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Nataliya A. Mayorova · Olga A. Khazova
Vladimir S. Bagotzky

Methanol electrooxidation on platinum mesh electrodes bonded to solid polymer electrolytes

Abstract Methanol electrooxidation on smooth platinum electrodes bonded to solid polymer electrolytes was studied in water and acid solution by voltammetric measurements with different scanning rates. An enhancement of the oxidation rates was observed in these systems as compared to identical platinum electrodes in contact with liquid electrolytes. This electrocatalytic effect strongly depends on the measuring conditions and on the electrode potential. The reasons for the catalytic effects at different potentials are discussed.

Key words Solid polymer electrolyte · Electrode · Methanol · Electrooxidation

Introduction

During recent years, solid polymer electrolytes (SPE) have been increasingly applied in methanol and hydrogen-oxygen fuel cells, electrolyzers, sensors and other electrochemical devices. Mostly, membranes of the types Nafion-117 or Nafion-315 are used for these purposes.

In some investigations, a substantial increase in the specific oxidation rate of methanol in solutions [1–4], methanol vapor [5, 6] on platinum, carbon monoxide on gold [7], hydrogen on platinum [8, 9] and formic acid on palladium electrodes [10] contacting with SPE as compared with the same catalysts immersed in liquid electrolytes without SPE was observed. Different explanations for such an enhanced catalytic activity were proposed. Aramata et al. [1–3] supposed the reason for the increased activity of Pt-SPE (about 10–20 fold) to be an increased number of redox-couples Pt(II)/Pt(0) and Pt(IV)/Pt(0), which act as mediators for methanol oxidation. At the same time, the state of methanol and

water absorbed in the pores of the membrane is characterized by a lowering of the strength of the hydrogen bonds. In [1], a lowered surface coverage with adsorbed methanol on Pt-SPE electrodes was also observed, which, according to the author's view, leads to an increased oxidation rate and to an increased stability of these electrodes.

In [4], an increased (fivefold) oxidation rate of dissolved methanol was observed on Pt-SPE-C electrodes (dispersed platinum on a carbon support soaked with liquid Nafion). This increase was explained by a lowering of the inhibiting effect of specifically adsorbed anions due to their lower concentration in Nafion.

In [11], a change in the adsorption state of CO on Pt–SPE–Au electrodes (electrochemically deposited platinum on gold support covered with a thin film of Nafion) was fixed as compared with the state on Pt–Au electrodes. This change manifests itself by a change in the IR spectrum measured by adsorption reflectance spectroscopy: the adsorption maximum at 2077 cm^{-1} is replaced by a broader double maximum. According to the authors, this change is linked with an influence of Nafion on the adsorption properties of platinum.

In all investigations mentioned, the electrodes were prepared in the form of dispersed platinum, palladium, platinum alloys, or gold deposited on polymer film or membranes. For pure platinum and platinum alloys, the method of chemical deposition was mostly used in which a solution of salts of the corresponding metals is reduced by a solution of borohydride or hydrazine diffusing through the membrane from the other side [1–3, 8, 12]. Electrochemical deposition of platinum on SPE films on gold or carbon supports was also used [4, 10, 11]. In both these cases, the structure of the deposited catalyst can be different from the structure of electrochemically deposited platinized platinum (without SPE), and this can be one of the reasons for the different catalytic activity.

The aim of the present investigation was a thorough comparison of the oxidation rates of dissolved methanol in liquid electrolytes and in SPE on platinum electrodes with a well-defined structure and state of the surface.

N.A. Mayorova · O.A. Khazova · V. S. Bagotzky (✉)
A.N. Frumkin Institute of Electrochemistry,
Russian Academy of Sciences, 117071 Moscow, Russia
Fax: +7 095 952 0846

For this purpose, relatively smooth platinum mesh electrodes were used, both in the liquid electrolyte and in SPE. The ratio of true to apparent surface of the mesh electrodes was 8.

Experimental procedure

The measuring cell consisted of two half-cells for the working and the auxiliary electrodes separated by a Nafion 117 membrane. Two platinum mesh electrodes (working and auxiliary) were pressed onto the membrane, one on each side. In order to assure a good contact between electrodes and membrane, a hot pressure method was used [13]. The assembly, consisting of the two platinum electrodes and the Nafion membrane, was placed into a mold and heated to 90–100 °C; then the pressure was increased to 50 kg/cm² and was held for 90 s. This procedure allowed the formation of electrochemical groups Pt–SPE–Pt with a low resistance. The resistance was measured at different frequencies from 20 Hz to 100–200 kHz and extrapolated to infinite frequency. The measured values were between 0.6 and 2.0 ohm · cm², which corresponds to the data in [14].

In a second version, a platinum mesh electrode (working) was pressed onto one side of the membrane only. The auxiliary electrode was placed in the liquid electrolyte at some distance from the membrane. The compartment for the auxiliary electrode was filled with a solution of the background electrolyte (0.5 M H_2SO_4), and the compartment for the working electrode was filled with a solution of methanol either in water or in the background electrolyte. The reference electrode was placed in a special compartment – the tip of the Luggin capillary adjacent to the membrane. In the case of a background solution in the working compartment of the cell, the reference electrode can be placed in the same compartment, the tip of the Luggin capillary adjacent to the platinum mesh.

For the preparation of solutions, double-distilled water and double-distilled methanol "Chempure" were used. The values of the electrode potentials E_r chemical pure to the reversible hydrogen electrode (rhe).

Prior to experiments, the membranes were thoroughly purified from possible organic admixtures. The following steps were used:

1. Treatment for 30 min in a hot solution of 2 M KOH
2. Washing in water
3. Boiling for 1 h in an oxidative mixture: H_2SO_4 ($\rho = 1.84$ g/cm³) + 30% H_2O_2 + H_2O (1 : 1 : 1)
4. Washing in water
5. Boiling for 30 min in 0.5 M H_2SO_4
6. Boiling 3 times for 15 min each in new portions of water
7. Stabilization in water for 3 days.

After this treatment, the membranes were stored in water in hermetically sealed vessels with periodical renewal of water. Voltammetric measurements in water with purified and non-purified membranes showed the appearance for the latter of additional maxima between $E_r = 0.4$ and $E_r = 1.6$ V not connected with oxygen adsorption or desorption. Platinum mesh electrodes pressed onto non-purified membranes gradually lost their catalytic activity for methanol oxidation as a result of poisoning by admixtures extracted from the membrane. The main criterion for purity of the membrane was the coincidence of the voltammetric curves measured on a Pt–SPE electrode in water and on the same kind of Pt mesh electrode in 0.5 M H_2SO_4.

The catalytic activity for methanol electrooxidation was compared in the following electrode systems: (1) Pt–SPE–water (Pt–SPE in water), (2) Pt–SPE–acid (Pt–SPE in 0.5 M H_2SO_4), and (3) Pt–acid (Pt in 0.5 M H_2SO_4).

Voltammetric curves were measured at scanning rates v from 2 to 1000 mV/s in 10^{-3}–0.5 M solutions of methanol in water or in 0.5 M H_2SO_4. Prior to measurements, the working compartment of the cell was thoroughly deoxygenated with argon.

A conventional anodic-cathodic pretreatment of the electrode was applied. Then the starting potential $E_r = 0.4$ V was applied for 20 s and the voltammetric curves for methanol oxidation were measured. All oxidation currents are referred to unit value of the true electrode surface measured by hydrogen adsorption.

Experimental results and discussion

In Fig. 1, voltammetric curves for Pt–SPE–water electrodes without (curve 1) and with 10^{-3} M methanol (curve 2) are shown, as well as for a Pt–acid electrode without methanol (dotted curve). A comparison of curve 1 and the dotted curve shows only minor differences. The potential of oxygen reduction in the presence of SPE is slightly shifted to more negative values, pointing to some lowering of the reaction rate. The currents in the double-layer region are somewhat higher, and the maxima of hydrogen adsorption are slightly flattened (the lowering of hydrogen adsorption is about 5%). The curve for Pt–SPE–acid practically coincides with the curve for Pt–acid.

In the presence of 10^{-3} M methanol and at a scanning rate of 20 mV/s, two maxima due to methanol oxidation appear on the voltammetric curve for Pt–SPE–water: maximum I at $E_r = 0.68$ V and maximum II at $E_r = 1.35$ V. At higher scanning rates and higher methanol concentrations, these maxima are shifted to more positive potentials.

The rate of methanol electrooxidation on the electrode systems mentioned were compared at three potentials: potential $E_r = 0.55$ V on the ascendant part of the voltammetric curve and the potentials of maxima I and II (which depend on the scanning rate and methanol concentration).

At potential $E_r = 0.55$ V, the steady-state reaction rate is limited by the rate of interaction of chemisorbed
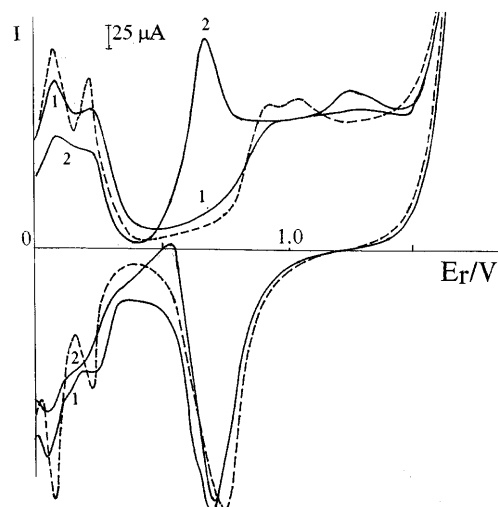

Fig. 1 Voltammetric curves for Pt–SPE–water electrodes without (*curve 1*) and with addition of 10^{-3} M methanol (*curve 2*); *dotted line* voltammetric curve for a Pt–acid electrode (0.5 M H_2SO_4) without methanol; scanning rate $v = 20$ mV/s

methanol and OH species on the surface of the electrode [15] (kinetic region). At the potential of maximum I, the overall reaction rate is in addition influenced by the rate of methanol adsorption on the platinum surface (transition region), which becomes predominant at more positive potentials. At the potential of maximum II, the overall reaction rate depends only on the adsorption rate. At this potential, the platinum surface is completely covered with adsorbed oxygen.

In Fig. 2, the dependence of the oxidation current densities for 0.1 M CH_3OH on the scanning rate v is shown. At the potentials of maximum I, the highest oxidation rate is observed for Pt–SPE–water; it declines when passing to Pt–SPE–acid and then to Pt–acid. This catalytic effect depends on the scanning rate. At $v = 2$ mV/s (which is close to steady-state conditions), the difference between Pt–SPE–water and Pt–acid is 15-fold; at $v = 1000$ mV/s the currents are almost the same.

At the potentials of maximum II, the catalytic effect is very low, and a difference of about 50% can be seen only at the lowest scan rate. At the potential $E_r = 0.55$ V, the differences are also low: 2.5-fold at $v = 2$ mV/s and much less at higher scan rates. It must be stressed that, in contrast to maximum I, the currents for Pt–SPE–water and Pt–SPE–acid at this potential are almost equal.

Figure 3 shows the dependence of current density on methanol concentration at $v = 20$ mV/s. At potentials of maximum I, the highest currents are observed for Pt–SPE–water. The dependence of log i on log c is almost linear, with a slope $b = 0.7$. Such a dependence

$(i = kc^b)$ is characteristic of oxidation processes on platinum electrodes under Temkin adsorption conditions. For methanol oxidation on platinum in liquid solutions in the kinetic region, the value of b is usually 0.5 [15]. The higher value of b in Fig. 3 is due to the beginning of the influence of the rate of methanol adsorption (at higher potentials, when methanol adsorption becomes the rate-determining step, a first-order reaction kinetics is observed).

On Pt–SPE–acid and Pt–acid electrodes, the oxidation rates are almost the same and 4–6 times lower than on Pt–SPE–water electrodes. The dependence on the methanol concentration remains the same ($b = 0.8$); deviations at lower concentrations are probably due to the insufficient accuracy of measurements at low current densities. From the equality of the oxidation rates on Pt–SPE–acid and Pt–acid electrodes, it can be stated that, in the region of maximum I, the catalytic effect on Pt–SPE–water electrodes is mainly due to the difference in concentration of free anions in the liquid electrolyte and in SPE.

At the potential of maximum II, no differences in activity for all systems studied can be observed.

At the potential $E_r = 0.55$ V, the oxidation rates for Pt–SPE–water are also the highest. For 0.1 M methanol, they exceed 2.5 times the rates for Pt–acid. In contrast to the behavior at the potential of maximum I, an enhanced reaction rate can also be observed for Pt–SPE–acid. Thus, in the kinetic region, the catalytic effect of SPE membranes is connected not only with a lowering of the inhibiting influence of anions.

At $E_r = 0.55$ V, the log i, log c dependence is also linear, but its slope is 0.2–0.4. This lower value is
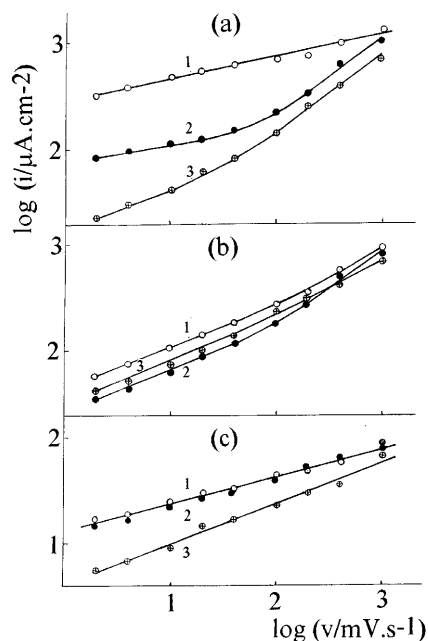

Fig. 2a–c Dependence of current densities for oxidation of methanol (0.1 M) on the scanning rate at potentials of maximum I (a), of the maximum II (b), and at $E_r = 0.55$ V (c) for the systems Pt–SPE–water (1), Pt–SPE–acid (2), and Pt–acid (3)
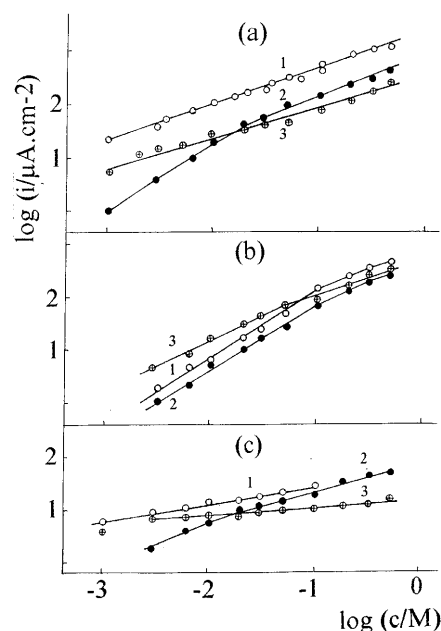

Fig. 3a–c Dependence of oxidation current densities on the concentration of methanol at $v = 20$ mV/s (potentials and systems as in caption for Fig. 2)

probably linked with the insufficient rest time at 0.4 V (20 s) in our experiments, which seems to be not enough to reach steady-state conditions; therefore dehydrogenation currents due to remaining slow adsorption processes possibly influence the oxidation currents at low methanol concentrations. In [2], on Pt–SPE–acid electrodes, a slope of 0.2–0.6 was reported; at the same time the kinetic parameters for the reaction were the same as for Pt/Pt–acid, in spite of a difference in catalytic activity of about two orders of magnitude.

Conclusions

1. For relatively smooth platinum electrodes (roughness factor about 8) bonded to SPE, a distinct catalytic effect in comparison with the system Pt–acid can be observed, but this effect is lower than that on highly dispersed platinum deposited on polymer membranes [1–3].

2. The degree of rate enhancement depends on the measuring conditions; it increases when approaching steady state conditions.

3. The catalytic effect depends on the electrode potential:

(a) At the potential of the current maximum I, it depends only on the concentration of the free anions and is probably related to the inhibiting influence of these anions on the methanol adsorption rate.

(b) In the kinetic region ($E_r = 0.55$ V), the system Pt–SPE–acid also shows an enhanced reaction rate in comparison with the system Pt–acid; this catalytic effect is obviously not linked to the inhibiting influence of anions.

(c) At the potential of the current maximum II, where the platinum surface is oxidized, no catalytic effect appears.

In order to clarify the reasons for the catalytic effects in the lower potential range, additional experiments in steady-state conditions must be undertaken, as well as investigations into the adsorption behavior of Pt–SPE systems. A comparison of catalytic effects at equal surface coverages with adsorbed methanol would be beneficial for a better understanding of these phenomena.

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