

Effect of hydrogen on discharge behaviour of the nickel oxide electrode

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The effect of hydrogen on the discharge behaviour of the nickel oxide electrode has been investigated in 30% KOH solution at 25°C. Open-circuit potentials of the nickel oxide electrodes, previously fully charged, decrease more rapidly in a hydrogen atmosphere than in an argon environment. Voltammograms of the nickel oxide electrode show that the amount of cathodic charge decreases considerably when the nickel oxide electrode is exposed to hydrogen rather than to argon. These results, along with X-ray diffraction data, indicate that hydrogen can increase the self-discharge rate of the nickel oxide electrode as a result of reduction of β -NiOOH to β -Ni(OH)₂ and the simultaneous oxidation of hydrogen. In addition, hydrogen can produce changes in the nickel oxide electrode during charge that persist to modify discharge behaviour and open-circuit potential.

1. Introduction

The electrochemical behaviour of the nickel oxide electrode has been the subject of investigations for several decades, due to its application as the positive plate in Ni-Cd, Ni-Fe, and Ni-H₂ batteries [1-4]. The nickel-hydrogen battery, which is now used in telecommunication satellites, exhibits a high energy density, long cycle life, direct indication of state of charge or discharge and tolerance to overcharge or overdischarge [5-8]. In it, the hydrogen pressure generally rises from about 0.5 MPa in the fully discharged state to 3-10 MPa when charged. This can be used to monitor the state of charge or discharge. However, the self-discharge rate is about 10% per day at 20°C, which is much greater than the expected reaction rate between hydrogen and nickel oxide.

Changes in the structural characteristics of the nickel oxide electrode have been studied by several researchers [9-12]. X-ray diffraction data suggest that the transformation of α - or β -Ni(OH)₂ to β - or γ -NiOOH occurs during cycling. It has been reported that the nickel oxide electrode is the life limiting component of the nickel-hydrogen battery due to the gradual expansion of the nickel oxide active material during charge/discharge cycling [13].

A fundamental understanding of the effect of hydrogen on the electrochemical mechanisms of the nickel oxide electrode is still lacking. In this paper, the effect of hydrogen at 1 atm pressure on the electrochemical behaviour of the nickel oxide electrode in 30% KOH solution at 25°C is reported. This enables a better understanding of its contribution to the rapid self-discharge of the nickel-hydrogen cell.

2. Experimental details

Nickel oxide electrodes were prepared by electrochemical deposition of Ni(OH)₂ on nickel foil substrates (13 × 27 × 0.127 mm, 99.998% purity, Alfa Products). The following procedure was used: the foils were cleaned electrochemically in 1 M HCl solution at an anodic current of 10 mA cm⁻² for 1 minute, then rinsed with acetone and deionized water. Electrochemical deposition was then carried out in a Pyrex cell on the nickel foil by applying a cathodic current of 35 mA cm⁻², in a boiling 50% 2 M Ni(NO₃)₂ 50% ethanol solution. Electrolysis was carried out for 2 hours using a nickel foil counter-electrode. Additives were not incorporated in the electrolyte. After electrochemical deposition, the electrode was washed in deionized running water and then charged at C/5 for 1 hour. Following this procedure, it was discharged at C/2 to 1.0 V (Zn/ZnO) in 30% KOH solution before use. This cycle was carried out three times to stabilize its capacity. The latter was calculated to be 20 mAh (theoretical), based on the one electron transfer reaction from Ni(OH)₂ to NiOOH.

The nickel oxide electrodes were examined by scanning electron microscope (SEM) and X-ray diffraction (XRD). The XRD pattern for the electrochemically deposited film gave a pattern characteristic of β -Ni(OH)₂. That for the fully charged electrode (C/10, 12 hours) showed β -NiOOH peaks which were confirmed in other studies [4, 11].

The electrochemical cell consisted of a nickel oxide working electrode, a Pt counter electrode and a Zn wire reference electrode. The reference electrode was isolated from the test solution by means of a Luggin capillary. Analytical reagent grade KOH was used to prepare 30% KOH solution in deionized water and

ultra-purity gas (H_2 or Ar) was purged through this solution during experiments.

Electrochemical measurements were conducted using an EG & G Model 273 Potentiostat/Galvanostat and a X-t linear chart recorder. A Keithley 220 Programmable Current Source was used for constant current charge and discharge. Open-circuit potential (OCP) behaviour, charge/discharge characteristics and cyclic voltammograms were measured in 30% KOH under either hydrogen or argon at 25°C.

3. Results and discussion

3.1. Effect of hydrogen during discharge

Figure 1 shows typical charge/discharge characteristics of a nickel oxide electrode. It was first charged at C/10 for 12 hours, to obtain β -NiOOH; this treatment was followed by discharge at three different rates down to 1.0 V in 30% KOH under argon at 25°C. Two voltage plateaux appear during slow discharge (C/10). It has been suggested that the upper voltage plateau is controlled by the Gibbs free energy change of the reaction (the rate determining step is proton diffusion within the active material) and the lower plateau by the resistance of a poorly conductive phase formed at the interface between the nickel substrate and the active material [14, 15].

Open circuit potentials of nickel oxide electrodes, previously fully charged at C/10 for 12 hours in argon-purged 30% KOH solution, were measured in 30% KOH at 25°C as a function of time in the presence of hydrogen or argon. Results in Fig. 2 show that hydrogen consistently shifts the OCP in a negative direction. These plots were obtained for three different electrodes and were found to be quite reproducible. Figure 3 shows OCPs of nickel oxide electrodes in 30% KOH at 25°C with argon bubbling. The electrodes had previously been fully charged at C/10 for 12 hours in 30% KOH under argon, which was followed by continuous immersion in 30% KOH at 25°C for 6 days under either hydrogen or argon. The OCP of the nickel oxide electrode exposed to a hydrogen atmosphere decreases more rapidly than that of the nickel oxide electrode in an argon environment. These results suggest that hydrogen increases

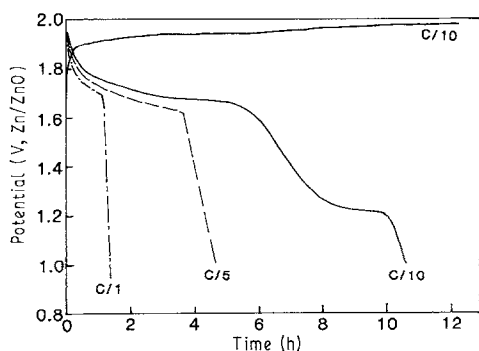


Fig. 1. Charge/discharge behaviour as a function of time for the nickel electrode in 30% KOH at 25°C with argon.

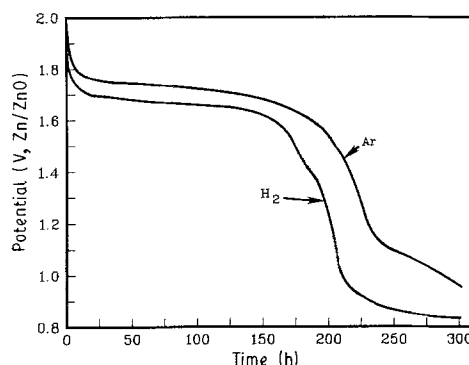


Fig. 2. Open-circuit potential behaviour as a function of time for the completely charged nickel oxide electrode (β -NiOOH) in 30% KOH at 25°C with hydrogen or argon bubbling. Charge at C/10; discharge at open-circuit.

the rate of reduction of β -NiOOH to β -Ni(OH)₂ itself being simultaneously oxidized. However, the mechanism of self-discharge of the nickel oxide electrode in argon environment is not clear at the present time.

Figure 4 shows cathodic voltammograms of nickel oxide electrodes in 30% KOH under argon bubbling at 25°C; these electrodes had been fully charged in an argon environment in the same electrolyte, then exposed to hydrogen or argon for 6 days. The amount of cathodic charge, represented by the area of the peak, is considerably less when the nickel oxide electrode had been exposed to hydrogen rather than to argon. This is further illustrated in Fig. 5, showing that nickel oxide electrodes exposed to hydrogen lost more capacity than those exposed to argon by about 30% after 12 day open-circuit immersion. It was also observed that the XRD pattern for the nickel oxide electrode exposed to hydrogen for 6 days at 2θ angles of 33.1° and 39.1° is increased in intensity (X-ray source: CuK α). This demonstrates the transformation of β -NiOOH to β -Ni(OH)₂. However, there is no significant intensity change in the XRD pattern for the nickel oxide electrode exposed to argon for 6 days. These results indicate that hydrogen enhances the transformation of the conductive β -NiOOH layer to the less conductive β -Ni(OH)₂ on nickel foil substrates.

It has been reported that (i) self-discharge of the nickel oxide electrode occurs in KOH solution saturated with oxygen, (ii) loss of capacity is accompanied

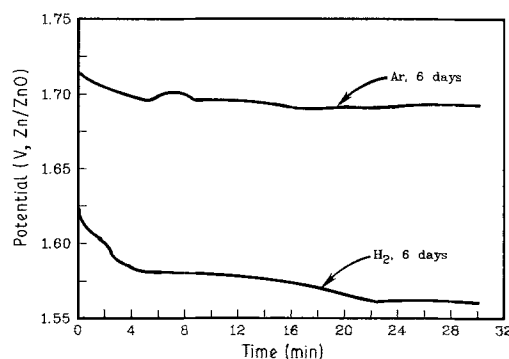


Fig. 3. Open-circuit potential behaviour as a function of time for the nickel oxide electrode in 30% KOH with argon at 25°C, after complete charge with argon in 30% KOH and subsequently 6-day immersion in 30% KOH with hydrogen or argon at 25°C.

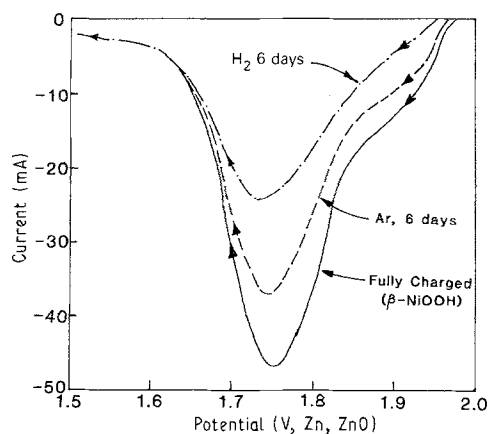
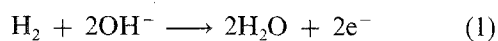


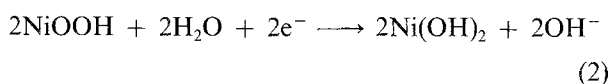
Fig. 4. Cathodic portion of cyclic voltammograms of the nickel oxide electrode in 30% KOH at 25°C with argon after complete charge and 6-day immersion in 30% KOH with hydrogen or argon. Scan rate = 10 mV s⁻¹.

by oxygen evolution, and (iii) the OCP of the nickel oxide electrode depends on KOH concentration [16, 17]. Also, Barnard *et al.* [18] have studied the oxidation state of the nickel oxide electrode as a function of OCP. They found that the OCP for the β -Ni(OH)₂/ β -NiOOH couple is independent of the degree of oxidation of the nickel cation between 25% and 70% states of charge.

Figures 2–5 indicate that hydrogen can increase the self-discharge rate of the nickel oxide electrode by reduction of β -NiOOH to β -Ni(OH)₂. However, the kinetics of hydrogen oxidation on the nickel oxide and/or on the nickel foil substrate are not clear. If the kinetics involve electrochemical reactions, then the oxidation process for hydrogen will be



accompanied by simultaneous reduction of β -NiOOH to β -Ni(OH)₂ according to



The following reactions are probably intermediates for process (1):

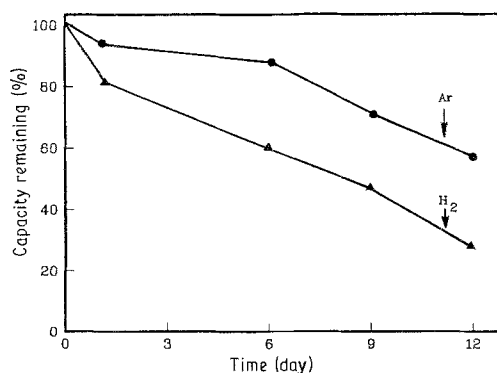
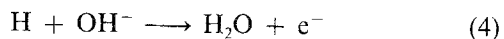


Fig. 5. Capacity change as a function of time for the nickel oxide electrode after complete charge and open-circuit immersion in 30% KOH with hydrogen or argon at 25°C.

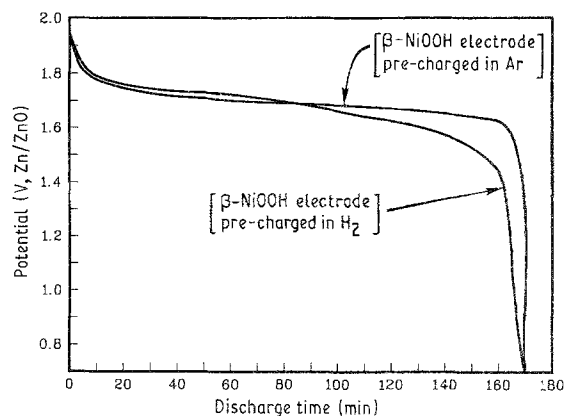
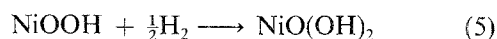


Fig. 6. Effect of pre-charging condition of the nickel oxide electrode on discharge behaviour as a function of time in 30% KOH at 25°C with argon. Charge at C/10; discharge at C/2.

The rate of reactions (3) and (4) will vary as a function of electrode potential or state of charge or discharge. If a direct chemical reaction occurs between hydrogen and nickel oxide, the reduction reaction will be:



This process is probably independent of the electrode potential, or state of charge or discharge. However, a more extended investigation of the role of hydrogen oxidation may produce valuable insight into the mechanism of self-discharge of the nickel oxide electrode.

3.2. Effect of hydrogen during charge

It is well known that hydrogen has deleterious effects on the mechanical properties of most metals and alloys, particularly as a result of embrittlement [19–23]. Oriani [19] explained that stresses generated by permeation of dissolved hydrogen during gaseous or electrochemical charging, or via a corrosion reaction, weakens the cohesive force between metal atoms and permits nucleation of the hydrogen-assisted micro-crack within the plastic deformation regions.

Two sets of experiments were carried out to observe

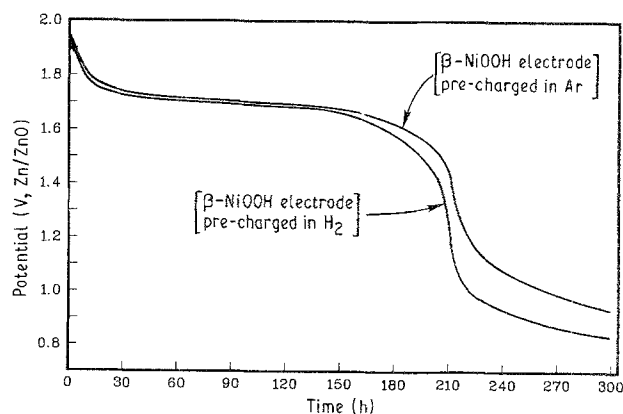


Fig. 7. Effect of pre-charging condition of the nickel oxide electrode on open-circuit potential behaviour as a function of time in 30% KOH at 25°C with argon. Charge at C/10; discharge at open-circuit.

any residual effect of hydrogen on the nickel oxide electrode during charge. Nickel oxide electrodes, previously charged at C/10 for 12 hours in 30% KOH under hydrogen bubbling or argon, were removed from the electrolyte, cleaned with deionized water, and immediately reimmersed in fresh 30% KOH under argon at 25°C to measure discharge behaviour and OCP.

Figure 6 shows lower discharge potentials on a nickel oxide electrode that had been previously charged in a hydrogen environment. There was no significant difference concerning charge potential behaviour. However, the nickel oxide electrode, after charging in a hydrogen atmosphere, developed lower OCPs upon subsequent immersion in 30% KOH with argon at 25°C, as shown in Fig. 7. It is therefore clear that hydrogen produces changes in the nickel oxide electrode during charging and modifies both discharge behaviour and OCPs in 30% KOH with argon at 25°C. Probably the mechanical properties of the nickel oxide electrode are altered, and γ -NiOOH may be partly formed during charge under hydrogen atmosphere in 30% KOH. For example, it has been reported that γ -NiOOH discharges at a lower potential than β -NiOOH [4, 24].

4. Conclusions

The electrochemical behaviour of the nickel oxide electrode was investigated in 30% KOH at 25°C in a hydrogen or argon environment in order to understand the effect of hydrogen on the rapid self-discharge characteristics of the nickel-hydrogen battery. From X-ray diffraction studies, it was concluded that hydrogen can increase the self-discharge rate of the nickel oxide electrode by 30% after 12-day open-circuit immersion. The self-discharge occurs by the reduction of β -NiOOH to β -Ni(OH)₂, with simultaneous hydrogen oxidation on the active nickel oxide and/or the nickel foil substrate according to reactions expressed by Equations (3), (4) and (2), respectively. In addition, hydrogen can alter the mechanical and/or structural properties of the nickel oxide electrode during charge, so that these modify both discharge behaviour and open circuit potential.

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