ELECTROREDUCTION OF CARBON DIOXIDE ON A TIN ELECTRODE

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The kinetics of the cathodic reduction of carbon dioxide gas on a tin electrode has been studied. The tin electrode is particularly suitable for this particular reaction. The steady-state polarization curves recorded with a rotating disk electrode in buffer solutions have two Taffel regions, the first of which lies in the region of potentials more positive than −1.15 V with a slope of 110-120 mV. The value of the slope remains constant over a wide range of pH. The experimental dependences in this region can be explained if we assume that CO_2 and the CO_2^- radical with water as the proton donor, are absorbed. The mechanism of the electroreduction of the CO_2 in this region can be represented in a form with two stages:

$$CO_2(ads)+e_M \rightleftharpoons CO_2^-(ads); \quad CO_2^-(ads)+H_2O+e_M \rightarrow HCO_2^-+OH^-.$$

The study using a photoelectron-emission method of the process at the metal/solution boundary has made it possible to establish that the slow stage is the transfer of the second electron.

The electroreduction of CO_2 has attracted the attention of many research workers, in particular in connection with the problem of the electrosynthesis of various organic materials from CO_2 [1]. The studies carried out in [2, 3] show that the cathode material has a strong effect on the overvoltage of the CO_2-electroreduction reaction. Thus, the overvoltage of the reduction of CO_2 on a tin electrode was found to be almost 1.0 V lower than on an Hg electrode [4]. The reduction of CO_2 on tin is also observed over a wider range of pH than in the case of Hg or Cu and this suggests that the tin electrode is a very promising electrode for practical use in the reduction of CO_2 in electrochemical systems.

We have studied the kinetics of the electroreduction of CO_2 on a rotating smooth-tin electrode (type OVCh-000). We made the measurements by recording the steady-state polarization curves ($v = 0.0125$ V/sec) in argon or CO_2 atmospheres with a PO-5122, model 03, oscillographic polarograph and in various buffer solutions: carbonate, phosphate, acetate, or formate.

The partial currents of the CO_2 electroreduction were determined by subtracting the hydrogen deposition currents measured in an argon atmosphere from the currents measured in a CO_2 atmosphere. In this case it was assumed that, in the first approximation, the partial currents of the hydrogen deposition and the electroreduction of CO_2 can be added together in the potential region where there is a marked deposition of hydrogen on the tin, i.e., there is no observable catalytic acceleration of the hydrogen deposition process in the presence of CO_2. All the values of the currents are related to the geometrical surface of the electrode. Otherwise the experimental method was analogous to that described in [3].

In order to study the kinetics of the electroreduction of CO_2 on tin, we examined the photoelectron-emission at the metal/electrolyte-solution interface which has been found to be promising in the study of a number of multistage processes [5, 6].

The electrode was illuminated by a DRShch-250 mercury lamp with a wavelength of 365 nm; the intensity of the illumination was ac modulated. A system of narrow-band amplifiers and a synchronous detector was used to record the photocurrent. These measurements were carried out in a 0.95 M KCl + 0.05 M $KHCO_3$ solution whose pH was 6.1.

There are two Taffel regions on the polarization curve of the electroreduction of CO_2 on a tin electrode (Fig. 1). The first is in the region of potentials more positive than 1.15 V and has a slope of 110−120 mV. In the case of a tin electrode with a developed surface, this region extends over approximately two orders of

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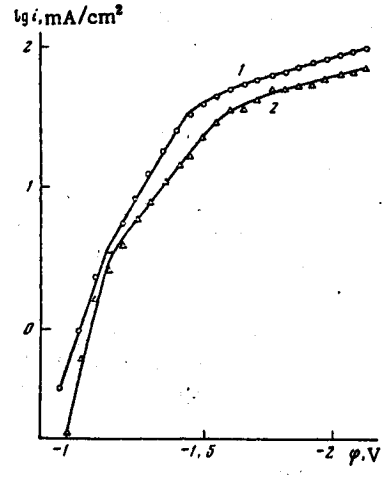

Fig. 1

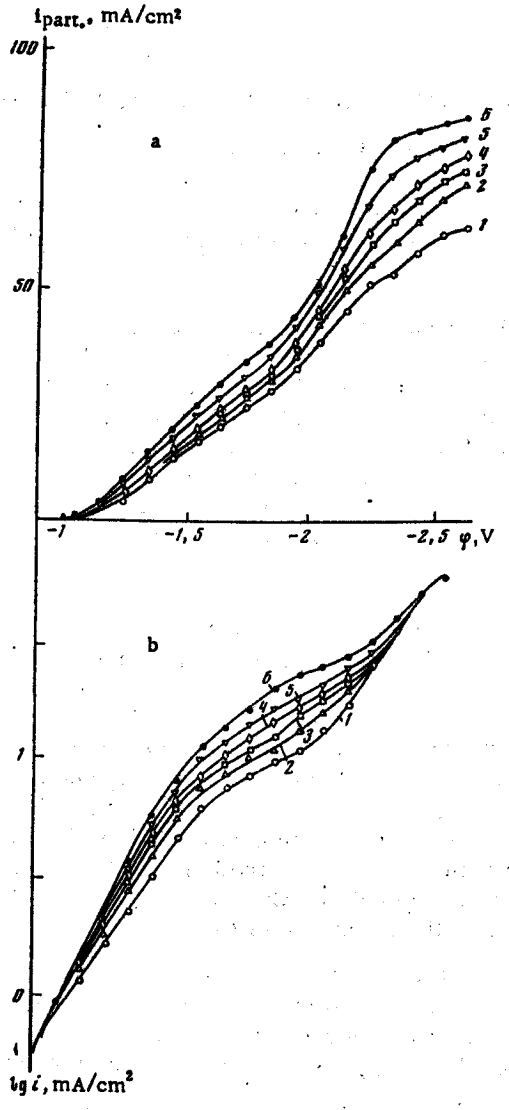

Fig. 2

Fig. 1. The polarization curves in a CO_2 atmosphere in phosphate (1) and carbonate (2) buffer solutions with a pH of 6.75.

Fig. 2. The potential dependence of the partial current of CO_2 electroreduction (a) and the hydrogen-deposition current in an argon atmosphere (b) in a phosphate buffer solution with a pH of 6.0 at various rotation rates, rev/min: 1) 600; 2) 1110; 3) 1900; 4) 2900; 5) 3950; 6) 5750.

magnitude of current. In the second region of potentials from −1.15 to −1.5 V, the slope is 300−350 mV. In this region of potentials, the separation of the partial current of the CO_2 electroreduction is difficult since the hydrogen-deposition currents acquire the same order of magnitude as the CO_2-electroreduction currents and depend on the mixing (Fig. 2) and on the buffering conditions of the solution (Fig. 3). Ohmic drops in potential are also marked at such high current densities.

The general form of the polarization curves in semilogarithmic coordinates and the Taffel slopes for both regions remain to a first approximation the same in different buffer solutions as is clear from Fig. 3.

A deviation from the Taffel dependence in the region of higher current densities of CO_2 electroreduction (Fig. 2a) is caused by the deficit of CO_2 molecules in the electrode layer.

The effect of the pH of the solution on the rate of the CO_2 electroreduction was studied in two buffer solutions: phosphate and carbonate. It is clear from Fig. 4a and b, that in the phosphate solution, the partial

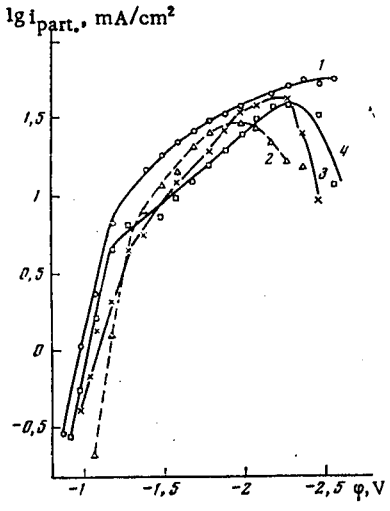

Fig. 3. The dependence on potential of the partial electroreduction currents of CO_2 in the following buffer solutions, pH 5.5: 1) phosphate; 2) carbonate; 3) formate; 4) acetate.

rate of electroreduction of CO_2 on a tin electrode with a constant potential in the first Taffel region in the experimental pH range of 2 to 6.75 does not depend on the pH of the solution. With a change to solutions with pH > 6.75 the partial currents drop sharply as a result of the CO_2 being converted to bicarbonate ions which are not subject to electroreduction [4, 7].

The big differences in the overvoltage of the hydrogen deposition and the CO_2 electroreduction on tin made it possible for us to study the effect of the pH on the rate of CO_2 electroreduction over a fairly wide range of pH and to conclude that the mechanism of the process does not change over the whole range of pH and that in the first Taffel region of the polarization curve the hydrogen ions do not participate in the slow stage or in the stages preceding it.

With large current densities it is observed that in the second region of the polarization curve the pH has a slight effect but this may only be apparent and be due to the strong increase in the hydrogen deposition currents subtracted from the total current or to a decrease in the concentration of dissolved CO_2 (Fig. 4c).

In its general form the CO_2 reduction process on a tin electrode, like the reduction process on Hg [6, 8], Pb [9], and Cu [4] electrodes, can be represented in the form of two successive electron-transfer reactions:

$$CO_2 + e_M \rightarrow CO_2^{\cdot-} \qquad (I)$$

and

$$CO_2^{\cdot-} + BH + e_M \rightarrow HCO_2^- + B^-, \qquad (II)$$

where BH is the proton donor.

The complex character of the polarization curve of the electroreduction of CO_2 on tin shows that the limiting stage is shifted when the potential is changed. In order to define this mechanism more precisely we studied the photoemission of electrons from a tin electrode into solutions containing CO_2.

According to Schiffrin [6] who first studied photoemission from a Hg electrode in solutions containing CO_2 molecules as the electron acceptors, the following processes occur:

$$CO_2 + e_{aq} \rightarrow CO_2^{\cdot-} \quad \text{(in solution)}, \qquad (I')$$

$$\left.\begin{aligned} CO_2^{\cdot-} + BH + e_M &\rightarrow HCO_2^- + B^- \\ CO_2^{\cdot-} &\rightarrow CO_2 + e_M \end{aligned}\right\} \text{(on electrode surface)}. \qquad \begin{matrix}(II)\\(III)\end{matrix}$$

The symbol e_{aq} refers to a hydrated electron which takes part in the reaction with CO_2 molecules (reaction (I')) at a distance of 10–30 Å from the surface of the electrode. The remaining reactions are the same as in the case of reduction in darkness.

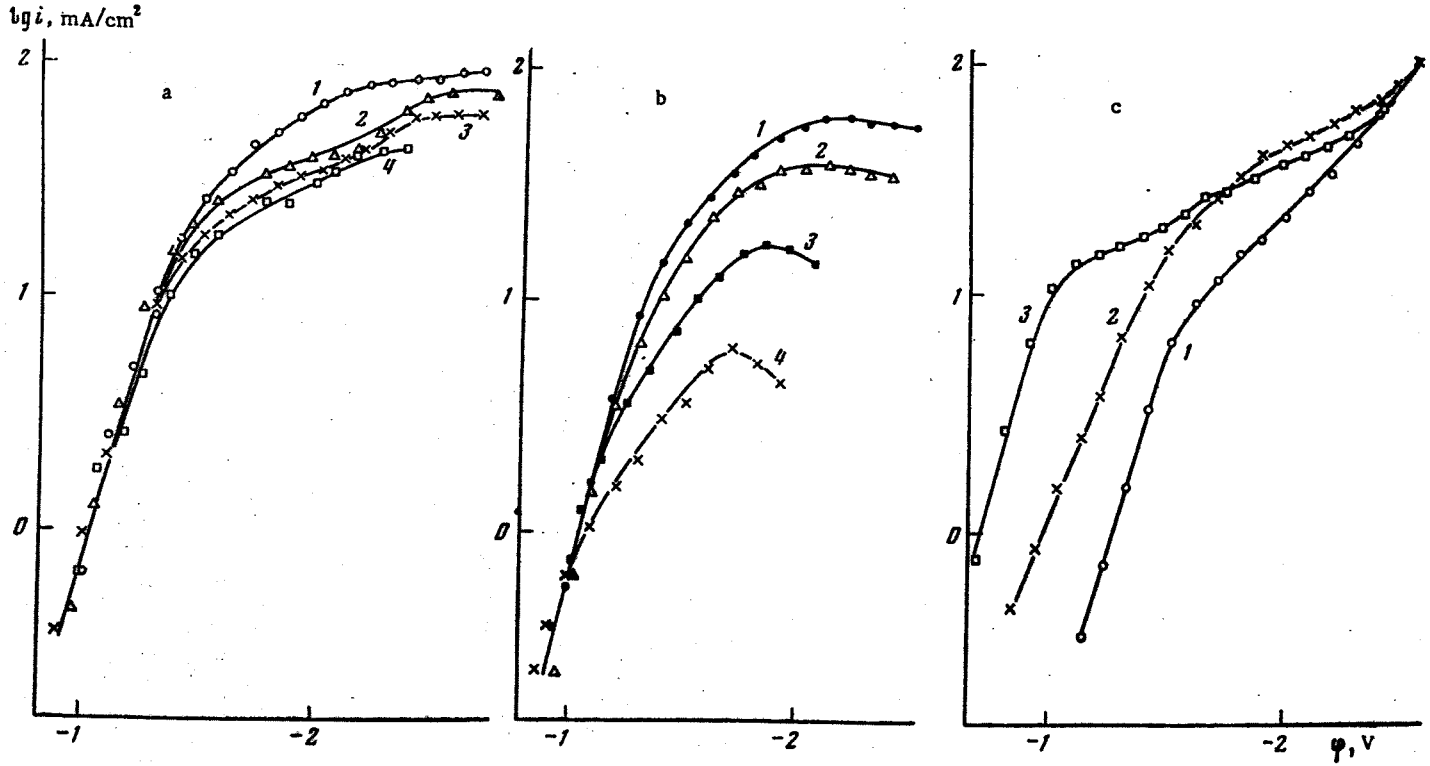

Fig. 4. The partial currents of CO_2 electroreduction in phosphate (a) and carbonate (b) buffer solutions and also the polarization curves of the hydrogen deposition in an argon atmosphere in a phosphate buffer solution (c) with various pH: a: 1) 6.75; 2) 6.0; 3) 5.0; 4) 3.0; b: 1) 6.75; 2) 5.5; 3) 3.0; 4) 2.0; c: 1) 6.75; 2) 5.0; 3) 3.0.

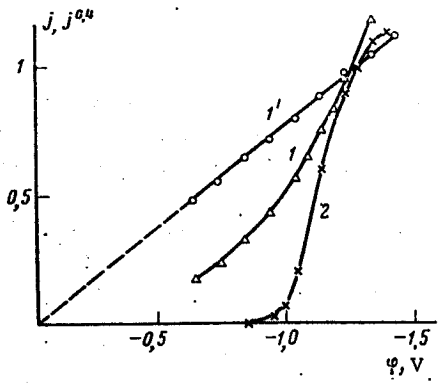

Fig. 5

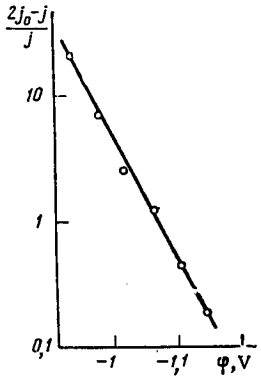

Fig. 6

Fig. 5. The dependence of the photocurrent on potential in $j(\varphi)$ (1, 2) and $j^{0.4}(\varphi)$ (1') coordinates for a 0.95 M KCl + 0.05 M $KHCO_3$ solution saturated with N_2O (1, 1') and CO_2 (2).

Fig. 6. The treatment of the experimental data from Fig. 5 in accordance with Eq. (V).

We believe that the CO_2^- ion radical formed with the trapping of a solvated electron when the electrode is illuminated is identical to the CO_2^- formed electrochemically in reaction (I) under dark conditions.

The HCO_2^- oxidation reaction on tin, as on mercury, can be ignored in this particular region of potentials as is indicated by direct measurements.

Figure 5 shows the potential dependence of the photocurrents for two acceptors: N_2O and CO_2. In the first case the photocurrent is observed over the whole region of potentials available for the measurements and the character of its dependence on potential can be described approximately by the "5/2 law" (curve 1'); in this case the threshold potential is very similar to the values for other metals. In the solution containing CO_2 as the acceptor, a photocurrent of a significant value only appears when $\varphi < -0.90$ V. In the region of more positive potentials, as in the case of the Hg electrode, photocurrent is virtually absent although, by contrast to the Hg electrode when $\varphi = -0.9$ V, marked dark currents are observed at the Sn electrode. At these potentials the product of the trapping of a hydrated electron by a CO_2 molecule [the CO_2^- radical) is completely oxidized at the electrode [reaction (III)] while with more negative potentials, reaction (II) occurs in addition to the oxidation of CO_2^-, i.e., the reaction of further reduction. Allowing for reactions (I'), (II), and (III), the steady state photocurrent is [5]

$$j = \frac{2j_0 \vec{k} e^{-\alpha F\varphi/RT}}{\vec{k} e^{\beta F\varphi/RT} + \vec{k} e^{-\alpha F\varphi/RT}}, \qquad \text{(IV)}$$

where j_0 is the electron-emission current after the subtraction of the return current to the electrode of hydrated electrons which do not react with the CO_2 molecules; $\vec{k}$ and $\vec{k}$ are the rate constants of reactions (II) and (III), respectively, when $\varphi = 0$ V; α and β are the corresponding transfer coefficients. The coefficient 2 in Eq. (IV) denotes the total number of electrons transferred across the interphase boundary for one emitted electron.

Equation (IV) describes the experimental data shown in Fig. 5. With positive potentials where the first term in the denominator is significantly greater than the second, the photocurrent tends to zero. In the negative-potential region where the equation is reversed, $j = 2j_0$, i.e., the character of the potential dependence of the photocurrent is the same as in the case of the N_2O solution (in the case of the latter, the product of the electron trapping by the acceptor, the OH^- radical, throughout the region of potentials where the measurements are taken, is reduced only at the electrode).

It is clear from Fig. 5 that the photocurrent for both acceptors in the negative-potential region ($\varphi < -1.2$ V) are very similar and the $j(\varphi)$ curves are parallel, i.e. in this region of potentials, the photocurrent in CO_2 solutions is also described by the "5/2 law." Therefore the photocurrent $2j_0$ in Eq. (I) can be assumed to be equal to the current in the N_2O solutions on such a scale as to match the CO_2 photocurrent in the $\varphi < -1.2$ V region. In this case if we know $2j_0$ over a wide range of potentials, we can find the ratio between the rate constants of reactions (II) and (III) and the sum of the transfer coefficients $(\alpha + \beta)$ for different φ. To do this we rewrite Eq. (I) in the form of a linear function of φ:

$$\varphi = \frac{2.3RT}{F(\alpha+\beta)}\left\{\log\left(\frac{2j_0}{j}-1\right)+\log\frac{\vec{k}}{\bar{k}}\right\}. \qquad \text{(V)}^*$$

The treatment of the experimental data in accordance with Eq. (V) is illustrated in Fig. 6. The value of $(2j_0/j - 1)$ is equal to the ratio between the $CO_2^{\cdot-}$ radical oxidation rates (reaction (III)) and those of the later reduction in accordance with reaction (II). It is clear from Fig. 6 that the rates of the two reactions become equal one to the other at a potential of −1.08 V. With more positive potentials corresponding to the first Taffel region of the polarization curve of the CO_2 electroreduction, the oxidation rate of the CO_2^- radical is significantly higher than its reduction rate, i.e., in this region the first stage of the CO_2 reduction process on Sn will be reversible while the next reduction stage is a slow one. With more negative potentials, the oxidation rate of the $CO_2^{\cdot-}$ radical in the second Taffel region of the polarization curve can be ignored by comparison with the rate of reduction. At these potentials, the stage in which the first electron is combined with the CO_2 molecule occurs at the same rate as that in which the second electron is combined. The potential at which the oxidation rate and the reduction rate of the $CO_2^{\cdot-}$ radicals become equal was found to be significantly more positive in the case of a tin electrode than that for a mercury electrode in the same electrolyte (−1.23 V [6]). This difference between the potentials for the two electrodes can be interpreted in two ways: either the $CO_2^{\cdot-}$ reduction on Sn is more rapid or the $CO_2^{\cdot-}$ oxidation is slower than in the case of a Hg electrode. It follows from the slope of the line in Fig. 6 that $\beta + \alpha = 0.6$ for Sn but is 0.96 in the case of Hg.

It is interesting to note that if the overvoltage of the processes for the photocurrents on Hg and Sn differ by only ~0.150 V, in dark conditions the overvoltage of the CO_2 reduction on Hg and on Sn differ by almost 1.0 V. This means that the nature of the electrode material has a significant effect on the rate of the first stage but only a slight effect on the rate of the second stage. This suggests that the CO_2 discharge mechanisms are different on the two metals.

Bewick and Schiffren [10] pointed out that one of the main difficulties in interpreting the kinetic data for the reduction of CO_2 on Pb and Hg is the problem of whether the intermediate product is or isn't adsorbed on the surface. Different measurements have indicated [9] that there is no great filling of the surface by intermediate particles by contrast to the hypotheses proposed in [8]. In Parson's view [11], the question of whether intermediate adsorption occurs or not can be solved by studying the effect on the kinetics of the nature of the cathode material. Our studies in [3] indicate the important effect of the cathode material, i.e., the presence of adsorption of the participants in the process.

However, the surface filling by adsorbed particles on Sn, as on Pb [9], is not great and we were unable to demonstrate it using a pulse method.

It follows from the experimental data obtained that in the first Taffel region of the polarization curve of the electroreduction of CO_2 on Sn by contrast with Hg, the slow stage is the transfer of the second electron. Therefore, the Taffel slope should be $2.3RT/(1+\alpha)F$, i.e., should be at least 60 mV lower. The weaker dependence indicates that a particle whose surface concentration drops with an increase in the negative value of the potential participates in the process. This particle is probably $CO_2^{\cdot-}$. Moreover, the character of the effect of the pH shows that over this particular region of pH the proton donor will be the water molecule. The CO_2 electroreduction mechanism in the first Taffel region can be represented in the following form:

$$CO_{2(ads)} + e_M \rightleftarrows CO_{2(ads)}^{\cdot-}, \qquad \text{(VI)}$$

$$CO_{2(ads)}^{\cdot-} + H_2O + e \rightarrow HCO_2^- + OH^-. \qquad \text{(VII)}$$

In the second Taffel region of the polarization curve where the attachment of the second electron becomes the slower stage, the weak dependence of the reduction rate on potential is probably associated with the fact that in the slow stage the electron is attached to the physically adsorbed CO_2 molecules at these potentials which are significantly more negative than the maximum-adsorption potential, and are dislodged from the surface of the Sn electrode as the negative value of the potential is increased.

On a mercury electrode, as was shown in [6, 8], the slow stage is the transfer of the first electron; however, the intense change in the CO_2 adsorption energy with the change from Hg to Sn accelerates the first stage so much that the second stage, i.e., reaction (V), becomes the slow stage on a Sn electrode. Moreover, the effect of the nature of the electrode material on the photocurrents and the dependence (weaker than would

* Equation (V) refers to the case where the $CO_2^{\cdot-}$ radical is involved in reactions (II) and (III) either from the solution or from the adsorbed states, i.e., the initial states for the two concurrent processes are the same.

be expected for the slow stage of the second electron transfer) of the rate of the CO_2 electroreduction on the potential of Sn indicate the need to allow for adsorption and for the intermediate ion-radical $CO_2^{-\cdot}$ which is formed.

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