

INFLUENCE OF HEAT TREATMENT OF IRON ON ITS BEHAVIOR IN THE ELECTRODES OF ALKALINE STORAGE CELLS

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Iron powder with a high content of metallic iron is used for production of sintered iron electrodes, used as negative plates in iron-nickel storage cells. The powder is made by thermal reduction of iron oxides in a hydrogen atmosphere or in presence of other reducing agents. The temperature varies from 600 to 1000°C, dependent on the technological conditions.

Little information is available in the literature on the influence of preliminary heat treatment on the behavior of iron electrodes. The influence of the reduction temperature on sintering of iron powders and on the effective capacity of powder electrodes has been studied [1, 2]. We have investigated the influence of the annealing temperature on the electrochemical and adsorption properties of smooth iron [3].

In this paper we report a study of the influence of the reduction and annealing temperatures on the electrochemical properties of iron powder in alkaline solutions.

Powdered Fe_3O_4 was prepared by the method of Platonova and Levina [4] from iron obtained from iron pentacarbonyl; Fe_3O_4 was then reduced by hydrogen for 3 h at 600° (powder I, Fe_{met} 98.9%) or for 2 h at 750° (powder II, Fe_{met} 99.1%). The powders were classified by screening in order to obtain similar specific surfaces in the powder electrodes. The particle sizes were determined with the aid of a microscope. The average particle size of powders I and II was 2μ . Weighed portions (1 g) of powder, containing 0.3% S in the form of FeS for activation [5], were pressed onto an iron grid with an attached conductor under 400 kg/cm² pressure in a rectangular mold. The dimensions of the electrodes were 1.5 • 0.3 cm.

In order to establish a constant discharge capacity, the electrodes were subjected to cathodic and anodic cycling at 40 mA per g of powder. The charging time was 16-18 h. Three series of specimens were used for the measurements. Each series consisted of eight electrodes, four from powder I and four from powder II. The electrolyte was 5 N KOH solution previously purified by cathodic polarization for 10-12 h at an iron electrode ($i_c = 20 \text{ mA/cm}^2$).

In order to maintain a high effective capacity, as described earlier [6], during the first three cycles the discharge was continued until oxygen was evolved, and during the subsequent cycles to a potential of -0.75 V, corresponding to completion of the first anodic process. The potential was measured against a mercury oxide electrode in the same solution.

Electrodes made from iron powder I had a discharge capacity of 0.25 A-h/g, which is higher by 15-25% than the capacity of electrodes made from powder II. The lower capacities of electrodes made from powder II probably cannot be attributed to decrease of the true area of the powder as the result of sintering, despite the fact that screening did not ensure completely equal specific surfaces. The agreement between the cathodic polarization curves shows that the true surface area of the electrodes made from powders I and II were similar (Fig. 1). It should be pointed out that the overpotential of the anodic process was lower on powder I (at $i = 1 \cdot 10^{-2} \text{ A/g}$ of powder) than on powder II by 25-30 mV.

The difference between the electrochemical properties of powders subjected to different heat treatments is also manifested on addition of $\text{Sb}(\text{OH})_3$ (0.02% of the weight of electrolyte) to the electrolyte. Antimony was deposited uniformly on electrodes I during cathodic polarization, raising the hydrogen overpotential by 20 mV (Fig. 1). This effect persisted during subsequent cycling. On electrodes II sponge was formed and no increase of overpotential was observed. Introduction of $\text{Sb}(\text{OH})_3$ lowered the rate of spontaneous dissolution of electrodes made from powder I, but had virtually no effect on the rate of spontaneous

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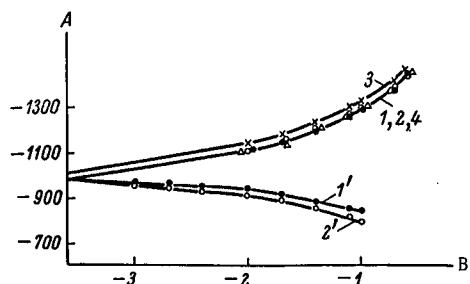


Fig. 1. Polarization curves of electrodes made from iron powders reduced at 600° (1, 1', and 3) and at 750° (2, 2', and 4), in 5 N KOH (1, 1' and 2, 2') and in 5 N KOH + 0.02% Sb(OH)_3 (3, 4). A) Potential, ϕ_{HgO} (mV); B) $\log i$ (A/g).

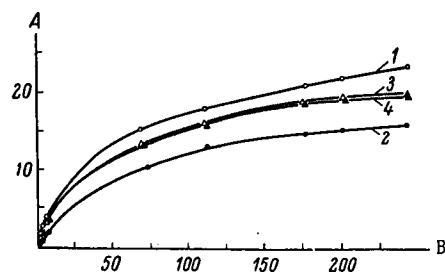


Fig. 2. Curves for gas evolution on electrodes made from powders reduced at 600° (1, 2) and at 750° (3, 4), in 5 N KOH (1, 3) and in 5 N KOH + 0.02% Sb(OH)_3 (2, 4). A) Volume of gas, V_{H_2} (ml/g); B) time (h).

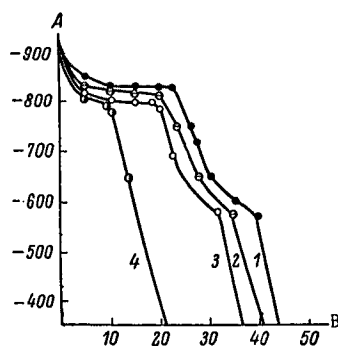


Fig. 3. Charging curves of smooth iron electrodes in 1 N KOH + $1 \cdot 10^{-4}$ N Na_2S . A) Potential, ϕ_{HgO} (mV); B) time (sec). 1) Not annealed; annealing temperature (°C): 2) 200; 3) 600; 4) 800.

dissolution of electrodes II (Fig. 2). The dissolution rate was also calculated from the difference between the electrode capacity at the preceding cycle and the residual capacity after gas evolution. The results were in agreement with the results obtained in determinations of the gas evolution rates.

Comparison of these results with data obtained for a smooth electrode shows that variations of the adsorption and electrochemical properties of powder and smooth electrodes with the annealing temperature follow a similar course. For example, polarization curves determined in 5 N KOH showed that smooth electrodes* annealed at 600° (6 h) had considerably higher adsorption capacity than electrodes annealed at 750°. On addition of 10^{-5} N Sb(OH)_3 the increase of the hydrogen overpotential is 100-150 mV in the first case and almost zero in the second.

As in the case of smooth electrodes, the decrease of the adsorption capacity of powder electrodes with increase of the annealing temperature is apparently due to processes associated with recrystallization. According to Bochvar [7], recrystallization of iron at an appreciable rate begins only at 750°. This is confirmed by our x-ray diffraction patterns of powders reduced at 600 and 750° and of smooth electrodes made from Armco iron and zone-refined iron. In the latter case the difference is especially pronounced [7]. The x-ray diffraction pattern of smooth iron annealed at 600° for 6 h consisted of a series of almost continuous diffuse lines, while that of iron annealed at 750° consisted of separate sharp spots. This shows that the crystal growth and formation of blocks, accompanied by ordering of the crystal faces proceeds at an adequate rate only at $t \geq 750^\circ$. In addition to ordering of the faces, recrystallization is accompanied by decrease of the number of dislocations and other defects serving as active adsorption sites, which leads to decreased rates of electrochemical processes and less effective action of additives.

This conclusion is confirmed by results of experiments with specially deformed smooth Armco iron electrodes. Thin plates were previously annealed for 6 h at 800° to release residual stresses after rolling. The electrodes were then deformed by extension (5% of electrode length) in order to raise the defect concentration in the iron lattice, and annealed in a hydrogen atmosphere at various temperatures: 200, 400, 600, and 800° (6 h) in order to lower the defect concentration. Charging curves were determined in 1 N KOH with addition of 10^{-4} N Na_2S , at 10^{-4} A/cm² current density at 20°. Figure 3 shows that the halts corresponding to anodic processes I and II become shorter with increase of the annealing temperature. In this case it can be assumed that shortening of the duration of the anodic processes is not caused by changes of the true electrode areas after

* The iron plates were previously cold-rolled.

annealing. Special determinations of the capacity of the double layer on iron, performed in acid solutions, showed that the surface area of the iron electrodes is almost unchanged during deformation and subsequent annealing. The results are in good agreement with data on discharge capacities of powder electrodes made from iron I and II.

CONCLUSIONS

Determination of polarization curves and charging curves on powder and smooth iron electrodes showed that the effectiveness of additives $[Sb(OH)_3, Na_2S]$ diminishes with increase of the temperature of reduction and annealing of iron. These results can be attributed to decrease of the concentration of adsorption sites during recrystallization of the metal.

LITERATURE CITED

- 1/ L. L. Kuz'min, Proceedings of the Second All-Union Conference on Theoretical and Applied Electrochemistry [in Russian], Kiev (1949), p. 405; L. L. Kuz'min and V. S. Poroikova, Zh. Prikl. Khim., 22, 572 (1949).
- 2/ A. M. Filippova and L. L. Kuz'min, Tr. Ivanovsk. Tekhn. Inst., 7, 75 (1958).
- 3/ Z. A. Iofa, V. V. Batrakov, and Yu. A. Nikiforova, Vestn. Mosk. Gos. Univ., Khimiya, 6, 11 (1967).
- 4/ I. Platonova and S. Levina, Zh. Fiz. Khim., 21, 331 (1947).
- 5/ S. A. Rozentsveig and Z. V. Shcherbakova, Zh. Fiz. Khim., 35, 2547 (1961).
- 6/ S. A. Rozentsveig and T. K. Teplinskaya, Zh. Fiz. Khim., 38, 2176 (1964).
- 7/ A. A. Bochvar, Metal Science [in Russian], ONTI (1947).