mavrikakis, J.A. Valerio and F. Uribe, Top Catal, **46** (3-4), 249-262, (2007).
2.S.R. Brankovic, J.X. Wang and R.R. Adzic, Surf Sci, **474** (1-3), L173-L179, (2001).
3.M.F. Mrozek, Y. Xie and M.J. Weaver, Anal Chem, **73** (24), 5953-5960, (2001).
4.Y.G. Kim, J.Y. Kim, D. Vairavapandian and J.L. Stickney, J Phys Chem B, **110** (36), 17998-18006, (2006).
5.M. Fayette, Y. Liu, D. Bertrand, J. Nutariya, N. Vasiljevic and N. Dimitrov, Langmuir, **27** (9), 5650-5658, (2011).
6.N. Jayaraju, D. Vairavapandian, Y.G. Kim, D. Banga and J.L. Stickney, J Electrochem Soc, **159**, D616-D622, (2012).
7.J. Nutariya, M. Fayette, N. Dimitrov and N. Vasiljevic, Electrochim Acta, **DOI 10.1016/j.electacta.2013.01.052**, (2013).
8.M. Baldauf and D.M. Kolb, Electrochimica Acta, **38** (15), 2145-2153, (1993).
9.X.-M. Wang, M.-E. Wang, D.-D. Zhou and Y.-Y. Xia, Phys. Chem. Chem Phys., **13**, 13594-13597, (2011).