In conclusion the authors consider it a pleasant duty to thank V. E. Kazarinov and V. N. Andreev for a helpful discussion of the results of the present work.

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ELECTROCHEMICAL BEHAVIOR OF CO_2 ON ELECTRODES WITH MEDIUM AND HIGH HYDROGEN OVERVOLTAGE

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UDC 541.138.3

Although CO_2 has extreme electrochemical stability, the possibility of its electroreduction to various organic products is of considerable interest as an electrochemical analog of natural photosynthesis. It has been shown in earlier works that a mercury electrode and amalgams reduce CO_2 only to formic acid. This is effected in a neutral solution at high overvoltage, within a very narrow pH range, through acceptance of an electron in a slow stage [1-3].

Ito [4] has also produced formic acid on zinc, lead, tin, indium, and cadmium; the reactions took place at lower overvoltages than on mercury. A number of studies on platinum [5-7] and results that we obtained on adsorption of CO_2 on metals of the platinum group [8] showed that electroreduction of CO_2 occurs readily on platinum and rhodium, through hydrogen adsorption, to form chemisorbed particles with a higher degree of reduction than HCOOH. On the other hand, no reductive chemisorption of CO_2 occurs on other metals of the platinum group containing adsorbed hydrogen, indicating that the metal itself plays a highly electrocatalytic role in the electroreduction of carbon dioxide.

In the present work, we studied this reaction on various electrodes with medium and high hydrogen overvoltage: lead, zinc, cadmium, tin, copper, nickel, iron, molybdenum, tungsten carbide, gold and vitreous carbon. These materials were fabricated as rotating disk electrodes. Polarization curves were obtained at a scan rate of 0.0125 V/sec using a PO-5122 oscillographic polarograph (model 03) in an argon and CO_2 atmosphere. The main electrolyte was a solution of 0.1 N $LiCH_3COO$ + 0.1 N CH_3COOH. In the range where pH > pK = 6.3, sparging with CO_2 was replaced by adding an amount of K_2CO_3 equivalent to the solubility of CO_2 in an acid solution of 2×10^{-2} M. The current used for the polarization curves was divided by the geometric surface area of the electrode. In the case of the copper electrode the current was corrected for pseudocapacity, measured as a rapid pulse between the initial potential ($\varphi_h = 0$ V) and the potential of the evolved hydrogen. Current for the gold electrode was dependent on its true surface measured through oxygen adsorption.

Figure 1 shows polarization curves in buffered acetate solutions for a flat, rotating copper cathode. In acid and alkaline solutions, the curves were similar with argon or CO_2; i.e., no additional CO_2 electroreduction current was observed. The curves had two sections: The first was a linear Tafel section, and the second a gently sloping nonlinear section in log i vs φ coordinates. In acid and alkaline solutions the slope of the first

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 13, No. 12, pp. 1818-1823, December, 1977. Original article submitted October 26, 1976.

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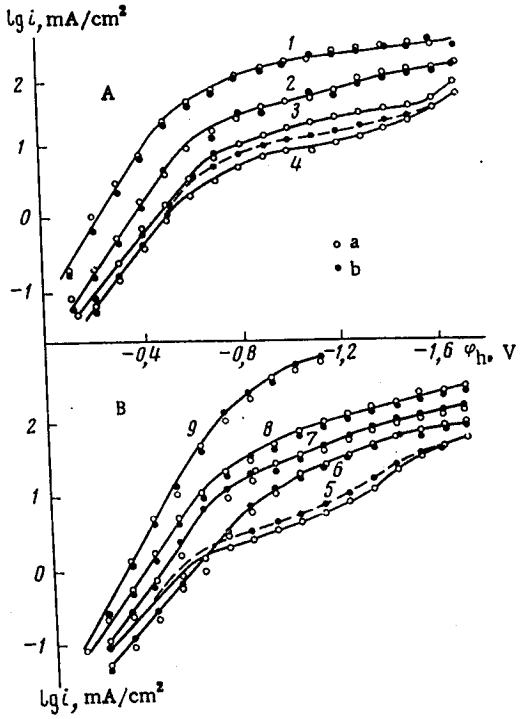

Fig. 1. Polarization curves for a rotating copper electrode (5800 rpm) in the following buffered solutions: A) in acid solutions with pH 1.12 (1); 2.3 (2); 5.0 (3); and 5.5 (4); B) in neutral and acid solutions with pH 6.12 (5); 7.5 (6); 10.75 (7); 12.0 (8); and 13.62 (9). a) Ar; b) CO_2.

section was about 120 mV and Tafel deviations were observed only at very high current densities. On passing to neutral solutions, the Tafel deviation increased with lower current densities causing an apparent slope increase even in the first section. Appearance of the second section is probably due to insufficient buffer and to a change in pH near the electrode at high current densities. A considerable current increase was observed with a copper electrode in neutral solutions at a narrow pH range of 5 to 6.5, as a result of electroreduction of CO_2 (Fig. 2A and B).

Partial polarization curves were calculated on the assumptions that the hydrogen evolution current of a copper electrode is the same whether in the presence of CO_2 or argon and that, in the presence of CO_2, the hydrogen evolution and CO_2 electroreduction currents are additive. In the initial section, the partial CO_2 electroreduction current shows a Tafel relation with a slope of ~140 mV. The curve then deviates from linearity and at $\varphi_h = -1.2$ V it passes through a maximum (Fig. 2B). Upon increasing the rotation rate of the copper electrode in a solution with pH 5.5, differences increase between curves obtained in argon and CO_2, showing that the CO_2 reduction current is diffusion limited at potentials of −1.1 to −1.2 V.

It is evident from Fig. 3 that the hydrogen overvoltage of a copper electrode at constant current density in acid solutions increases with an increase in pH, i.e.; $\eta = \text{const} + \gamma \cdot \text{pH}$, where $\gamma = 60$ to 80 mV and increases somewhat with current density. It may thus be postulated that hydrogen ion discharge is the slow stage of the hydrogen evolution reaction in solutions with pH < 5. In alkaline solutions, on the other hand, hydrogen overvoltage decreases with increasing pH, i.e.; $\eta = \text{const} - \gamma \cdot \text{pH}$, where $\gamma = 50$ to 60 mV, and with pH > 8 hydrogen evolution occurs on a copper electrode through discharge of water molecules.

Neutral solutions in the presence of CO_2 give rise to a CO_2 electroreduction current that has no dependence on pH at constant potential φ (Fig. 2D). It then follows that hydrogen ions do not participate in slow or earlier slow stages of CO_2 reduction on a copper electrode. Considering that the Tafel slope is about 120 mV, it may be assumed that the slow stage, even on mercury, comprises a transfer of electrons from the electrode to the CO_2 molecule. We observe this process only in neutral solutions since in acid solutions it is overshadowed by hydrogen evolution due to hydrogen ion discharge. Upon shifting to pH > pK = 6.3, the transfer rate quickly drops owing to a decrease in concentration of CO_2 and its conversion to the HCO_3^- anion which is not reduced. We found that at constant potential relative to a hydrogen electrode kept in the same solution the partial CO_2 reduction current increased initially with a rise in pH and then dropped.

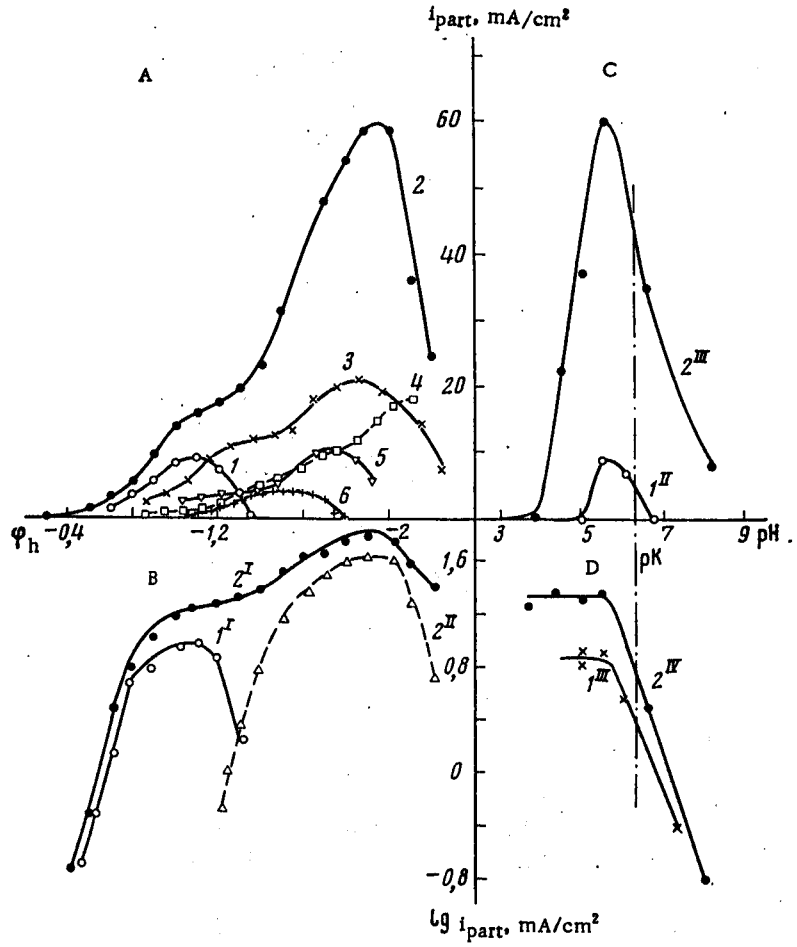

Fig. 2. Relation of partial CO_2 reduction current to potential (A and B) and to pH (C and D) for rotating electrodes of copper (1, 1^{I}, 1^{II}, 1^{III}), tin (2, 2^{I}, 2^{II}, 2^{III}, 2^{IV}), zinc (3), lead (4) cadmium (5), and gold (6). A, B) in a buffered solution at pH 5.5; C) at $\varphi_h = -1.1$ (1^{II}) and −1.9 V (2^{III}); D) at $\varphi = -1.44$ (1^{III}) and −2.18 V (2^{IV}).

Measurements at various temperatures from 20 to 85°C conducted with copper in a neutral solution enabled us to determine the apparent activation energies for hydrogen evolution and CO_2 electroreduction. They conform to the equation $A = A_0 - \alpha nF\eta$ in the same potential region as that in which polarization curves for copper obey the Tafel relation (Fig. 4). In the calculations we took into account the change in CO_2 solubility with temperature. Extrapolations of A_0 for the CO_2 electroreduction reaction and the hydrogen evolution reaction yielded 100.3 kJ and 66.9 kJ, respectively. Slopes of the curves for both reactions were about 100 mV for 4.18 kJ, i.e., $\alpha n \simeq 0.4$, which is in good agreement with the values of αn from Tafel slopes at the same temperature.

The patterns observed with copper were also the case for a tin electrode (Fig. 2). The partial CO_2 electroreduction current for tin, however, considerably exceeded that for copper. The polarization curve shows a wave from −1.1 to −1.2 V and a second maximum at −1.9 V. The limiting current at the wave and that at the maximum depend on the electrode rotation rate; i.e., they are diffusion-controlled. Presence of the two waves indicates that the reduction of CO_2 on tin occurs in two stages. Since the height ratio of the first and second waves is $i_{2,lim}/i_{1,lim} = 60/19 \simeq 3$, we may postulate that, like copper, the first wave represents reduction of CO_2 to formic acid by the general reaction: $CO_2 + 2e + 2H^+ \rightarrow HCOOH$ and that the second wave is probably an indication of further reduction, possibly to methanol.

The higher partial currents for tin and the greater difference in hydrogen evolution and CO_2 reduction overvoltages lead to the conclusion that the CO_2 reduction current can occur within a wider pH range ($4 < pH < 8$) for tin than for copper and mercury. The dependence of partial currents on pH and the similar slopes of the

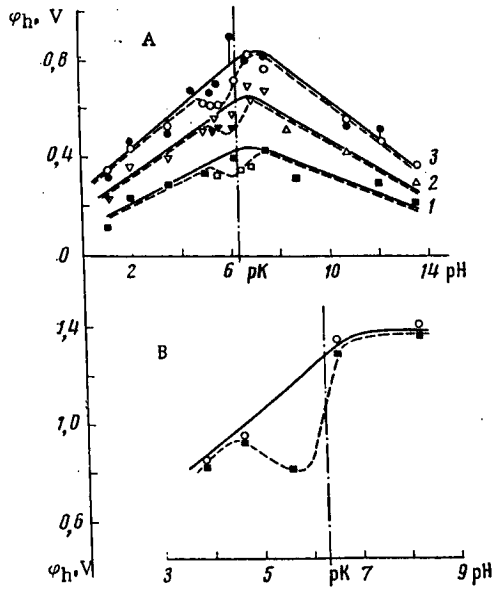

Fig. 3

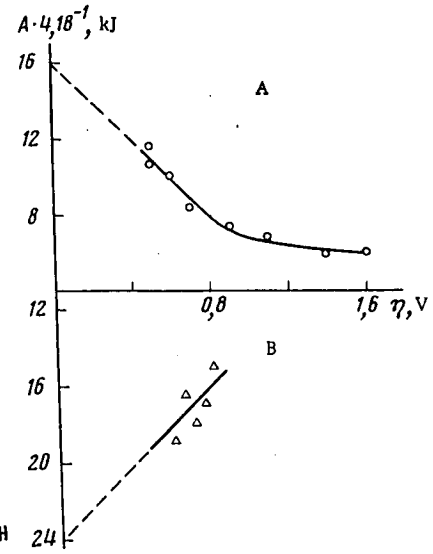

Fig. 4

Fig. 3. Relation of potential at constant current density to solution pH in the presence of CO_2 (dashed line) and in argon (continuous line) for the following electrodes: A) copper at values of log i (in units of mA/cm^2) = −0.5 (1); 0.1 (2); and 0.5 (3); B) tin at log i = 1.0.

Fig. 4. Relation of activation energy to copper potential in a buffered solution with a pH of 5.5 for the hydrogen evolution reaction (A) and the CO_2 electroreduction reaction (B).

partial polarization curves indicate that the CO_2 electroreduction mechanism for tin is generally analogous to the mechanism for mercury and copper (Fig. 2).

A zinc electrode in neutral solutions also gives rise to considerable CO_2 partial reduction currents the nature of which is generally analogous to the partial currents for a tin electrode. The polarization curve also displays a wave between −1.1 and −1.3 V that may represent CO_2 reduction to formic acid, and a maximum at −1.8 V. With zinc however, $i_{2,lim}/i_{1,lim} = 2$; i.e., electroreduction proceeds at the second wave through addition of four electrons, pointing to a reduction to formaldehyde.

Small, partial CO_2 reduction currents were also observed for gold, cadmium, and lead (Fig. 2). Carbon dioxide and inert gases have the same polarization curves for electrodes of tungsten, molybdenum, tungsten carbide, and vitreous carbon. Steady-state currents for platinum, nickel, and iron are much lower in the presence of CO_2 than in an argon atmosphere. This is due to strong CO_2 chemisorption on the electrode and effect of the chemisorbed species on the hydrogen evolution rate. In this case, partial CO_2 reduction currents are unobtainable just from the polarization curves.

Figure 2 shows that the CO_2 reduction overvoltage is strongly dependent on the nature of the electrode material and increases in the order: tin < copper < zinc < cadmium < lead < gold. This series does not fully correspond to the hydrogen overvoltage series. Catalytically active metals of the platinum group with low hydrogen overvoltage easily engender electroreduction through a mechanism of reaction with adsorbed hydrogen; however, bond strength of the chemisorbed particles is too great to permit their subsequent desorption. It is therefore to be expected that cathodes made from metals having medium hydrogen overvoltage are the most suitable for electroreduction of CO_2 to organic substances. The effect of the cathode material on the reaction overvoltage indicates that the slow stage of electron transfer from the electrode to the electroreduced CO_2 molecule is accompanied by a weak, physical adsorption of intermediate particles undetectable by the pulse method.

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EFFECT OF SOLUTION COMPOSITION ON THE RATE OF REACTION OF HYDROGEN PEROXIDE ON A PLATINUM ELECTRODE

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UDC 541.138

The heterogeneous decomposition of hydrogen peroxide is one of the most common model reactions in the study of the catalytic activity of metals. This process is also of independent interest since hydrogen peroxide and its derivatives are intermediates in a number of electrochemical reactions.

It has been repeatedly assumed [1-4] that the decomposition of hydrogen peroxide on a platinum electrode occurs by both an electrochemical and chemical mechanism. Direct evidence for the simultaneous occurrence of electrochemical and chemical reactions leading to the heterogeneous decomposition of hydrogen peroxide was obtained using the heavy isotope of oxygen ^{18}O [5]. This permitted the concrete formulation and significant simplification of the proposed schemes for this process.

In the present work the effects of pH and the ionic composition of the solution on the rate of the electroreduction, electrooxidation, and chemical decomposition of hydrogen peroxide on a platinum electrode were studied.

Polarization and gasometric measurements were carried out on a rotating platinum disk electrode of 1 cm^2 area. The experimental technique was described in detail in our earlier work [6]. The observed values for the current and rate of gas liberation in current units were extrapolated to an infinite rotation rate in coordinates of $1/I$ vs $1/\sqrt{\omega}$. The potentials are given relative to the normal hydrogen electrode ($\varphi_{H_2}^0$) or hydrogen electrode in the same solution (φ_r). The hydrogen peroxide concentration was varied from 10^{-3} to $2 \cdot 10^{-1}$ N.

The solutions were prepared in doubly distilled water using high-purity reagents. The invariance of the ionic strength of the electrolyte with changing pH was maintained by the addition of the required amount of twice recrystallized potassium sulfate.

In Fig. 1, the pH dependence is shown for the rate of decomposition of hydrogen peroxide at a stationary potential by electrochemical and chemical mechanisms. These data were calculated from the results of polarization and gasometric measurements. In a wide pH range (from 0.3 to 12), the rates of the electrochemical and nonelectrochemical reactions are independent of pH. In the strongly basic region with pH above 12, the rates of both processes increase.

The results of the polarization measurements in solutions with different values of pH containing sulfate ion are given in Figs. 2 and 3. The slope ($\partial\varphi/\partial \log I$) both for the anodic and cathodic branch of the curve is ~120-130 mV for all values of pH. This may indicate a slow stage with the participation of the first electron. However, it is difficult to correlate this proposal with the value of $\partial\varphi_c/\partial$pH (or $\partial\varphi_a/\partial$pH) equal to about -60 mV observed in a broad pH range. The order of the reaction relative to hydrogen peroxide obtained from concentration measurements is close to 1 for both the oxidation and reduction reactions.

Thus, the electrochemical reaction of hydrogen peroxide in the pH range from 0.3 to 12 is described by the following kinetic parameters:

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. Translated from Élektrokhimiya, Vol. 13, No. 12, pp. 1823-1825, December, 1977. Original article submitted October 21, 1976.

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