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Abstract

Full Text

Physical Chemistry

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On the Question of the Properties of Intermediate Carbon-Oxygen Compounds

(Presented by Academician A. N. Frumkin, 21 V 1957)

The existence of intermediate carbon-oxygen compounds formed during the activated sorption of oxygen by carbon may be regarded as an established fact.

Ideas concerning intermediate oxides of carbon were invoked, in particular, by us (1,2) to substantiate the mechanism of the phenomena responsible for the occurrence of a large overvoltage on carbon anodes in aluminum baths. According to this mechanism, the primary result of the discharge of oxygen-containing ions on a carbon anode is the formation of electrochemically active intermediate carbon-oxygen compounds. The bonds of chemisorbed oxygen with the carbon lattice are redistributed and strengthened with time, and the final result of this process is the formation and desorption of gaseous oxides of carbon. Owing to the energetic nonuniformity of the carbon surface, at low current density the discharge proceeds on its most active regions, with the formation of the strongest oxygen-carbon bonds at a comparatively low anode potential (almost corresponding to the free energy of the reaction $Al_2O_3 + 3C = 2Al + 3CO$). With increasing current density, the discharge also spreads to less active regions, where, because of the lower energy of oxygen sorption, discharge is possible only at a higher potential. Correspondingly, ionic exchange by oxygen between the intermediate oxides formed at a higher current density in the anode and the oxygen-containing ions in the electrolyte occurs at a higher potential; this is observed over many tens of minutes, even after the current density has been reduced by 30%. At the industrial current density, apparently, pure CO_2 is evolved as a result of electrochemical desorption.

The above-mentioned stage of formation and desorption of gaseous oxides of carbon is the slowest one, determining the presence of anode overvoltage in aluminum baths.

The present communication contains one more proof that, at 960°, the potential of the carbon anode is determined not by the partial pressure of O_2 in the gas bubbles under the carbon anode, as was previously believed, and not by the overvoltage of its evolution, but specifically by electrochemically active carbon-oxygen compounds formed at a high anode potential, and that the overvoltage is due to the slowness of their decomposition.

The arrangement of the experiments described below is based on a method used

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Fig. 1. Measuring cell with a carbon test tube—anode, inside which is the carbon-oxygen reference electrode

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Fig. 2. Dependence of the overvoltage on the inner, polarized surface of the carbon anode on the time after electrolysis is switched on. Electrolyte KCl—NaCl—Na2SO4 at 650°

Figure 2: Fig. 2. Dependence of the overvoltage on the inner, polarized surface of the carbon anode on the time after electrolysis is switched on. Electrolyte KCl—NaCl—Na2SO4 at 650°

in the case of aqueous solutions since 1937 (3).

The carbon anode 2 (Fig. 1), having the shape of a test tube, is polarized from the outside. Inside it there is also a small amount of electrolyte and a carbon rod 1, serving as an oxygen-carbon reference electrode (4). Measurements of the potential of the carbon anode (on its diffusion side) relayed—

with respect to the oxygen-carbon electrode were carried out by means of a lamp potentiometer with an input resistance of $2 \cdot 10^7$ ohms*. The current between the anode and the iron diaphragm cathode was usually kept constant during the experiments. In the first series of experiments the electrolyte was a mixture of KCl—NaCl—Na_2SO_4 (m.p. 565°). The bottom thickness of the carbon test tube was 1.0-1.5 mm, and the outside diameter 13 mm.

Fig. 1. Measuring cell with a carbon test tube—anode, inside which is the carbon-oxygen reference electrode

After the current was switched on, after some time the potential of the anode began to increase on the inner, diffusion side. Thus, in one of the experiments, the results of which are shown in Fig. 2, after switching on a current of 1.0 A, already after 20 sec the potential of the diffusion side of the anode became 0.24 V more positive than that of the carbon reference electrode.

Fig. 2. Dependence of the overvoltage on the inner, polarized surface of the carbon anode on the time after electrolysis is switched on. Electrolyte KCl—NaCl—Na_2SO_4 at 650°.

When the current was switched off there was no jump in the anode potential (which indicates the absence of a component due to IR); the potential began to decrease slowly and after 2 min became equal to the potential of the reference electrode. The same pattern was observed when the current was switched on again. The curve in Fig. 2 was plotted from records of the anode potential on the diffusion side during one of these switch-ons (at a current of 0.3 A and a temperature of 650°).

Fig. 3. Dependence of the overvoltage on the inner, unpolarized surface of the carbon anode on the time after electrolysis is switched on. Electrolyte—cryolite-alumina melt at 950°

Figure 3: Fig. 3. Dependence of the overvoltage on the inner, unpolarized surface of the carbon anode on the time after electrolysis is switched on. Electrolyte—cryolite-alumina melt at 950°

In another series of experiments the electrolyte was a cryolite-alumina melt (Na_3AlF_6 60.5 wt. %, Al_2O_3 4 wt. %, AlF_3 35.5 wt. %). During 30 min of electrolysis at a current of 1.3 A, the potential of the diffusion side increased by 0.125 V and continued to rise (Fig. 3). In this case the bottom thickness of the carbon test tubes—anodes was as much as 3 mm before the experiment, and the potential of the diffusion side increased very slowly; by the end of the experiment the bottom thickness was only about 0.5-0.7 mm. When the current was switched off, the potential of the diffusion side, in contrast to the experiments of the first series, fell practically at once to zero. Possibly, this is fully or partially explained by the higher temperature (100° higher). It is interesting that if the current is reduced by only 30%, the potential on the diffusion side remained unchanged for at least 2 min. (as long as the observation continued). This observation agrees with our measurements on the polarized side ([1],2).

Fig. 3. Dependence of the overvoltage on the inner, unpolarized surface of the carbon anode on the time after electrolysis is switched on. Electrolyte—cryolite-alumina melt at 950°.

The gradual appearance of an overvoltage on the unpolarized, inner side of the carbon tube—the anode—confirms the mechanism of overvoltage formation set forth above and cannot at all be explained from the standpoint of earlier views.

In addition to this principal conclusion, it is appropriate to point out the following. The linear rate of consumption of the carbon anode in the last experiment (at 770°) was about 5 mm per hour. Consequently, the rate of penetration of chemisorbed oxygen to the diffusion side was no less than this value. Judging from Fig. 2, the rate of oxygen penetration through the carbon at 670°, i.e., at a lower temperature, may be considerably greater, namely more than 1 mm per minute.

Qualitatively the same correspondence of rates was also observed in other experiments. There is nothing paradoxical in this, since the potential difference between the diffusion side of the anode and the oxygen-carbon reference elec-

* With the small volume of electrolyte, changes in its composition because of the formation of double electrolytic layers and selective absorption of components of the melt are probably large, but this is of no importance because both the anode and the reference electrode are made of the same material.

trode arises only at the expense of carbon–oxygen compounds of nonequilibrium composition, formed at a potential considerably higher than the equilibrium one. At a higher temperature the rate of redistribution of oxygen bonds with the carbon lattice is higher, and the combustion reaction is completed in a thinner layer of carbon on its polarized side.

Finally, the strictly logarithmic form of the dependence between the overvoltage on the diffusion side and time (Fig. 2) is noteworthy.

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