THE IRON-CARBON CELL

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In this paper the results of an investigation of certain processes, occurring at the iron and carbon electrodes of the iron-carbon cell, are set forth.

THE IRON ELECTRODE

The use of iron as an electrode in a galvanic cell became possible only after the development of methods of preparing semipassive iron, i.e., iron having electrochemical activity and little self-discharge. There are now a number of methods of preparing semipassive electrodes. R. Kh. Burshtein and co-workers [1, 2] showed that if iron powder is poured after reduction into benzene or other organic solvent, without contact with air, and then dried in air, an electrode prepared from this powder has electrochemical activity which is retained for several years. Semipassive iron also may be obtained by treating the reduced powder with a 1% solution of an inhibitor: water glass or sodium phosphate.

To find out the causes of the semipassive state in iron electrodes, it is expedient to investigate the effect of organic solvents and thin oxide films on gas evolution and the processes of cathodic and anodic polarization of powdered iron.

Experiments were performed with iron powders of two types. The first of these was prepared from iron oxide of the kind used in alkaline storage batteries; the second, which was purer, was prepared by decomposing iron pentacarbonyl and freeing the product from organic admixtures [3]. For security from autoignition, these powders, after reduction in hydrogen at 500-550°, were poured into benzene or water, without contact with air, and then filtered out and dried at room temperature. The electrodes under investigation had the form of lamellas containing 0.2 g of iron powder. A setup was used, in which electrode reduction and determination of the quantity of absorbed oxygen could be combined with electrochemical measurements [4].

The rate of gas evolution and the technological capacity were determined, and polarization curves were taken for electrodes of storage-battery iron which, after additional reduction, were covered with an oxide film containing 2×10^{15} oxygen molecules per cm^2 of true surface. Gas evolution was not observed at this electrode in 9.5 N KOH. The electrode potential was equal to 50-60 mv, with respect to the hydrogen electrode in the same solution; i.e., it corresponded to the potential of the iron electrode in the charged state. The utilization of iron of this type amounted to 41% of the theoretically possible value at a current density of 35 ma per g of powder when the electrode was discharged to a potential of +280 mv with respect to the hydrogen electrode. Thus, electrodes bearing a thin surface film of oxide are similar in their properties to electrodes prepared from solid iron after treatment with organic solvents.

The self-discharge of such electrodes may be diminished by the effect of the oxide film either on hydrogen evolution or on anodic oxidation of iron. In Fig. 1 are shown curves expressing the relation between the electrode potential (with respect to the hydrogen electrode in the same solution) and the logarithm of the current density. As is evident from these curves, the presence of an oxide film on the iron surface has no substantial effect on the path of the anodic curves. Cathodic polarization curves for semipassive electrodes are identical among themselves, but lie considerably lower than the curve of hydrogen overvoltage for an electrode without an oxide film. Removal of the oxide film leads to gas evolution at a stationary potential. The reduction of

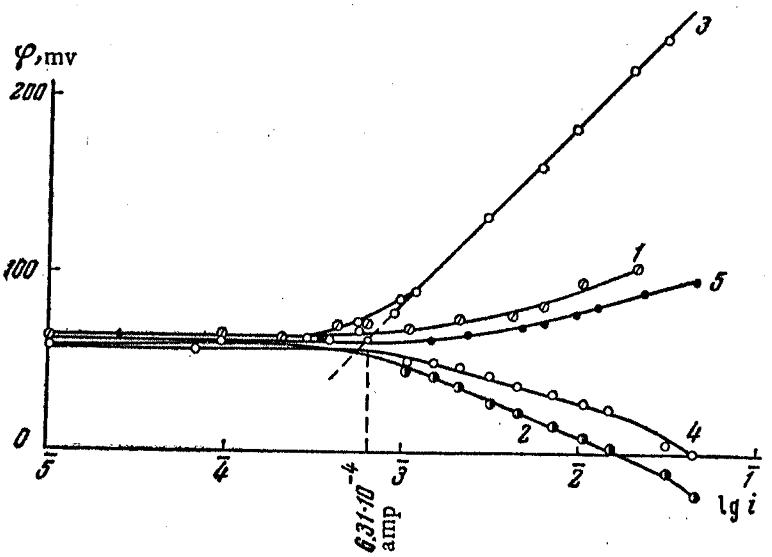

Fig. 1. Polarization curves. 1 and 2) Curves of cathodic and anodic polarization of electrodes with a thin oxide film; 3 and 4) curves of cathodic and anodic polarization of electrodes without oxide film; 5) curve of cathodic polarization of a semipassive iron electrode prepared by treatment with benzene.

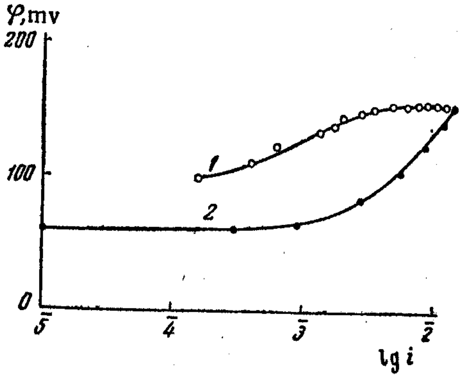

Fig. 2. Cathodic polarization curves. 1) Electrode with oxide film. The amount of hydrogen, used up in the removal of oxygen is taken into account; 2) same electrode after removal of the oxide film.

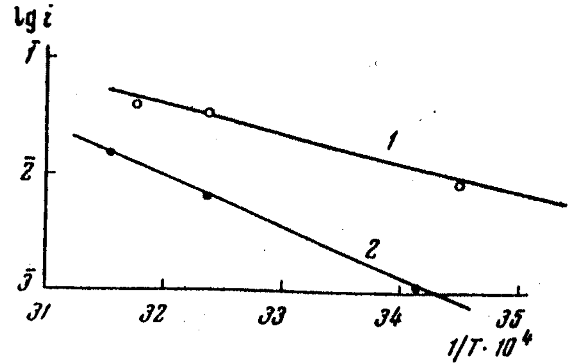

Fig. 3. Relation between the logarithm of the rate of hydrogen evolution and 1/T. 1) For an electrode without oxide film; 2) for an electrode with oxide film 6 A thick.

hydrogen overvoltage for iron, covered with an oxide film, indicates, as it were, an increase in the self-solution current and, therefore, should lead to an increase in gas evolution, which contradicts experimental data given earlier. In order to elucidate this contradiction the rate of gas evolution from a semipassive iron electrode with cathodic polarization by a current of 2.6×10^{-3} amp was measured. These measurements showed that the rate of hydrogen evolution at the beginning of polarization is considerably less than that predicted by Faraday's law; hence, it follows that part of the electricity is consumed in the removal of the oxide film. If the amount of electricity going into the removal of the oxide film is taken into account (as the difference between the observed rate of gas evolution and the rate of gas evolution, corresponding to the current being passed), the hydrogen overvoltage for this electrode will be expressed by Curve 1 (Fig. 2). Curve 2 relates to the hydrogen overvoltage for the same electrode after complete removal of the oxide film. As is evident from the figure, the lower points of Curve 1, determined in the presence of oxygen at the surface of the iron, lie above the corresponding points

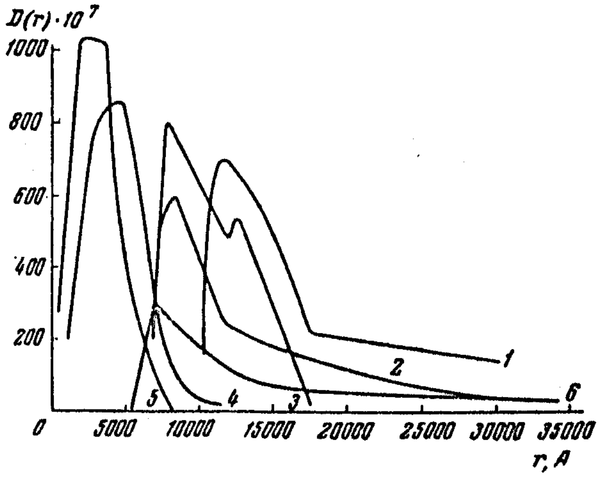

Fig. 4. Curves of the relation between the pore-distribution function and the radius. 1) Electrode of unground activated charcoal; 2) electrode of charcoal ground for 5 hours; 3 and 4) electrodes of a pressed mass prepared from charcoal ground for 5 and 10 hours, resp.; 5) electrode prepared similarly to the preceding , but pressed at a higher pressure; 6) electrode prepared by the Daniel'-Bek method.

of Curve 2. This indicates that the hydrogen overvoltage for iron, covered with an oxide film, is higher, which agrees with literature data [5, 6]. Thus, the presence of an oxide film on semipassive iron causes an increase in the hydrogen overvoltage, which leads to a decrease in the rate of self-solution. Measurement of gas evolution on removal of the oxide film from the iron electrode by cathodic polarization also permits determination of the film thickness, if the extent of the surface is known, or the extent of the surface if the film thickness is known.

The effect of thin oxide films on the self-solution of thermally reduced iron was also investigated. The experiments were performed with chemically pure iron prepared from iron pentacarbonyl. The results of measurement of gas evolution in the temperature interval 17-44° are compared in the table for the cases of iron without an oxide film and iron, on which are adsorbed 2×10^{15} oxygen molecules per cm^2 of true surface (thickness of the oxide film – 6 A, calculated for Fe_2O_3). From these results it follows that thermally reduced iron has an appreciable rate of self-solution, which decreases in the presence of a thin oxide film to 1/10, 1/5, and 1/3 of the original value at 20, 35 and 42°, respectively.

Effect of an Oxide Film on Iron on Gas Evolution at Various Temperatures

Temperature, °C	Quantity of evolved gas, cc/g-hour		b/a
	with oxide film, a	without oxide film, b	
17	–	0.086	–
20	0.0012	(0.012)*	10
36	0.0065	0.034	5
42	(0.013)*	0.039	3
44	0.0154	–	–

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* Values in parentheses were obtained by interpolation from curves of the relation between the rate of gas evolution and temperature.

The relation between the logarithm of the rate of hydrogen evolution in the absence of current and the inverse temperature (Fig. 3), both for iron without an oxide film (Curve 1) and for iron bearing a surface film 6 A thick (Curve 2), is linear. Apparent activation energies, calculated from Curves 1 and 2, are 11.3 and 19.7 kcal., respectively. Therefore, the decrease in the rate of self-solution of iron in the presence of a surface film of oxide is due to an increase in the apparent activation energy of the electrochemical process.

THE CARBON ELECTRODE

The principal shortcoming of the air-depolarized carbon electrode consists of its impregnation, which hinders the diffusion of oxygen thru the pores of the electrode and thus impairs its electrochemical characteris-

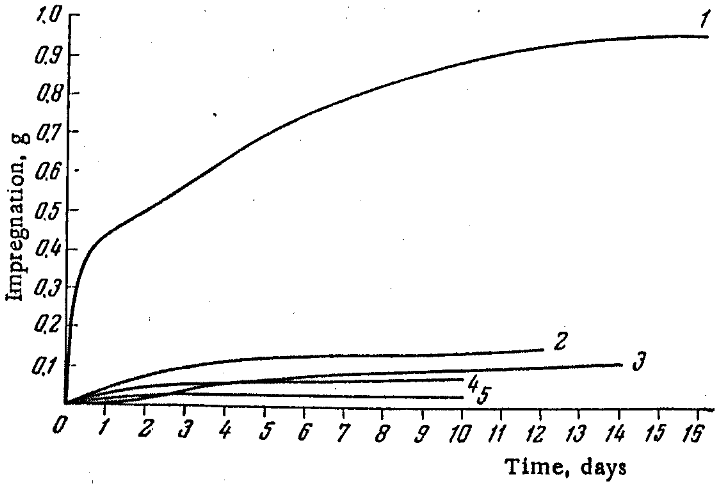

Fig. 5. Curves of impregnation of carbon electrodes with time. 1) Electrode of unground charcoal; 2) electrode of charcoal ground for 5 hours; 3) electrode of a pressed mass prepared from charcoal ground for 10 hours; 4) paraffined electrode of charcoal ground for 5 hours; 5) paraffined electrode prepared without soot, from charcoal ground for 12 hours.

tics. As is generally known [7]*, the impregnation of an air-depolarized electrode is a function of its potential and increases on both sides of the point of zero charge of the carbon surface. In KOH solution the impregnation minimum lies near the rest potential (without current) of the air-depolarized electrode. It was to be expected that the impregnation of the electrode at the rest potential would depend to a considerable degree on its structure. In connection with this, R. Kh. Burshtein and D. L. Kondrashov investigated the distribution of pores with respect to radii and its effect on the electrochemical characteristics and impregnation of electrodes prepared from carbon having various degrees of dispersity [8].

The pore distribution was measured by forcing mercury in, according to an improved form of the method of Ritter and Drake [9, 8]. The impregnation of the electrode on keeping in the electrolyte was determined by the change in its weight. The carbon electrodes were prepared from a mixture of 67% activated charcoal and 33% soot. The grain size of the activated charcoal was changed by grinding in a ball mill. Rubber cement (solution of rubber in benzene) was used as a binder. The electrodes had the form of a tumbler with a wall thickness of 5 mm and were prepared by pressing the carbon mass on an iron grid. The electrolyte was a KOH solution (sp. gr. 1.3-1.4) located inside the tumbler. The working area of the electrode was equal to 80 cm^2.

In Fig. 4, are shown curves expressing the distribution function of pores, with respect to radii. From the data obtained, it follows that the grinding and subsequent pressing of the carbon mass shift the distribution of pores in the electrodes toward smaller diameters. Electrode 6, prepared by the method of V. S. Daniel'-Bek, has only wide pores for the most part.

In Fig. 5, are given curves characterizing the impregnation of carbon electrodes. They show the increase in the weight of the electrode with time on keeping in an electrolyte. From comparison of the data on pore distribution with the data on impregnation of carbon electrodes, it is evident that electrodes, the distribution curve of which is shifted into the region of pores of lesser diameter, are impregnated to a much lesser degree. In the presence of very large pores hydrophobic substances are ineffective. The data given relate to charcoal roasted at 900°. At this temperature oxides are removed from the charcoal surface. The presence of acidic oxides on the charcoal surface improves the wetting properties and, therefore, should lead to increased impregnation. In Fig. 6, are given the volt-ampere characteristics of electrodes of charcoal with various degrees of dispersity. As is evident from the curves, grinding of the charcoal leads to improvement in the electrochemical characteristics of the electrode. Similar data were obtained with gas carbon electrodes.

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*Gas-carbon electrodes were used in the cited work.

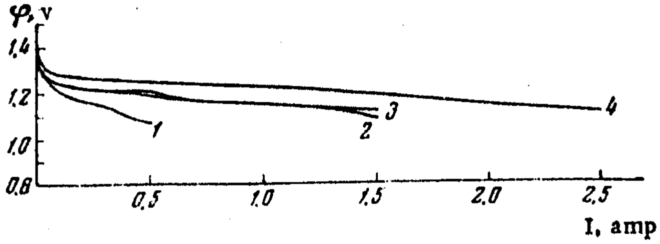

Fig. 6. Volt-ampere curves of carbon electrodes. 1) Electrode of unground charcoal; 2) electrode of charcoal ground for 5 hours; 3) electrode of a pressed mass prepared from charcoal ground for 10 hours; 4) paraffined electrode prepared without soot, from charcoal ground for 12 hours.

Determination of the total porosity of the carbon electrodes showed that it decreases as the pore radius decreases. However, the electrochemical characteristics of the electrode are improved in this case. This indicates that the process of air depolarization limits not the rate of diffusion of oxygen through the carbon mass but the rate of penetration of oxygen through the gas-electrode interface to the carbon surface. Apparently, grinding of the carbon causes an increase in the surface at which the electrochemical reaction takes place, and this leads to a decrease in the polarization of the carbon electrode. However, the pore diameter can be decreased only to a definite limit, beyond which diffusion inhibition sets in.

Thus, the results obtained show that the structure of air-depolarized electrodes is of substantial importance in determining their electrochemical characteristics.

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