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Anomalous effect of the presence of methanol on the oxygen electroreduction rate on rhodium electrode in sulfuric acid solution

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By the example of Rh electrodes, it was observed for the first time that, in certain cases, the presence of methanol can lead to an increase in the oxygen electroreduction rate.

It is known[1,2] that the methanol crossover through a fuel-cell membrane to the cathode leads to a decrease in the oxygen electroreduction current. A wide quest for methanol-tolerant electrocatalysts of oxygen reduction is carried on.[3] When studying the electrochemical behaviour of mixed MeOH + O_2 solutions on a Rh electrode, we observed an unusual effect of methanol present in solution on the oxygen electroreduction current. This publication is devoted to this effect.

Polarization measurements were carried out at room temperature (19±1 °C) in a three-electrode cell according to a procedure described elsewhere.[4,5] A Pt plate with the visible surface $S_{\text{geom}} = 1.1$ cm^2 and covered with a layer of porous Rh electroplate ($E_{\text{dep}} = -0.020$ V[6])[†] served as the working electrode; the ratio of the true surface to visible was determined based on the copper adsorption[7] to be 250–500. The contribution of the Pt surface free of Rh to the overall surface area can be neglected, from hereon the studied electrode is called the Rh electrode. Stationary polarization curves were measured in both anodic and cathodic directions under potentiostatic conditions; the criterion of stationarity corresponded to the current variations by no more than 2% per min.

Figures 1 and 2 show stationary polarization curves of oxygen electroreduction (curves *1*), methanol electrooxidation (curves *2*), and in mixed solutions O_2(sat.) + MeOH (curves *3*) for the methanol concentrations of (*a*) 5×10^{-2} and (*b*) 1.0 mol dm^{-3}. Curves in Figure 1 were recorded from 0.9 to 0.3 V; curves in Figure 2 were measured from 0.3 to 0.9 V in 50 mV steps (the Rh electrode pretreatment is shown in the figures). It is evident that the current depends on the initial state of the electrode surface (first of all, its degree of oxidation). This is associated with the larger hysteresis between the curves of oxygen adsorption and desorption on a Rh electrode.[8] According to published data,[9] the irreversible nature of oxygen adsorption manifests itself at $E > 0.45$ V on Rh electrodes and only at $E > 0.9$ V on Pt. On the preliminarily oxidized Rh surface, the oxygen reduction current is sufficiently lower (curve *1*, Figure 1) than on a pre-reduced surface [to make the comparison easier, curve *1* from Figure 2(*a*) is also shown in Figure 1(*a*) in a dashed line].

However, irrespective the direction of measuring polarization curves, the methanol electrooxidation currents in the absence of oxygen were insignificant [on the scale used, they were discernible only in 1 M MeOH, Figures 1(*b*) and 2(*b*)]. This means that, with the observed principle of current additivity,[10] in mixed solutions, the oxygen electroreduction currents (curves *1*) should not undergo considerable changes in the methanol presence. The real currents in mixed solutions (curves *3*) considerably deviated from the individual currents of oxygen electroreduction; moreover, this effect increased with the increase in the methanol concentration.

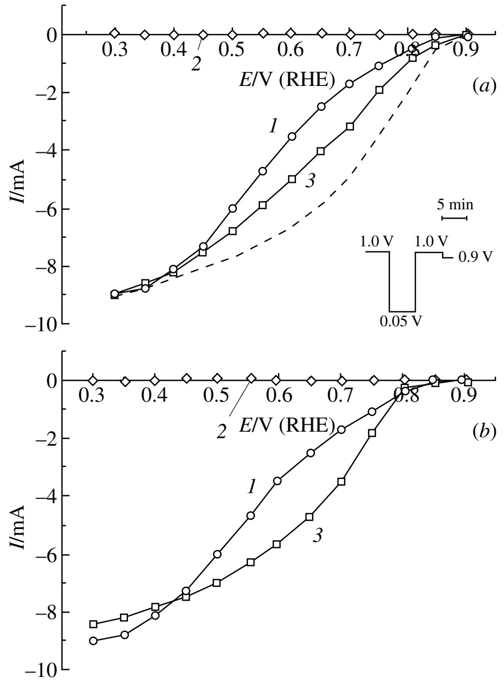

Figure 1 Stationary polarization curves recorded from 0.9 V in solution of (*1*) O_2(sat.), (*2*) *x* mol dm^{-3} MeOH, (*3*) *x* mol dm^{-3} MeOH + O_2(sat.). (*a*) $x = 5\times10^{-2}$; (*b*) $x = 1.0$. Supporting electrolyte, 0.5 M H_2SO_4. Dashed line is the curve *1* from Figure 2(*a*).

Thus, the same as found earlier for Pt electrode,[3–5,11] on Rh electrodes too, the principle of current additively was not observed in O_2 + MeOH solutions. However, the fundamental difference of the Rh behaviour as compared with Pt deserves mention, namely, in considerable potential intervals, the oxygen reduction current in the presence of methanol increased rather than decreased (especially, when the polarization curves were measured from 0.9 V, Figure 1). So long as the methanol electrooxidation currents were insignificant in the absence of oxygen (curves *2*), this effect unambiguously points to the increase in the oxygen electroreduction current in the presence of methanol. If the methanol electrooxidation currents increased in a mixed solution, then the real increase in the O_2 electroreduction current should be still higher.

[†] Electrode potentials are shown with respect to reversible hydrogen electrode (RHE) in the same solution.

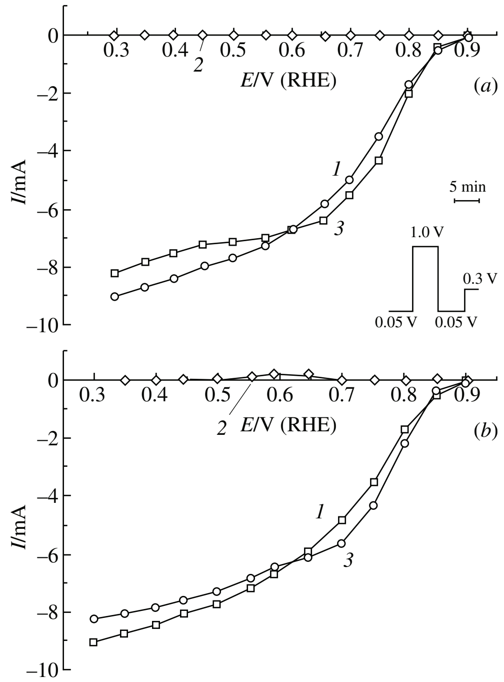

Figure 2 Stationary polarization curves recorded from 0.3 V. Curve numbers correspond to those in Figure 1.

A decrease in the Rh surface coverage with adsorbed oxygen in the presence of methanol as a result of direct catalytic interaction between MeOH and O_{ads} (without electron exchange *via* the electrode)[‡] can be assumed as the reason for the observed phenomenon. It is known[12] that O_{ads} inhibits the oxygen electroreduction on Rh electrodes. The possibility of a catalytic interaction between MeOH and O_2 was assumed[3–5,11] for Pt electrodes (most probably, *via* O_{ads}). A concept of direct interaction of HCO-compounds with O_{ads} was used previously[13,14] in the interpretation of transients of open-circuit potential.

An attempt was undertaken to quantitatively compare the CO_2 yield when an electrode was polarized in 1 M MeOH in the absence and the presence of oxygen in solution. For this purpose, we used a procedure of CO_2 absorption in an Ascarite-filled tube, which was applied earlier[15] to find the composition of propane chemisorption products. However, for the methanol electrooxidation in a deaerated solution (1 M MeOH + 0.5 M H_2SO_4, Ar, 0.6 V, 2 h), the CO_2 yield was found to be 0.3±0.2 mg (five experiments), which exceeded the calculated value ~1.5-fold (assuming the 100% yield of CO_2). It was found that the low accuracy in determination of the CO_2 yield was caused by the difficulty in the removal of MeOH traces from the gas flow. Hence, we only managed to roughly determine the upper limit of the increase in the CO_2 yield with the substitution of O_2 for Ar as not exceeding 50%. Insofar as the MeOH electrooxidation currents were small at 0.6 V, the obtained result allowed us to conclude that the rate of the direct catalytic interaction between MeOH and O_{ads} on a Rh electrode is very low. It is typical that the observed effect of the increase in the O_2 electroreduction current in the presence of MeOH was still sufficiently pronounced at $c_m = 5\times10^{-2}$ mol dm^{-3} [Figures 1(*a*) and 2(*a*)], *i.e.*, in a solution where the rate of the reaction between MeOH and O_{ads} was still lower.[14]

The stability of the effect of oxygen reduction current increase in the presence of MeOH is proved by the following fact. Namely, we have observed after 2 h even same increase in this electroreduction current (~10%) in experiments carried out for determination of CO_2 current efficiency at 0.6 V in 1 M MeOH + O_2(sat.).

Thus, in this study, by the example of a Rh electrode, it was shown for the first time that oxygen electroreduction currents can increase in the presence of methanol in solution. The effect was explained by the changes in the O_{ads} coverage (state) as a result of its direct interaction with methanol.

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[‡] The surface coverage with O_{ads} cannot be determined as on Pt[5] by the method of cathodic pulses due to the wide overlap of hydrogen and oxygen adsorption regions on Rh.[8,9]