A simple experimental protocol for platinum deposition on gold electrodes

For many electrochemical applications, the platinum group metals (PGM) are the most active electrocatalysts available. Amongst these metals, platinum itself displays the highest catalytic activity for a wide range of electrochemical processes and its exceptional properties are well documented in the literature. Unfortunately, the use of platinum as an electrode material has two major drawbacks related to one another: its scarcity and its price. These disadvantages constitute an important obstacle to the introduction of PGM dependent applications like DMFCs and PEMFCs (Direct Methanol and Proton Exchange Membrane Fuel Cells).

To solve this issue, several solutions have been proposed. One alternative consists in synthesizing new materials that are able to mimic the electrochemical properties of the PGM. Another approach aims at drastically reducing the amount of platinum used, either by alloying platinum with other metals or by dispersing small platinum particles, in the order of a few nanometers, on a technologically relevant substrate.

Recent advances in material science have highlighted the existence of so-called electronic effects that can significantly enhance the activity of bi-metallic systems. The promoting effect of a gold substrate on the electrocatalytic activity of platinum nanoparticles has been discussed in several recent papers. In most cases, a dramatic increase in activity, attributed to the gold substrate, was reported for important reactions such as the oxidation of CO and the reduction of oxygen.

This application note describes a very simple procedure that can be used to produce small deposits of platinum on a gold substrate. This simple procedure is based on an electrochemical process known as *displacement deposition*, during which the deposition of a noble metal occurs by the oxidation of a precursor metal adlayer deposited on the substrate, at open-circuit potential. In this application note, the spontaneous oxidation of a copper adlayer by hexachloroplatinate (IV) ions has been used to produce small deposits of platinum on a gold electrode, according to:

$$2Cu/Au + PtCl_6^{2-} \rightarrow Pt/Au + 2Cu^{2+} + 6Cl^{-}$$

Experimental

All the measurements were performed using a microAutolab 3 in combination with the GPES 4.9.005 software. A three electrode electrochemical cell, with a KCl saturated Ag/AgCl reference electrode and a platinum grid counter electrode, was used. The working electrode was a polycrystalline gold electrode. The gold electrode was mechanically polished prior to each experiment, using sand papers and diamond paste. The electrode was sonicated after the polishing in water. Copper deposits were obtained from a 10 mM $CuSO_4$ in 0.1 M $HClO_4$ solution. All the solutions were deareated by bubbling nitrogen. The copper adlayers were deposited potentiostatically in the under-potential region (UPD). Open-circuit deposition of platinum was performed from a 1 mM H_2PtCl_6 solution. A diluted nitric acid solution, ca. 0.5 M was used to remove the residual copper after the displacement reaction. Characterization of the platinum modified gold electrode was done in 0.1 M $HClO_4$. All the potentials given in this application note are expressed relative to the RHE.

To perform the displacement deposition of platinum on gold, a precursor adlayer was deposited on the electrode. Copper was deposited in the UPD region, which limits the amount of copper to one monolayer. Fig. 1 shows a typical cyclic voltammogram recorded for copper deposition.

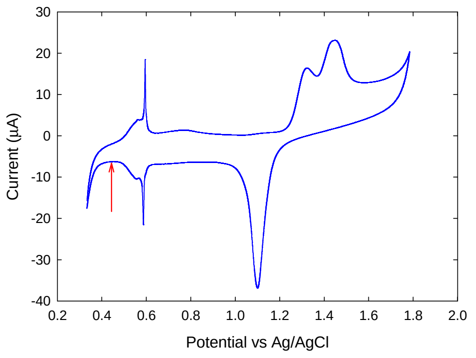

Figure 1 - Cyclic voltammogram for copper deposition on gold, recorded in 0.01 M CuSO4 in 0.1 M HClO4 at 50 mV/s.

The high-potential end of the cyclic voltammogram shown in fig. 1 corresponds to the formation and the reduction of gold oxides. The two sharp symmetric peaks in the low-potential end of the cyclic voltammogram correspond to the formation and the dissolution of the copper adlayer. Charge integration of both peaks indicate that the amount of copper on the gold electrode corresponds to a full monolayer. For the displacement deposition of platinum on gold, a potentiostatically deposited precursor copper adlayer was used. The deposition potential was 0.45 V (and corresponds to the red marker arrow in figure 1). The deposition time was 20 seconds. After the deposition of the copper adlayer, the electrode was rinsed and immersed in the hexachloroplatinic acid solution during 180 seconds, at open circuit. Thereafter, the electrode was rinsed and immersed into the diluted nitric acid solution for 10 seconds in order to remove residual copper from the surface. Finally, the platinum modified gold electrode was rinsed once more and was placed into an electrochemical cell for characterization in $HClO_4$.

Fig. 2 shows a typical cyclic voltammogram recorded in perchloric acid medium with the Pt/Au modified electrode. While the high-potential end of the curve does not deviate significantly from cyclic voltammogram displayed in fig. 1, the low potential-end of the curve shows a sharp cathodic peak around 0 V, attributed to the hydrogen UPD and the onset of hydrogen evolution. When the scanning direction is reversed a smaller anodic peak, related to the oxidation of adsorbed hydrogen, is recorded.

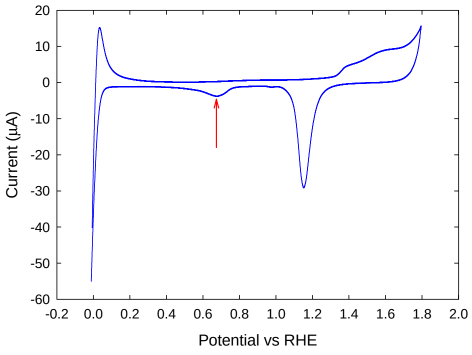

Figure 2 - Cyclic voltammogram recorded on a platinum modified gold electrode in 0.1 M HClO4 at 50 mV/s.

Fig. 2 also shows the presence of a small cathodic peak located around 0.8 V, which corresponds to the reduction of Pt-OH species formed during the potential cycling in the high potential region. Both the platinum oxide reduction peak and the hydrogen adsorption/evolution confirm the presence of platinum on the surface of the gold electrode. Moreover, the cyclic voltammetry displayed in fig. 2 is consistent with data reported in the literature.

References

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