

Application Area: Electrocatalysis

A Simple Experimental Protocol for Platinum Deposition on Gold Electrodes

Keywords

Electrodeposition; Platinum deposition; Gold electrode; Exchange reaction

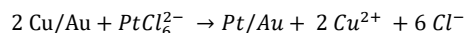
Summary

For many electrochemical applications, the Pt group metals (PGM) are the most active electrocatalysts available. Among these metals, Pt 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 each other: 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 were 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 Pt used, either by alloying platinum with other metals or by dispersing small Pt 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 an Au substrate on the electrocatalytic activity of Pt nanoparticles has been discussed in several papers. In most cases, a dramatic increase in activity, attributed to the Au 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 Pt on an Au 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 Cu adlayer by $PtCl_6^{2-}$ ions has been used to produce small deposits of Pt on a Au electrode:



1

Experimental and discussions

All the measurements were performed using a Metrohm Autolab PGSTAT204. A three electrode electrochemical cell, was used. A Ag/AgCl, saturated KCl, was the reference electrode, while a Pt sheet was the counter electrode. The working electrode was a polycrystalline Au electrode.

The Au electrode was polished prior to each experiment, using sand paper and diamond paste. After the polishing, the electrode was sonicated in water. Cu deposits were obtained from a 10 mM CuSO_4 in 0.1 M HClO_4 solution. All the solutions were deaerated by bubbling nitrogen. The Cu adlayers were deposited potentiostatically in the underpotential region (UPD). Open-circuit deposition of platinum was performed from a 1 mM hexachloroplatinic acid H_2PtCl_6 solution. A diluted 0.5 M HNO_3 solution was used to remove the residual Cu, after the displacement reaction. Characterization of the platinum modified gold electrode was done in 0.1 M HClO_4 . All potentials given in this application note are expressed relative to Ag/AgCl, satd. KCl reference electrode

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

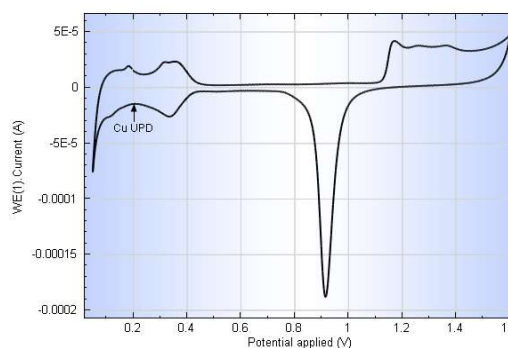


Figure 1 - Cyclic voltammogram for Cu deposition on Au, recorded in 0.01 M CuSO_4 in 0.1 M HClO_4 , 50 mV/s.

As shown in Figure 1, at the positive potentials, the oxidation of Au and the reduction of Au oxides take place.

The two sharp symmetric peaks in the low-potential end of the cyclic voltammogram correspond to the formation and the dissolution of the Cu monolayer. Charge integration of both peaks indicates that the amount of Cu on the Au electrode corresponds to a full monolayer.

For the displacement deposition of Pt on Au, the Cu adlayer was used as a precursor. The deposition potential was 0.2 V and corresponds to the arrow in Figure 1. The deposition time was 20 seconds. After the deposition of the Cu adlayer, the electrode was rinsed and immersed in the hexachloroplatinic acid solution for 180 s, at OCP. Thereafter, the electrode was rinsed and immersed in the diluted HNO₃ solution for 10 seconds in order to remove residual Cu from the surface. Finally, the Pt modified Au electrode was rinsed once more and was placed into an electrochemical cell for its characterization in HClO₄.

Figure 2 shows a typical cyclic voltammogram of the Pt/Au modified electrode recorded in HClO₄. While the positive end of the curve does not deviate significantly from the cyclic voltammogram displayed in Figure 1, at the negative end of the voltammogram, a sharp cathodic peak around -0.2 V can be seen. This is 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.

Also, a small cathodic peak located around 0.4 V can be discerned in the voltammogram shown in Figure 2. This corresponds to the reduction of the Pt oxide species formed during the potential cycling in the high potential region.

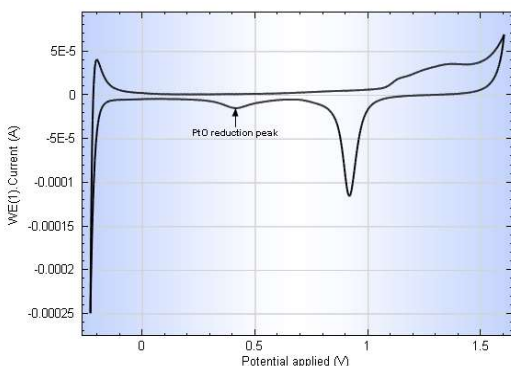


Figure 2 - Cyclic voltammogram recorded on a Pt modified Au electrode in 0.1 M HClO₄, 50 mV/s.

Both the Pt oxide reduction peak and the hydrogen adsorption/evolution confirm the presence of platinum on the surface of the Au electrode. Moreover, the cyclic voltammetry

displayed in Figure 2 is consistent with the data reported in the literature.

References

- K. Kusmierczyk, M. Lukaszewski, Z. Rogulski, H. Siwek, J. Kotowski, A. Czerwinski, Polish J. Chem. 76 (2002) 607
- S.R. Brankovic, J.X. Wang, R.R. Adžić, Surf. Sci. 474 (2001) L173

Date

May 2019

AN-EC-006

For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **www.metrohm.com/electrochemistry**.