Short communication

Role of graphite in self-discharge of nickel(III) oxyhydroxide

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Abstract

The rate constants for the self-discharge of the cathode material nickel(III) oxyhydroxide (NiOOH) in an alkaline medium are determined using a galvanostatic titration technique. By examination of a number of common graphite materials used in battery cathodes it is found that both the type and the amount of graphite present in the electrode influence the self-discharge rate. Two competing self-discharge phenomena exist, namely, reaction of NiOOH with surface active sites on the graphite, as well as the graphite catalyzing oxygen evolution. Their respective contributions to the overall self-discharge are evaluated.
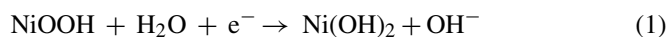© 2007 Elsevier B.V. All rights reserved.

1. Introduction

The ongoing evolution of hand-held electronic devices has placed an increased demand on the battery systems used to power them. The alkaline MnO_2/Zn cell has in recent years been a reliable performer; it is able to cope with the demands of standard hand-held electronic devices. The advent of digital technology, however, has seen a switch towards higher drain applications that are beyond the rate capabilities of the manganese dioxide electrode. A viable alternative is nickel(III) oxyhydroxide (NiOOH), which has already demonstrated its high discharge rate capability in applications that involve rechargeable cells, most notably NiOOH/metal hydride and NiOOH/Cd cells.

One of the problems that arises when using the NiOOH electrode in primary cells is that, in an alkaline electrolyte, the NiOOH is prone to self-discharge and this results in shorter battery life. In a rechargeable system, self-discharge is much less of a problem since the cell can simply be recharged. If the NiOOH is to be used in a primary cell, self-discharge must be minimized to the point where the cell is stable for at least five years.

The components of the self-discharge reaction are as follows:

reduction:

$$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^- \tag{1}$$

oxidation:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \tag{2}$$

overall:

$$4NiOOH + 2H_2O \rightarrow 4Ni(OH)_2 + O_2 \tag{3}$$

This process has been discussed by a number of authors who have studied self-discharge in the $NiOOH/H_2$ system [1–3]. They found that this reaction was only a minor contributor to the high self-discharge rates that were observed, and was only a significant factor at higher potentials. At lower potentials, the direct oxidation of H_2 by NiOOH was found to be the major cause of self-discharge. Recently Barde et al. [4] studied the self-discharge of various cationic-substituted γ-NiOOH phases and concluded that the mechanism for self-discharge was related to a dissolution–recrystallization process that progressed from γ-NiOOH to β-Ni(OH)$_2$, through an intermediate α-Ni(OH)$_2$ phase, which is generally unstable in concentrated alkaline electrolytes, and reverts to the β-Ni(OH)$_2$ phase. It is the relative solubilities of these phases which govern the rate of

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self-discharge. They found that certain cations, namely cobalt and iron, stabilized the α-Ni(OH)$_2$ structure, which is less soluble than the β-Ni(OH)$_2$ and thus forms a passive layer on the surface of the γ-NiOOH and protects it from self-discharge.

Questions not clearly answered by the literature include the following. Does the oxygen evolution reaction (OER) occur on the surface of the NiOOH or on the surface of the carbon which is included in the cathode mixture to improve its conductivity? Does the catalytic activity of the conductor towards oxygen evolution accelerate the rate of self-discharge?

Arikado et al. [5] have suggested that the graphite surface in alkaline medium can be oxidized to form an oxide layer, and at oxidation potentials above 0.4 V (vs. Hg/HgO) the oxide layer can form a surface quinone structure. Anderson et al. [6] also determined the initial open-circuit voltage (IOCV) of cells containing electrolytic manganese dioxide (EMD) and graphite in the cathode mix. They demonstrated that the presence of graphite lowered the IOCV of a cell containing EMD as the active cathode material. They also found that the IOCV was influenced by the quantity of graphite and the activity of the manganese dioxide that was used. It was determined that the presence of an EMD-to-graphite ratio of 1:3 resulted in a drop in IOCV of 60 mV due to the graphite reducing the potential-determining Mn^{4+} before discharge was initiated.

There has also been significant study into the use of graphite as an anode in lithium-ion batteries [7–10]. These studies tend to focus on the effect that the graphite has on the irreversible capacity that is lost due to the consumption of lithium and electrolyte. It has been observed that the graphite surface can be divided into different areas, namely, a flat or basal surface, and an edge or prismatic surface, both of which exhibit different characteristics in terms of chemical and electrochemical behaviour [7]. It has been found that the prismatic surface is the main site for reactions that lead to capacity loss in lithium-ion cells. It has also been shown that the conductivity of graphite in the direction parallel to the basal surface is orders of magnitude higher than in a direction perpendicular to the basal surface [11].

This study aims to determine what affect the type of conductor and their NiOOH-to-graphite ratio have on the stability of a standard NiOOH sample.

2. Experimental

2.1. Sample preparation

NiOOH was produced by precipitation of Ni(OH)$_2$ from a solution of 1 M NiSO$_4$ added to an equal volume of 2 M NaOH solution so as a double excess of OH$^-$ ions was present. This solution was then filtered to collect the precipitate, which was washed with reverse-osmosis water and dried at 60 °C for 48 h. The solid was then ground and sieved, and the portion that passed through a 45-μm sieve was collected and oxidized with a large excess of sodium hypochlorite solution at a constant pH of 11, for 12 h. This was then washed and dried again as specified above. An X-ray diffraction pattern of the resultant NiOOH material (γ-phase) is shown in Fig. 1.
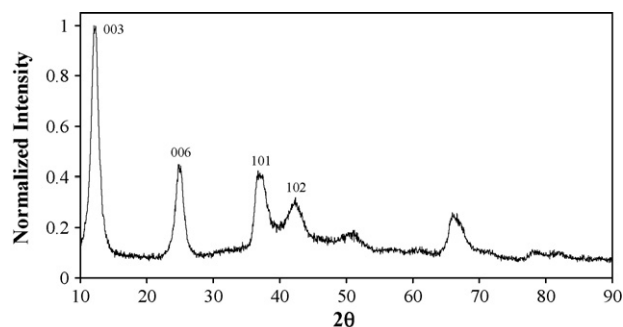

Fig. 1. XRD pattern of γ-NiOOH phase used in this work.

2.2. Electrochemical stability test

The stability of NiOOH was evaluated by constructing a series of identical cells, allowing them to sit under open-circuit conditions for different periods of time, and then discharging them to determine the remaining capacity. A similar approach was used by both Wang et al. [12] and Yazami and Reynier [13], although their focus was on a non-aqueous, carbon-based, negative electrode. Cell construction involved mixing the active NiOOH with a known proportion of graphite, with an additional 10 wt.% of 1 M KOH added to aid the binding process. The appropriate amount of blackmix that corresponded to 8–10 mg of active NiOOH was placed on to the base of a Teflon-lined (side walls) C-size battery can, covered with three layers of separator paper, and then compressed under 1 t to ensure good electrical contact with the current-collector. After compaction, a perforated Perspex disc was placed on top of the separator papers and held in place with a cylindrical stainless-steel counter electrode. A Perspex cap was placed in the top end of the counter electrode, and then each of the components was held in placed under a constant pressure with a securing frame. The cell was almost filled with 1 M KOH electrolyte ($\sim$15 mL) and then an Hg/HgO reference electrode inserted into the cell through the cap.

To measure NiOOH stability, a series of identical cells was assembled from the same cathode mixture, and then allowed to rest under open-circuit conditions for varying lengths of time before the cell was discharged, with the remaining capacity compared with the initial discharge at time zero. Discharge was preformed under constant-current (75 mA g^{-1}) conditions.

In this work, the stability of a standard β-NiOOH sample was evaluated with the cathode mixture varying in the type of graphite used, and in ratio of active material to graphite. The graphites used were TIMREX$^{®}$ synthetic graphite powders KS6, KS15, KS44, SFG6, and SFG44.

3. Results and discussion

3.1. Measuring stability

Previously reported papers have relied on a variety of techniques to measure stability. Huggins et al. [14] used a potentiostatic technique, in which the NiOOH was held at a constant potential and the anodic current passed to maintain this

potential was measured. Barde et al. [4] prepared a series of alkaline NiOOH/Zn button cells which were aged at 60 °C for 24 h to enhance self-discharge, with the capacity remaining in these cells compared with that of cells which were discharged immediately. Several other methods have also been used and include measurement of the amount of oxygen produced when the NiOOH was soaked in electrolyte [15]. Whilst these methods give an indication of the stability, they have yet to produce a calculated self-discharge rate constant that allows for a quick comparison. The method employed here is again a type of accelerated test whereby there is only a small amount of NiOOH that, by the end of the experiment, will have been self-discharged to close to 100% of its original capacity. The large amount of conductive graphite additive and the excess electrolyte used further aid in a fast rate of self-discharge. The benefits of this method are that measurements of the remaining capacity are taken at various stages of self-discharge. It also allows for the calculation of a self-discharge rate constant. Fig. 2 shows an example of the experiment used to obtain the data for calculation of the rate constant. Using the capacity of the NiOOH electrode down to a cut-off voltage of −0.1 V from the different cells at varying rest times, the normalized capacity can be plotted and a first-order decay curve (exponential) fitted to the experimental data and a rate constant calculated, i.e.,

$$Q = Q_0\, e^{-kt} + D \tag{4}$$

where Q is the normalized capacity at time t, Q_0 is the maximum available capacity, k is the rate constant, and D is a constant reflecting the amount of charge remaining at infinite time. Fig. 3 shows an example of this calculation. A cut-off voltage of −0.1 V was chosen because it is a region of the curve which is most vertical so as to reduce error, as well as occurring after the main discharge process has occurred.

3.2. Effect of NiOOH:graphite ratio

The effect of graphite content (weight percent) has a large effect on the rate of self-discharge. Typically, a standard cathode mix used in battery manufacture would contain 5–10% graphite [11]. In these tests, however, a larger amount of graphite was used to improve the conductivity of the cathode and enhance any self-discharge process related to the graphite content (Fig. 4).
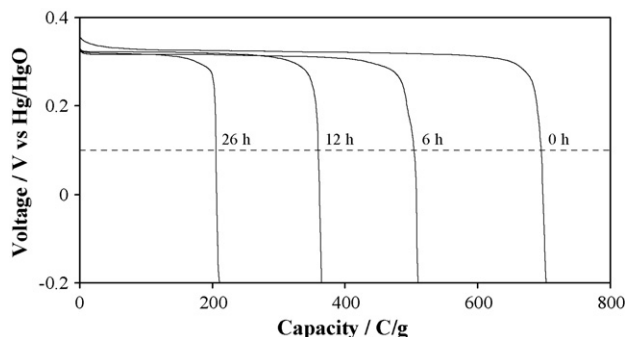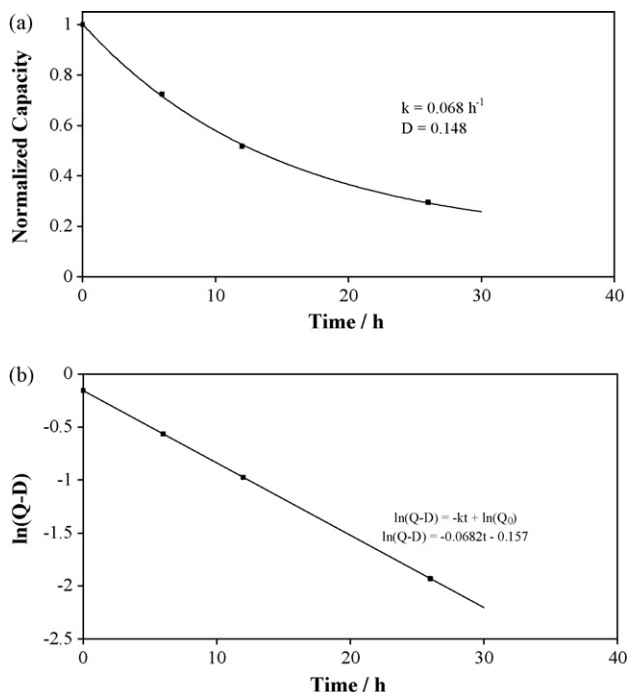
Fig. 3. Example of rate constant determination: (a) normalized plot; (b) logarithmic plot.

The rate constants for a cathode mixture containing all types of graphite and conductive carbons increase as the amount of conductor is increased. In this situation, it assumed that there are two mechanisms for self-discharge. The first is the presence of oxidizable surface sites on the conductor that when in contact with the NiOOH and electrolyte would reduce the NiOOH and hence lower the capacity, as has been previously observed for the alkaline manganese dioxide system [6]. Second, there is NiOOH decomposition due to its reaction with water in the electrolyte, to produce Ni(OH)$_2$ and oxygen. The nature of this latter reaction is quite complex since we suspect it requires a three-phase boundary between the NiOOH, electrolyte and conductor. For the NiOOH to be reduced, both a proton and electron must be inserted into its structure. The proton certainly comes from water decomposition in the electrolyte. It is subsequently inserted through the NiOOH|electrolyte interface. The electron source is certainly water oxidation to evolve oxygen;

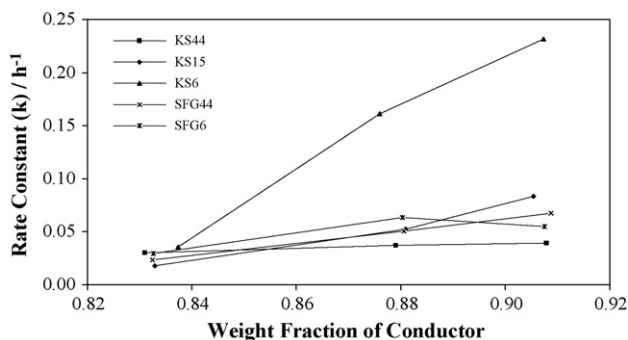Fig. 2. Resultant discharge curves after various rest periods on identical cells.

Fig. 4. Effect of type and weight fraction of conductor in electrode on rate constant of self-discharge.

but the location (interface) within the electrode where this reaction occurs is of considerable interest. The possibilities are that it occurs at the NiOOH|electrolyte interface, with the associated proton insertion, or at the conductor|electrolyte interface, with the transferred electron passing through the conductive network to the sites where they are needed to reduce NiOOH to Ni(OH)$_2$. The data presented here indicate that the majority of oxygen evolution occurs at the conductor|electrolyte interface, given that the rate of self-discharge increases as the amount of conductor in the electrode is increased. This raises the point that the catalytic activity of the conductor towards oxygen evolution has an impact on the rate of NiOOH self-discharge. Slowing this oxygen evolution reaction offers a possibility to improve NiOOH stability. As shown above, this can be achieved by optimizing the amount of conductor within the cathode so as to maintain overall conductivity without having excess conductor present to facilitate oxygen evolution. This will also be dependent on the nature of the conductor.

3.3. Effect of conductor type

An examination has been made of a range of graphite and conductive carbon samples that are used within the battery industry to enhance overall cathode electrical conductivity. Comparison of the Timcal KS series, which vary only in surface area and mean particle size, shows that as the surface area increases, so does the self-discharge rate. One reason for this may be that a decrease in the size of the particles increases the number of exposed edges or prismatic surfaces and these have been shown to be more active than flat surfaces [7–10]. Arikado et al. [5] investigated the oxidation of graphite in alkaline medium. The resulting data suggested that oxidation occurred more at the edges due to the presence of exposed bonds that can form an oxide layer. This would account for the portion of self-discharge that is related to oxidation of the graphite in the cathode mix. Such behaviour is not observed, however, for the SFG-type graphites. This suggests that there are fewer sites on the graphite surface that can be oxidized and hence reduce the NiOOH. In this case, the catalytic evolution of oxygen evolution may be the major aspect of the self-discharge process.

To examine oxygen evolution on the graphite samples, anodic linear sweep voltammetry was used, the results from which are shown in Fig. 5. The data further confirmed the trend within the
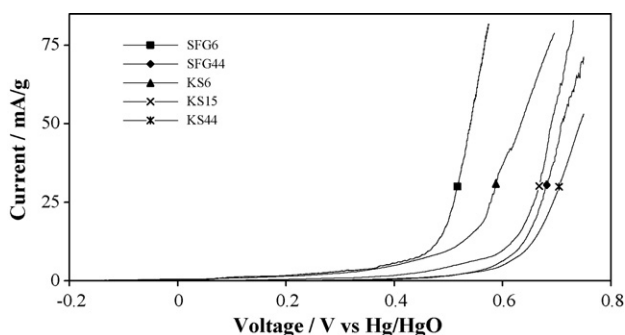

Fig. 5. Linear sweep voltammograms showing oxygen evolution on a variety of conductors.
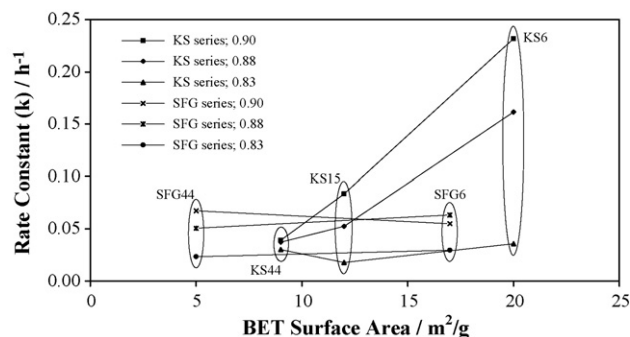

Fig. 6. Measured self-discharge rate constant as a function of the BET surface area and mass fraction of the conductor (number after each series).

KS series, with KS6 evolving oxygen at a lower potential than the KS15 and KS44 samples. This suggests that there may be more oxidizable material on the KS6 surface compared with the KS15 and KS44 samples, which may also enhance the trend. Comparing the BET surface area of this series with their self-discharge rate constants (Fig. 6) indicates a good correlation. This suggests that an increased surface area implies more exposed active sites that can either be oxidized by the NiOOH, or can catalyze the oxygen evolution reaction. The SFG samples, however, exhibit different behaviour, with the SFG6 sample evolving oxygen at a lower potential, yet the cathode mix using this type of graphite has a lower rate constant than the SFG44. Olivier and Winter [7] studied the KS series and calculated the contribution of each surface type (either prismatic/edge, or basal or flat surfaces) to the total surface area. They also made mention of the defect surfaces that arise from the milling process. It was found that in the lithium-ion system there was a correlation between irreversible capacity loss and increase in the BET surface area. It should also be noted that the prismatic surface area increases with increasing surface area in these graphite types.

4. Conclusions

The self-discharge rate of a γ-NiOOH sample has been determined by means of an accelerated test that employs a small amount of active material with an excess of conductor in a flooded electrolyte environment. Rate constants are determined for various conductor types and conductor:NiOOH ratios. For all types of graphite, the rate of self-discharge increases with the increased fraction of graphite present. For the KS-type graphite, there also appears to be a correlation between increasing BET surface area and increase in the self-discharge rate. This appears to be due to the greater number of more active prismatic (edge) sites in the higher surface area material. This correlation is not apparent for the SFG graphites, however, which may have different surface characteristics.

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