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Mendeleev Commun., 2013, **23**, 157–159

Mendeleev
Communications

Open-circuit potentials established on platinum and gold electrodes in $PtCl_4^{2-}$ solutions after the displacement of copper adatoms

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DOI: 10.1016/j.mencom.2013.05.013

The steady-state potentials E_{st} established on Pt and Au upon the substitution of platinum for Cu_{ad} are shown to be determined by adsorbed oxygen (OH_{ads}).

The open-circuit potentials established on platinum metals carry important information on the structure of the electrode/solution interface and the kinetics of electrode reactions. Thus, open-circuit potential transients recorded at the irreversible adsorption of uncharged species or ions in the absence of faradic processes make it possible to determine variations in the electrode total charge and find the zero total charge value.[1–3] Open-circuit potential transients can be used for monitoring the galvanic displacement (GD) of a non-noble metal M_1 (Cu, Pb, Ni, *etc.*) by a noble metal M_2 (Pt, Pd, Au, *etc.*).[4–7] For synthesizing electrocatalysts (catalysts), the following two GD versions are of the greatest interest: (i) the displacement of M_{1ad} adatoms from a foreign support by irreversibly chemisorbed M_2^0 atoms[8,9] and (ii) the formation of a dense M_2 layer on the micro- or nanoparticles of M_1, *i.e.*, the formation of the core(M_2)–shell(M_1,M_2) structure.[6,10–12] The steady-state (or quasi-steady-state) potential established upon the end of the displacement process is an important parameter of the observed potential transients. At present, this parameter is mainly used for the attestation of the complete displacement of M_{1ad} or the complete formation of a core–shell structure. However, many factors concerning the nature of the established potential (the potential-determining reaction, the effect of the support material, the effect of the original M_{1ad} coverage, *etc.*) still remain virtually unclear.

In this study, attention is focused on steady-state potentials at the displacement of copper adatoms from the surface of polycrystalline (pc) Pt and Au in a solution of $PtCl_4^{2-}$ (0.5 M H_2SO_4 as the supporting electrolyte). To explain the results, we compared the time variations of the open-circuit potential in the presence and in the absence of copper adatoms on the surface of noble metals. This also allowed us to put forward certain assumptions on the mechanism of reduction of $PtCl_4^{2-}$ anions.

The procedure of measuring open-circuit potential transients upon the contact of $PtCl_4^{2-}$ anions with a pc Pt electrode (a plate with the geometrical surface of 1.0 cm^2) in the absence and in the presence of a Cu_{ad} monolayer ($MLCu_{ad}$) was described in detail elsewhere.[5] The measurements on the Au electrode were carried out mainly by the same procedure. The Au electrode potential was cycled in 0.5 M H_2SO_4 in the range of 50–1700 mV in order to obtain a steady-state voltammogram.[13] The true surface of the Au electrode (a plate with a geometrical surface area of 1.0 cm^2) was determined from the oxygen electrodesorption peak under the assumption that at E = 1.68 V, the O_{ads} layer corresponds to the charge of 420 μC cm^{-2}.[13] The true surface area of platinum was determined by hydrogen adsorption.[14,15] Figure 1 shows typical cyclic voltammograms of Pt and Au electrodes. The roughness factor was 4.8±0.2 for Au and 4.6 for Pt. The Cu_{ad} monolayer was formed on pc Au (the same as on pc Pt[5]) in a 2 mM $CuSO_4$ + 0.5 M H_2SO_4 solution at E = 290 mV; the charge corresponding to $MLCu_{ad}$ was 400±10 μC cm^{-2} (for the surface found by the above procedure). The potential variation by less than 0.4 mV min^{-1} served as a steady-state criterion in the solutions of 0.5 M H_2SO_4 + + 10^{-4} M K_2PtCl_4 and 0.5 M H_2SO_4 + 2 mM $CuSO_4$ + 10^{-4} M K_2PtCl_4 (E_{st}). After the establishment of the steady-state potential, the gold electrode was thoroughly washed with the supporting electrolyte solution (0.5 M H_2SO_4). Next, in the same solution, a CVA was recorded in order to determine the surface coverage of the Au electrode with the Pt deposit. All potentials are shown with respect to a reversible hydrogen electrode in the same solution; current densities i and capacitances C were calculated per cm^2 of the true surface.

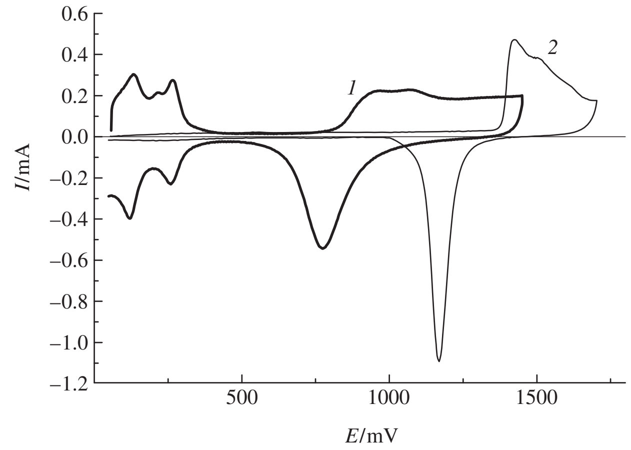

Figure 1 Cyclic voltammograms on (*1*) pc Pt and (*2*) pc Au electrodes in 0.5 M H_2SO_4; v = 50 mV s^{-1}.

Open-circuit potential transients observed upon bringing the Pt and Au electrodes covered with a Cu_{ad} monolayer into contact with $PtCl_4^{2-}$ clearly demonstrate the arrests corresponding to the desorption of adatoms (curves *1* and *2*, Figure 2). On the Au electrode, after the displacement of Cu_{ad}, a substantially lower potential was established (curve *2*) than that on the Pt electrode (curve *1*): 860±10 mV and 920±10 mV, respectively. It is well known that Pt (up to ~0.9 V) and Au (up to ~1.2 V) electrodes behaved as perfectly polarizable electrodes in 0.5 M H_2SO_4 (according to the Plank and Frumkin terminology[14]). The total polarization capacitance of pc Pt (in contrast to pc Au) sharply increased at potentials of >800 mV, as shown in Figure 1. This is due to the fact that oxide in the form of O_{ads} or OH_{ads} was accumulated on Pt much earlier than on Au (this process is

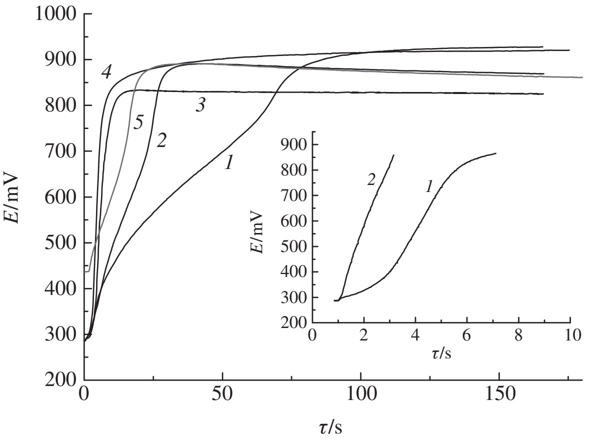

Figure 2 Open-circuit potential transients (OPT) corresponding to the displacement of Cu_{ad} by Pt atoms in a solution of 0.1 mM K_2PtCl_4 + 2 mM $CuSO_4$ + 0.5 M H_2SO_4: (*1*) $MLCu_{ad}Pt$, (*2*) $MLCu_{ad}Au$, (*5*) $0.5MLCu_{ad}Au$. OPT in 0.1 mM K_2PtCl_4 + 0.5 M H_2SO_4: (*3*) Au, (*4*) Pt.

reversible at low coverages[14]). Note that the form in which oxide is present at small coverages is still an open question;[16] however, this is of no importance for solving the problem under consideration. We assume that, at low anodic potentials, adsorbed oxygen is present as OH_{ads}.

At first glance, due to the much later oxygen adsorption on Au, one can expect that after the displacement of Cu_{ad} by the reaction

$$Cu_{ad} + PtCl_4^{2-} \rightarrow Cu^{2+} + Pt^0 + 4\,Cl^-, \tag{1}$$

more positive potentials will be attained on an Au electrode, as compared with a Pt electrode. Experimental data do not confirm this assumption. Hence, the system of reactions that determine the potential and the factors which affect the rate of reaction

$$PtCl_4^{2-} - 2e \rightarrow Pt^0 + 4\,Cl^- \tag{2}$$

should be considered more thoroughly.

To find the role of reaction (2) in the attainment of E_{st}, important information can be acquired by analyzing the potential shift on clean Au and Pt electrodes after bringing them into contact with $PtCl_4^{2-}$ anions (curves *3* and *4*, Figure 2). Even with the small-scale time axis shown in Figure 2, one can see that in the potential range below 800 mV in which the capacitance variations due to oxide formation can also be neglected on the Pt electrode, the rate at which the Pt electrode potential shifts is higher, as compared with the gold electrode. For $E > 800$ mV, the difference becomes still more pronounced. The rate of the open-circuit potential shift under these conditions is determined by the reduction rate of $PtCl_4^{2-}$ anions (and hence by the rate of Pt^0 deposition) according to reaction (2). This is accompanied by an increase in the total charge Q[2,14] of the M/solution interface, where M = Pt or Au.

The quantitative comparison of $PtCl_4^{2-}$ discharge rates on Pt and Au can be carried out using the equation

$$i_{Pt}^{M} = \frac{dQ_M}{d\tau} = C_M\frac{dE}{d\tau}, \tag{3}$$

where i_{Pt}^{M} is the hidden current of reduction of $PtCl_4^{2-}$ anions on M; C_M is the total differential capacitance of pc Pt or pc Au calculated per cm^2 of true surface; $dE/d\tau$ is the rate of potential shift in the $PtCl_4^{2-}$ + 0.5 M H_2SO_4 solution (curves *3* and *4* in Figure 2).

To assess C_M, we measured galvanostatic charging curves on pc Pt and pc Au from 290 to 800–900 mV (insert in Figure 2) by using the currents such that the time of potential increase to ~800 mV was close to the time of the attainment of these potentials in the $PtCl_4^{2-}$ solution (curves *3* and *4*). Next, the calculations were carried out according to the relationship

$$i_{Pt}^{M} = i_{g}^{M}\frac{d\tau_g}{dE}\,\frac{dE}{d\tau}, \tag{4}$$

where i_g^M is the current density of galvanostatic curve measurements calculated per cm^2 of the true surface; $d\tau_g/dE$ is the reciprocal rate of potential variation during the galvanostatic curve measurements. From the found i^M *vs*. E dependences shown in Figure 3, it is evident that the reduction currents of $PtCl_4^{2-}$ anions are substantially lower on Au than on Pt. Note that i_{Pt}^{M} weakly depends on potential, namely, the mean slopes of polarization curves ($dE/d\lg i$) in the potential range of 450–700 mV (dashed lines) were ~500 mV for Au and ~400 mV for Pt. This result suggests that the Pt deposition process on both platinum and gold is probably determined by a certain chemical stage of $PtCl_4^{2-}$ destruction rather than by the stage of electron transfer. This assumption for pc Pt was put forward earlier.[5] The calculation of i_{Pt}^{Au} is only approximate because the variations of C_{Au} with potential in Figure 2 (curve *3*) somewhat differed from the C_{Au} *vs*. E dependence for clean pc Au. The reduction of $PtCl_4^{2-}$ as a result of changes in the total charge of the Au electrode leads to a certain coverage of the Au electrode surface with Pt^0 atoms (Figure 4, curve *2*). However, this coverage is as small as 0.15 (±0.03) at the steady-state potential in curve *3* (Figure 2). The

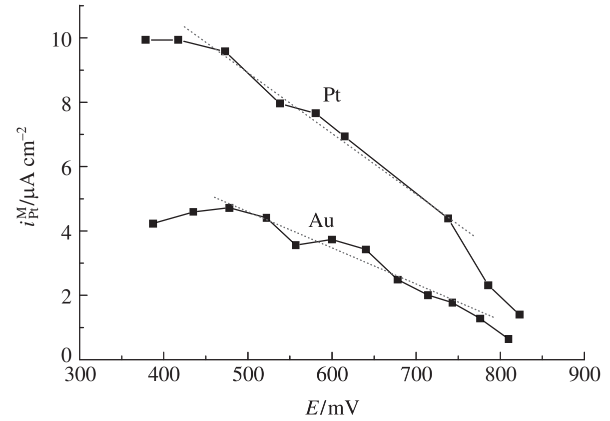

Figure 3 The dependence of reduction currents of $PtCl_4^{2-}$ anions on the potential in a solution of 0.1 mM K_2PtCl_4 + 0.5 M H_2SO_4 at open circuit on pc Pt and pc Au.

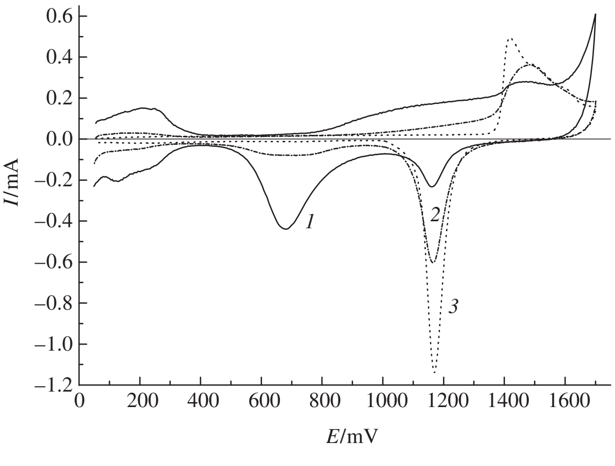

Figure 4 Cyclic voltammograms of Au electrode in the presence of Pt deposits formed on the surface (*1*) at the displacement of $MLCu_{ad}$ (after measuring curve *2* in Figure 2), (*2*) at the reduction of $PtCl_4^{2-}$ anions at open circuit (after measuring curve *3* in Figure 2) and (*3*) in the absence of Pt^0 on the surface.

C_M values for Pt and Au in the electric double layer region (insert in Figure 2) were $C_{Pt} = 55\pm4$ μF cm^{-2} and $C_{Au} = 35\pm3$ μF cm^{-2}. Hence, the capacitance of Au should be expected to increase by no more than 5% due to the Pt deposition, and this gain can be neglected. Thus, the specific activity of pc Pt in the reaction of $PtCl_4^{2-}$ reduction is higher, as compared with pc Au.

According to published data,[7,17,18] the virtually complete removal of Cu_{ad} from pc Pt and pc Au electrodes takes place upon the attainment of $E \sim 0.75$ V. In the absence of Cu_{ad} from the surface, the further increase in E is associated with changes in the total surface charge Q by reaction (2). The total charge of the Pt surface is mainly determined by the reaction

$$Pt^0 + H_2O \leftrightarrow Pt^0(OH)_{ads} + H^+ + e, \qquad (5)$$

which is reversible at low coverages with OH_{ads} as mentioned above. Evidently, this reaction is potential determining.

With the displacement of the Cu_{ad} monolayer from pc Au, a Pt coating that approaches a monolayer but fails to reach it (as regards the Au sites suitable for oxygen adsorption). This is evident from the potentiodynamic curve recorded after washing the electrode (curve *1*, Figure 4). The retained small electrodesorption peak of oxygen adsorbed on gold (at $E = 1.17$ V) made it possible to assess the degree of pc Au surface blocking as 0.75–0.85 (the scatter is determined by the reproducibility of results). The fact that, at $E > 0.8$ V, the potential shift rate on Pt^0Au (curve *1*, Figure 2) was smaller than that on pc Pt (curve *3*) and a lower steady-state potential was reached could be due to the formation of an incomplete Pt monolayer and/or the different properties of the monolayer of Pt atoms formed on the gold surface, as compared with Pt atoms deposited on Pt. The published results[5] mainly point to the epitaxial deposition of Pt on pc Pt at the displacement of Cu_{ad}. On gold, the formation of Pt islets was assumed.[8,17] The effect of the support on the electrochemical and electrocatalytic behaviour of noble-metal monolayer coatings was theoretically substantiated.[19,20] The predominance of this effect is also evident from the difference in E *vs.* τ curves *1* and *2* in Figure 2 at $E > 800$ mV. In contrast to monotonically increasing potential on curve *1*, curve *2* demonstrates a well reproducible potential decay after the maximum. Probably, this is associated with a structure rearrangement of the Pt layer formed on Au as a result of Cu_{ad} displacement in time. This can hardly be associated with a decrease in the surface coverage with OH_{ads}. It is most likely that the chemical potential of OH_{ads} (μ_{OH}) changed. Although the established potential is determined by OH_{ads} species, the accumulation of the latter on the surface proceeds by reaction (2). The rate of this reaction on Pt, like the rates of many electrode processes, apparently slows down due to the blocking of active sites with adsorbed oxygen.

For the accumulation of small amounts of Pt on gold by reaction (2) under open-circuit conditions (curve *3* in Figure 2 and curve *2* in Figure 4), OH_{ad} species appear only on a small surface part occupied with Pt. The lower reaction rates on pc Au, as compared with pc Pt, are probably the reason for the lower E_{st} on Au.

As mentioned previously,[6] the establishment of the final potential of core (Pt, Cu)–shell (Pt) particles formed by galvanic displacement can be strongly affected by Cl$^-$ anions that appear in the solution after the reduction of $PtCl_4^{2-}$ and also by the oxidation of $PtCl_4^{2-}$ to $PtCl_6^{2-}$ at sufficiently high potentials. Calculations analogous to those reported previously[6] have shown that, in our experiments, Cl$^-$ and $PtCl_6^{2-}$ species could appear in solution in concentrations of $\sim10^{-5}$ and $\sim10^{-6}$ M, respectively (approximately one order of magnitude lower than published values[6]). This is close to trace concentrations (for example, oxygen traces that remain even after the thorough deaeration of solution), which allows us to assume that the reaction $PtCl_4^{2-} + 2Cl^- \rightarrow PtCl_6^{2-} + 2e$ has an insignificant effect on E_{st} under these conditions. At the same time, Cl$^-$ anions are adsorbed on the Au electrode in considerable amounts even at concentrations of 10^{-5}–10^{-6} M.[21,22] This should be assumed as the main reason for the inhibition of reaction (2) on gold electrode surface areas unoccupied by platinum at potentials where oxygen is not yet adsorbed on Au.

Curve *5* in Figure 2 was recorded after the accumulation of Cu_{ad} at 450 mV. At this potential, as was shown in a special experiment, ~0.5 MLCu_{ad} was formed on gold. Curve *5*, like curves *2* and *3*, passes through a maximum. As could be expected, E_{st} is intermediate between the values corresponding to the zero and monolayer Cu_{ad} coverages.

Thus, the above analysis allowed us to assume that it is the OH_{ads} species formed as a result of conjugated reactions (2) and (5) that determine the potential of Pt and Au after the displacement of Cu_{ad}.

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Received: 10th January 2013; Com. 13/4044