AN ELECTROANALYTICAL STUDY OF NICKEL HYDROXIDE AND COBALT CODEPOSITED NICKEL HYDROXIDE ELECTRODES

By

ANIL KUMAR

(SOOD)

THESIS SUBMITTED TO

INDIAN INSTITUTE OF TECHNOLOGY, DELHI

FOR THE AWARD OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

March 1985

CENTRE FOR ENERGY STUDIES

INDIAN INSTITUTE OF TECHNOLOGY

NEW DELHI-110 016

INDIA

CERTIFICATE

This is to certify that the thesis entitled " An electroanalytical study of nickel hydroxide and cobalt codeposited nickel hydroxide electrodes" being submitted by Mr. Anil Kumar to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy is a record of bonafide research work carried out by him. Mr. Anil Kumar has worked under my guidance and supervision and has fulfilled the requirements for the submission of the thesis, which to my knowledge has reached the requisite standards.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any Degree or Diploma.

(P.N. SAHGAL)

Professor & Head

Department of Chemical Engineering

Indian Institute of Technology

New Delhi-110016

ABSTRACT

The thesis examines the effect of the addition of lithium and cobalt to the α - and β- nickel hydroxide electrodes over a wide range of conditions by using constant current studies, atomic absorption/emission spectroscopy, x-ray diffraction studies, linear sweep cyclic voltammetry, energy dispersive x-ray analysis and scanning electron microscopy.

Lithium addition is found to increase the oxygen overvoltage thereby allowing for increased charging of the β- $Ni(OH)_2$ electrodes in lithiated electrolytes compared to the potassium hydroxide electrolytes. K ion uptake by the β-$Ni(OH)_2$ electrodes is suppressed by the presence of lithium in the electrolyte without affecting any β-phase to γ-phase transformation in the process. Li ion uptake, on the other hand, is independent of the lithium concentration in the electrolyte. Beneficial effects of lithium addition to the electrolyte are also observed by cyclic voltammetry in the initial periods of cycling. Improvement in the performance of β-$Ni(OH)_2$ electrodes due to the addition of lithium to the electrolyte is attributed to the formation of a lithiated surface on the electrodes.

Cobalt codeposition on the β-$Ni(OH)_2$ electrodes does not account for any appreciable change in the oxygen overpotential in 5M KOH electrolytes though beneficial increase of the overpotential is observed in the presence of lithium in the electrolyte . K^+ uptake is effectively suppressed by the presence of Co in β-nickel hydroxide electrodes on cycling in 5M KOH, though no change in K^+ uptake is shown in the

lithiated electrolytes. These confirm the existence of the lithiated surface which is further corroborated by the similar levels of Li uptake by the β-electrodes in the presence or absence of the codeposited Co. Presence of Co in the β-Ni/CO hydroxide electrodes results in an increase in the useful life of the electrodes in 4M KOH+1M LiOH electrolyte without affecting any changes in the reaction mechanism.

α-Ni/Co hydroxide electrodes show unstable behaviour due to ageing of the α-electrodes to the β-electrodes during repeated cycling.

The surface characteristics observed under electron micsroscopy show tne α-electrode surface to be better resolved with an unswollen, but flaked, surface. The β-Ni/Co hydroxide electrode has a swollen and irregularly flaked surface in 5M KOH as against an unswollen lithiated surface with small fissures in the 4M KOH-1M LiOH electrolyte. This surface accounts for better performance of the β-Ni/Co hydroxide electrodes in lithiated electrolytes, especially in the commercial applications by reducing the iron poisoning effects on the performance of the electrodes.

Low temperatures of $0^{o}C$ and $-20^{o}C$ are found to be unsuitable for the operation of β-Ni/Co hydroxide electrodes. This is accounted by a hard, closed electrode surface at these temperatures. For higher temperatures of $40^{o}C$, the β-Ni/Co hydroxide electrodes give better performance due to the litniated surface in 4M KOH+1M LiOH as compared to their performance in 5M KOH. However, with further increase of temperature, 5M KOH is the better suited electrolyte since the litniated surface in 4M KOH+1M LiOH gets ruptured at such temperatures resulting in a poor performance.

It is concluded that the role of Li and Co is complimentary to each other in improving the performance and life of the nickel hydroxide electrodes.

ACKNOWLEDGEMENTS

The author wishes to express his deep gratitude to Prof. P.N. Sahgal, Department of Chemical Engineering, IIT, Delhi and Dr. R.D. Armstrong, Electrochemistry Research Laboratories, University of Newcastle-upon-Tyne, U.K. for their advice, help and constant encouragement given throughout the course of this work.

Thanks are also due to all friends and laboratory staff for their assistance during the conduct of the work.

(ANIL KUMAR)

Date: March 1985

NEW DELHI

CONTENTS

			Page
ABSTRACT			vi
ACKNOWLEDGEMENTS			ix
Chapter	1	INTRODUCTION	1
Chaapter	2	EXPERIMENTAL	6
	2.1	Working electrode preparation	6
		2.1.1 Electrode substrates	6
		2.1.2 α-Nickel hydroxide electrodes	6
		2.1.3 β-Nickel hydroxide electrodes	7
		2.1.4 α-Ni/Co hydroxide electrodes	7
		2.1.5 β-Ni/Co hydroxide electrodes	8
	2.2	Mercury/mercuric oxide reference electrodes	8
	2.3	Counter electrodes	9
	2.4	Cell disigns	10
		2.4.1 Electrodeposition cell	10
		2.4.2 Room temperature working cell	10
		2.4.3 Low/High temperature working cell	11
		2.4.4 Recrystallisation cell	11
	2.5	Instrumentation	12
		2.5.1 Constant current studies	12
		2.5.2 Atomic absorption/emission spectrocopy	12
		2.5.3 Cyclic voltammetry	12
		2.5.4 X-Ray diffraction	13
		2.5.5 Heating & cooling equipment	13
		2.5.6 EDAX & Scanning electron microscopy	14
	2.6	Experimental procedures	14
		2.6.1 Constant current charge/discharge	14

2.6.2 Atomic absorption/emission spectroscopy 16
2.6.3 Cyclic voltammetry 16
2.6.4 X-Ray diffraction 16
2.6.5 EDAX & Scanning electron microscopy 17
2.7 Electrode composition 17
Chapter 3 CATION UPTAKE BEHAVIOUR OF THE NICKEL HYDROXIDE & Ni/Co HYDROXIDE ELECTRODES 29
3.1 Introduction 29
3.2 Constant current studies on β-nickel hydroxide electrodes 30
3.2.1 Li effect on β-$Ni(OH)_2$ electrodes 31
3.2.2 X-Ray diffraction studies 31
3.3 Constant current studies on Ni/Co hydroxide electrodes 34
3.3.1 α-and β-Ni/Co hydroxide electrodes in 5M KOH 34
3.3.2 Effect on Co addition to β-$Ni(OH)_2$ electrodes 35
3.3.3 Effect of Li addition to the electrolyte 35
3.4 Uptake studies on α-$Ni(OH)_2$ electrodes 38
3.4.1 Potassium uptake 38
3.4.2 Lithium effect 42
3.4.3 Lithium uptake 42
3.4.4 Li/K preference 43
3.5 Uptake studies on β-$Ni(OH)_2$ electrodes 43

		3.5.1 Potassium uptake	43
		3.5.2 Lithium effect	47
		3.5.3 Lithium uptake	47
		3.5.4 Li/K preference	48
	3.6	Uptake studies on β-Ni/Co hydroxide electrodes	48
		3.6.1 Potassium uptake	48
		3.6.2 Lithium effect	50
		3.6.3 Lithium uptake	53
		3.6.4 Li/K preference	53
	3.7	Further discussions	54
Chapter	4	ELECTROCHEMICAL RESPONSE OF NICKEL HYDROXIDE & Ni/Co HYDROXIDE ELECTRODES	70
	4.1	Introduction	70
	4.2	β-Nickel hydroxide electrodes	71
		4.2.1 5M KOH electrolyte	71
		4.2.2 Lithium effect	75
	4.3	β-Ni/Co hydroxide electrodes	76
		4.3.1 5M KOH electrolyte	76
		4.3.2 Lithium effect	79
		4.3.3 Effect of lithium concentration	81
	4.4	α-Ni/Co hydroxide electrodes	82
Chapter	5	ENERGY DISPERSIVE X-RAY ANALYSIS & ELECTRON MICROSCOPY STUDIES ON Ni/Co HYDROXIDE ELECTRODES	91
	5.1	Introduction	91
	5.2	EDAX studies	91
	5.3	Scanning electron microscope studies	93

		5.3.1 α-Ni/Co hydroxide electrodes in 5M KOH	93
		5.3.2 β-Ni/Co hydroxide electrodes in 5M KOH	94
		5.3.3 β-Ni/Co hydroxide electrodes in 4M KOH + 1M LiOH	95
	5.4	Discussions	95
Chapter	6	ELECTROCHEMICAL BEHAVIOUR OF Ni/Co HYDROXIDE ELECTRODES AS A FUNCTION OF TEMPERATURE	100
	6.1	Introduction	100
	6.2	Constant Current studies	100
		6.2.1 β-Ni/Co hydroxide electrodes in 5M KOH	100
		6.2.2 β-Ni/Co hydroxide in 4M KOH + 1M LiOH	101
	6.3	Cyclic voltammetry	104
		6.3.1 β-Ni/Co hydroxide in 5M KOH	107
		6.3.2 β-Ni/Co hydroxide in 4M KOH 1M LiOH	110
	6.4	Scanning electron microscopy	111
		6.4.1 Low temperature studies on β-Ni/Co hydroxide	111
		6.4.2 High temperature studies on β-Ni/Co hydroxide in 5M KOH	111
		6.4.3 High temperature studies on β-Ni/Co hydroxide in 4M KOH + 1M LiOH	112

	6.5	Energy dispersive X-ray analysis	113
	6.6	Discussion	115
Chapter	7	STUDIES ON THE EFFECTS OF IRON POISONING OF $Ni(OH)_2$ & Ni/Co HYDROXIDE ELECTRODES	125
	7.1	Introduction	125
	7.2	Constant current studies	126
		7.2.1 Studies in 5M KOH sat. with Fe	126
		7.2.2 Studies in 4M KOH + 1M LiOH sat. with Fe	128
	7.3	Energy dispersive X-ray analysis	128
	7.4	Discussion	131
Chapter	8	CONCLUSIONS	134
REFERENCES			140
PUBLICATIONS BY THE AUTHOR			143