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The effect of ferric ions on the behaviour of a nickelous hydroxide electrode

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Nickelous hydroxide electrodes bulk and surface-poisoned with ferric ions were studied. It was found that the effect on the efficiency of electrode charging was greater with ferric compounds precipitated on the hydroxide surface rather than inserted in their structure.

1. Introduction

Edison and Junger were the first to observe that ferric compounds poison the active positive material, $Ni(OH)_2$, in alkaline storage batteries. Tichenor [1], Zlatnikowa [2], Troilius and Alfelt [3] described the influence of iron contamination on the capacity of positive electrodes. The contamination is generated in different parts of the alkaline battery. According to these authors the negative influence of ferric compounds on the capacity of positive electrodes is caused by a decrease in the oxygen evolution overpotential on the ferric compounds and this causes a decrease in the charge efficiency. During the technological process and battery cycling the ferric ions can be precipitated on the surface or introduced into the bulk of the active material. The influence of the ferric ion deposition procedure in the active material was the object of this study.

2. Experimental details

2.1. *Methods of electrode preparation*

Microelectrodes sintered from nickel powder with dimensions 15 × 10 mm provided with welded terminals were impregnated with nickelous hydroxide. The impregnation was done by Kandler's method, using conditions given in the paper by Paszkiewicz [4]. The degree of impregnation of the sinter was estimated by the increase of hydroxide mass in the sinter. Microelectrodes with a similar content of nickelous hydroxide, capacity 14.3 mAh, were chosen for the tests. Ferric compound was precipitated onto the electrode surface by immersing the standard electrodes in 10% ferric nitrate aqueous solution. Ferric hydroxide was precipitated by immersing the electrodes in 25% KOH aqueous solution.

Using various impregnation times in the ferric ion solution, different ferric ion concentrations were precipitated on the nickelous hydroxide electrode.

The introduction of ferric compounds into the structure of nickelous hydroxide or rather a simultaneous precipitation of both kinds of ions was performed by the impregnation of microelectrodes in a mixture of nickel nitrate and ferric nitrate without current polarization. In order to precipitate hydroxides, microelectrodes saturated with nitrates were immersed in 25% KOH solution at 30 to 40° C. Afterwards the microelectrodes were washed and dried.

The correct proportion of nickel and iron was achieved by changing the components of the mixture used for impregnation.

2.2. *Test methods*

Cyclic voltammetric measurements were made by applying the method described by Paszkiewicz and Walas [5], using a 25% KOH solution and a rate of change of the potential, 5 mV min^{-1}. The volume of oxygen evolved during charging was determined by a volumetric method. The oxygen evolved on the electrodes was collected in burettes placed over the electrodes. Burettes were initially filled

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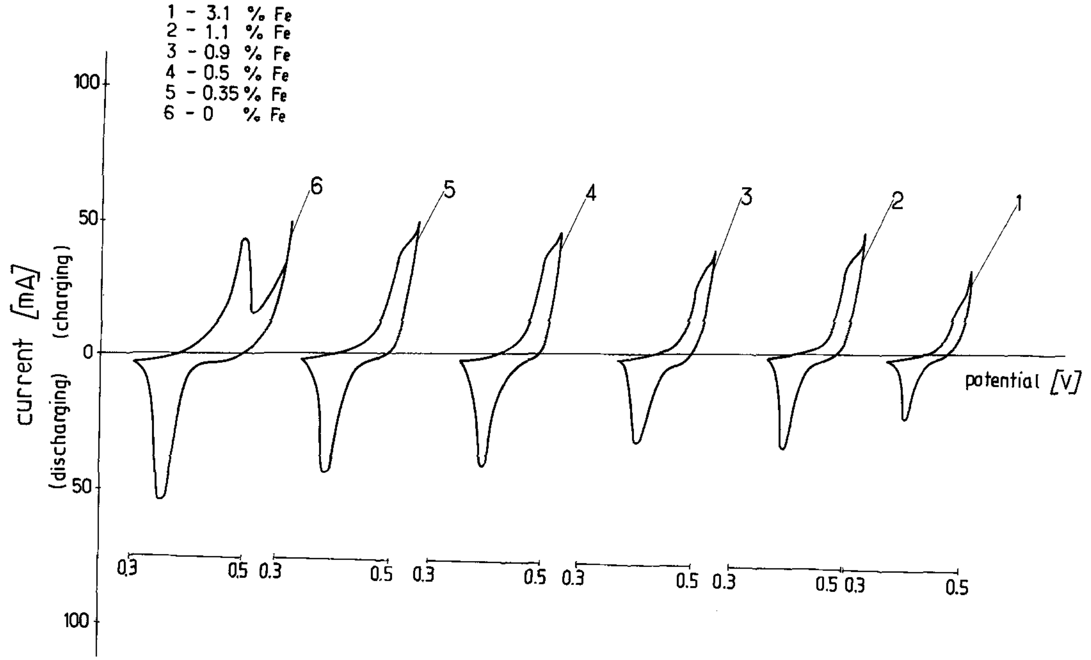

Fig. 1. Cyclic voltammetry curves showing electrode behaviour. The electrodes were made of nickel hydroxide contaminated at the surface by ferric compounds.

with electrolyte solution and as the oxygen evolved the solution was displaced. Measurement of the oxygen evolution rate was performed on the electrodes at the end of voltammetric cycles. At the end of the electrochemical tests the content of iron in the microelectrodes was determined. It was determined by an extraction–colorimetric method. A red complex of Fe^{3+} ions with ammonium rhodanate was formed in an acid environment. This was then extracted with isopentyl alcohol. The iron content was expressed as a percentage in relation to the electrochemically active $Ni(OH)_2$.

3. Results and discussion

Cyclic voltammetry curves of microelectrodes with ferric compounds precipitated in nickelous hydroxide surface are shown in Fig. 1.

On comparing the cathodic reduction curves for the oxyhydroxide, NiOOH, it is observed that as the content of ferric compounds on the active material surface rises, the microelectrode capacity decreases. Even as low a content of iron as 0.35% causes a change in the shape of the anodic part of the cyclic voltammetry curve. The value of the potential of initial oxygen evolution shows that this value decreases as the concentration of ferric compounds precipitated on the surface increases. It corresponds with the statement of the authors, cited in the introduction, that the negative effect of ferric compounds produces a decrease in the oxygen evolution overpotential compared to nickel compounds only.

The decrease of the oxygen evolution overpotential and the decrease in the efficiency of nickelous hydroxide oxidation can be also observed in the case of a simultaneous precipitation of nickel and ferric hydroxide (Fig. 2). A comparison of the cyclic voltammetric curves shows that in this case a distinct effect of electrode poisoning with ferric compounds can be seen, when the concentration of ferric compounds on nickelous hydroxide is one order of magnitude higher than the surface precipitation.

Comparing the test results of these two groups of electrodes (Figs. 1 and 2) it can be stated, that ferric compounds precipitated on the active material surface, i.e. at the interface of the solid phase and the liquid phase where the electrochemical reactions take place, has a negative

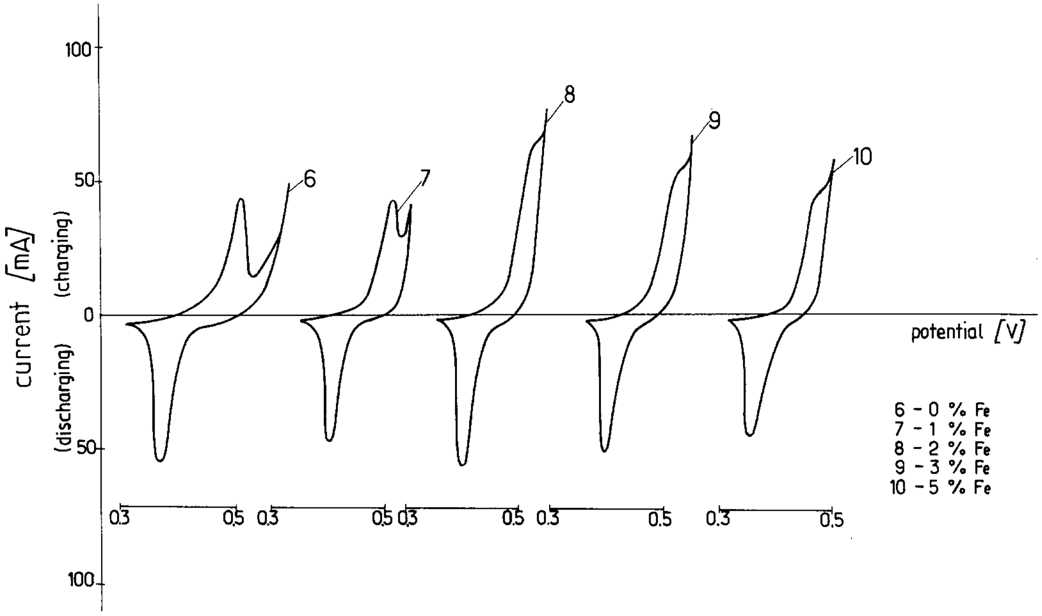

Fig. 2. Cyclic voltammetry curves showing electrode behaviour. The electrodes were made of nickel hydroxide contaminated in the bulk with ferric compounds.

influence on the charging efficiency, i.e. the oxidation of nickelous hydroxide.

The results of the cyclic voltammetric studies were confirmed by oxygen evolution rate measurements during the charging of the microelectrodes with a constant current (Figs. 3 and 4). The curves in Fig. 3 show that the increase of oxygen evolution rate follows the increase in ferric compound content on the nickelous hydroxide surface. Oxygen evolution begins almost instantly at the

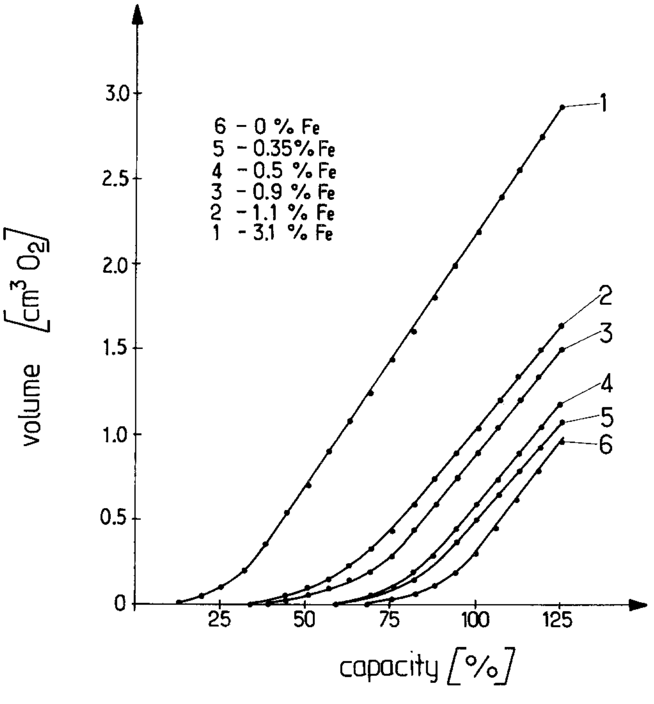

Fig. 3. Effect of iron contamination precipitated on the surface of nickel hydroxide on oxygen evolution rate as a function of charged capacity.

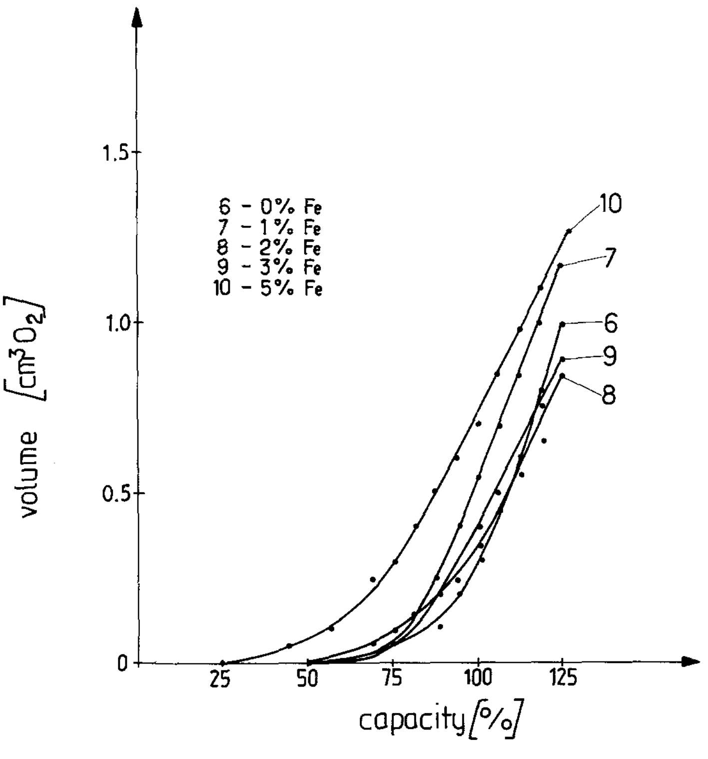

Fig. 4. Effect of iron contamination precipitated in the bulk of nickel hydroxide on oxygen evolution rate as a function of charged capacity.

beginning of charging when the concentration of ferric compounds is high.

When the electrodes are not contaminated with ferric compounds they oxidize at least to 75%, e.g. electrode no. 6, before the evolution of oxygen commences.

A similar effect of nickelous hydroxide contamination with ferric compounds can be observed when these two kinds of compounds are precipitated together (Fig. 4). However the conclusions drawn from the cyclic voltammetric studies confirm that the negative effect of ferric ions can only be seen, when they are precipitated in the hydroxide in an amount much larger than when precipitated at the surface. Even 1 or 2% content of ferric compounds (recalculated to Fe) in nickelous hydroxide does not provoke the decrease of electrode charging efficiency and it even rises slightly.

4. Final conclusions

Two basic reactions take place on the nickelous hydroxide electrode during its charging–oxidation

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e \qquad (1)$$

and

$$4OH^- \rightarrow O_2 + 2H_2O + 4e. \qquad (2)$$

In the potential range of these reactions the ferric ion precipitated in the form of the hydroxide or hydrated oxide is wholly oxidized electrochemically to Fe_3O_4 [6].

Among the many compounds which can form during the electrochemical reaction and ferric oxidation, this ferric–ferrous oxide is the best current conductor.

The reaction of oxygen evolution can proceed only at the interface and it is accompanied by an increase of free electrons. This ferric–ferrous oxide enables the electrons to flow easily because it is already oxidized: a part of the nickelous hydroxide (an insulator) is not yet oxidized to nickelous oxyhydroxide which is a better electric conductor than nickelous hydroxide. Obviously this easy flow of electrons through the Fe_3O_4 structure lowers the oxygen evolution overpotential, which results in an increase of Reaction 2 in relation to Reaction 1 and causes a smaller oxidation–charging of the whole electrode active material. When Fe_3O_4 is mixed with nickelous hydroxide in a solid phase, a part of it has no contact with the liquid phase and in this part the reaction of electrochemical oxygen evolution cannot proceed.

However, Fe_3O_4 inserted into nickelous hydroxide can simply act as a current conductor such as a nickelous sinter with a very fine structure. Then this ferric compound can even help the reaction of nickelous hydroxide oxidation and hence the increase in electrode capacity when the electrodes contain ferric compound in the bulk of electrochemically active material.

Acknowledgement

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References

[1] R. L. Tichenor, *Ind. Eng. Chem.* **44** (1952) 973.

[2] M. A. Zlatnikowa, Chemical Current Sources FTD-TT-66-7/1+2, AD 638 888 Foreign Tech. Div., Wright-Patterson, Air Force Base, Ohio (1966) pp. 102–12.

[3] G. Troilius and G. Alfelt, *Power Sources* **22** (1966) 337.

[4] M. Paszkiewicz, *J. Appl. Electrochem.* **11** (1981) 443.

[5] M. Paszkiewicz and J. Walas, *Electrochim. Acta* **24** (1979) 629.

[6] U. Falk and A. Salkind, 'Alkaline Storage Batteries', J. Wiley and Sons, New York, London, Sydney, Toronto.