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Galvanic replacement of copper adatoms from a Pt/Pt electrode surface in H_2PtCl_6 solutions

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Hidden currents of Cu_{ad} galvanic replacement in H_2PtCl_6 solutions have been measured for the first time and analysed in comparison with the hidden currents of Pt deposition in the absence of Cu_{ad}.

In the past decade, much attention has been given to the use of galvanic replacement as a method for the production and modification of nanostructured catalysts.[1–5] This is largely associated with the problem of decreasing the content of expensive and scarce platinum-group metals in catalysts (electrocatalysts) for fuel cells.[6] For example, platinum can be incorporated in catalysts in amounts corresponding to mono- and submonolayers by contact replacement of adatoms of a non-precious metal M_{1ad} by platinum atoms under open circuit conditions: $M_{1ad} + (n/z)\,Pt^{z+} \rightarrow M_1^{n+} + (n/z)Pt^0$.[1–3] The published data on replacement in adatom layers mostly concerned the surface structure of the resulting catalysts and their electrocatalytic activity in electrode reactions used in fuel cells.

This paper describes a study of the kinetics and mechanism of galvanic replacement, using the model reaction $2Cu_{ad} + PtCl_6^{2-} \rightarrow 2Cu^{2+} + Pt^0 + 6Cl^-$ as an example. Electrolytic deposits of platinum on platinum (Pt/Pt electrodes) with a small roughness factor ($f < 100$) were used as the substrate for Cu_{ad}.[†] This substrate was chosen for the following reasons: (i) the surface properties of Pt/Pt are well studied;[7,8] (ii) sufficiently ample data are available on the formation and properties of adatomic copper layers on Pt/Pt;[9,10] and (iii) the effect of trace amounts of dissolved oxygen decreases due to the growth of the true substrate surface.

Open-circuit potential transients (OCPTs) were recorded. Anodic galvanostatic pulses were used to determine the surface coverage with copper adatoms (θ_{Cu}) during an OCPT (Figure 1, curve *1*). Curve *1* was superimposed on an analogous curve in the supporting electrolyte solution (Figure 1, curve *2*) at a potential of 1400 mV, at which the substrate surface was assumed to reach the same state in both experiments. The amount of non-displaced copper was assessed as shown in Figure 1: $Q_{Cu} = i_{pulse}\Delta\tau$, where i_{pulse} is the pulse current density. To choose a current density such that the variation in θ_{Cu} during a pulse can be neglected, a series of experiments was carried out in which pulses with various current densities were triggered on reaching the same E values during the OCPT. At $i_{pulse} > \sim 0.07$ mA cm^{-2} of the true surface (S_{true}), the $Q_{Cu}-i_{pulse}$ plot reached a plateau (inset in Figure 1); $i_{pulse} = 0.1$ mA cm^{-2} of the true surface was chosen as the 'working' value. S_{true} was determined from hydrogen adsorption,[7] while θ_{Cu} was determined as the ratio of Q_{Cu} to the charge corresponding to a Cu_{ad} monolayer: $Q_{Cu}^0 = 420$ μC cm^{-2} of the true surface.[10–12] High purity reagents were used.[8]

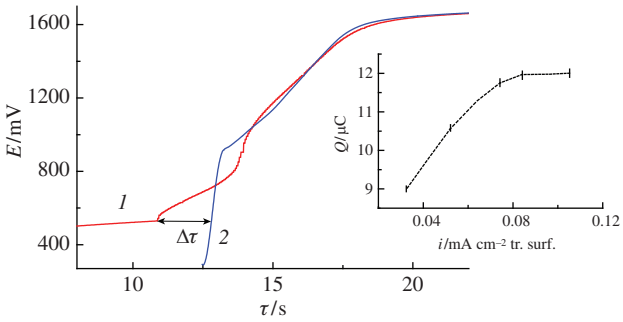

Figure 1 Anodic galvanostatic pulses obtained on a Pt/Pt electrode: (*1*) after partial replacement of Cu_{ad} with platinum in the course of OCPT in the 1 mM H_2PtCl_6 + 2 mM $CuSO_4$ + 0.5 M H_2SO_4 solution; (*2*) in the reference 0.5 M H_2SO_4 solution. Inset: plot of the charge consumed for the oxidation of non-replaced Cu_{ad} at 600 mV *versus* the current pulse.

Figure 2 represents an OCPT corresponding to the replacement of Cu_{ad} with Pt atoms due to the reaction $2Cu_{ad} + PtCl_6^{2-} \rightarrow 2Cu^{2+} + Pt^0 + 6Cl^-$ (curve *1*). It is important that, on reaching the potentials of total Cu_{ad} replacement (~750 mV) and washing the electrode with a reference solution, no appreciable changes in the true surface or in the energy spectrum of hydrogen adsorption in this solution were observed. This allows us to believe that Pt is deposited as an epitaxial layer. Based on the data obtained in H_2PtCl_6 solutions concerning Cu_{ad} replacement on Au and Pd[1–3] and Pt deposition on Pt/C,[13] the contribution of the reaction $Cu_{ad} + PtCl_6^{2-} \rightarrow Cu^{2+} + PtCl_4^{2-} + 2Cl^-$ can be neglected.

Based on pulse measurements, a $\theta_{Cu}-$potential plot during an OCPT was built (Figure 3, curve *1*). A plot of equilibrium θ_{Cu} on E

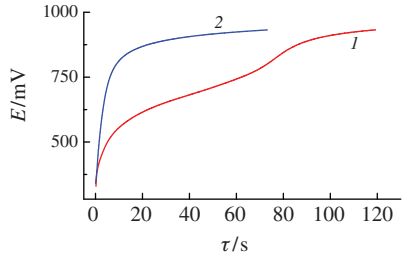

Figure 2 OCPTs corresponding to (*1*) replacement of Cu_{ad} with Pt ions in the 1 mM H_2PtCl_6 + 2 mM $CuSO_4$ + 0.5 M H_2SO_4 solution and (*2*) Pt deposition in the 1 mM H_2PtCl_6 + 0.5 M H_2SO_4 solution under open circuit conditions.

[†] The measurements were carried out at 20±1 °C in a three-electrode cell with separated anodic and cathodic spaces; the working solution was stirred with a magnetic stirrer. A monolayer of Cu_{ad} was formed at $E = 300$ mV (all potentials are given with respect to a reversible hydrogen electrode in the same solution) in a 2 mM $CuSO_4$ + 0.5 M H_2SO_4 solution. After that, the circuit was opened and a portion of deaerated H_2PtCl_6 + 0.5 M H_2SO_4 solution was quickly (< 1 s) injected into the working compartment to obtain a concentration of 1.0 mM H_2PtCl_6.

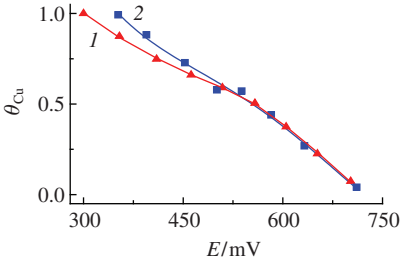

Figure 3 θ_{Cu} *vs.* potential: (*1*) in the course of Cu_{ad} replacement with platinum in the 1 mM H_2PtCl_6 + 2 mM $CuSO_4$ + 0.5 M H_2SO_4 solution under open circuit conditions; (*2*) under equilibrium conditions in the 2 mM $CuSO_4$ + 0.5 M H_2SO_4 solution.

(adsorption isotherm) in 2 mM $CuSO_4$ + 0.5 M H_2SO_4 (Figure 3, curve *2*) was also obtained using galvanostatic pulses (before applying the pulse, the electrode was kept for 1 min at the preset potential). One can see that curve *1* is not appreciably shifted with respect to curve *2*; hence, no significant violation of the reaction equilibrium $Cu_{ad} \leftrightarrow Cu^{2+} + 2e$ occurs during the replacement of copper adatoms. Small divergence between curves at $E <$ 500 mV, from our viewpoint, results from some experimental errors in the estimation of θ_{Cu} values. It is obvious that, if this divergence resulted from the electrochemical polarization of Cu_{ad} removal, curve *1* would pass higher than curve *2*.

On the basis of $Q_{Cu}-E$ and $E-\tau$ plots, hidden currents of Cu_{ad} replacement with platinum in 2 mM $CuSO_4$ + 1 mM H_2PtCl_6 + + 0.5 M H_2SO_4 solution under open-circuit conditions were calculated using the relationship:

$$i_{hid}^{Cu} = -\frac{d\theta_{Cu}}{dE}\frac{dE}{d\tau}Q_{Cu}^{0}, \qquad (1)$$

where $d\theta_{Cu}/dE$ and $dE/d\tau$ are the derivatives of curves *1* in Figures 3 and 2, respectively. The plot obtained using equation (1) is represented by curve *1* in Figure 4.

We used the following relationship to calculate the hidden current of Pt deposition due to the charging of the Pt/solution interface in the absence of copper (i_{hid}^{Pt}):

$$i_{hid}^{Pt} = \frac{i_{pdc}}{v}\frac{dE}{d\tau}, \qquad (2)$$

where i_{pdc} is the current on the potentiodynamic curve in 0.5 M H_2SO_4, and $dE/d\tau$ is the derivative of curve *2* in Figure 2.

The dashed line in Figure 4 shows the experimentally determined limiting diffusion current of Pt electrodeposition from the 1 mM H_2PtCl_6 + 0.5 M H_2SO_4 solution with respect to 1 cm^2 of the true surface. One can see that copper replacement currents (curve *1*) correspond to mixed kinetics (especially at $E \leqslant 500$ mV).

Two effects can be found by a comparison of i_{hid}^{Cu} (curve *1* in Figure 4) and i_{hid}^{Pt} (curve *2*): $i_{hid}^{Cu} > i_{hid}^{Pt}$ at $E < 0.5$ V; furthermore, i_{hid}^{Cu}, unlike i_{hid}^{Pt}, starts to increase appreciably at $E \geqslant 600$ mV. The

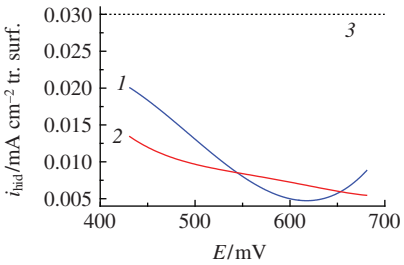

Figure 4 Dependence of the following values on potential: (*1*) hidden current of Cu_{ad} replacement with Pt in the 1 mM H_2PtCl_6 + 2 mM $CuSO_4$ + 0.5 M H_2SO_4 solution; (*2*) hidden current of Pt deposition in the 1 mM H_2PtCl_6 + 0.5 M H_2SO_4 solution under open circuit conditions; (*3*) limiting diffusion current of Pt electrodeposition in the 1 mM H_2PtCl_6 + 0.5 M H_2SO_4 solution.

first effect suggests that Pt deposition accelerates at high θ_{Cu}, which is likely due to the direct chemical reaction of copper adatoms with $PtCl_6^{2-}$ anions. The weak dependence of i_{hid}^{Pt} on E (curve *2*) allows us to conclude that Pt deposition in the absence of Cu_{ad} is mostly determined by a chemical stage, most likely, $PtCl_6^{2-}$ destruction, rather than by the electron transfer stage. Copper adatoms that are comparatively weakly bound with the surface at $E < 500$ mV catalyse this destruction. At high θ_{Cu}, one can speak of some similarity in the mechanism of Cu_{ad} reaction with $PtCl_6^{2-}$ and that of O_{ads} reaction with a number of organic compounds at high θ_O.[14]

The second effect, namely, the increase in i_{hid}^{Cu} at $E > 600$ mV, is most likely due to the effect of adsorption of small amounts of oxygen at these potentials on Pt in sulfuric acid solutions,[11,12,15] *i.e.*, reactions of the type: $Pt–OH_{ad} + Cu_{ad} + H^+ \rightarrow Cu^{2+} + Pt + H_2O + e$; $PtCl_6^{2-} + H_2O + 3e \rightarrow PtOH + H^+ + 6Cl^-$.

It is known,[15] that many oxidative reactions on Pt electrodes that occur at potentials of 'quasi-double layer' region cannot be explained without assuming the presence of at least traces of active adsorbed oxygen species on the surface.

As one can see in Figure 4, $i_{hid}^{Cu} < i_{hid}^{Pt}$ in the potential range of 550–650 mV. These potentials correspond to the strongly bound Cu_{ad} form,[9–12] which, unlike the weakly bound Cu_{ad} form (high coverages), is likely to inhibit the destruction of $PtCl_6^{2-}$ anions. Note that, according to published data,[16,17] a two-dimensional phase transition of Cu_{ad} occurs in the test potential range.

Thus, we conclude that the kinetics and mechanism of the galvanic replacement of Cu_{ad} in H_2PtCl_6 solutions on Pt/Pt is mostly determined by the direct reactions of Cu_{ad} with $PtCl_6^{2-}$ and the destruction of the latter.

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