

Studies on the lithium and potassium uptake of nickel hydroxide electrodes

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Received 17 July 1984

The extent of lithium and potassium uptake by both α - and β -Ni(OH)₂ electrodes has been studied by atomic absorption/emission spectroscopy. It was found that lithium ions are preferentially taken up into the bulk of the electrodes. The increase in the end-of-charge potential on constant current charging in lithiated electrolyte compared with pure potassium hydroxide is attributed to the bulk incorporation of lithium into the Ni(OH)₂ electrodes. X-ray studies have indicated no change in the phases present in the lithiated electrolytes either in the charged or discharged states. Cyclic voltametric measurements to 100 cycles showed no significant benefit due to lithium ions in terms of charge retention.

1. Introduction

It is generally assumed that the presence of lithium ions in the electrolyte improves the capacity of Ni(OH)₂ electrodes in Ni-Cd batteries [1-4].

There are suggestions that lithium causes increased γ -phase formation [2, 5] while some others suggest the contrary [6]. In the present work we have set out to investigate the Li effect using atomic absorption/emission spectroscopy, constant-current studies, X-ray analysis and repetitive linear sweep cycling.

2. Experimental details

The experimental cell was a three-compartment unit with the central compartment used for the working electrode. The outer compartments were used for Pt auxiliary electrodes. Hg/HgO reference electrodes in the same solution as that under investigation were used.

Nickel electrodes of 2 cm × 2 cm were cut from a sheet of pure Ni(4N) of 0.25 mm thickness. A nickel wire of 0.25 mm diameter was spot welded to each of these electrodes to provide electrical contacts. Nickel hydroxide was then electrodeposited onto the cleaned surface of the electrodes from a 0.05 M Ni(NO₃)₂ bath with a

cathodic current of 1 mA cm⁻² for 10 min. This treatment gave a deposit of α -Ni(OH)₂ on the Ni sheets. β -Ni(OH)₂ electrodes were then obtained by ageing the α -Ni(OH)₂ electrodes for 5 days in 5 M KOH at 40°C.

Both the α -Ni(OH)₂ and the β -Ni(OH)₂ electrodes were charged at a constant current of 0.2 mA cm⁻² in 5 M KOH. The electrodes were discharged at the same rate upon completion of the charge cycle. These experiments were repeated using saturated LiOH (4.6 M) and 4 M KOH + 1 M LiOH as the electrolytes. All electrodes were cycled three times before using them for atomic absorption/emission or X-ray studies.

X-ray analysis of the various deposits was carried out by scraping the electrode material into a 0.3 mm Lindemann capillary. This was then mounted onto a 57.5 mm Debye-Scherrer powder camera and subjected to a 50 min exposure using CoK α Fe filtered radiation at 40 kV.

For atomic absorption/emission spectroscopy, β -Ni(OH)₂ electrodes charged in 5 M KOH were washed in 40 ml of triply distilled water for different times and then placed in 10 ml of 1 M HCl for 2 h so as to dissolve the deposit for analysis. The experiments were repeated using similar procedures in saturated LiOH and 4 M KOH + 1 M LiOH electrolytes. Samples so obtained were

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analysed for Li, K and Ni using a Perkin Elmer 2380 Atomic Absorption Spectrophotometer. Nickel was analysed under the absorption mode while Li and K were analysed under the emission mode.

All experiments were carried out at room temperature of $22 \pm 2^\circ\text{C}$. The linear sweep results were obtained using an Apple II microcomputer into which ADC and DAC converters were inserted [7]. The microcomputer was connected to a potentiostat, thus allowing multiple cycling to be carried out with recording of the results onto floppy disks.

3. Results

Constant current charge-discharge curves for the III cycle for $\beta\text{-Ni(OH)}_2$ electrodes in 5 M KOH, saturated LiOH and 4 M KOH + 1 M LiOH as electrolytes are shown in Fig. 1. Maximum charging potentials for different electrolytes are given in Table 1. Addition of lithium in the electrolyte is found to increase the maximum charging potential without significantly changing the efficiency of the charging process. There is an increase of 50 mV for the lithiated potassium electrolyte as against pure potassium hydroxide.

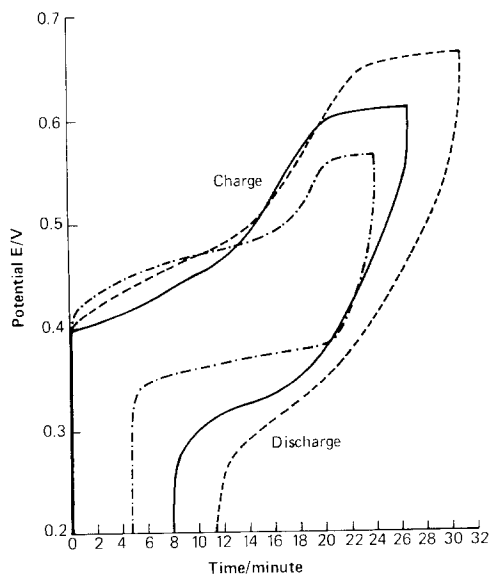


Fig. 1. Constant current charge/discharge curves for beta phase electrodes vs Hg/HgO reference electrode. ——— saturated LiOH, ——— 4 M KOH + 1 M LiOH, - - - - 5 M KOH.

Table 1. Maximum charging potential of β -electrodes in different electrolytes

Electrolyte	Potential (mV)
5 M KOH	560
4 M KOH + 1 M LiOH	610
LiOH saturated	670

The results are in general agreement with the observations of other authors [3].

The results of X-ray powder photographs are shown in Fig. 2. The positions and intensities of reflections show that the phases present are typical of β -phase Ni(OH)_2 and $\beta\text{-NiOOH}$, as reported by other authors [8]. No difference in d -spacings or intensities was seen in the lithiated electrolyte suggesting that there is no gross phase difference in electrodes in lithiated electrolytes. This indicates the absence of any substantial amounts of $\gamma\text{-NiOOH}$ or lithium nickelates in charged β -electrodes.

The atomic absorption/emission results shown in Figs. 3-6 indicate uptake of lithium and potassium by the Ni(OH)_2 or NiOOH deposits.

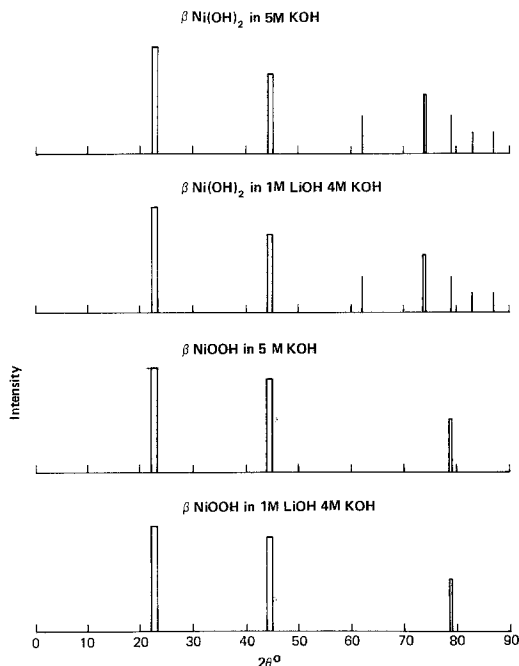


Fig. 2. X-ray diffraction patterns of charged and discharged beta phase electrodes in 5 M KOH and 4 M KOH + 1 M LiOH.

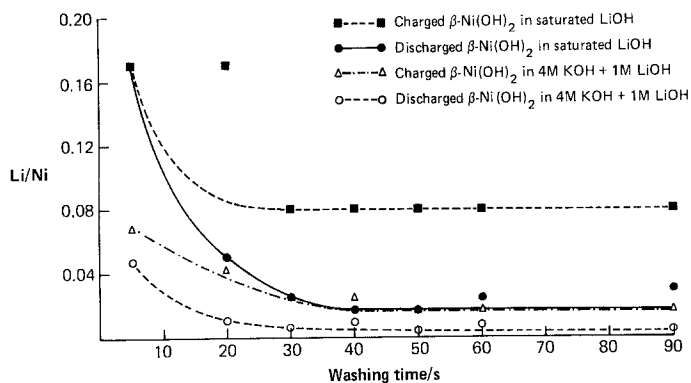


Fig. 3. Li/Ni atom ratios for charged and discharged beta phase electrodes in saturated LiOH and 4 M KOH + 1 M LiOH as a function of washing time.

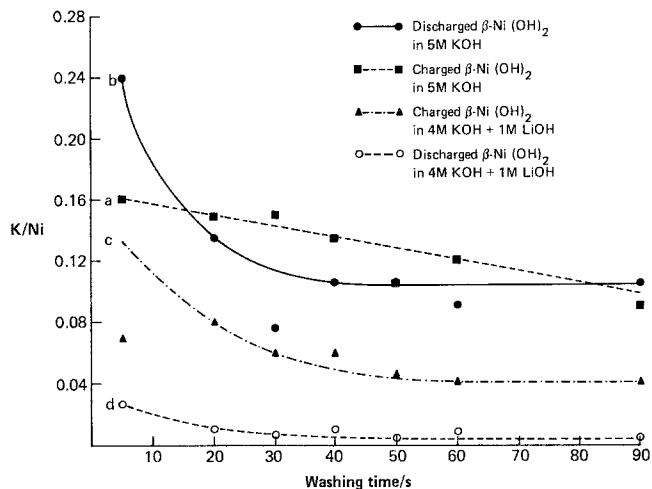


Fig. 4. Li/Ni atom ratios for charged and discharged beta phase electrodes in 5 M KOH + 1 M LiOH as a function of washing time.

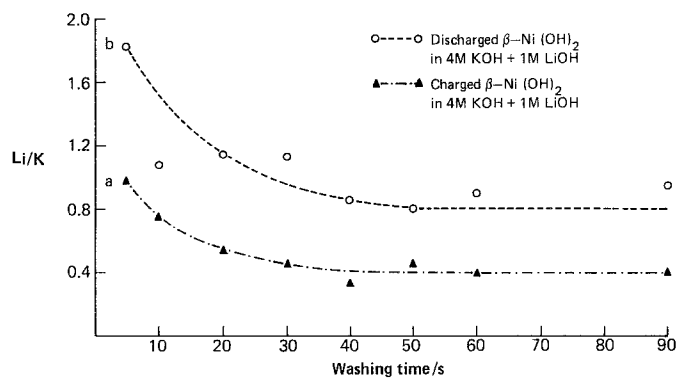


Fig. 5. Li/Ni atom ratios for charged and discharged beta phase electrodes in 4 M KOH + 1 M LiOH as a function of washing time.

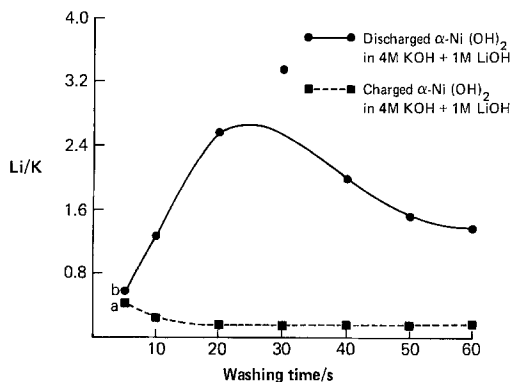


Fig. 6. Li/K atom ratios for charged and discharged alpha phase electrodes in 4 M KOH + 1 M LiOH as a function of washing time.

A steep fall in all the curves in the initial portions can be attributed to the washing out of surplus electrolyte from the electrodes. Stabilization of curves in Figs. 3 and 4 after washings of 40 s suggests that Li and K enter the bulk of the electrolytes. It is also observed that uptake of lithium in the charged states is significantly higher than in the discharged state of β -electrodes. It is seen from Fig. 5 that Li is taken up preferentially over K compared with the Li/K ratio present in the electrolyte. The peak of the curve in Fig. 6 indicates that K is removed more rapidly than Li in the washing procedure in the case of α -electrodes.

The results of linear sweep cycling of electrodes are shown in Figs. 7 and 8. It is observed that the peak currents increase slightly on prolonged cycling in 5 M KOH while there is a slight decrease in the corresponding results in lithiated electrolyte. X-ray analysis of charged material after

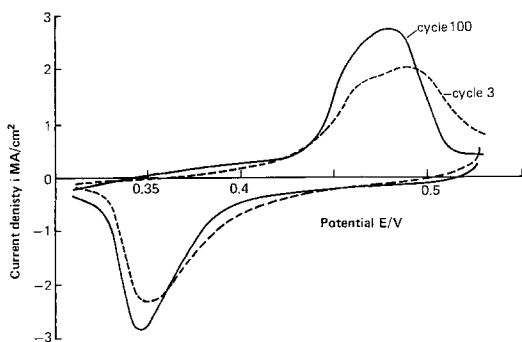


Fig. 7. Cyclic voltamograms for charge/discharge cycle of beta phase electrodes in 5 M KOH. Sweep rate 1 mV s⁻¹.

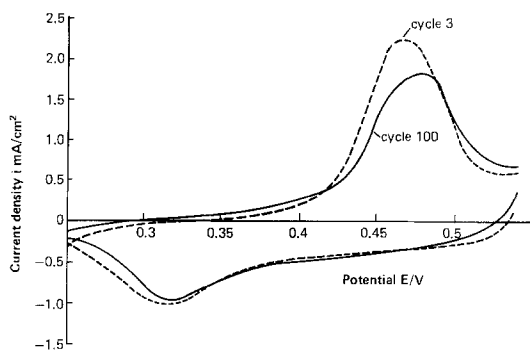


Fig. 8. Cyclic voltamograms for charge/discharge cycle of beta phase electrodes in 1 M LiOH + 4 M KOH. Sweep rate 1 mV s⁻¹.

100 cycles in 5 M KOH and 4 M KOH + 1 M LiOH electrolytes showed no signs of γ -NiOOH.

4. Discussion

The results reported here show that lithium and potassium are firmly retained by the active material of both charged and discharged electrodes, after the surplus electrolyte has been removed by washing with water. Although the evidence clearly demonstrates this retention, it is not conclusive as to the precise way in which the ions are retained. No major disturbance of the crystal lattice is revealed by X-ray power photographs, and previous authors have claimed [9] that the compact β -structures are unable to accommodate alkali cations. There remains the possibility of surface adsorption, or of the presence of an expanded γ -phase, either in a small amount, or in a degree of crystallinity which renders detection by X-ray diffraction difficult.

The most significant effect of LiOH is the raising of oxygen overvoltage, which strongly suggests the presence of a lithiated surface phase. No noticeable improvement in capacity was found on repetitive cycling of flat thin film electrodes in the presence of lithium at room temperature. However, since 100 cycles were completed within a period of about 12 h, any effect of ageing during a prolonged stand in alkaline solution would not be observed in these experiments. There also remains for investigation the possibility that LiOH acts by preventing loss of capacity caused by the presence of other ions such as Cd²⁺, Fe³⁺, Bi³⁺, etc.

Acknowledgements

A.K.S. wishes to thank the British Council and the Department of Science and Technology, Government of India, New Delhi, for a Queen Elizabeth Fellowship. M.M. wishes to thank Marathon Alcad Ltd. for sponsorship. We wish to thank Dr G. W. D. Brigs for useful comments.

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