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Carbon monoxide adsorption and electrooxidation at a Pd(Mo) electrode prepared by galvanic displacement

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The deposition of Pd particles on Mo substrate leads to an increase in their catalytic activity in the electrooxidation of both adsorbed and dissolved carbon monoxide.

Electrocatalytic systems containing palladium were proposed for the acceleration of electrode processes in fuel cells. A significant catalytic effect on oxygen electroreduction was found for Pd–Co and Pd–Mo electrodes.[1,2] The electrooxidation of formic acid was performed at Pd–MoO_x electrodes,[3] however, the catalytic effect was extremely small and disappeared after division on the true electrode surface of palladium.

Palladium electrodes do not exhibit significant catalytic activity towards CO and methanol electrooxidation in acid solutions. Such a behaviour is due to a high positive potential of Pd oxide formation (~0.8 V;[4,5] hereinafter, all potentials are given *vs.* a reversible hydrogen electrode in the same solution). The acceleration effect of molybdenum can be caused by molybdenum oxides formed at the electrode surface at relatively low potentials. Small currents of methanol electrooxidation were found[6] on Pd(Mo) electrodes at $E \le 0.4$ V. The purpose of this work was to study CO adsorption on Pd(Mo) electrodes prepared by galvanic displacement.[6]

The Pd(Mo) electrodes were produced by the galvanic displacement of molybdenum by palladium. The molybdenum plates (99.9% Mo, geometrical surface area of 2 cm^2) were immersed in a solution containing 0.01 M $PdCl_2$ + 0.5 M H_2SO_4 at open circuit potential. The time of galvanic displacement was 1 min, ~25 μg of Pd on 1 cm^2 of molybdenum plate were deposited.[6] The mass of palladium was determined by its dissolution in aqua regia and further analysis by inductively coupled plasma atomic emission spectroscopy (ICP-AES). 3D palladium clusters formation on the surface of molybdenum was detected by transmission electron microscopy (Figure 1, inset). The size of these clusters was 10–20 nm. Electrochemical measurements were performed in a three-electrode cell in an argon atmosphere in 0.5 M H_2SO_4.

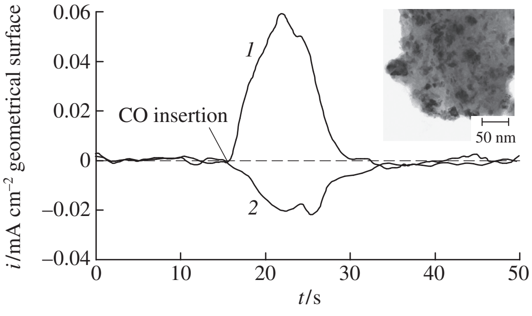

Figure 1 Potentiostatic current transients recorded after insertion of carbon monoxide in contact with Pd(Mo) electrodes in 0.5 M H_2SO_4 at E_{ads} of (*1*) 90 and (*2*) 300 mV. Inset shows the TEM image of a Pd(Mo) electrode.[6]

The true surface area of Pd particles was calculated from the charge corresponding to desorption of hydrogen on cyclic voltammograms (CVAs) (0.09–0.30 V, anodic scan). The contribution of absorbed hydrogen was subtracted from the overall charge. The evaluation of absorbed and adsorbed hydrogen contributions to the overall charge was performed by suppression of hydrogen adsorption caused by copper adatoms[6,7] or a CO monolayer (see below). The adsorption of carbon monoxide was carried out under potentiostatic conditions. To remove dissolved CO from the solution, argon was bubbled through the cell for 30 min. Some measurements were performed on palladium deposits on Pt (Pd was deposited in such amounts that the influence of a Pt substrate was negligible).

Current transients of carbon monoxide adsorption (E_{ads} = 0.09 and 0.30 V) correlated with data on the electrolytic deposits of Pd (Figure 1).[8,9] Cathodic currents measured at 0.3 V are associated with changes in double electric layer caused by CO adsorption on Pd. Anodic currents at E_{ads} = 0.09 V are connected with H_{ads} displacement from the surface of palladium. The total zero charge potential of Pd significantly shifts to positive values in the process of CO adsorption.[9] The charge that corresponded to CO adsorption at 0.30 V was ~40 μC cm^{-2} of true Pd surface. This value measured on the electrolytic deposits of Pd was slightly higher (52 μC cm^{-2}).[8] The decrease of the adsorption charge can be associated with the influence of Mo on the adsorbed dipoles of carbon monoxide at the electrode surface.

Carbon monoxide adsorbed on a Pd surface suppresses hydrogen adsorption. It results in a charge reduction measured on cyclic voltammograms at potentials of 0.09–0.30 V (Figure 2, curves *1* and *2*). From a comparison of CVAs recorded after CO adsorption at 0.30 V (curve *2*) and after deposition of copper adatoms (curve *3*), one can see that the degrees of hydrogen adsorption suppression in these two cases are almost the same. Consequently, carbon monoxide forms a monolayer on Pd at 0.30 V. This result correlates with the data obtained on electrodeposited Pd.[8]

The estimation of the true surface area of palladium calculated from the suppression of hydrogen sorption by a CO monolayer has led to a value of ~20 m^2 g^{-1}. It was found from the difference in areas corresponding to hydrogen portions of *I*–*E* curves *1* and *2* in Figure 2 on anodic scans. It was taken into account that the part of Pd surface occupied by hydrogen atoms (θ_H) is ~0.6 at 0.09 V.[10] The calculated average diameter of Pd clusters on the assumption of their spherical shape was ~25 nm. The size of Pd particles determined from transmission electron microscopy was slightly smaller (Figure 1, inset). Taking into account the

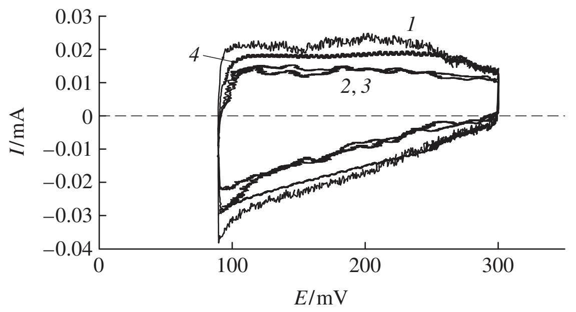

Figure 2 Cyclic voltammograms of Pd(Mo) electrodes in 0.5 M H_2SO_4: (*1*) Pd(Mo); (*2*) Pd(Mo)–CO_{ads} (E_{ads} = 300 mV); (*3*) Pd(Mo)–Cu_{ads}; (*4*) Pd(Mo)–CO_{ads} (E_{ads} = 400 mV). Scan rate, 1 mV s^{-1}.

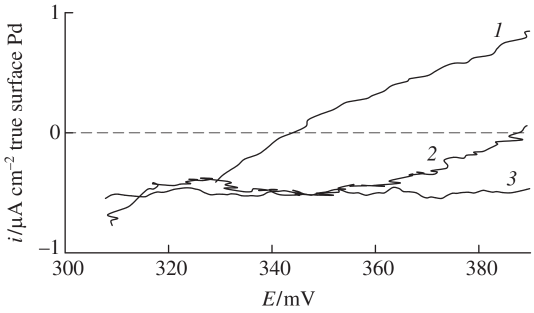

Figure 4 Potentiodynamic polarization curves of (*1*,*2*) Pd(Mo) and (*3*) Pd/Pt electrodes in 0.5 M H_2SO_4 (scan rate, 1 mV s^{-1}): (*1*,*3*) solution saturated with CO; (*2*) bare solution.

disadvantages of a model of spheres,[11] the discrepancy between these values may be considered as insignificant.

In the case of CO adsorption at 0.40 V, the degree of currents suppression in hydrogen portion of CVs was significantly lower (Figure 2, curve *4*). Consequently, the area blocked by CO molecules at E_{ads} = 0.40 V was less than that at E_{ads} = 0.30 V. This fact can be explained by the assumption that carbon monoxide does not form a monolayer on Pd surface at 0.40 V. Thus, this result differs from that on Pd/Pt electrode[8] where CO monolayer existed at Pd surface at $E > 0.40$ V (to ~0.6 V). Evidently, the decrease of CO_{ads} amount is associated with the partial oxidation of adsorbed carbon monoxide molecules by molybdenum oxides formed at the Pd/Mo boundaries. The variation in charges measured in hydrogen portions of CVAs (curves *2* and *4*) was 950 μC. This value corresponds to a surface area of ~4 cm^2 (total true Pd surface area was ~11.5 cm^2). This part of surface (~30%) was free from CO molecules at E = 0.40 V. Probably, a significant decrease of the area blocked by carbon monoxide is related to the high length of Pd/Mo boundaries due to the formation of Pd nanoclusters on the surface of molybdenum. The oxidation of adsorbed CO molecules occurs at these boundaries.

The partial oxidation of CO_{ads} at 0.40 V was confirmed experimentally: after the accumulation of a CO monolayer at 0.30 V, the electrode potential was changed to 0.40 V. In the first second after potential change, the anodic currents were observed (Figure 3, curve *1*). Note that these currents were significantly higher than currents measured on a Pd(Mo) electrode without CO_{ads} (curve *2*). The charge consumed for the oxidation of CO_{ads} was determined by the integration of current transients. It was 1200 μC. It is necessary to take into account that carbon monoxide can adsorb in linear and bridged forms.[8,12,13] The value of 320 μC cm^{-2} corresponds to the desorption of CO_{ads} from Pd surface.[12] Using this value, we estimated the area cleared from carbon monoxide adlayer at 3.7 cm^2 (~30%), which is in good agreement with the estimation made from hydrogen portions of CVAs. Note that the calculation gives approximate values only. Changes in double electric layer occur in the course of carbon monoxide adsorption (desorption). It is difficult to take proper account for the currents of double electric layer charging.[14]

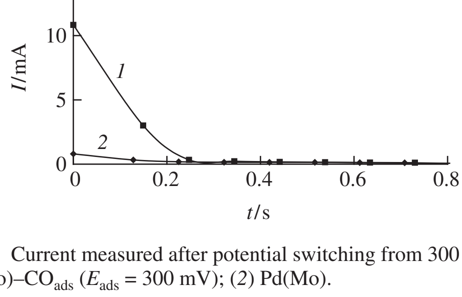

Figure 3 Current measured after potential switching from 300 to 400 mV: (*1*) Pd(Mo)–CO_{ads} (E_{ads} = 300 mV); (*2*) Pd(Mo).

Pd(Mo) electrodes prepared by galvanic displacement exhibit good catalytic activity towards the oxidation of dissolved carbon monoxide. The oxidation started at ~0.33 V (Figure 4, curve *1*). Very small cathodic currents observed at $E < 0.33$ V were associated with the reduction of oxygen, which remained in trace amounts in the cell even after argon bubbling for 30 min. On the other hand, it was impossible to observe any currents of CO oxidation on Pd/Pt electrodes at potentials of 0.30–0.45 V (curve *3*). Small anodic currents at $E > 0.39$ V indicated the beginning of molybdenum electrooxidation.

The potential of dissolved CO electrooxidation on Pd(Mo) electrodes was rather close to the values observed for Pt–Mo/C electrodes.[15] The oxidation of dissolved carbon monoxide likely occurred through the weakly bounded forms of CO on the parts of electrode surface, which were free from the adsorbate.

Thus, we found that the partial oxidation of CO_{ads} occurs on Pd(Mo) electrodes at $E < 0.4$ V. The electrooxidation of carbon monoxide dissolved in the electrolyte on Pd particles proceeds at potentials that are significantly less positive than those in the absence of molybdenum substrate. Pd(Mo) electrodes prepared by galvanic displacement can be applied in fuel cells and as catalysts for organic reactions.

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