

Structurally heterogeneous electrodes can occur, not only as polycrystals but also as materials which are homogeneous with respect to their electrochemical properties and which contain impurity-type inclusions occupying an insignificant part of the working surface area. Such inclusions can also exist on polycrystalline electrodes, e.g., at the grain boundaries. The influence of the inclusions will extend to distances substantially larger than their own size (Fig. 6). It is evident that this is bound to affect the accuracy of the electrochemical parameters measured at the electrode.

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CARBON DIOXIDE ADSORPTION ON SMOOTH PLATINUM ELECTRODES AT DIFFERENT TEMPERATURES

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Carbon dioxide adsorption on smooth platinum electrodes was studied by potentiodynamic sweeps at different temperatures. The desorption of chemisorbed products was examined. The activation energy of the adsorption process was determined.

An important aspect of the electrocatalytic reduction of carbon dioxide is its adsorption. Many papers have dealt with the adsorption of CO₂ on platinum electrodes at room temperature, but little attention was paid to the effect of temperature on this process.

In view of the great importance of electrocatalytic CO₂ reduction, the effect of temperature on the adsorption has been studied in the present work, and the description of the chemisorbed products has also been examined.

It was first found by Giner [1] that CO₂ interacts with the hydrogen adsorbed on the platinum electrode, forming a chemisorbed species which is oxidized in the same potential range as the species produced during the adsorption of organic substances such as methanol, formaldehyde, and formic acid. Subsequently CO₂ adsorption on platinum electrodes was the concern of many investigations [2-10], where it was demonstrated that the chemisorbed species is strongly bound to the surface, and does not desorb on rinsing. Johnson and Kuhn [10] analytically did not find desorption products such as CO, formaldehyde, or formic acid in the solution. The chemisorbed species remains stable during cathodic polarization [6, 8], and is removed only upon anodic polarization. But it was found in [11] that methane is produced at 80°C when the electrode is subjected to prolonged polarization in methanol, which gives rise to the same chemisorbed species.

The reaction of CO₂ with adsorbed hydrogen is slow, and its rate increases with temperature. The effect of temperature had been studied by Sobkowski and Czerwinski [8] at platinized platinum over the relatively narrow temperature range from 20 to 50°C. Over this range the authors did not find any dependence of surface coverage on temperature or carbon dioxide concentration. The activation energy of adsorption was calculated by them using an equation for processes occurring on homogeneous surfaces; it was 12 kcal at $\varphi_r = 0.05$ V and 9.6 kcal at $\varphi_r = 0.2$ V. But at platinum electrodes one must take into account that the heat of adsorption and the activation energy of adsorption are changing with coverage [4, 12, 13].

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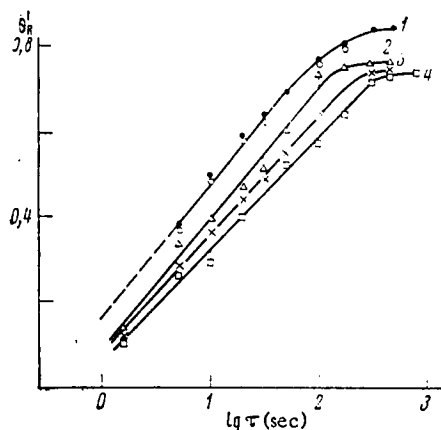


Fig. 1. Kinetic isotherms of CO_2 adsorption on the smooth platinum electrode in 1 N H_2SO_4 at $\varphi_r = 0.1$ V and $p_{\text{CO}_2} \approx 1$ atm, at different temperatures: 1) 83, 2) 65, 3) 35, and 4) 25°C.

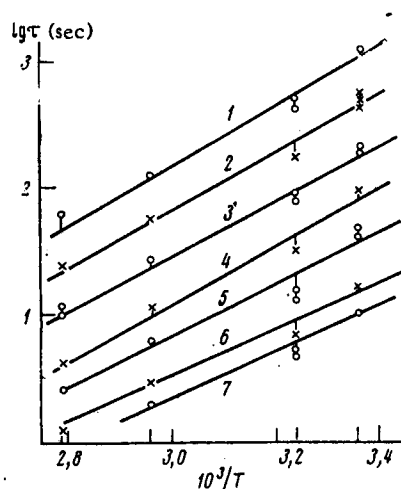


Fig. 2

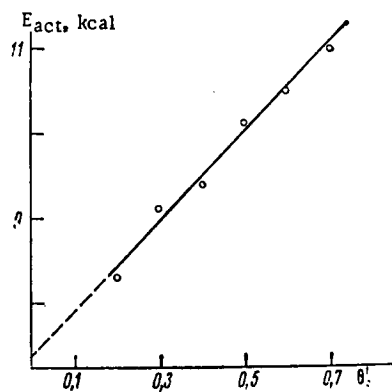


Fig. 3

Fig. 2. The logarithm of the time required to reach a specified value of coverage, as a function of reciprocal temperature for different θ_R' values: 1) 0.7, 2) 0.6, 3) 0.5, 4) 0.4, 5) 0.3, 6) 0.2, and 7) 0.15 (with $c_{\text{CO}_2} \approx 3.7 \cdot 10^{-3}$ M).

Fig. 3. The activation energy of CO_2 adsorption on the smooth platinum electrode in 1 N H_2SO_4 at $\varphi_r = 0.1$ V as a function of surface coverage by chemisorbed species.

The adsorption of CO_2 at smooth platinum electrodes in 1 N H_2SO_4 solution was studied at temperatures from 25 to 83°C using complex potentiodynamic sweeps in the technique described in [14]. Higher demands on solution purity are presented when working at elevated temperatures. Additional solution purification was carried out directly in the measuring cell at a large platinized platinum screen the potential of which was maintained for 1 h at 0.2 V at 83°C. During purification the system was purged with argon.

Data on the kinetics of CO_2 adsorption at temperatures from 25 to 83°C on the smooth platinum electrode in 1 N H_2SO_4 at 0.1 V are presented in Fig. 1. The coverage of the electrode surface by chemisorbed species

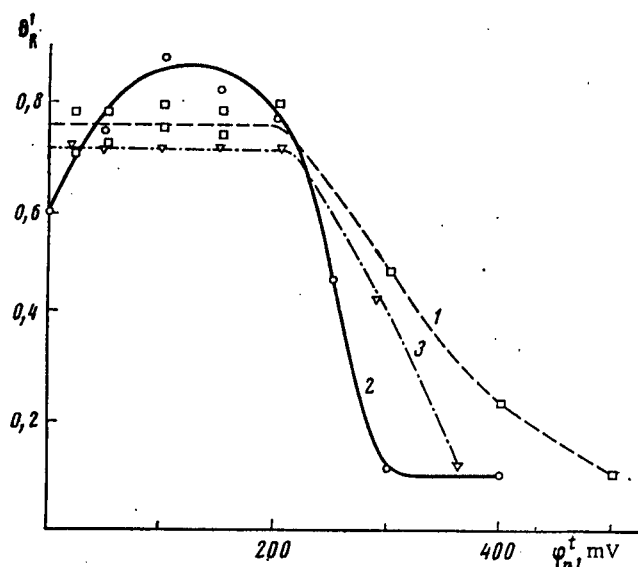


Fig. 4. The stationary surface coverage of the smooth platinum electrode by chemisorbed organic species in 1 N H_2SO_4 solution saturated with CO_2 at $p \approx 1 \text{ atm}$, as a function of electrode potential at different temperatures: 1) 25, 2) 83, 3) 40°C (curve 3: from data of [4]).

rises rapidly at first at all temperatures as the adsorption time increases, but then it attains a stationary value which increases with temperature ($\theta_R' = 0.75$ for $t = 25^\circ\text{C}$, and $\theta_R' = 0.85$ for 83°C).

At intermediate values, the surface coverage of the platinum electrode by the product of CO_2 chemisorption is increasing linearly with the logarithm of adsorption time at all temperatures:

$$\theta_R' = B + \frac{1}{\alpha f'} \ln \tau \quad (1)$$

while quantity $\alpha f'$ is decreasing with increasing temperature [13]. It can be seen from Fig. 1 that the rate of adsorption increases with temperature. The activation energy of carbon dioxide adsorption was determined from the kinetic adsorption curves obtained at different temperatures (in going from the kinetic isotherms to isosteres, the quantity τ_t was divided by $K = c_{\text{CO}_2}^{25^\circ} / c_{\text{CO}_2}^{t^\circ}$) after correcting them for the change in CO_2 solubility with temperature (this changes by a factor of five over this range of temperatures [15]). To do so we plotted the logarithm of the time necessary to attain a specified value of coverage of the electrode surface by chemisorbed organic species as a function of the inverse of absolute temperature (Fig. 2). The isosteric differential activation energies (at $\theta_R' = \text{const}$) were determined from these plots [13].

It can be seen from Fig. 3 that the activation energy of carbon dioxide adsorption on the smooth platinum electrode at $\phi_R = 0.1 \text{ V}$ to a first approximation is increasing linearly with the coverage of the electrode surface [12, 13, 16], i.e.,

$$E_{\text{act}} = E_0 + \alpha f' RT \theta_R', \quad (2)$$

where $E_0 = 7.4 \text{ kcal}$ and $\alpha f' = 8.3$

But this value of the activation energy at constant potential is an apparent value, and disregards the variation of surface coverage by the second adsorbed hydrogen, which occurs with temperature at constant potential.

The potential dependences of stationary surface coverage by chemisorbed organic species in CO_2 solution are strongly different at 25 and 83°C (Fig. 4). At room temperature, the surface coverage by chemisorbed species does not change with potential between $\phi_R = 0$ and 0.2 V , but then decreases strongly (almost linearly with increasing anodic potential).

At 83°C, the potential dependence of adsorption is a curve with maximum at $\varphi_R = 0.1$ V. The coverage falls rapidly at potentials more positive than 0.15 V, so that at these potentials, the surface coverage by chemisorbed species is lower at 83°C than at room temperature. For comparison we report in Fig. 4 the potential dependence of CO₂ adsorption on the smooth platinum electrode obtained by Brummer [4]. At potentials above $\varphi_R = 0.25$ V, the surface coverage by chemisorbed organic species in CO₂ solutions decreases sharply as the temperature is increased from 25 to 40°C and further to 83°C. This probably is due to the strong decrease in surface coverage of the platinum electrode by adsorbed hydrogen which is found to occur with increasing temperature in this potential range [17, 18].

It is interesting to note that at 83°C, the coverage of the electrode surface by chemisorbed species near $\varphi_R = 0$ V is lower than that at 0.1 V. Such a decrease in coverage of the electrode surface by chemisorbed species when the potential is displaced in the negative direction could be attributed to hydrogenation of the chemisorbed species. However, if after CO₂ adsorption at the potential of maximum adsorption ($\varphi_R = 0.1$ V) the potential is switched over to φ_R values between -0.025 and -0.05 V, the surface coverage by the species chemisorbed in advance does not decrease to a lower stationary value.

Failure of the species adsorbed from CO₂ solution in 1 N H₂SO₄ at $\varphi_R = 0.1$ V and 83°C to desorb was also demonstrated by blowing the CO₂ from the solution, both after maintaining the electrode under these conditions and after chemisorption at negative potentials (φ_R between -0.025 and -0.05 V). Thus, the decrease in stationary surface coverage by chemisorbed organic species in CO₂ solution at 83°C which occurs when the potential is shifted from $\varphi_R = 0.1$ V to $\varphi_R = 0$ is not due to hydrogenation of the chemisorbed species.

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