

INFLUENCE OF THE CONCENTRATION AND NATURE OF THE ELECTROLYTE ON THE BEHAVIOR OF AN IRON ELECTRODE

A. P. P'yankova and Z. A. Iofa

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A problem of great significance for the theory of the iron electrode of the alkaline storage cell is determination of the dependence of the technological capacity and other parameters on the concentration and nature of the electrolyte.

The influence of alkali concentration was studied earlier [1-3]. Kabanov and Leikis [3] showed that the capacity q_1 of the first anodic process of a smooth iron electrode increases with increase of the KOH concentration (to 3.5 N) at constant current density in accordance with the equation

$$q_1 = K[\text{OH}^-]^{1/2}. \quad (1)$$

We verified this relationship for a powdered-iron electrode over a wider range of alkali (KOH and NaOH) concentrations. The role of lithium ions and of sulfide sulfur added as an activator to the active material of the electrode (0.1% of sulfur in the form of FeS on the weight of iron powder [4, 5]).

For preparation of the iron powder, pentacarbonyl iron was dissolved in HNO_3 , the nitrate was calcined, and the oxide was reduced in a current of hydrogen at 600° . The electrodes were made by pressing the iron powder (0.35 g) onto fine nickel gauze. Before the experiments they were cathodically polarized at 20 mA for 20 h. The electrolyte was also purified by cathodic polarization for 20 h at 20 mA/cm² current density with the aid of an Armco iron plate.

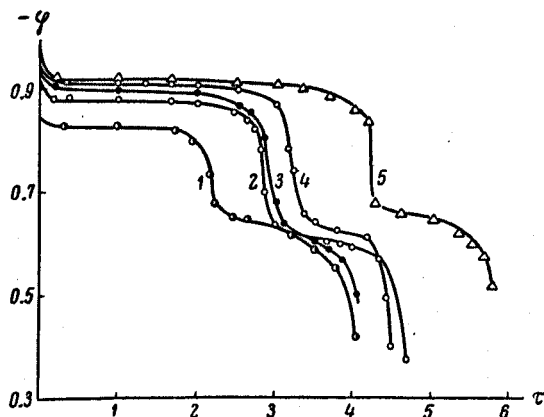


Fig. 1. Discharge curves of powdered-iron electrodes, containing an activator (0.1% of sulfur in the form of FeS), in KOH solutions. φ) Potential (V); τ) time (min). KOH concentration (N): 1) 1.0; 2) 3; 3) 4.6; 4) 7.0; 5) 10.

Figure 1 shows discharge curves recorded at 30 mA in a KOH electrolyte at 20° at the sixth or seventh cycle, when the A-h capacity became established at a constant level, for powdered-iron electrodes prepared as described above and containing an activator. The curves have two halts of potential, corresponding to the processes $\text{Fe} \rightarrow \text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_2 \rightarrow \text{FeOOH}$. It follows from Fig. 1 that the potentials of these anodic processes become more negative at a given current strength with increase of KOH concentration, and the A-h capacity of the first anodic process (q) increases substantially. Electrodes of this type gave similar results in an NaOH electrolyte (Table 1). In both cases the stationary potential (φ_s) shifts in the negative direction, in accordance with thermodynamic principles, with increase of the alkali concentration.

It is noteworthy that the capacity of the second anodic process (q_2) varies little with the alkali concentration.

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TABLE 1. Technological Capacity of the First (q_1) and Second (q_2) Anodic Processes on an Iron Electrode in Relation to the Concentration and Nature of the Alkali

Alkali	Cycle No.	Electrode capacity (mA-h/g) and alkali concentration (N)																			
		1		2		3		4		4.6		5		7		7.4		10		10.8	
		q ₁	q ₂	q ₁	q ₂	q ₁	q ₂	q ₁	q ₂	q ₁	q ₂	q ₁	q ₂	q ₁	q ₂	q ₁	q ₂	q ₁	q ₂	q ₁	q ₂
KOH (with activator in electrode)	6	131	79	—	—	200	83	—	—	—	—	230	100	265	94	—	—	—	—	357	88
	7	110	88	—	—	113	88	—	—	—	—	176	88	220	77	—	—	—	—	262	92
KOH (without activator in electrode)	2	—	—	71	34	—	—	—	—	108	68	—	—	—	—	—	—	57	0	—	—
	3	—	—	72	34	—	—	—	—	100	63	—	—	—	—	71	55	0	—	—	—
	5	—	—	85	34	—	—	—	—	—	—	—	—	—	—	48	48	—	—	—	—
	6	—	—	82	30	—	—	—	—	100	57	—	—	—	—	0	0	—	—	—	—
12	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	

TABLE 2. Currents I at the Maxima of the Potentiodynamic Curves and Capacities q of Powdered-Iron Electrodes

Electro-lyte	Concn. (N)	Cycle No.	Cur. stren. at max. (mA)				Tech. cap. (mA-h/g)			
			I ₁	I ₂	I ₃	I ₄	q ₁	q ₂	q ₃	q ₄
Electrodes with activator										
KOH	1	1	128	104	102	—	57	49	17	—
	3	1	188	130	126	—	80	76	42	—
	4.6	1	166	100	86	—	86	71	29	—
NaOH	7	1	196	122	96	—	94	71	25	—
	1.2	1	110	105	80	—	50	42	26	—
	3	1	150	116	88	—	57	42	33	—
LiOH	5	1	168	117	96	—	63	44	35	—
	4.3	2	130	194	50	—	94	74	28	—
	4.3	8	120	89	40	—	91	71	70	—
Electrodes without activator										
KOH	2	1	42	34	33	22	14	8	4.3	3
	4.6	1	47	34	39	29	15	8	7	3
	7.4	1	93	46	49	70	20	9	6	6
	10	1	60	32	30	71	17	9	5	4
	10	5	2	1	0	—	0	0	0	0
LiOH	4.3	1	113	0	14	113	8	0	0	7
	4.3	2	63	0	0	72	2	0	0	1.4

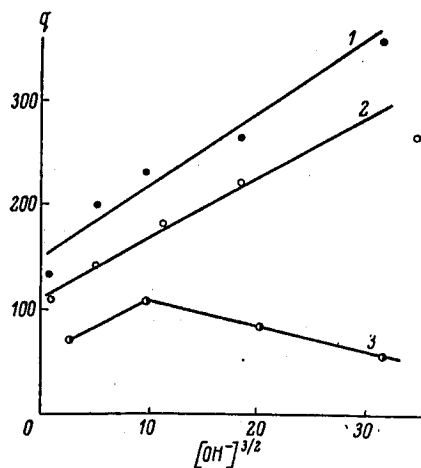


Fig. 2. Dependence of the capacity q (mA-h/g) of iron electrodes containing the activator on $[\text{OH}^-]$ in KOH (1) and NaOH (2) solutions, and of electrodes without the activator in KOH solutions (3).

higher in 7.0 than in 4.6 N KOH. Accordingly, the capacities q_1 and q_2 are higher in 7.0 N KOH than in the less concentrated electrolyte. The curves have one cathodic maximum, corresponding to reduction of ferric to ferrous oxide; the latter is reduced to the metal probably simultaneously with evolution of hydrogen.

It follows from Fig. 3b that the presence of the activator in the electrode more than doubles the maximum currents of the first and second anodic processes, with a corresponding increase of the capacity (Table 2), while oxidation of ferrous to ferric oxide begins at a more positive potential. It is seen from the curves that the activator raises the hydrogen overpotential and the overpotential for reduction of ferrous oxide. Therefore the curve has only one cathodic maximum, whereas in the case of electrodes without the activator there are two distinct maxima, corresponding to the reactions $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ and $\text{Fe}^{2+} \rightarrow \text{Fe}$, the second maximum being considerably higher than the first. Thus, the activator in the electrodes increases the yields of the first and second anodic processes substantially and raises the hydrogen overpotential. However, the latter does not facilitate reduction of the oxides, as the additive raises the overpotential for reduction of iron oxides to a greater extent. Addition of nickel sulfate to the active material has been proposed [4] for lowering the overpotential for reduction of iron oxides and for improving the chargeability of iron electrodes.

Addition of sulfide sulfur also increases the discharge capacity substantially in LiOH electrolyte.

The potentiodynamic curves for an iron electrode in 4.3 N LiOH (Fig. 3c) show that when the above-named additive is introduced into the electrode material a high maximum corresponding to the second anodic process is obtained. The second maximum is virtually absent in the case of the electrode without the activator. The cathodic branch has a small current maximum at $\varphi = -0.93-0.92$ V and a high maximum at $\varphi = -1.12$ V, corresponding to reduction of ferrous oxide to the metal.

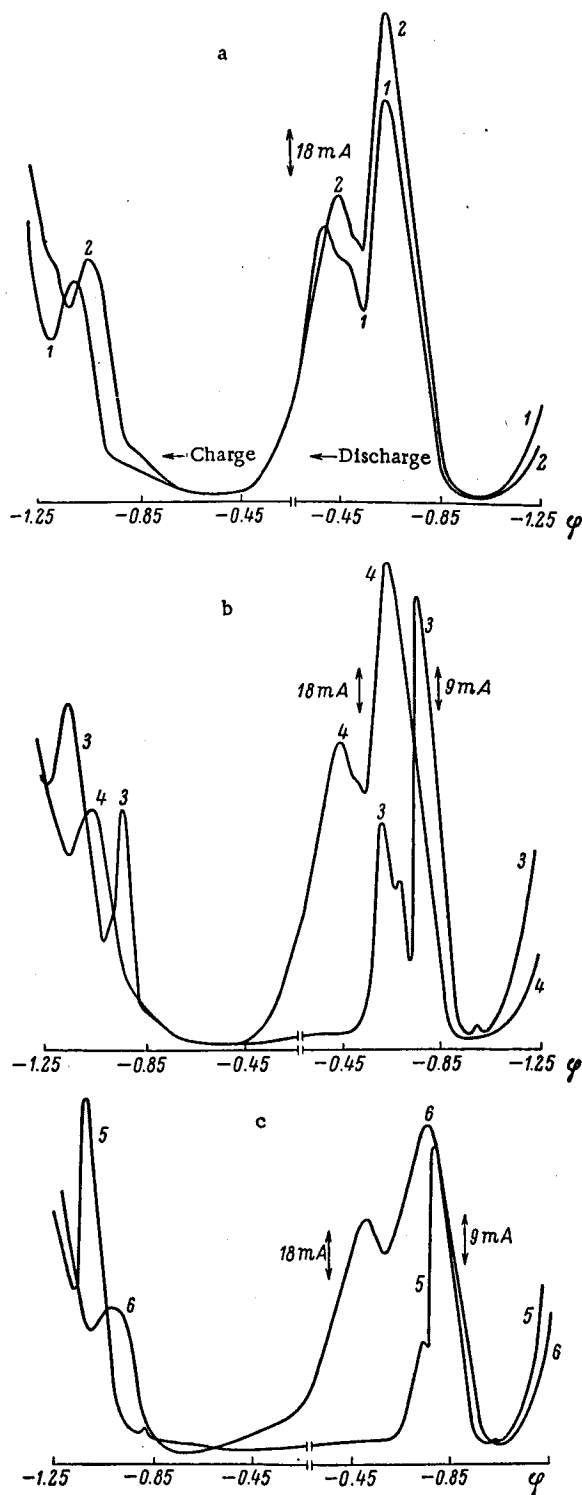


Fig. 3. Potentiodynamic curves for discharge and charge of iron electrodes. φ) Potential (V). a) With activator (first cycle) in KOH solutions: 1) 4.6 N; 2) 7.0 N; b) in 7.0 N KOH: 3) without activator; 4) with activator in electrode; c) in 4.3 N KOH (second cycle): 5) without activator; 6) with activator in electrode.

In absence of the activator the oxides are reduced with difficulty in the LiOH electrolyte, and the technological capacity therefore falls to zero at the third cycle.

The difficult reduction of iron oxides in LiOH solutions has been attributed [1, 8, 9] to formation and accumulation of the compound LiFeO_2 , which is difficult to reduce; but it was not explained how small amounts of sulfide sulfur can eliminate this difficulty and prevent formation of LiFeO_2 .

The curves for discharge of an iron electrode, containing the activator, in a solution of 2.3 N LiOH + 2.3 N KOH, show a somewhat lower capacity than in 4.6 N LiOH, but the capacity alters little with successive cycling. The i vs φ potentiodynamic curve for an electrode without the activator, recorded in 2.3 N LiOH + 2.3 N KOH solution, has a high current maximum at $\varphi = -0.69$ V while the second anodic maximum is absent. The cathodic branch has only one current maximum, corresponding to reduction of ferric to ferrous oxide. Reduction of the latter to the metal is probably simultaneous with evolution of hydrogen. Addition of 15 g of LiOH per liter to 4.6 N KOH raises the technological capacity both in presence and in absence of the activator, which is in agreement with literature data [10, 11].

CONCLUSIONS

1. The A-h capacity of powdered-iron electrodes containing an activator (0.1% of sulfuric in the form of FeS) increases with increase of the electrolyte (KOH or NaOH) concentration to 10 N, and at $i = \text{const}$ it conforms to the equation $q_1 = K + b[\text{OH}^-]^{3/2}$.

2. The capacity is somewhat lower in NaOH solutions, and higher in LiOH solutions, than in KOH of the same concentrations. In absence of the activator the capacity decreases in the course of cycling in NaOH and KOH solutions of above 5 N concentration; the decrease is especially rapid in LiOH solution.

3. Addition of 15 g of LiOH per liter to 4.6 N KOH solution raises the electrode capacity and prevents its decrease during cycling.

4. Potentiodynamic curves for the systems studied showed that the presence of the activator in the electrode raises the capacity of the first anodic process substantially and lowers that of the second, and increases the hydrogen overpotential and the overpotential for reduction of iron oxides. The latter leads to disappearance of the current maximum corresponding to the reaction $\text{Fe}^{2+} \rightarrow \text{Fe}$ from the curves, as the reaction proceeds simultaneously with hydrogen evolution, and to more difficult charging.

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