The electrodeposition and electrocatalytic properties of copper–palladium alloys

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Abstract

The codeposition of copper and palladium from solutions of CuSO₄ and PdSO₄ in 0.6 M HClO₄ is investigated using microdisc voltammetry. It is shown that good quality coatings of CuPd may be deposited and the composition may be controlled either through the deposition potential or the Cu(II)/Pd(II) ratio in solution. While the deposits seem to be amorphous and the copper can be dissolved anodically, the voltammetry indicates that the palladium stabilises the copper to dissolution. The CuPd alloys are effective catalysts for nitrate reduction in alkaline media.

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1. Introduction

While alloys are routinely electroplated [1,2], the electrodeposition of CuPd alloys has received little attention [3–5]. This is surprising since CuPd alloys are attracting interest as hydrogen transport membranes [6–8], as materials with good corrosion resistance [9] and as catalysts, for example, for the liquid phase reduction of nitrate [10]. In addition, various Pd/Cu surfaces (although not alloys) have been demonstrated as effective electrocatalysts for the reduction of alkyl halides [11] as well as the cathodic reduction of nitrate [12–14]. This paper therefore reports a study of the electrodeposition of CuPd alloys plated from simple, non-complexing aqueous acid media and also some of their electrochemical properties.

2. Experimental

Perchloric acid (Fisher, 60%), palladium(II) sulfate dehydrate (Alfa Aesar, 99%) and copper(II) sulfate pentahydrate (BDH, AnaLaR®) were all used as received. All aqueous solutions were freshly prepared using deionised water from a Whatman Analyst water purifier system. The glassware used was soaked for several hours in a Decon/deionised water solution and washed thoroughly with deionised water prior to use.

All electrochemical experiments were carried out using a laboratory built PC controlled potentiostat/galvanostat and two-electrode glass cell. The reference/counter electrode was a laboratory made Hg/Hg₂SO₄, saturated K₂SO₄ electrode (SMSE). This cell configuration works well with an aqueous electrolyte, conductivity 0.49 Ω⁻¹ cm⁻¹ and experimental currents generally well below 1 μA. Before each cyclic voltammogram and potential step experiment, the platinum microdisc electrodes (25 μm diameter), made by sealing microwires into soda glass, were polished with successively finer grades of alumina/water slurries (alumina powder: 1.0, 0.3 and 0.05 μm on a Microcloth®, Buehler) and rinsed well with water.

All voltammograms were recorded in a small glass, three-necked, pear-shaped cell in a Faraday cage. The voltammetry was carried out at room temperature after the solution had been thoroughly deoxygenated with a fast stream of nitrogen and a stream of nitrogen was passed over the electrolyte surface during experiments.
The morphology of the electrodeposits and their composition were examined using an environmental scanning electron microscope (Philips model XL30 ESEM) incorporating an energy dispersive X-ray (EDX) unit and software for elemental analysis. To confirm the uniformity of composition, multiple EDX spectra were recorded at different points over the surface.

3. Result and discussion

3.1. Electrodeposition from 0.6 M HClO₄

As preliminary experiments, the voltammetry of the Pt microelectrodes was investigated in solutions containing only a single metal ion. Fig. 1 illustrates the results with a 25 μm diameter Pt microdisc electrode. With the 5 mM CuSO₄ + 0.6 M HClO₄ solution, curve (a), the deposition of copper commences at \(-0.7\) V vs the Hg/Hg₂SO₄ reference electrode and a well formed reduction wave is observed although with a sloping limiting current density plateau; the limiting current density is \(\sim 6\) mA cm\(^{-2}\) corresponding to a diffusion coefficient for Cu(II) of \(6 \times 10^{-9}\) cm\(^2\) s\(^{-1}\). The reverse scan shows significant hysteresis consistent with the metal deposition reaction involving nucleation as well as growth of the copper layer and deposition continues to \(-0.46\) V. Immediately positive to this potential, copper dissolution is seen as a sharp stripping peak. There is a good charge balance between that for copper dissolution and for copper deposition confirming that there are the only processes occurring in the potential range employed. With the 5 mM PdSO₄ + 0.6 M HClO₄ solution, curve (b), palladium deposition is seen as a well formed reduction wave with a defined limiting current density plateau. Palladium deposition commences at \(-0.40\) V vs the Hg/Hg₂SO₄ reference electrode and the reverse scan again shows substantial hysteresis with deposition continuing to \(-0.10\) V. In contrast to copper, however, there is no peak for palladium dissolution although small features for surface oxidation and reduction (on a second cycle) are seen at \(+0.4\) and \(+0.1\) V, respectively. As expected, the limiting current density for palladium deposition is very similar to that for copper deposition with the same metal ion concentrations. If the negative potential limit is extended, even to \(-0.65\) V, a large current density is observed for hydrogen absorption into the palladium lattice and the reverse scan shows a sharp, symmetrical peak for the desorption reaction at \(E_p = -0.56\) V. It is clear that in experiments with only one metal ion in solution, the deposition of palladium occurs at potentials well positive to those essential to initiate copper deposition, at least on the timescale of the voltammetry, although copper deposition is thermodynamically possible close to the potential where palladium deposition occurs (as seen from the scan back towards more positive potentials).

Fig. 2 reports a cyclic voltammogram for the solution containing both 5 mM Cu(II) and 5 mM Pd(II) in 0.6 M HClO₄ at the Pt microdisc electrode. The forward scan shows at least two cathodic waves positive to \(-0.80\) V, with deposition commencing close to \(-0.40\) V and the limiting current density negative to \(-0.60\) V having the value expected for the deposition of both copper and palladium at a mass transport controlled rate; it should be noted that this limiting current density is reached at a potential where the voltammogram for the solution containing only Cu(II) shows the absence of copper deposition during the forward scan. The further increase in current density negative to \(-0.70\) V is associated with proton reduction. The reverse scan shows substantial hysteresis over the whole potential range where metal deposition is to be expected and metal deposition continues to at least \(-0.20\) V. Although the negative limit for the voltammogram of Fig. 2 is \(-0.80\) V, the reverse scan does not show large anodic peaks that can be assigned to the desorption of hydrogen from the metal lattice. Hence unlike palladium itself, the CuPd does not seem

![Fig. 1. Cyclic voltammograms for a Pt microdisc electrode (diameter 25 μm) in solutions of (a) 5 mM CuSO₄ and (b) 5 mM PdSO₄, both also containing 0.6 M HClO₄. Potential scan rate 10 mV s\(^{-1}\).

![Fig. 2. Cyclic voltammograms for a Pt microdisc electrode (diameter 25 μm) in a solution containing 5 mM CuSO₄ + 5 mM PdSO₄ + 0.6 M HClO₄. Potential scan rate 10 mV s\(^{-1}\).]
to be absorbing hydrogen, at least within this potential range. Also, surprisingly, there is no stripping peak for the reoxidation of the copper but at more positive potentials there are features that might be assigned to the surface oxidation and reduction of palladium. The interpretation of the absence of anodic peaks is, however, complicated by the possibility that the composition of the metal deposited is likely to change with potential, leading to a deposit with a composition that varies through its thickness. Certainly, the form of the reverse scan depends on the negative potential limit (see later).

Voltammograms were also recorded for two other solution compositions. Curve (b) in Fig. 3 reports the response for a solution, 15 mM Cu(II) and 5 mM Pd(II) in 0.6 M HClO₄ at the Pt microdisc electrode. Again, cathodic current is observed negative to −0.40 V with three reduction waves prior to the limiting current density negative to −0.70 V. The total limiting current density is larger than for the solution containing 5 mM Cu(II) and 5 mM Pd(II), curve (a), and close to that expected for a total metal ion concentration of 20 mM. For the solution 5 mM Cu(II) and 15 mM Pd(II) in 0.6 M HClO₄, only a single reduction wave is observed and its limiting current density has the expected value for 20 mM metal ion. Certainly, proton reduction shifts to less negative potentials with an increasing Pd(II)/Cu(II) ratio in solution and the proton reduction currents become large negative to −0.60 V for the 5 mM Cu(II) and 15 mM Pd(II) solution. With the negative potential limit of −0.75 V, only the solution containing 15 mM Cu(II) and 5 mM Pd(II) showed substantial anodic peaks that could be attributed to the dissolution of copper.

In order to obtain more uniform deposits, a series of electrodepositions were carried out with Pt microdiscs at constant potential and these were followed by SEM/EDX. The experiments were carried out as a function of the deposition potential and the Cu(II)/Pd(II) ratio in the 0.6 M HClO₄ solution. Fig. 4 shows a scanning electron micrograph of the layers produced by electrodeposition at −0.50 V vs the Hg/Hg₂SO₄ (total charge density 1.4 C cm⁻²) from a solution containing 5 mM Cu(II) and 5 mM Pd(II). It can be seen that the deposit is rather smooth and uniform with only a minor edge effect. Layers could be formed at all potentials negative to −0.40 V and from all the solution compositions studied. The layers were generally smooth and uniform although there was a trend to roughness and dendritic growth at the perimeter of the microdiscs at the more negative potentials. For each of the deposits, EDX analysis was carried out at several points over the surface in order to confirm that the compositions of the deposits were uniform and the elemental compositions are reported in Table 1. As expected, the copper content in the deposit increased with the Cu(II)/Pd(II) ratio in the solution. The variation of the deposit composition with deposition potential is more complex. Over the range −0.40 to −0.50 V, copper is the major element in the deposit and this is contrary to the expectation based

**Fig. 3.** Linear potential scans for a Pt microdisc electrode (diameter 25 µm) in solutions (a) 5 mM CuSO₄ + 5 mM PdSO₄, (b) 15 mM CuSO₄ + 5 mM PdSO₄ and (c) 5 mM CuSO₄ + 15 mM PdSO₄ all also containing 0.6 M HClO₄. Potential scan rate 10 mV s⁻¹.

**Fig. 4.** SEM images (a) top view and (b) side view with sample at 65.5°, of a CuPd layer deposited at −0.50 V vs SMSE onto a Pt microdisc electrode (diameter 25 µm) in a solution containing 5 mM CuSO₄ + 5 mM PdSO₄ + 0.6 M HClO₄. Deposition charge 1.4 C cm⁻². Composition by EDX: 82 at.% Cu/18 at.% Pd.
on the voltammetry of the single ions clearly showed that Pd(II) reduces at a less negative potential and nucleation of the copper phase was unlikely at these potentials. On the other hand, the reverse scan of the voltammogram for Cu(II) alone in Fig. 1 shows that copper deposition is favourable at $-0.46 \text{ V}$ and the formation of a CuPd alloy will shift this potential further positive. Such reversals in deposition potentials with electrolytes containing two electroactive metal ions are, however, not uncommon [15] and have been termed ‘anomalous codeposition’ [16]. Moreover, palladium centres are known to have a strong catalytic effect in electroless copper deposition [17–19]. It is also clear that over this range, the copper content increases as the potential is made more negative; this is largely due to an increase in the rate of reduction of Cu(II) with overpotential. Negative to $-0.50 \text{ V}$, the trend reverses and the palladium content increases as the potential is made even more negative. This will be partially due to the mass transport limitation on the availability of Cu(II) at the surface during the deposition. On the other hand, the voltammetry of the solutions clearly show more than one wave in this potential region and this implies different electrode reactions, perhaps the formation of particular CuPd phases.

Deposition of the alloys were also carried out onto gold coated glass slides and the deposits were examined by X-ray diffraction. But no patterns compatible with the presence of the intermetallic compound phases, PdCu, Pd$_3$Cu$_5$, PdCu$_3$ or PdCu$_5$ [20–22] were identified. This was also the case, when the deposits were subjected to a heat treatment, 573 K for 3 h. Hence, such experiments did not provide any evidence as to the structure of the alloy deposits; it remains uncertain whether the deposits are amorphous or polycrystalline, perhaps consisting of many single alloy micro- and/or nano-crystals.

In order to learn more about the alloy deposits, a further set of experiments were carried out with a Pt microdisc in the solution 5 mM Cu(II) and 5 mM Pd(II) in 0.6 M HClO$_4$. A CuPd layer was formed at a series of constant potentials for 30 s and then a potential scan between the deposition potential and +0.60 was recorded in the same solution. The transients during deposition are shown as Fig. 5a and the responses during the potential scans are shown in Fig. 5b for four deposition potentials and further data from the experiments are presented in Table 2. With a
deposition potential of $-0.40$ V, the current is very low throughout the 30 s although a slight increase with time is seen; the rate of deposition is very low and only a very thin layer of alloy ($\sim 6$ nm) is deposited. Even so, a well-defined copper stripping peak is seen as well as features for the surface oxidation/reduction of palladium. The stripping peak for copper is, however, broader than seen for a solution containing only Cu(II), see Fig. 1. When the deposition potential is $-0.45$ V, a rising $I-t$ transient is clearly seen during the deposition stage. The ‘steady state’ rate of deposition after the current increase is substantially higher than when the potential was $-0.40$ V although the layer is still relatively thin. The copper stripping peak is much larger but is shifted $\sim 100$ mV positive from that for the copper dissolution peak when only Cu(II) is present in solution, Fig. 1. The anodic peak is also substantially broadened with a shoulder on the positive side. Hence, it appears that there are interactions between the copper and palladium in the deposit that stabilise the copper to dissolution. The charge associated with copper dissolution corresponds to $66\%$ of the total deposition charge, very close to all the copper as assessed from the elemental composition, see Table 1. After dissolution of the copper, the features associated with the oxidation of the palladium surface at more positive potentials and its reduction on a second cycle remain visible. By a deposition potential of $-0.60$ V, rising transient occurs at very short times and the ‘steady state’ rate has again increased; the layer thickness approaches 0.2 $\mu$m. The copper dissolution is seen as two overlapping stripping peaks and the charge associated with these peaks (see Table 2) is substantial but corresponds to only $21\%$ to that expected if all the copper dissolves anodically. Probably with the rather thick deposit layer, not all the copper is exposed to the solution, at least on the timescale of the potential scan. The overall charge balance ratio, $Q_{\text{anodic}}/Q_{\text{deposition}}$ is only 0.31, consistent with the palladium being the dominant element in the deposit and this metal only undergoing surface oxidation. Indeed, the peaks associated with the formation of PdO and its reduction are now markedly more prominent features. As the deposition potential is made more negative, the anodic peaks do not grow markedly indicating that hydrogen evolution contributes substantially to the cathodic charge. It is interesting to note, however, that an anodic peak for the desorption of hydrogen is never seen confirming that, in contrast to pure palladium, the CuPd alloys deposited do not easily adsorb or absorb hydrogen.

Overall, it may be concluded that deposits with a range of Cu/Pd ratios may be deposited. Over all the range of deposition potentials, a substantial fraction of the deposited copper redissolves anodically but there is also clear evidence that the palladium stabilises the copper to dissolution and this is consistent with other observations in the literature [21,22]. Moreover, the observation of the two stripping peaks suggest that two different CuPd phases are being deposited. Surprisingly, in view of the application of CuPd membranes for hydrogen transport [6–8], the voltammetry does not show evidence for facile hydrogen adsorption/absorption.

### 3.2. Catalysis of the cathodic reduction of nitrate in an alkaline medium

Fig. 6 reports cyclic voltammograms for a palladium film, a copper film and a 30 at.% Cu + 70 at.% Pd film in 2 M NaOH. The Cu film electrode shows no significant current density for H$_2$ evolution positive to $-1.80$ V vs SMSE. In contrast, the Pd film electrode shows current density for water reduction at all potentials negative to $-1.40$ V vs SMSE. The proportion of the charge leading to H$_2$ gas and hydrogen adsorption/absorption was not investigated but the reverse scan for the Pd only film shows a large anodic peak due to removal of hydrogen from the palladium surface/lattice. The electrochemistry of palladium in base has, of course, been widely investigated [23–26]. The response during the forward scan for the CuPd film shows intermediate behaviour; water reduction commences at $\sim -1.60$ V vs SMSE. Again, however, it can be seen that the anodic current density for hydrogen desorption during the reverse scan is very low confirming that the alloys do not readily absorb hydrogen.

Fig. 7 reports the cyclic voltammograms for the three surfaces when the solution contains 30 mM NaNO$_3$ in addition to 2 M NaOH. As reported earlier [27], nitrate is not reduced at the Pd surface, at least at potentials positive where water reduction occurs rapidly. In contrast, nitrate reduction occurs at the CuPd surface and two slightly peaked cathodic waves are observed at $-1.33$ and $-1.54$ V vs SMSE. Moreover, reduction is clearly occurring at potentials $\sim 250$ mV positive to that necessary for reduction at a copper surface; the CuPd is an effective catalyst for nitrate reduction. We would note two other fea-
tures of the voltammogram for the CuPd surface. Firstly, while one cannot attribute the two waves to reactions leading to particular products, the plateau current density for the first wave is close to that expected for a diffusion controlled, $2e^-$ reduction – i.e. reduction is occurring at a high rate. Secondly, the potential of the first wave is very similar to that found for the reduction of nitrite at palladium [27]. This may suggest similarity in the reduction mechanisms and one could postulate that the first step is the reaction of nitrate adsorbed on a copper site with hydrogen adsorbed on a palladium site. We have discussed elsewhere [28], and in some detail, the mechanism of nitrate reduction.

Voltammograms were obtained for a series of CuPd electrodeposits in $30 \text{mM NaNO}_3 + 2 \text{M NaOH}$ where the Pd content varied between 18 at.% Pd and 79 at.% Pd. All showed two cathodic waves for nitrate reduction and the first reduction stage occurred at a similar potential. Hence, even a small addition of Pd to Cu produces the positive shift in the nitrate reduction response. Moreover, the limiting current density was found to increase with decreasing Pd content; the value was $\sim 10 \text{mA cm}^{-2}$ for 79 at.% Pd to $37 \text{mA cm}^{-2}$ for 18 at.% Pd.

It is necessary to emphasise the way in which all the voltammograms were obtained. Firstly, although the responses in Fig. 7 are reported only from $-1.00 \text{V}$, the scans were, in fact, started from 0 V vs SMSE. If the voltammograms were started at $-1.00 \text{V}$, the waves were substantially smaller and a similar effect has been reported for the reduction of nitrate at CuTl surfaces in alkali [29]. It was also observed that, at least initially, the waves for nitrate reduction increase in height by cycling the potential through the potential range where surface oxidation/reduction occurs. Such behaviour has also been reported with other catalytic surfaces for nitrate reduction in alkaline solution [30]. While, for the CuPd surface in base, the potential range between 0 and $-1.00 \text{V}$ includes that where the surface oxidation/reduction of both copper [31] and palladium [27] occurs, it cannot be stated with certainty whether the increased response arises because of cleaning of the surface, a change in the elemental composition (e.g. due to Cu dissolution), an increase in surface area or a more fundamental change in the catalyst centre.

4. Conclusions

It has been shown that CuPd alloys with a wide range of compositions could be electrodeposited from a simple acidic electrolyte and the composition could be controlled through the deposition potential or the Cu(II)/Pd(II) ratio in solution. While the alloys appear to be amorphous, they show significantly different electrochemical properties. The copper in the alloy is stabilised to anodic dissolution by the presence of the palladium while the presence of copper in the alloy reduces the ability of the palladium to absorb hydrogen. The CuPd alloys in alkaline media are significantly superior catalysts for nitrate reduction than either palladium or copper; nitrate reduction is not observed on smooth palladium and on copper the reduction occurs at a potential 250 mV more negative. Moreover, a relatively small addition of palladium to the copper is sufficient to obtain the potential shift.

References


Fig. 7. Linear potential scans for (a) Pd film, (b) Cu film and (c) CuPd film (30 at.% Pd + 70 at.% Cu) in 2 M NaOH + 30 mM NaNO3. Potential scan rate 10 mV s$^{-1}$. Potential scans were commenced at 0 V. All films were deposited from 0.6 M HClO$_4$ containing 5 mM metal ions at a potential giving a smooth deposit. Substrate: Pt microdisc electrode (diameter 25 μm). Deposition charge: 1.4 C cm$^{-2}$. 

- Reduce the potential range between 0 and $-1.00 \text{V}$.
- The surface oxidation/reduction of both copper and palladium occurs.
- Nitrate reduction is not observed on smooth palladium and on copper the reduction occurs at a potential 250 mV more negative.
- A relatively small addition of palladium to the copper is sufficient to obtain the potential shift.