

Formation of Au/Pd–Sn trimetallic particles onto vitreous carbon

L. A. Meier,^a J. Ferron,^b S. G. García^{a*} and D. R. Salinas^{a†}

The sequential deposition process of Pd and Sn on Au microcrystals, previously electrodeposited onto vitreous carbon (VC) was investigated in sulphuric acid solution by cyclic voltammetry and Auger electron spectroscopy (AES). Scanning electron microscopy was used to characterize Au deposits. The results reveal that the deposition of Pd and Sn is selective on the Au microcrystals, uniformly distributed on the VC surface, due to the strong interaction energy between the three metals. From the cyclic voltammetric and AES measurements in the VC/Au/Pd/Sn system, the existence of a Sn core–shell structure with Pd can be inferred. Similar voltammetric results were obtained for the VC/Au/Sn/Pd system, where in this case, the Pd adsorbed layer screened the Sn deposits on the VC/Au interface. However, the AES spectrum shows that Sn is still present on the surface, indicating that probably, the Sn deposits have diffused to the surface, or they are not completely covered by Pd. The VC/Au/Pd/Sn modified substrate appears as an interesting electrocatalyst material for the reduction of nitrate ions. Copyright © 2013 John Wiley & Sons, Ltd.

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Introduction

The formation of bimetallic or trimetallic particles distributed onto a conductor substrate is a method to obtain superficially modified electrodes that may have electrocatalytic properties for some reactions of technological interest. This is the case of the Au–Pd–Sn trimetallic system, which presents interesting properties for the electroreduction of nitrate ions.^[1]

In some cases, ultrathin metallic layers can be generated onto nano or microparticles potentiostatically formed, by underpotential deposition (UPD)^[2–4] or by spontaneous deposition using the so-called immersion technique.^[5] Rodes *et al.*^[6,7] studied the spontaneous adsorption of tin on polycrystalline and single-crystal gold surfaces by cyclic voltammetry and concluded that the deposition process could be explained by the adsorption of Sn^{II} species followed by a disproportionation reaction in which the product with the lower valency state is adsorbed. They indicated that the tin adlayers on the different gold single-crystal surfaces are strongly dependent on the solution pH and the superficial redox reaction undergone by the tin adatom is structure sensitive. Particularly, in the case of the Au(111) surface, these authors indicated that the adsorbed tin is directly oxidized to Sn^{IV} species. In addition, the adsorption of tin could change the Au(111) surface by the formation of a Sn–Au surface alloy.^[7] This was also suggested, from *in situ* scanning tunneling microscopy experiences using single-crystal substrates.^[8]

Some studies indicated that the UPD process of Pd on Au single crystals begins with the adsorption of [PdCl₄]^{2–} complex.^[9–11] This also occurs during the spontaneous deposition of Pd where the complex can be reduced with a proper polarization routine in a free Pd(II) ions solution.

In the present work, the sequential deposition of Au, Pd and Sn on vitreous carbon (VC) was investigated by cyclic voltammetry. Scanning electron microscopy (SEM) was used to characterize the Au microcrystals, and the formation of Pd–Sn bimetallic deposits obtained onto the VC/Au modified surface was analysed by Auger

electron spectroscopy (AES). Cyclic voltammetry was also used to evaluate qualitatively the electrocatalytic properties of the modified surface towards the reduction of nitrate ions.

Experimental

VC rods sealed into a Teflon holder with a diameter of 3 mm were used as working electrodes. The substrate surface was mechanically polished with diamond paste of decreasing grain size down to 0.25 μm.

The solutions used throughout the study were prepared from suprapure chemicals (Merck, Darmstadt) and fourfold distilled water. A 0.5 M H₂SO₄ solution was used as test electrolyte. The solutions employed for metal deposition were: 1 mM HAuCl₄ + 50 mM H₂SO₄, 1 mM SnSO₄ + 0.5 M H₂SO₄ and 0.23 mM PdCl₂ + 6 mM HCl + 0.1 M H₂SO₄. In order to evaluate the electrochemical reduction of nitrate ions, 0.1 M NaNO₃ + 0.1 M Na₂SO₄ and 0.1 M Na₂SO₄ solutions were used.

Conventional electrochemical studies were performed in standard three-electrode electrochemical cells. The counter electrode was a platinum sheet (1 cm²), and the reference electrode was a Hg/Hg₂SO₄/K₂SO₄ saturated electrode (SSE). All potentials in this study are referred to the SSE. The measurements

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were carried out with an EG&G Princeton Applied Research Model 273A potentiostat–galvanostat.

SEM studies were performed using a JEOL 35CF microscope, with an accelerating voltage of 15 KeV.

Elements concentration profiles were carried out in an Auger electron spectrometer, PHI SAM 590A, equipped with a single cylindrical mirror analyzer working in the 10^{-10} Torr range. The AES spectra were acquired in differentiated way exciting with 3 keV, 1 μ A electron beam.

Results and discussion

The SEM image in Fig. 1 shows the distribution of Au particles deposited on VC from a 1 mM AuHCl₄ + 0.05 M H₂SO₄ solution using the double-potential pulse technique. This electrochemical technique is useful for controlling size, density and distribution of the metal deposits varying the polarization conditions. After an initial potential of 0.8 V, a nucleation pulse of -0.15 V during 0.25 s was first applied, followed by a growth pulse of 0.1 V during 20 s. With these chosen parameters, the particle size distribution is homogeneous, and the particles (about 50–150 nm in diameter) are distributed over the entire surface.

The Pd deposits were obtained following a similar procedure found in the literature.^[1] The VC/Au modified surface was immersed in a 0.23 mM PdCl₂ + 6 mM HCl + 0.1 M H₂SO₄ deaerated solution under open-circuit conditions during 15 min, to facilitate the adsorption of the [PdCl₄]²⁻ complex. Then, the electrode was rinsed with water, transferred to a 0.5 M H₂SO₄ solution and polarized at $E = -0.3$ V for 90 s, in order to reduce the palladium complex. This procedure was repeated three times. Subsequently, the electrode was immersed in a 1 mM SnSO₄ + 0.5 M H₂SO₄ solution, during 1 h, to generate the Sn deposits spontaneously. The electrode thus prepared is denoted as the VC/Au/Pd/Sn electrode.

The cyclic voltammogram obtained for this modified surface, in the 0.5 M H₂SO₄ solution, is shown in Fig. 2. The response of the VC/Au and VC/Au/Pd surfaces were also included for comparison. The scan was started at $E = -0.5$ V towards the cathodic direction. It is clearly observed that the deposition of Sn on the VC/Au/Pd modified surface is evidenced by the inhibition of the H₂ evolution reaction at the more negative end. During the anodic sweep, a broad peak was identified in the potential range $-0.4 \leq E/V \leq 0.0$, corresponding to the Sn desorption. This result is consistent with those obtained by Rodes *et al.* for the deposition

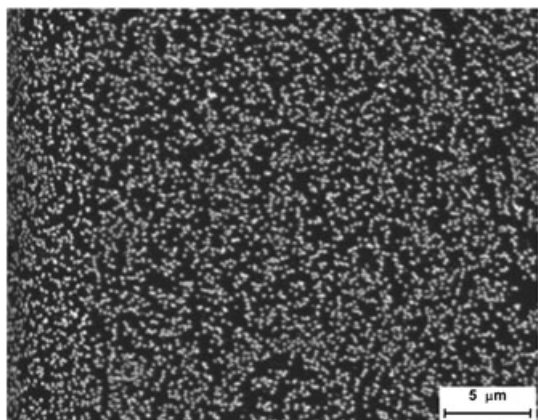


Figure 1. SEM image of Au particles electrodeposited onto VC. Electrolyte: 1 mM AuHCl₄ + 0.05 M H₂SO₄.

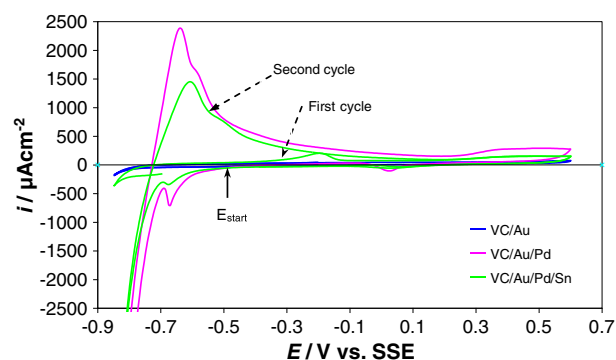


Figure 2. Cyclic voltammograms of VC/Au and VC/Au/Pd before and after the immersion in 1 mM SnSO₄ + 0.5 M H₂SO₄ solution for 1 h. Electrolyte: 0.5 M H₂SO₄, $|dE/dt| = 50$ mV s⁻¹.

of Sn on polycrystalline Au.^[6] Once the tin adlayer has been removed, in a second potential cycling, the typical hydrogen adsorption peak on Pd is recorded at $E \approx -0.65$ V, previous to the onset of hydrogen evolution indicating the presence of Pd exposed on the surface. On the reverse scan and after the anodic peaks related to the hydrogen oxidation and desorption processes, an anodic current density peak is observed at potentials positive to $E > 0.3$ V, related to the Pd deposit oxidation. This result clearly shows that the Sn present on the surface covered the Pd deposit, forming a core–shell structure. No characteristic peaks for the VC/Au system were found in the potential range considered.

In order to take more insight about the behaviour of Pd–Sn bimetallic deposits, a VC/Au/Sn/Pd modified surface was prepared with the procedure previously described, inverting the deposition order for Sn and Pd. In this case, by cyclic voltammetric measurements, the presence of Sn after depositing Pd on VC/Au/Sn modified surface could not be observed. The voltammetric response was similar to that obtained for the VC/Au/Pd electrode (Fig. 2), and it is in agreement with that reported for the Au(hkl)/Sn/Pd interfaces.^[12] The presence of Pd on the Au(hkl)/Sn/Pd modified substrate is clearly verified by the significant current increase for the hydrogen evolution reaction at the cathodic end. Furthermore, no peaks were observed in the voltammogram that could indicate the presence of Sn on the surface. These results suggest that the Pd adlayer covers the Sn deposits previously formed or even that, due to a displacement effect, these deposits are oxidized during the spontaneous reduction of Pd. The occurrence of one or another process cannot be deduced using only voltammetric techniques. Anyway, if the amount of Sn exposed on the surface is small, the corresponding peaks in the voltammogram could not be appreciated.

Figures 3 and 4 show the evolution of the Auger spectra for VC/Au/Pd/Sn and VC/Au/Sn/Pd systems and the variation of concentration of the various elements, to different times of bombardment (t_b) with argon ions of 4 keV. In both samples, the appearance of the Au peak at low energy (70 eV) was observed, which grows in intensity for longer bombardment times. The C is always visible, so the metal coverage is not complete on the VC surface. The spectrum for the VC/Au/Pd/Sn system (Fig. 3a) shows important peaks of Sn and O; the latter may be due to the existence of surface oxides. The Pd signal is weaker, which may indicate that the surface is partially covered by the above elements. The peak of Sn tends to disappear, while the Pd signal initially increases and then decreases with

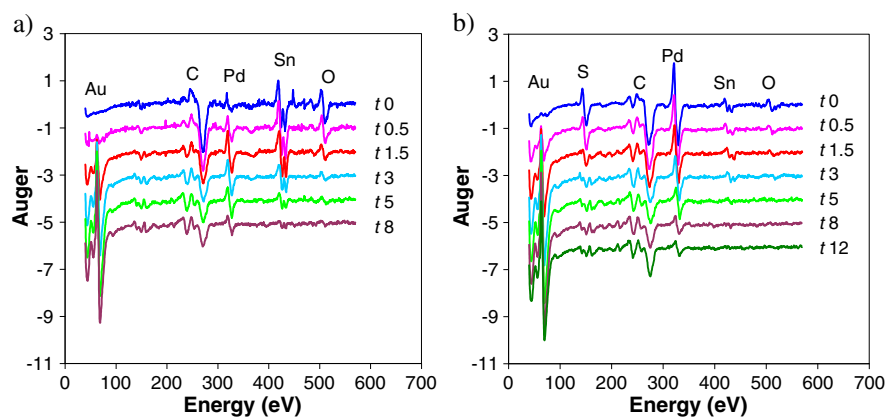


Figure 3. Auger spectra for the modified surfaces: a) VC/Au/Pd/Sn, b) VC/Au/Sn/Pd.

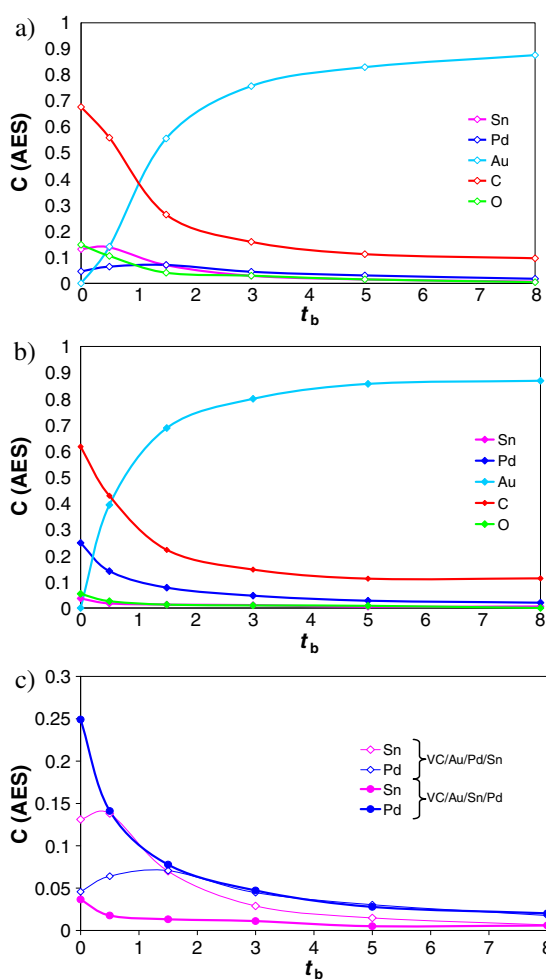


Figure 4. Auger concentration profiles of the modified surfaces: a) VC/Au/Pd/Sn, b) VC/Au/Sn/Pd, c) comparison of the variations in concentration of Sn and Pd in each case.

increasing bombardment time. This is consistent with the sequence in which the metals were deposited. This is also observed in the variation of concentration of the various elements to different times of bombardment (Fig. 4a). The spectrum for the VC/Au/Sn/Pd system shows a large peak of Pd and a smaller one for the Sn, indicating a more concentration of Pd on the surface

(Figs. 3b and 4b). Both peaks decrease simultaneously suggesting that either the Sn deposits have diffused to the surface, or they are not completely covered by Pd. Moreover, the presence of an S peak was observed, which could be related to the existence of adsorbed sulphate ions. The fast decrease of the C signal at the beginning of the depth profile is due to the removal of the adsorbed carbon species. Taken into account that, for 3 KeV impinging electrons, the relative elemental sensitivity factors^[13] for Pd (0.80) and Sn (0.85) are practically identical, all our conclusions can be reached from a direct comparison of peaks heights in the differentiated spectrum. Figure 4c shows a comparison of the variation of Sn and Pd concentration on both modified surfaces.

In order to examine the electrocatalytic effect for the reduction of nitrate ions, Fig. 5 shows cyclic voltammograms of the systems VC/Au, VC/Au/Pd and VC/Au/Pd/Sn in 0.1M NaNO₃ + 0.1M Na₂SO₄. The cyclic voltammograms in 0.1M Na₂SO₄ were also presented. The VC/Au modified with Pd and Sn deposits were obtained by immersing the electrode during 5 min and 30 s in the respective solutions. In the case of the VC/Au electrode, a slight current increase in the cathodic limit related to the hydrogen evolution reaction was observed, which started at $E < -1.7$ V and was relatively similar in both solutions, indicating a poor catalytic activity for the nitrate reduction. The presence of Pd in the VC/Au/Pd substrate resulted in a significant increase in the reduction current corresponding to the hydrogen reaction but an increase even more important related to the reduction of

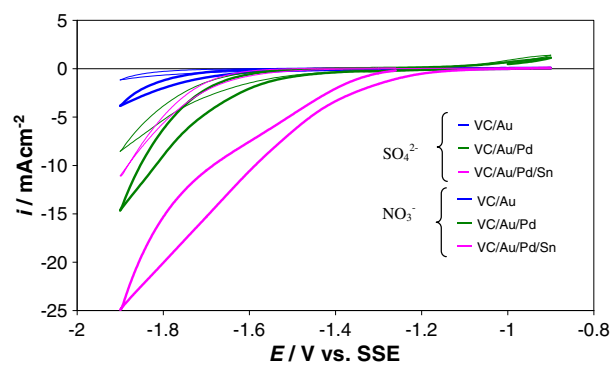


Figure 5. Comparison of the voltammetric response of the VC/Au, VC/Au/Pd and VC/Au/Pd/Sn systems in 0.1 M Na₂SO₄ and 0.1 M NaNO₃ + 0.1 M Na₂SO₄ solutions. $|dE/dt| = 50 \text{ mV s}^{-1}$.

nitrate ions was observed. Also, this current increase started at potentials slightly more positive ($E = -1.4$ V) than those registered for VC/Au substrates. Taking into account that the hydrogen evolution reaction is an unwanted secondary reaction, which would produce a decrease in efficiency for the nitrate reduction reaction, the VC/Au/Pd/Sn modified surface was tested. Hydrogen evolution reaction occurred at more negative potentials ($E = -1.55$ V) on this modified surface than on the VC/Au/Pd substrate, suggesting that hydrogen adsorption might be better facilitated at the latter than at the VC/Au/Sn/Pd substrate. It is important to note that the presence of Sn on the surface is responsible for the potential displacement at which the hydrogen evolution reaction starts due to its poor catalytic activity for this reaction. However, the behaviour of the VC/Au/Pd/Sn modified substrate in the presence of nitrate ions led to interesting results. An increase in the cathodic current at more positive potentials ($E = -1.1$ V) was observed which was not associated with the hydrogen evolution reaction and indicated an enhancement of the catalytic activity for the reduction of nitrate ions. These results are in accordance with those obtained by Shimazu *et al.* for the Pd and Sn deposits on gold films.^[1] Because VC/Au and VC/Au/Pd electrodes without Sn deposits have no significant activity, the increase in the activity is due to the synergetic effect of Pd and Sn.

Conclusions

Sn and Pd deposits were prepared onto Au microparticles previously electrodeposited on VC, through the immersion technique, followed by an appropriate polarization routine for the case of Pd. The voltammetric behaviour of the VC/Au/Pd/Sn modified surface and the corresponding AES analysis indicated that the Sn adlayer formed a core-shell structure with the Pd deposits.

In the VC/Au/Sn/Pd system, the Pd adsorbed layer screened the Sn deposits on the VC/Au modified surface. However, in this case, the AES spectrum shows that Sn is still present on the surface, indicating that probably, they have diffused to the

surface, or they are not completely covered by Pd. Further work is required in order to determine the existence of a Sn-Pd surface alloy which is now in progress.

In both systems, the Au particles were not detected on the surface, indicating that the Pd or Sn ultrathin layers on the surface are most likely formed selectively on the Au microcrystals.

The VC/Au/Pd/Sn modified substrate can be used as electrocatalyst material because it exhibits a high activity for the reduction of nitrate ions due to a synergetic effect between the metal components.

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