

PLASTIC-BONDED ELECTRODES FOR NICKEL-CADMIUM ACCUMULATORS.

IV. SOME SPECIFIC PROBLEMS OF THE POSITIVE ACTIVE LAYER

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(Received July 17, 1979; in revised form November 29, 1979)

Summary

The active layer of plastic-bonded nickel oxide electrodes undergoes expansion during discharging and contraction during charging; the latter however does not fully compensate for the expansion. These volume changes can be made reversible by the action of an external pressure. The electrochemical behaviour of the conductive components, carbon black and graphite, shows more or less severe corrosion during anodic current loading.

Introduction

In studying the life of nickel oxide electrodes for alkaline accumulators, attention has been paid in the literature to the effect of various admixtures both to the active mass and to the electrolyte [1]. With plastic-bonded nickel oxide electrodes developed in recent years [2 - 4], no systematic investigation of the factors influencing their life has been made hitherto except for the effect of the current collector and external pressure [5]. The present work deals with volume changes of the active mass during cycling and with the behaviour of the conductive component during oxidation.

Experimental

Electrodes for electrochemical cycling tests were 3.1 cm discs, pressed from a mixture of 82.5% KBL active material (Lachema, Bohumín, CSSR) used for pocket-type electrodes [4] and 17.5% Teflonised acetylene black (55% PTFE + 45% black) at a pressure of 120 MPa. Their thickness was measured with a micrometer at five points and an average was taken. Nickel nets of 1.08 mm mesh size and 0.175 mm wire diameter were pressed on both

sides of the discs to improve the current conduction. The electrodes were held between two nickel screens of 1.3 mm mesh size and 0.7 mm wire diameter provided with current leads. The resistance of a dry disc between the screens was of the order of 1 ohm. The electrolyte was 5M KOH (density 1.2 g/cm^3), the counter electrode was nickel sheet, the reference electrode was Hg/HgO in the same electrolyte. The charging current was 50 mA (*i.e.*, 3.3 mA/cm^2) for 16 - 18 h, the discharging current was 70 mA (4.6 mA/cm^2) for an assumed discharge time of 4.5 h (corresponding to a content of 2.10 g of KBL active material of theoretical capacity $C_t = 0.214 \text{ A h/g}$). For comparison, some electrodes were prepared by rolling and subsequent pressing of the active material with Teflonised carbon black onto a nickel-plated iron screen (central collector) of 3.88 mm mesh size and 1.12 mm wire diameter. These were cut in the form of $3 \times 3 \text{ cm}$ squares and one or two wires of the screen were cut longer and made use of as current leads. The corresponding charging current was 65 mA and discharging current 90 mA for an assumed discharge time of 4.5 h (corresponding to a content of 2.70 g of KBL active material).

Electrodes prepared by pressing the Teflonised carbon black without the active material were typically hydrophobic and did not accept any charge during galvanostatic polarization. It was, hence, necessary to modify the starting material in order to obtain semihydrophobic electrodes, *i.e.*, to add some inert hydrophilic particles. Plaster of Paris seemed most suitable for this purpose since it was available in a sufficiently fine, powdered form and, after solidification, it improved the mechanical strength of the test electrodes. It was mixed with carbon black in the ratio of 1:1. Experiments were made with: Acetylene black P 1042 (Stickstoffwerke Piesteritz, GDR), furnace black Nigros (Urxovy závody, Valašské Meziříčí, CSSR), powdered graphite CR-2 of particle size around $2 \mu\text{m}$, and graphite VA of a particle size in the range $10 - 200 \mu\text{m}$ (Rudné doly, Týn nad Vltavou, CSSR) containing a certain portion of graphite flakes.

Electrodes for anodic oxidation tests were prepared by pressing 0.3 g of the given mixture at 120 MPa in the form of a 1 cm diameter disc together with a fine nickel gauze of 0.08 mm mesh size and 0.05 mm wire diameter (as in ref. 4). The tablets obtained were placed in groups of three between two nickel screens of 1.3 mm mesh size and 0.7 mm wire diameter provided with current leads. The oxidation current was 20 mA for one or more hours, the reduction current was 15 mA. The electrolyte, counter electrode, and reference electrode were the same as with the nickel oxide electrodes.

Results and discussion

Expansion measurements

The dependence of the electrode thickness on the number of cycles (dilatation curve) is shown in Fig. 1. At the end of the fourth cycle, the thickness of six electrodes increased by 21 - 29%, at the end of the ninth

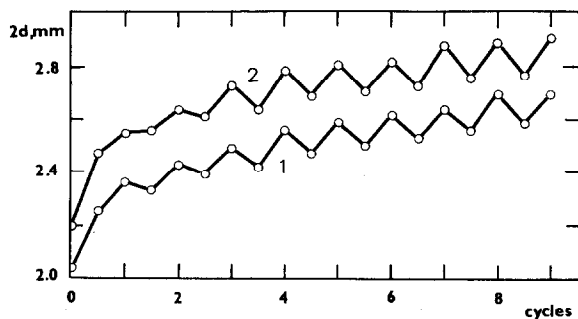


Fig. 1. Dependence of the thickness on the number of charge-discharge cycles for two nickel oxide electrodes (1 and 2) cycled simultaneously.

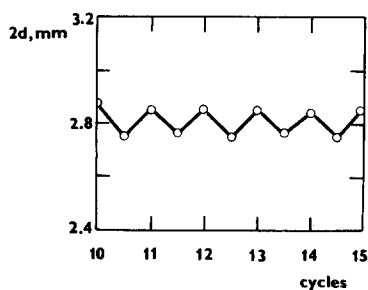


Fig. 2. Continuation of curve 2 from Fig. 1 with the difference that the electrode was pressed by steel springs at about 0.05 MPa.

cycle by 30 - 38% (with four electrodes). These figures refer to the rolled electrodes with pressed-in nickel screen, but the results were similar for the pressed electrodes with nickel screens on both sides. The largest increments in thickness were measured always after the first cycle. In parallel with the increasing thickness, a gradual decrease of the discharge capacity was observed, namely, from 63 to about 52% of the theoretical capacity C_t at the end of the 9th cycle.

The character of the dilatation curves suggests that we have to deal with a superposition of two effects: (a) volume changes due to different molar volumes of the oxidised and reduced forms of the active material, and (b) volume changes due to a gradual loosening of the active mass particles and loss of their cohesion. This can be suppressed by a mechanical external pressure [5]. In Fig. 2 are shown the dilatation curves of an electrode pressed at about 0.05 MPa by means of steel springs in the electrolyte. Here, obviously, only the periodic effect (a) takes place, which has no influence on the electrode capacity. The same electrode was used as that from which curve 2 in Fig. 1. was obtained; the pressure caused a slight decrease in its thickness (from 2.91 to 2.85 mm) and at the same time its capacity increased from the last value of 52 to 57 - 60% C_t . The amplitude

of the oscillations, however, showed practically no change, as would be expected. If the electrode is in the pressed state from the first cycle, its expansion during the initial cycles is similar to that in the unpressed state.

If we assume that the oxidised form is NiOOH with a molar volume of $19.0 \text{ cm}^3/\text{mol}$ (density 4.83 g/cm^3 [6]) and the reduced form is $\beta\text{-Ni(OH)}_2$ with a molar volume of $24.1 \text{ cm}^3/\text{mol}$ (density 3.85 g/cm^3 [7]), then the volume increase during reduction is 27% and the linear dimensions increase by 8.2%. Since the electrodes contained about 52 vol% Ni(OH)₂ in the solid phase (without considering the pores) prior to charging, their dilatation should be correspondingly smaller, namely 4.3%. The measured increments were in the range 5 - 6%, hence, in satisfactory agreement.

The oscillations in the thickness of the nickel hydroxide electrode suggest that the volume changes of the solid phase do not occur at the expense of the pores, as with the electrodes of the lead-acid accumulator [8], but at the expense of the electrode volume. This difference is apparently due to a different electrode reaction mechanism: in the electrodes of the lead-acid battery a new phase is formed during discharge by precipitation from the pore electrolyte, whereas in the nickel hydroxide electrode the solid phase undergoes a continuous change with the formation of a solid solution of both the oxidised and reduced forms [9], hence the volume of the solid phase must change also. This would lead — similarly to thermal expansion — to a linear transformation of all dimensions of the electrode, including pores, on the assumption that the electrode would not be acted upon by any external forces. However, as a result of the rigidity of the current collector, changes in the diameter of the disc electrode are partially hindered. The diameter increased after the 4th cycle by only 2 mm, *i.e.*, 6%, as compared with the increase in thickness of 25 - 27% (referred to the same electrode prior to the first charge). It is probable that the internal tension caused by the mechanical strength of the current collector pressed into the electrode causes a somewhat larger increase in the thickness of the disc during reduction than that calculated (5 - 6% against 4.3%).

When the Teflonised acetylene black added to the electrode mix was replaced by an analogous mixture of PTFE and graphite VA, the electrode gave a similar dilatation curve to Fig. 1. Hence, this phenomenon is characteristic for the active material proper and not for the admixtures.

Oxidation tests

Figure 3 shows the dependence of the potential on time during the 10th discharge-charge cycle for Teflonised acetylene black containing 35% PTFE at a current of 15 mA. Two cathodic steps, A at 0.35 - 0.40 V and B at -0.1 to -0.15 V on the descending branch correspond to two nearly reversible anodic steps, C and D. When the electrode stands on open circuit for about 2 h after charging and then the discharge $E-t$ curve is recorded, only step B appears. If graphite VA is used instead of acetylene black, the $E-t$ curve shows only step A, and step B appears only after a longer oxidation (20 h), it is, however, much smaller than with acetylene black.

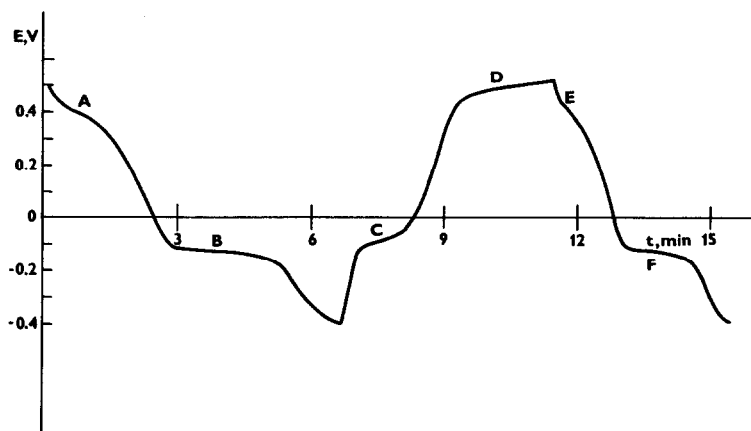


Fig. 3. Cyclic galvanostatic curve for acetylene black after the 10th cycle (pseudo-stationary state). A, B, E, and F, cathodic steps; C and D, anodic steps. A and B after 1 h of anodic oxidation, E and F immediately after recording the step D. Electrolyte 5M KOH.

If the same experiment is repeated with the nickel screens (see Experimental) without graphite or carbon black, then only step A appears, which diminishes with time when the screens are left standing on open circuit after charging (namely to 1/3 after 2.5 h or to 1/7 after 16 h). Hence, it follows that step A corresponds to reduction of an oxide film on the nickel screens and its decrease with time is due to self discharge. The other step, B, corresponds obviously to reduction of an oxide film on the carbon black. The experiments with graphite show that oxygen dissolved in the electrolyte or perhaps occluded in the electrode pores exerts no effect on the cathodic $E-t$ curve and that graphite is much more resistant against anodic oxidation than the carbon black.

The self discharge of the oxide film on the nickel screens is appreciably accelerated by the presence of carbon black. With electrodes from furnace or acetylene black, step A had already disappeared after 2 - 3 h standing on open circuit, whereas with graphite electrodes, it was distinctly observable even after 23 h. These observations can be discussed in terms of local galvanic elements formed by the carbon black and oxidised nickel.

Electrodes from furnace black containing 35% PTFE give similar curves to Fig. 3, but the steps on the $E-t$ curve become more elongated and ill-defined, while the electrolyte turns brown after the 7th cycle, evidence for a strong electrochemical corrosion of the black and its dissolution. Acetylene black is much more stable in this respect since the $E-t$ curves had practically the same form up to the 10th cycle (the end of the experiment) and the electrolyte turned only very light brown.

Prolonging the charging time above 1 h had no marked influence on the steps on the $E-t$ curve, however, they were smaller in the first one or two cycles ("formation" of electrode). The charge passed was relatively

small: in step B with acetylene black, 1.08 - 1.26 A s for one tablet, *i.e.*, 11.1 - 12.9 A s/g of carbon black without PTFE (with furnace black 9.2 - 10.5 A s/g); if we assume that one oxygen anion occupies a surface area of $4 \times 10^{-16} \text{ cm}^2$ and the specific surface area of acetylene black (according to the manufacturer) is $74 \text{ m}^2/\text{g}$, then the charge consumed for full coverage of the surface with a monolayer of oxygen atoms would be $8 \times 10^{-4} \text{ A s/cm}^2$ or 592 A s/g. Hence, it is apparent that the surface of the black in our experiments was utilized to only a very small extent.

It is interesting in this respect to evaluate the slope of the linear portion of the $E-t$ curve (Fig. 3). Between steps A and B we have $dE/dt = 5.56 \times 10^{-3} \text{ V/s}$. At a current of 15 mA, an acetylene black content in all three tablets of 0.293 g (without PTFE) and a specific surface area of $74 \text{ m}^2/\text{g}$ we obtain $C = 12.5 \mu\text{F/cm}^2$ for the capacity of the double layer on the black. The slope in the part C-D is only $8.89 \times 10^{-3} \text{ V/s}$, whence $C = 7.8 \mu\text{F/cm}^2$. In the portion A-B the charging of the double layer is apparently accompanied by reduction of the nickel oxide film. Therefore we recorded another cathodic curve E-F immediately after finishing the anodic curve C-D, so that the nickel oxide film could not be fully formed. This time the wave of nickel oxide (E) was smaller and the linear portion of the curve (E-F) more steep, $dE/dt = 1.06 \times 10^{-2} \text{ V/s}$, $C = 6.5 \mu\text{F/cm}^2$. It is obvious that this latter value is least distorted by the faradaic current. Hence, the capacity of the double layer on the studied electrode is very small — the common value is about $16 - 18 \mu\text{F/cm}^2$. Gagnon [10] measured the capacity of the double layer on carbon black as $10 \mu\text{F/cm}^2$ and he attributed this low value to the effect of the space charge layer in the solid phase, as is usual in the case of semiconductors. Our value, which is still smaller, is probably lowered by blocking a part of the surface of the black by the adsorbed PTFE.

It is known that the chemical reactivity of carbon black is conditioned by the presence of chemically bound oxygen on its surface [11, 12]. We therefore attempted to remove this oxygen by heating the acetylene black for 1 h in an atmosphere of argon at 1600°C . The heated acetylene black gave similar galvanostatic curves as in Fig. 3, but the cathodic step B became much smaller and the corresponding specific charge was (in the 2nd - 5th cycles) in the range 4.8 - 6.2 A s/g, that is about one half of that prior to heating the black. The temperature mentioned is not sufficient to cause graphitization of the black and it is probable that heating at a higher temperature would lead to a still more stable product.

Measurements on powdered graphites CR-2 and VA (without PTFE) showed that after 1 or several hours of anodic oxidation, step B was, in both cases, on the limit of detection and after 21 - 26 h of oxidation it attained a size corresponding to 3.6 A s/g of graphite (Fig. 4). It is, hence, apparent that even graphite is not quite inert, which is in agreement with the observations of other authors [1, 13].

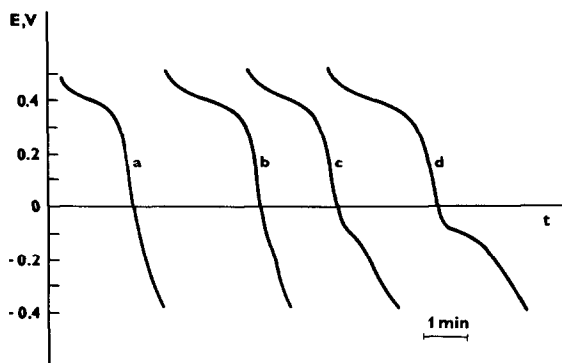


Fig. 4. Cathodic galvanostatic curves for graphite CR-2: (a) after 1 h, (b) after 4.5 h, (c) after 6.5 h, (d) after 26 h of anodic oxidation in 5M KOH.

Conclusions

Volume changes of plastic-bonded nickel hydroxide electrodes during charging and discharging can be attributed both to a difference between the molar volumes of $\text{Ni}(\text{OH})_2$ and NiOOH and to a loss of cohesion of the active material particles. The latter effect can be eliminated by means of a mechanical external pressure. Anodic corrosion of the conductive components increases in the order: graphite < acetylene black < furnace black, hence addition of graphite into the active mass is preferable.

Acknowledgement

The authors are indebted to Dr. M. Longauer, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, for furnishing acetylene black modified by heating.

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