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Modification of platinum electrodeposits with an ultralow amount of palladium through the galvanic displacement of hydrogen and copper adatoms

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Pd^0_{Cu}(edPt) and Pd^0_H(edPt) electrodes demonstrated considerable differences in the kinetics of methanol and formic acid oxidation.

In view of the synthesis of highly efficient catalysts for fuel cells, attention is focused on mixed platinum–palladium catalysts.[1–9] Of special interest are core–shell structures, which allow the consumption of expensive metals to be reduced and/or the catalyst activity to be increased as compared with monometallic catalysts due to a synergistic effect.[1,3–8] Galvanic displacement (GD) is an efficient method of synthesizing core–shell structures.[9–13] Among the Pt–Pd systems synthesized by GD, the systems with the Pd(core)–Pt(shell) structure were studied most thoroughly.[1,4,6] However, information on the platinum–palladium catalysts with Pd shells is scarce and corresponds to catalysts synthesized by methods other than GD.[5,8] The mixed Pt–Pd catalysts demonstrate the high activity in the reactions of oxygen reduction and methanol electrooxidation.[1–7,9]

Earlier,[14–20] we studied the properties of Pt and Pd electrodeposits (ed), such as hydrogen sorption, adsorption of copper atoms, galvanic displacement of Cu_{ad} and electrocatalytic activity in methanol and formic acid electrooxidation reactions. In this work, we investigated (i) the possibility of modifying the surface of edPt with Pd microamounts (corresponding to a Pd submono- or monolayer) by displacing Cu_{ad} and H_{ad} in $PdSO_4$ solutions and (ii) the structural and electrocatalytic properties of the Pd^0(edPt) deposit surface layer and their dependence on the displaced atom. The electrocatalytic activity of Pd^0(edPt)/C was tested in the oxidation of methanol and formic acid.

The electrochemical studies were carried out in a three-electrode cell with separated anodic and cathodic compartments at 19±1 °C. A reversible hydrogen electrode (RHE) in the same solution was used as a reference electrode (all potentials E are shown in the RHE scale). The supports were polished glassy carbon plates with S_{geom} = 1 cm^2 to which a layer of Vulcan XC-72 carbon black mixed with Nafion was applied[12] (below, this support is designated as C). Platinum electrodeposits were synthesized from a solution of 2×10^{-3} M K_2PtCl_4 + 0.5 M H_2SO_4 at E^{dep} = 0.25 V. The quantity of electricity passed in the electrolysis corresponded to the deposition of ~80 μg of Pt. After the repeated washing of the cell from platinum ions with a supporting electrolyte solution (0.5 M H_2SO_4), the latter was changed for a solution containing copper ions (5×10^{-3} M $CuSO_4$ + 0.5 M H_2SO_4) in which a monolayer (ML) of Cu_{ad} was formed at E = 0.29 V[12,20] (in a separate experiment, 0.5 ML of Cu_{ad} was formed at E = 0.4 V). The working compartment of the cell was washed with the supporting electrolyte solution in a flow of argon; the circuit was opened, and the supporting electrolyte solution was changed for a deaerated solution of 10^{-3} M $PdSO_4$ + 0.5 M H_2SO_4. A transient of open-circuit potential (E *vs.* τ) was recorded, after which the electrode was washed with the supporting electrolyte solution. For comparison, the experiments on the displacement of hydrogen adatoms by palladium ions were performed. For this purpose, the potential of edPt/C was stabilized at 60 mV in the supporting electrolyte solution, then the circuit was opened and the procedures similar to those used at the displacement of Cu_{ad} were carried out. The deposits obtained by the GD of Cu_{ad} and H_{ad} were designated as Pd^0_{Cu}(edPt)/C and Pd^0_H(edPt)/C, respectively.

The surfaces of all electrodes were determined with respect to Cu_{ad}.[12,16,17] Note that, for Pd^0(edPt)/C electrodes, the overall surface (Pt + Pd) was determined because the electrodesorption of Cu_{ad} from these metals proceeds in the same potential region. To estimate the activity of Pd^0(edPt)/C, cyclic voltammograms (CVAs) and steady-state polarization curves were recorded in 0.5 M MeOH + 0.5 M H_2SO_4 and 1 M HCOOH + 0.5 M H_2SO_4 solutions. All the currents were recalculated per unit of the true surface determined based on copper adatoms. The steady-state criterion corresponded to variations in the current by less than 2% per minute at the established potential E.

The morphology of the deposit surface was studied by means of a JEOL JSM – 6490 LV scanning electron microscope. The Pd mass in samples was determined by electrochemical methods (m^{elch}_{Pd}) and also by dissolution of the deposit in aqua regia followed by the ICP-AES analysis of the resulting solution (m^{anal}_{Pd}). The composition of the surface layer was analyzed by XPS (Axis Ultra DLD spectrometer).

Figure 1 shows that the steady-state potentials (E_{st}) established after the substitution of palladium for both Cu_{ad} and H_{ad} are in the vicinity of 0.8 V. First, this corresponds to the potentials of the total removal of not only H_{ad} but also Cu_{ad} from the surface of Pt and Pd.[12,13,16,17] Second, the steady-state potentials are shifted by ~100 mV in the cathodic region with respect to the equilibrium

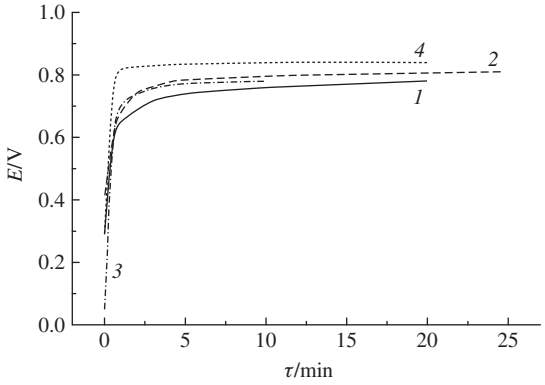

Figure 1 Transients of open-circuit potential recorded upon bringing the 10^{-3} M $PdSO_4$ + 0.5 M H_2SO_4 solution into contact with electrodes: (*1*) $MLCu_{ad}$(edPt)/C, (*2*) 0.5 $MLCu_{ad}$(edPt)/C, (*3*) MLH_{ad}(edPt)/C and (*4*) $MLCu_{ad}$(edPd)/Pt (1 mg Pd).

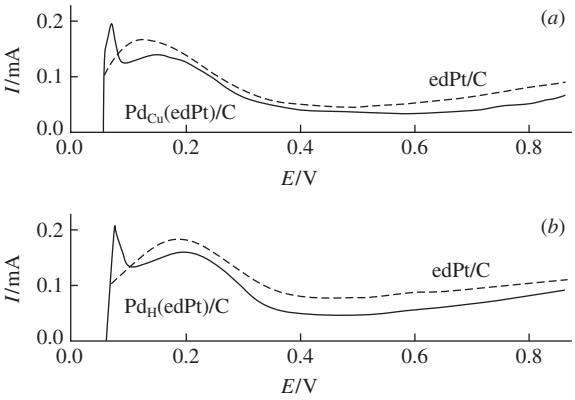

Figure 2 Anodic potentiodynamic curves in 0.5 M H_2SO_4 solution for (*a*) Pd^0_{Cu}(edPt)/C and (*b*) Pd^0_H(edPt)/C.

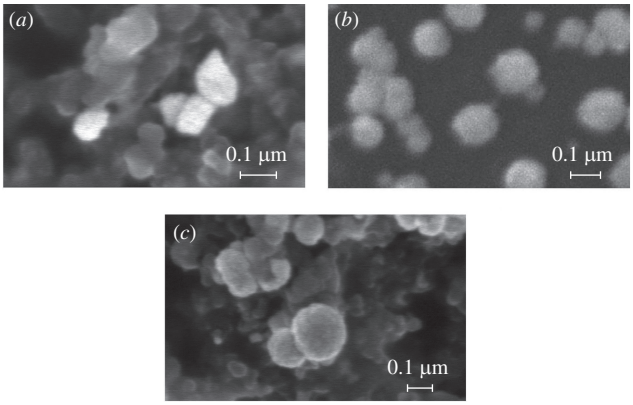

Figure 3 SEM images of the samples of (*a*) edPt/C, (*b*) Pd^0_{Cu}(edPt)/C and (*c*) Pd^0_H(edPt)/C.

potential of the Pd^{2+}/Pd pair at $[Pd^{2+}] = 10^{-3}$ mol dm^{-3}, *i.e.*, the system is non-equilibrium. A further increase in the potential is apparently impeded by the formation of oxides on both Pt and Pd.[12,16] The adsorption of oxygen on Pt starts at less positive potentials than that on Pd. This can explain the fact that, after the displacement of $MLCu_{ad}$ from edPt (curve *1*), E_{st} is considerably less positive as compared with the displacement of $MLCu_{ad}$ from edPd (curve *4*). This indirectly points to the non-monolayer distribution of Pd^0 on the surface of edPt/C.

Figure 2 depicts anodic potentiodynamic curves for the Pd^0(edPt)/C deposits prepared by the displacement of $MLCu_{ad}$ and MLH_{ad} (the real surface coverage with H_{ad} at 60 mV is ~0.8). For comparison, the curves for original edPt/C electrode (curve *2*) are shown. Changes in the curves induced by the deposition of Pd microamounts are close in both cases. The appearance of a peak in the initial region of curves denotes considerable dissolution of hydrogen in the palladium deposit. According to published data,[21] the mono- and bilayers of palladium do not dissolve hydrogen; the presence of these peaks points to the non-monolayer distribution of Pd over the edPt surface and also to the conglomeration of deposited Pd atoms. This can be expected bearing in mind the complicated porous structure of edPt with a lot of fine pores ($\leqslant$ 1 nm).[14] The changes in the morphology of edPt (Figure 3) upon the substitution of palladium for $MLCu_{ad}$ and MLH_{ad} are similar in both cases: the conglomerates are slightly rounded upon the deposition of Pd.

Based on the overall XPS spectra, the concentrations of Pd in the surface layer were estimated at ~80 at% after its substitution for $MLCu_{ad}$ and ~40 at% after substitution for adsorbed hydrogen (Pt + Pd = 100%). The ratio of these values is close to the ratio of palladium amounts deposited in place of $MLCu_{ad}$ and MLH_{ad} (Table 1). Insofar as the XPS signal is collected from the area with a diameter of ~600 μm and the layer 2–3 nm deep, the XPS data make it possible to infer that no coarse Pd conglomerates are formed. The Pd content of the surface layers exceeds its total content in Pd^0_{Cu}(edPt)/C and Pd^0_H(edPt)/C (~5 and ~3.5 at%, respectively) by more than one order of magnitude. Note that the Pd deposit is formed preferentially on the surface of Pt conglomerates [Figure 3(*a*)], and it does not penetrate into the depth being deposited only in small amounts in fine pores. Due to the close crystallographic parameters of Pt and Pd, transmission electron spectroscopy failed to provide additional information on the distribution of ultralow amounts of Pd over the surface of edPt.

Table 1 shows the averaged values of m^{elch}_{Pd} calculated based on the adsorption of hydrogen and copper found electrochemically (the charges Q^H and Q^{Cu}, respectively) on the original samples of edPt/C. For the stoichiometry of the displacement reaction $Cu_{ad}(2H_{ad}) + Pd^{2+} \rightarrow Cu^{2+}(2H^+) + Pd^0$, the ratio of $m^{elch}_{Pd}[Pd^0_{Cu}(edPt)]$ to $m^{elch}_{Pd}[Pd^0_H(edPt)]]$ should be 2.5 : 1.0 (for the displacement of $MLCu_{ad}$ and MLH_{ad}). The observed deviations from this value (see Table 1) can be explained by considerable scatter in the surface areas of edPt from one experiment to another and by errors in the Q^H and Q^{Cu} estimates due to the high capacitance of the support.

Data in Table 1 indicate that the amounts of deposited Pd, which were determined indirectly by ICP-AES, are considerably higher than those determined electrochemically. This is apparently due to the fact that in the electrochemical method only the displacement of Cu_{ad} or H_{ad} is taken into account and the deposition of Pd due to changes in the total electrode charge Q is ignored.[12,20] The contribution of changes in Q is significant because, in the test system, the total charge Q is determined by not only the overall differential capacitance of the metal particle surface but also the capacitance of the unoccupied support areas. Apparently, the co-deposition of palladium due to support capacitance should considerably smooth out differences in the behaviors of Pd^0_H(edPt)/C and Pd^0_{Cu}(edPt)/C.

When Pd is deposited to form a monolayer, such a modification of edPt induces no changes in the true surface value because a copper adatom occupies one surface atom on both Pt and Pd. However, it is beyond reason to expect considerable changes in S^{Pt+Pd} as compared with S^{Pt} at the formation of clusters. Thus, Pd deposited in its highly disperse form (*e.g.*, 100 m^2 g^{-1}) did not block the Pt surface, and the total surface of Pt and Pd determined with respect to copper adatoms would exceed the initial S^{Pt} by ~20%. This is associated with ultralow amounts of deposited Pd. Indeed, S^{Pt+Pd} for Pd^0_H(edPt) does not virtually differ from S^{Pt}

Table 1 Characteristics of edPd/C, edPt/C and Pd^0(edPt)/C.

Sample	Displaced layer	m^{elch}_{Pd}/μg cm^{-2} of geom. surface	m^{anal}_{Pd}/μg cm^{-2} of geom. surface	S^{Pt}, S^{Pd} or S^{Pt+Pd}/cm^2	E_{st}/V	i^{200}, i^{300}/A mg^{-1} Pd (HCOOH)
edPd	—	—	—	10±1		2.0×10^{-3}, 2.2×10^{-3}
edPt	—	—	—	7.4±1.5		
Pd^0(edPt)	0.8 MLH_{ad}	0.9±0.1	1.5	7.3±1.0	0.79±0.04	5.1×10^{-2}, 8.0×10^{-2}
	1.0 $MLCu_{ad}$	1.8±0.4	2.3	6.0±1.1	0.8±0.02	8.9×10^{-3}, 2.0×10^{-2}
	0.5 $MLCu_{ad}$	1.2	—	8.0	0.81	

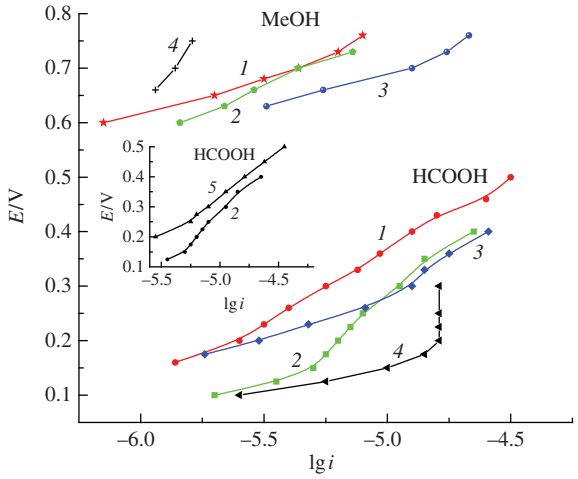

Figure 4 Steady-state polarization curves of methanol and formic acid oxidation for (*1*) Pd^0_{Cu}(edPt)/C, (*2*) Pd^0_H(edPt)/C, (*3*) edPt/C and (*4*) edPd/C. Insert: steady-state polarization curves of formic acid oxidation for (*2*) Pd^0_H(edPt)/C and (*5*) $Pd^0_{0.5\,Cu}$(edPt)/C.

(Table 1). At the same time, for Pd^0_{Cu}(edPt), we can speak of a slight decrease in the surface, which may be due to the fact that palladium blocks the entrance to some pores in edPt.[14] This effect was not observed for the displacement of 0.5MLCu_{ad} (see Table 1).

Figure 4 shows that the presence of untralow Pd amounts deposited by displacing copper from edPt (curve *1*) lowers down the specific steady-state currents of methanol electrooxidation as compared with Pt (curve *3*) by a factor of ~3 but increases them also by a factor of ~3, as compared with Pd (curve *4*). The deposit modified with Pd through displacing H_{ad} was also less active than edPt (curves *2* and *3*, respectively). These results agree with the well-known fact that Pd is a poor catalyst for MeOH electrooxidation (*cf.* curves *3* and *4*); hence, the partial blockage of the surface of edPt with Pd leads to a decrease in the specific rate of MeOH electrooxidation. Neglecting the methanol oxidation currents on Pd and assuming the total absence of the synergistic effect, the proportion of the blocked surface of edPt in Pd^0_{Cu}(edPt) can be assessed as ~2/3. A somewhat higher specific activity of Pd^0_H(edPt), as compared with Pd^0_{Cu}(edPt), can be caused by the weaker blockage of the Pt surface.

For the electrooxidation of formic acid, the deposits modified by displacing different adatoms behaved in a different manner (Figure 4). Pd^0_{Cu}(edPt)/C (curve *1*) demonstrated specific activity lower than that of not only edPd (curve *4*) but also edPt (curve *3*) (excluding potentials more cathodic that 0.2 V). As regards their activity, the Pd^0_H(edPt)/C catalysts at $E \leqslant 0.15$ V were comparable with edPd; at higher potentials, their activity decreased approaching that of Pt at ~0.3 V. The difference in the activity of Pd^0_H(edPt)/C and Pd^0_{Cu}(edPt)/C cannot be associated only with the substantially smaller amounts of Pd^0 at its deposition through the displacement of H_{ad} (see Table 1). The $Pd^0_{0.5Cu}$(edPt)/C electrode synthesized by the displacement of 0.5MLCu_{ad} also demonstrated the activity in HCOOH electrooxidation markedly different from that of Pd^0_H(edPt)/C (insert).

Based on the data presented in Figure 4, we can infer the absence of any substantial promoting action of Pd microamounts on the electrooxidation of HCOOH and MeOH. The more detailed analysis of *E vs.* log *i* curves was complicated due to the impossibility of separating the surface fractions corresponding to Pt and Pd.

We measured CVAs in 1 M HCOOH + 0.5 M H_2SO_4 under various conditions and obtained very different ratios between specific activities for Pd^0_H(edPt)/C and Pd^0_{Cu}(edPt)/C at low potentials. In certain cases, this ratio was even inverse to that found based on steady-state currents. The steady-state currents of oxidation of HCO compounds at relatively low anodic potentials (up to ~0.6 V) are of interest for fuel cells. However, in many publications the activities of different electrocatalysts were compared based on CVA peak currents. First, as a rule, these currents correspond to $E > 0.6$ V. Second, being nonsteady-state currents, they depend on many factors (electrode treatment, final and initial potentials, scan rate, exposure time at the initial and/or final potentials, *etc.*), which makes conclusions on their activity ambiguous.

Currently, attention is focused on currents related not to the true surface but to the mass of metal catalysts (so-called mass activity) because this value characterizes the degree of catalyst utilization in the target reaction, which is important for practice. It is interesting that, if to neglect the activity of platinum in the electrooxidation of HCOOH, the specific mass activity of Pd for Pd^0_H(edPt)/C and Pd^0_{Cu}(edPt)/C far exceeds that of edPd/C. In the region $E < 0.2$ V it can be assessed to exceed the activity of Pd in edPd/C (~40 μg, S^{Pd} ~ 20 $m^2\ g^{-1}$) by a factor of >25. This is mainly associated with the high dispersion of Pd deposited by galvanic displacement.

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