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Open-circuit potentials of a platinized platinum electrode in mixed oxygen–methanol solutions

Boris I. Podlovchenko* and Tatyana D. Gladysheva

Department of Chemistry, M. V. Lomonosov Moscow State University, 119992 Moscow, Russian Federation. Fax: +7 495 939 0171; e-mail: podlov@elch.chem.msu.ru

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A difference between stationary open-circuit potentials and mixed potentials corresponding to the additivity of currents in the individual solutions of MeOH and O_2 was found; the open-circuit potentials are shown to dramatically decrease with methanol concentration increasing in a narrow concentration range.

Considerable attention was paid to the effect of methanol in solution on the behaviour of an oxygen electrode.[1–4] This is associated with the crossover effect of methanol in direct methanol fuel cells, which results in the deterioration of characteristics of the cathode and the fuel cell as a whole.[5,6] It is known that, when the principle of additivity of currents is fulfilled,[7] the open-circuit potential (OCP) in a solution containing an oxidant and a reductant can be calculated based on polarization curves measured in individual solutions. However, as a rule, the principle of additivity is adequately fulfilled only for sufficiently simple reactions. The reactions of electroreduction of oxygen and electrooxidation of methanol on platinum electrodes are complex, include many stages and various adsorbed intermediate species.[8–12] Hence, the additivity principle is unlikely to be fulfilled in mixed solutions of oxygen and methanol on platinum electrodes. Indeed, it was shown[1–4] that the principle of additivity of currents is violated to a certain extent on platinum electrodes in solutions of O_2 + MeOH. The OCPs were compared with those expected in the case of fulfillment of the additivity principle and a deviation was observed.[4] These measurements were carried out on a carbon-supported Pt catalyst under nonstationary conditions.

Frumkin with co-workers[10,13] considered the nature of OCPs established in individual alcohol solutions on Pt/Pt. It seemed interesting to measure the OCP on such electrodes in mixed solutions of methanol and oxygen, determine the role of the anodic and cathodic reactions in the formation of OCPs and, particularly, elucidate the possibility of using OCPs in assessing the degree of fulfillment of the principle of additivity of currents.

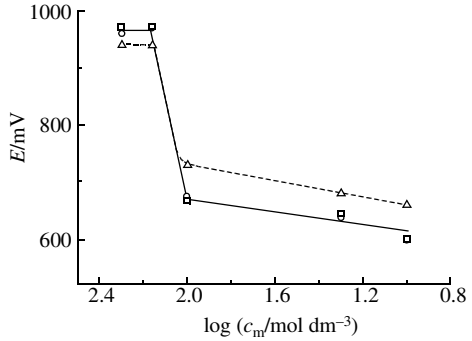

Figure 1 Dependence of the open-circuit potentials in solutions of MeOH + O_2 (sat.) on methanol concentration: circles – E_{oc}^{mix}; squares – OCP determined by the intersection of polarization curves in mixed solutions with the abscissa; triangles – OCP corresponding to the principle of additivity of currents. Supporting electrolyte 0.5 mol dm^{-3} H_2SO_4.

The studies were carried out in a three-electrode cell with cathodic and anodic compartments separated by a cock at 20±1 °C. The solution was stirred with a magnetic stirrer. The constant intensity of stirring was controlled according to the limiting diffusion current of O_2 electroreduction in its saturated solution (8.5±0.1 mA cm^{-2} of the geometric area). High-grade oxygen (99.999%), twice distilled methanol (reagent grade) and water, H_2SO_4 (Merck, analytical grade) were used. The procedure of OCP measurements was as follows. Oxygen was purged through a 0.5 M H_2SO_4 solution with an immersed Pt/Pt electrode up to the establishment of a stationary potential (1.040±0.020 V).[†] Then, a deaerated concentrated methanol solution (containing 0.5 mol dm^{-3} H_2SO_4) was added in an amount sufficient to yield a given MeOH concentration. Stationary OCPs and stationary currents were measured on a Pt/Pt electrode with the geometric surface S_{geom} = 1.1 cm^2 and the true surface area S_{true} = 170–220 cm^2 estimated from the hydrogen adsorption. The surface coverages with the chemisorption products of methanol and O_{ads} at stationary potentials were determined using cathodic potentiodynamic pulses (v = 1.0 V s^{-1}) as described earlier,[14,15] on a Pt/Pt electrode with S_{geom} = 0.4 cm^2 and S_{true}/S_{geom} = 100–200.

As can be seen in Figure 1 (circles), the greatest deviation E_{oc}^{mix} from the initial oxygen electrode potential was observed at MeOH concentrations of > 10^{-2} mol dm^{-3}. For $c_m < 10^{-2}$ mol dm^{-3}, OCP sharply shifts to more positive values up to the potential region of the beginning of oxygen adsorption on Pt/Pt.

Stationary polarization curves were measured in mixed solutions for which the values of E_{oc}^{mix} are shown in Figure 1, and also in individual solutions of O_2 (sat.) and MeOH (for the same c_m as in the mixed solutions). Figure 2 shows the examples of curves for O_2 electroreduction (curves *1*) and curves measured in solutions of MeOH + O_2 (curves *2*) and MeOH (curves *3*) for (*a*) $c_m = 5\times10^{-2}$ and (*b*) 7×10^{-3} mol dm^{-3}.

In Figure 1, squares correspond to zero current in mixed solutions $E_{I=0}$. They coincide with E_{oc}^{mix}, *i.e.*, E_{oc}^{mix} are indeed the mixed potentials determined by the equality of currents of MeOH electrooxidation and O_2 electroreduction, but this concerns only their partial current in mixed solutions. The latter currents may differ from the individual currents of methanol electrooxidation and oxygen electroreduction for two reasons,[3,4] namely, due to the effect of chemisorption products and a direct chemical reaction between MeOH and O_2.

For the deviations of individual currents of MeOH electrooxidation (I_m) and O_2 electroreduction (I_O) from their partial

[†] The potentials E are related to a reversible hydrogen electrode in the same solution.

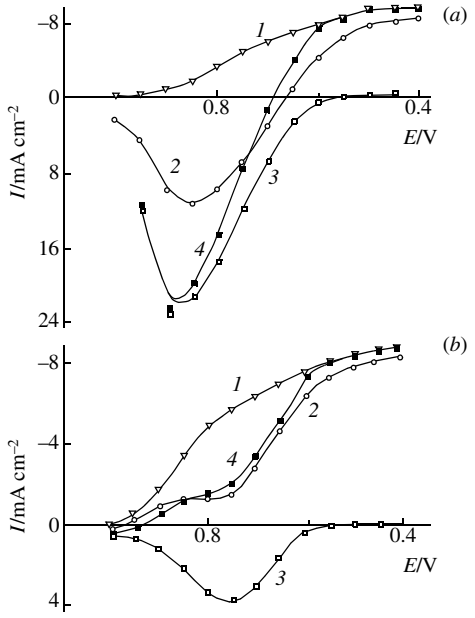

Figure 2 Stationary polarization curves in solutions of (*1*) O_2 (sat.), (*2*) *x* mol dm^{-3} MeOH + O_2 (sat.), (*3*) *x* mol dm^{-3} MeOH, (*4*) the sum of current of curves *1* and *3*. (*a*) $x = 5\times10^{-2}$; (*b*) $x = 7\times10^{-3}$.

currents in mixed solution to be insignificant, E_{oc}^{mix} should be close to the potential at which $I_{add} = I_m + I_O$ is zero. As can be seen in Figure 1 (triangles) the mixed potentials that correspond to the principle of additivity, *i.e.*, $E_{I_{add}=0}$, considerably deviate from the real OCP in mixed solutions. At potentials smaller than 0.7 V, E_{oc}^{mix} is 40–60 mV more negative than $E_{I_{add}=0}$. In this potential range the stationary currents in mixed solutions [Figure 2(*a*), curve *2*] are higher (with regard to the sign) than the total currents $I_{add} = I_m + I_O$ (curve *4*). This could be due to both an increase in the current of methanol electrooxidation in the presence of O_2 and a decrease in the current of oxygen electroreduction (in the absolute magnitude) in the presence of MeOH. The first factor appears to be most probable because we determined (by means of cathodic potentiodynamic pulses) that the presence of oxygen in solution leads to a decrease in the surface coverage with products of strong chemisorption of methanol. According to the generally accepted concept of the two-route mechanism of MeOH electrooxidation,[11,12] these products inhibit the electrooxidation of alcohol.

A solution of MeOH (5×10^{-2} mol dm^{-3}) + O_2(sat.) was analysed for the stable products of methanol electrooxidation at E_{oc}^{mix}. No formic acid was detected; formaldehyde was found in small amounts corresponding to the current efficiency of less than 3%. Thus, CO_2 is the main product of methanol oxidation at the OCP established in the mixed solutions.

For low methanol concentrations (< 10^{-2} mol dm^{-3}) in the presence of O_2, $E_{oc}^{mix} > 0.90$ V is established. As follows from experiments with potentiodynamic pulses (Figure 3), at 0.90 V, in a solution saturated with O_2, in the absence of methanol, oxygen is adsorbed in appreciable amounts (the wave in curve *1* with a maximum at ~0.65 V). A rough estimate of θ_O from the $Q_O/2Q_H^o$ ratio (where Q_O and Q_H^o are the charges consumed in the electrodesorption of O_{ads} and a monolayer of H_{ads}, respectively) produces a value of $\theta_O \sim 0.2$. In the presence of 5×10^{-2} mol dm^{-3} MeOH, the surface coverage with O_{ads} substantially decreases (Figure 3, curve *2*) but remains considerable. In solutions with $c_m < 10^{-2}$ mol dm^{-3} at $E_{oc}^{mix} > 0.90$ V, the surface coverages with oxygen are obviously higher than that at 0.9 V in 5×10^{-2} mol dm^{-3} MeOH. Apparently, the presence of O_{ads} on the surface stabilises E_{oc}^{mix} at such high values. The less positive $E_{I_{add}=0}$, as compared with E_{oc}^{mix} (in contrast to $E_{I_{add}=0}$ in the low-potential range), makes it possible to assume that the current

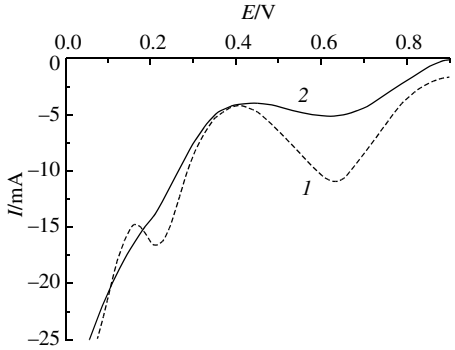

Figure 3 Cathodic potentiodynamic pulses (1 V s^{-1}) in the solutions of (*1*) O_2 (sat.) and (*2*) 5×10^{-2} mol dm^{-3} MeOH + O_2 (sat.).

of MeOH electrooxidation decreases. This agrees with published data[4] according to which the methanol oxidation current in the presence of O_2 decreased at $E > 0.7$ V. At $E > 0.7$ V, the methanol electrooxidation rate is limited by its dehydrogenation.[11,12,14,15] The decrease in the current of methanol electrooxidation in the presence of O_2 could be caused by both the suppressing effect of O_{ads} on the MeOH destruction and the direct catalytic reaction of O_2 with intermediate products of MeOH dehydrogenation. The strong displacement E_{oc}^{mix} in cathodic direction is required at $E < 0.9$ V to compensate by reduction currents (under constant low concentration O_2) the fast increase of oxidation currents with increasing MeOH concentration ($I_m \sim kc_m$).[11,12,15] Obviously it is due to appearence and increasing with *E* decreasing of diffusional limitings associated with oxygen. In such a qualitative manner, the strong variation of E_{oc}^{mix} (from ~ 0.9 to ~0.7 V) in a narrow interval of c_m can be explained (Figure 1).

Thus, the comparison of E_{oc}^{mix} with $E_{I_{add}=0}$ suggests the presence of deviations from the simple additivity of currents in mixed solutions of methanol and oxygen on a Pt/Pt electrode. Apparently, this should be explained by nonfaradaic interactions between MeOH and O_2 on the Pt surface. The fact that the OCP sharply decreased with the methanol concentration in a narrow concentration range is of practical interest.

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