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1963

SovietRxiv

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## Abstract

## Full Text

## Physical Chemistry

Academician A. N. FRUMKIN, E. A. PONOMARENKO, R. Kh. BURSHTEIN

# CHEMISORPTION OF OXYGEN AND ADSORPTION OF ELECTROLYTES ON ACTIVATED CARBON

According to the electrochemical theory of adsorption of electrolytes on carbon ($^1$), carbon activated at 900° behaves in electrolyte solutions as a gas electrode. The adsorption of electrolytes is determined by the formation of an electrical double layer as a result of the ionization of electrochemically active oxygen or hydrogen chemisorbed on the carbon surface. The potential difference between the carbon and the solution depends on the chemical potential of the adsorbed gases and the pH of the solution. The ionization of oxygen, depending on the conditions of chemisorption, may proceed with the addition of two or four electrons ($^2$). The validity of these ideas is confirmed by the existence of a linear relationship between the amount of adsorbed ions and the potential of the carbon electrode ($^3$).

From the standpoint of the chemical theory developed by Shilov and co-workers ($^4$), the adsorption of electrolytes on carbon is regarded as a process of salt formation as a result of the reaction between surface oxides and ions of the solution. The chemical theory was further developed by Garten and Weiss, who attempted to bring the conclusions of this theory closer to the results of electrochemical investigations ($^5$,$^6$ )*. Garten and Weiss believe that functional groups on the carbon surface participate in electrolyte adsorption, changing their structure upon oxidation or reduction. The adsorption of acid is explained by the presence of a chromene (benzpyran) structure, which, on interaction with oxygen and acid, forms a carbonium ion and $H_2O_2$:

**Fig. 1.** Dependence between the adsorption of $H_2SO_4$ (1), the amount of

Fig. 2 graph: dependence between adsorption of $H_2SO_4$ and amount of chemisorbed oxygen. Axes labeled $H_2SO_4$, meq/g and $O_2$, meq/g.

Figure 2: Fig. 2 graph: dependence between adsorption of $H_2SO_4$ and amount of chemisorbed oxygen. Axes labeled $H_2SO_4$, meq/g and $O_2$, meq/g.

chemisorbed oxygen (2), and the potential assumed by a carbon electrode in $0.01\,N$ $H_2SO_4$. The point on curve 1 at $\varphi = 0.65$ was obtained with access of air.

$$\text{[chromene structure]} \xrightarrow[\text{HCl}]{\text{O}_2} \text{[carbonium-ion structure]} + H_2O_2. \tag{1}$$

On the basis of this theory the authors derive an equation that may be represented in the form

$$E_h = E'_{1/2} - \frac{2.3RT}{2F} \lg \frac{1-\alpha}{\alpha}, \tag{2}$$

where $E_h$ is the potential of the oxidation-reduction system, $\alpha$ is the relative content of the oxidized form (carbonium ion), proportional, according to (1), to the adsorption of HCl, and $E_{1/2}$ is the value of $E_h$ at $\alpha = 1/2$.

Garten and Weiss consider the proof of the validity of their theory to be that the results to which the equation (2) derived by them leads are in agreement with the data of Kuchinskii, Burshtein, and Frumkin on the dependence of acid adsorption on a carbon electrode on the potential ([3]). Examination of the graph presented by Garten and Weiss ([5]) shows that equation (2) does indeed approximately reproduce the experimental data if one takes $E_{1/2} = 0.42$ and $\alpha = A/0.303$, where $A$ is the measured adsorption value in meq per 1 g of carbon. At the same time, however, the coefficient before the logarithmic term on the right-hand side of equation (2) must be assigned the value 0.24 instead of the theoretical 0.029, which deprives the test of the theory of meaning.

**Fig. 2.** Dependence between the adsorption of $H_2SO_4$ from 0.01 $N$ $H_2SO_4$ and the amount of chemisorbed oxygen

In our earlier investigations ([2,7,9]) it was shown that carbon, well degassed at 950°, does not adsorb anions from dilute solutions of $H_2SO_4$ or HCl. In studying acid adsorption on a carbon electrode whose potential is changed by cathodic polarization ([3]), it was found that the zero value of the carbon charge lies in the potential interval 0.05–0.15 V on the normal hydrogen scale.

* The carbon of high-temperature activation, whose properties are considered in the present article, Garten and Weiss, as well as some other foreign authors, call H-carbon.

It was of interest to determine directly the potential of degassed carbon and the change in potential upon adsorption of various amounts of oxygen on carbon whose surface had first been degassed by prolonged heating in vacuum at high temperature.

The procedure for degassing the electrolyte has been described previously ([8]). Determination of the dependence of the potential of a carbon electrode on the amount of adsorbed oxygen and electrolyte was carried out in an apparatus similar to that described in the same work. The lower part of the apparatus, where the carbon was placed, was made of quartz. Electrodes made of activated sugar carbon were degassed at a temperature of 950° for 72–96 h to a pressure of $2.5 \cdot 10^{-6}$ mm, after which the apparatus was sealed off from the vacuum system. In the experiments on oxygen adsorption, after the carbon had cooled to 20°, a definite portion of gas was admitted, and the apparatus was sealed off after adsorption equilibrium had been established. After this, an ampoule containing a degassed solution of 0.01 $N$ $H_2SO_4$ was broken, and, for exact determination of the concentration, which changes somewhat during degassing of the solution, the electrical conductivity of this initial solution was measured in a special cell sealed to the apparatus. Then the solution was brought into contact with the carbon, and the adsorption of acid on the carbon was determined from the change in electrical conductivity. The potential of the carbon electrode was measured relative to an Hg, $Hg_2SO_4$ electrode. Curve 1 in Fig. 1 expresses the dependence between the potential of the carbon electrode on the normal hydrogen scale and the amount of adsorbed acid.

The potential of a carbon electrode carefully degassed in vacuum

lay within 0.14–0.19 V, on average 0.16 V relative to the normal hydrogen electrode. At this potential, adsorption of $SO_4^{2-}$ ions from the solution did not occur. During oxygen adsorption, a shift of the carbon potential toward positive values is observed as the amount of adsorbed oxygen increases (Fig. 1, curve 2). With increasing positive value of the potential, adsorption of $H_2SO_4$ increases; moreover, beginning at 0.250 and up to 0.650 V, the dependence between acid adsorption and potential is linear.

As long as the amount of absorbed oxygen is small, the amount of adsorbed acid is equivalent to the amount of oxygen adsorbed by the carbon (Fig. 2); in other words, the process of acid adsorption proceeds according to the mechanism

$$C_{xO} + 2H^+ + SO_4^{2-} \rightarrow$$

$$\rightarrow C_x^{2+} \ldots SO_4^{2-} + H_2O. \tag{3}$$

Positive charges on the carbon and negative charges of the anions form two plates of the electric double layer. This result is in complete agreement with data obtained earlier ([9]); under the conditions of our experiments, hydrogen

Fig. 3

Figure 3: Fig. 3

peroxide is not formed. With an increase in the amount of absorbed oxygen, relation (3) is violated; oxygen adsorption increases more rapidly than acid adsorption (Fig. 1). In other words, not all the absorbed oxygen is exchanged with $SO_4^{2-}$ anions according to equation (3), and at equilibrium with the solution a certain fraction of chemisorbed oxygen remains on the carbon surface, whereas at potentials $\varphi < 0.32$ the concentration of chemisorbed oxygen in equilibrium with the solution may be neglected.

**Fig. 3.** Potential of a degassed carbon electrode: *a*—in $0.01\,N$ $H_2SO_4$, *b*—after alkalization of the solution, *c*—after admission of air, *d*—after acidification of the solution

The results presented here are in general agreement with those obtained earlier, although the curve expressing the dependence of adsorption on potential is shifted somewhat (by 0.05-0.1 V) toward more positive potentials in comparison with the curves given in ([3]), obtained for carbon subjected to cathodic polarization.

From the fact that degassed carbon does not adsorb anions from solution, it may be concluded that its surface does not bear a positive charge. On the other hand, from the fact that a minimal shift of its potential in the positive direction leads to adsorption of $SO_4^{2-}$ anions, it follows that the surface of degassed carbon also does not bear a negative charge, which might arise as a result of chemisorption of $OH^-$ ions from water (see below). Thus, the measured value of the potential of the degassed electrode should be regarded as the potential of zero charge of the carbon surface for the indicated method of its preparation.* The deviation of curve 1 in Fig. 1 from rectilinear behavior near this potential is possibly associated with the greater diffuseness of the double layer at small surface charges.

We also investigated the change in the potential of a degassed carbon electrode when acid was replaced by alkali. In the apparatus, without access of air, after contact of the carbon with acid, an ampoule containing alkali was broken, and the pH value was brought to $\sim 12$ (Fig. 3). It was found that the potential in alkali (section *b*) is shifted, in comparison with the potential in acid (section *a*), by almost 0.2 V toward more negative values. When air is passed through the system, the electrode potential is gradually shifted in the positive direction to 0.18 V (section *c*), and upon addition of acid the potential of the carbon in air reaches +0.65 V (section *d*).

The shift of the carbon potential in the negative direction was accompanied by

* The zero point of oxygen carbon that had undergone reduction by cathodic polarization apparently lies somewhat more negative (at $\varphi \sim 0.05$) ([3]).

adsorption of alkali (0.066 meq per 1 g), which, upon contact with air, fell to zero. Adsorption of alkali on degassed carbon had previously been observed by one of the authors[10]. This adsorption was explained by ionization of the hydrogen contained in activated carbon, which is not removed even by prolonged high-temperature degassing. This explanation, however, is not consistent with the results obtained here. Since the potential of degassed carbon in $0.01\,N$ $H_2SO_4$ is close to the potential assumed by carbon in alkali in the presence of air, i.e., under conditions in which chemisorbed oxygen is undoubtedly present on the carbon surface, it must be assumed that, on passing from an acidic to an alkaline solution, chemisorbed groups $>$ O or $-$OH appear on the surface of the degassed carbon through discharge of $OH^-$ ions. The negative charges that appear on the surface in this process attract $K^+$ ions, i.e., as a result adsorption of KOH takes place, accompanied by a shift of the potential in the negative direction:

$$C_x + \mathrm{OH}^- \rightleftarrows C_x^-(\mathrm{OH}), \tag{4}$$

where $C_x^-(\mathrm{OH})$ denotes the negatively charged carbon surface with chemisorbed OH (or O) groups. When oxygen is introduced into the system, the concentration of chemisorbed oxygen groups increases, reaction (4) proceeds in the reverse direction, which causes a shift of the potential in the positive direction and desorption of alkali.

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Received
18 I 1963

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*Note: Figure translations are in progress. See original paper for figures.*