ELECTROCHEMICAL STUDIES ON POROUS NICKEL OXIDE ELECTRODES FOR THE ALKALINE SECONDARY BATTERY SYSTEMS

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Abstract

Nickel secondary systems have high energy density, power density, rugged physical structure and good low temperature performance. Nickel secondary systems are mainly used in electric vehicles as well as in military and commercial aircraft. Electrochemical impregnation of active material onto porous nickel foam electrode containing different additives has been studied to give best electrochemical reversibility. The development of additives for nickel electrode is mainly aimed at increasing the discharge capacity and minimizing self-discharge. Porous nickel electrodes have been evaluated using cyclic voltammetry, potentiodynamic polarization and AC impedance measurements. All the addition agents favour the reversibility of the charge-storage reaction of nickel electrode. Addition of copper and thiourea increases the capacity values.

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Key words : Porous nickel electrodes, Alkaline electrolyte, Additives, Impregnation, Secondary battery

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INTRODUCTION

Nickel oxide electrodes are widely used as cathodes in alkaline batteries. The structure and electrochemistry of nickel oxides, hydroxides have been reviewed [1,2]. X-ray and IR studies indicated that the stoichiometry of oxides near oxygen evolution is relatively close to H_2NiO_2 and $HNiO_2^-$ [3]. Addition of 10% $Co(OH)_2$ decreases the diffusion resistance on the active material [4]. The addition of cobalt or cerium or manganese hydroxide to plastic bonded nickel electrodes has suppressed the second discharge step, sometimes referred to as the " graphite step" [5,6]. The addition of cobalt stabilized the α and γ phases of the active material [7]. The influences of addition agents were added separately in the nickel hydroxide electrodes and alkaline electrolyte have been studied by various electrochemical techniques [8-11]. In the present paper, the cyclic voltammetry technique is used to determine the reversibility of the porous nickel electrode. The role of additives impregnated into the nickel hydroxide electrodes are also examined together with the effect of discharge rate on the cyclic efficiency. Potentiodynamic polarization technique is used to find out the self-discharge current and corrosion inhibition efficiency of the nickel electrodes. The impedance technique is used to determine the charge-transfer resistance and double layer capacity for the electrodic reaction of the nickel hydroxide electrodes containing addition agents such as $Cu(NO_3)_2$, $(NH_2)_2CS$ and $Mg(NO_3)_2$.

EXPERIMENTAL DETAILS

Porosity measurement

The porosity of nickel foam electrode was 80 to 90% measured using xylene impregnation method. The weighed (Ag) nickel electrode was kept in xylene below 30mm mercuric pressure for one hour in vacuum desicator. The electrode was removed and weighed in air (Bg) and in water (Cg)

The percentage of porosity is

$$P = 100\,(B-A)d_w / (B-C)d_x$$

where d_w and d_x were the densities of water and xylene at room temperature respectively.

Preparation of nickel electrode by electrochemical impregnation method

The nickel foam electrodes (imported from UK) were impregnated cathodically in the solution prepared from 3M $Ni(NO_3)_2\ 6H_2O$ + 0.5M $NaNO_2$ solution (pH =2.5-3.5). The geometrical area of the nickel electrode is $1cm^2$. Copper (0.2-0.8M) and magnesium (0.2-0.8M) were incorporated along with nickel from their nitrate solution and thiourea (0.1-0.4M) was incorporated with nickel nitrate. A cathodic current of 40mA was applied using a constant current regulator for 90 minutes at 308 ± 2K. The anode was pure nickel mesh of area $30cm^2$. The electrode was dried at 373K for 60 minutes and dipped in 6M KOH solution at 373K for 60 minutes. The electrodes were washed free of nitrate ion, then kept in double distilled water for 30 minutes and dried at 373K for 75 minutes. Amount of nickel hydroxide impregnated into the electrode was determined by increase in weight. The sequence of impregnation was repeated until there was no appreciable weight gain.

Cyclic Voltammetry

The experimental set-up comprise a potentiostat, voltage scan generator and X-Y recorder. For this, cyclic voltammetry (CV27) made in USA was used. A three electrode glass cell assembly was used. Platinum foil as counter electrode, Hg/HgO as the reference electrode and nickel foam as the working electrode was used. Nickel electrodes were polarized from 700 to –550mV vs Hg/HgO at different sweep rates, 3 to 10mV/s. The potential was fixed at after several experiment to get reproducible E-i curves for different sweep rates.

Potentiodynamic polarization

Using the three electrode glass cell assembly, polarization experiments were performed in the potential range of 500 to –500mV vs Hg/HgO at a constant scan rate of 1mV/s using BAS 100A instrument.

Impedance Technique

The impedance measurements were carried out to determine the charge-transfer resistance, double layer and f_{max} values for the electrode reaction under study. The frequency range chosen was from 100mHz to 1000KHz and the amplitude of AC signal was 5mV. A PAR model 6310 impedance bridge was used for the studies.

RESULTS AND DISCUSSION

Cyclic voltammetry (CV)

Impregnated nickel hydroxide electrodes were prepared by cathodic impregnation of nickel nitrate solution with $NaNO_2$ of pH 2.5 to 3.5 into the nickel foam substrate at a current density of 40mA/cm^2. The porosity of the electrode was about 80 to 90%. The nickel hydroxide electrode (Blank) was polarized from +700mV to –550mV at different sweep rates (3, 5, 8 and 10 mV/s) in 6M KOH solution. The cyclic voltammogram revealed interesting features (Fig.1). The Zero current Crossing Potentials (ZCP) occur at +550mV followed by a broad cathodic peak at +200mV (I). The reverse scan revealed an anodic peak at 685mV (II) followed by a severe oxygen evolution. The charges flowed under the peaks increased with scan numbers suggesting that they are redox couple. The ZCP lies between the equilibrium potentials of reversible oxygen reaction and Ni_3O_2 / NiO_2. On repeated cycling, charges flowed under the peaks decreases, which causes the reduction in capacity of the nickel electrodes and also poor charging efficiency due to dominated oxygen evolution. The cathodic peak potential was shifted towards the active direction and anodic peak potential towards noble direction with increase in sweep rate. Voltammetric studies on β-$Ni(OH)_2$ in KOH solution revealed a single cathodic peak at 180mV[12-15].

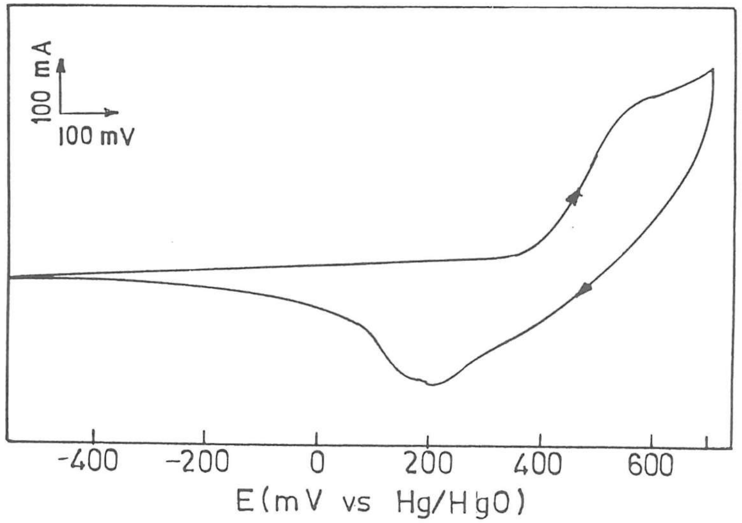

Fig. 1 Typical Cyclic Voltammogram for the impregnated nickel hydroxide foam electrode in 6M KOH solution .

$E_{\lambda,a}$ = +700 mV; $E_{\lambda,c}$ = -550 mV; Sweep rate 5 mV/s

Application to battery system

The growing need for the recycling of the resources requires that the discharged battery should preferably be reusable for a large number of times. Hence one looks for a rechargeable battery with long cycle life. Between periods of use, a loss in the available energy of the battery usually occurs partly due to the leakage of charge between the electrodes and partly due to a consumption of charge by parasitic reactions. A degree of charge retention is the valuable property of the battery. A long cycle life is achieved by use of electrodes of good reversibility. An ideal reversible battery requires that the positive and negative electrodes to be electrodes of the second kind [16] i.e a metal in contact with its sparingly soluble salt and solution saturated with the salt.

When the active mass in a battery electrode changes from the oxidant state to the reductant state or vice versa due to charge-discharge reactions, at least one of the states will be non-metallic. A porous electrode configuration is suitable to incorporate the active mass inside the pores of the structure.

In the case of nickel, the charge storage reaction is

$$\mathrm{NiOOH} + \mathrm{H_2O} + e^- \rightleftharpoons \mathrm{Ni(OH)_2} + \mathrm{OH^-}$$

In CV studies, the appearance of cathodic peak potential (I) and anodic peak potential (II) corresponds to Ni(III)/Ni(II) redox couple.

$$[E_p\,(I) - E_e] - [E_p\,(II) - E_e] = \Delta E_p$$

This ΔE_p is the measure of reversibility. The more the value of ΔE_p, the more is the irreversibility of the electrode process. The fact that the electrode potential varies from +0.7V to –0.55V at different sweep rates corresponds to a situation of the discharge of a porous electrode at different rates. A slower sweep rate in CV study represents discharging a battery at low rates of connecting to a load of high impedance and following a single electrode potential with time. A high sweep rate will correspond to a situation of short circuiting a battery. Hence, the extrapolation of peak potential separation ΔE_p to zero sweep rate will exhibit a maximum reversibility and will be a good battery electrode [10].

Effect of foreign ions in impregnated nickel hydroxide electrodes

Electrode preparation details and amount of active materials impregnated into the electrodes were given in Table –1. Fig.2. presents the electrochemical spectrum for copper co-precipitated with nickel hydroxide in 6M KOH solution at different scan numbers. During forward scan, ZCP occur at 585mV followed by a sharp cathodic peak at 180mV. The reverse scan revealed an anodic peak at 575mV along with oxygen evolution. On repeated cycling the reversibility of the redox couple increases. The addition of Cu^{2+} ions improve the charging efficiency of the nickel hydroxide electrode by shifting the anodic peak potential towards less positive regions with a difference of 100mV compared to nickel hydroxide electrode (Blank). ΔE_p values are minimum for all the concentrations of copper addition when compared to nickel hydroxide electrodes. Increase in sweep rates increases the charges flowed under the peaks. The cathodic peak potentials shifted towards negative values and anodic peak potentials towards noble values with increase in sweep rates.

TABLE-1

Electrode preparation details

S.No	Composition of impregnation solution	Weight of active material impregnated (mg)
1.	3M $Ni(NO_3)_2\,6H_2O$ + 0.5M $NaNO_2$ (Blank)	158
2.	Blank + 0.2M $Mg(NO_3)_2\,6H_2O$	125
3.	Blank + 0.4M $Mg(NO_3)_2\,6H_2O$	184
4.	Blank + 0.6M $Mg(NO_3)_2\,6H_2O$	165
5.	Blank + 0.8M $Mg(NO_3)_2\,6H_2O$	119
6.	Blank + 0.2M $Cu(NO_3)_2\,3H_2O$	195
7.	Blank + 0.4M $Cu(NO_3)_2\,3H_2O$	184
8.	Blank + 0.6M $Cu(NO_3)_2\,3H_2O$	165
9.	Blank + 0.8M $Cu(NO_3)_2\,3H_2O$	205
10.	Blank + 0.1M NH_2CSNH_2	183
11.	Blank + 0.2M NH_2CSNH_2	148
12.	Blank + 0.3M NH_2CSNH_2	119
13.	Blank + 0.4M NH_2CSNH_2	155

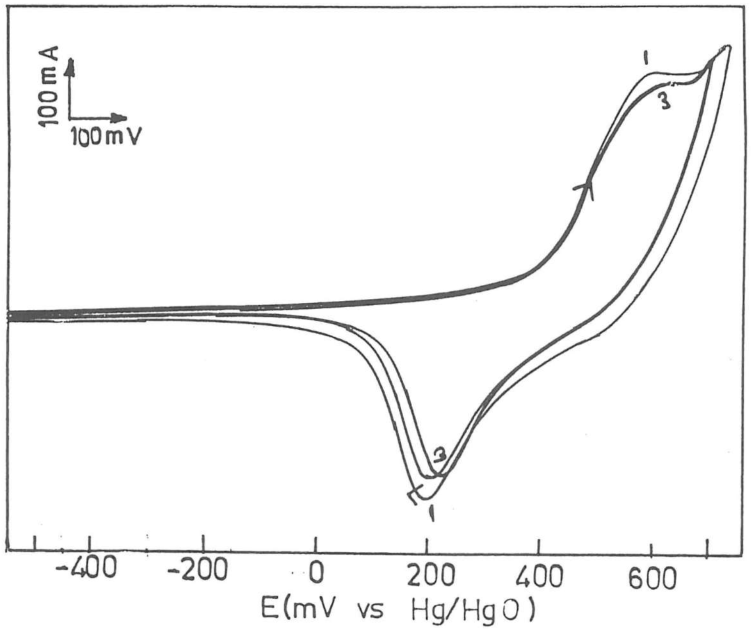

Fig.2. Typical cyclic voltammogram for copper co-precipitated with nickel hydroxide from 3M $Ni(NO_3)_2$ + 0.5M $NaNO_2$ + 0.4M $Cu(NO_3)_2$ in 6M KOH solution at different scan numbers

$E_{\lambda,a}$ = +700mV; $E_{\lambda,c}$ = -550mV; Sweep rate 3mV/s

In the case of thiourea co-precipitated with nickel hydroxide from 3M $Ni(NO_3)_2$ + 0.5M $NaNO_2$ + 0.4M Thiourea in 6M KOH solution at different scan numbers, forward scan revealed the cathodic peak at 190mV and the reverse scan revealed an anodic peak at 550mV followed by oxygen evolution at 625mV. Appearance of anodic peak at lower positive potential favours the good charging capability of nickel hydroxide electrodes, which improve the capacity and life of the electrode. On repeated cycling there is a small shift in the peak potentials which shows there is no reduction in capacity of nickel

electrodes with cycling. ΔE_p values are minimum for higher concentrations of thiourea when compared to nickel hydroxide electrode.

In $Mg(OH)_2$ co-precipitated in nickel hydroxide electrode, cathodic peak potential appears at 240mV to 300mV which is more positive than the other electrodes which favours the easier reduction of NiOOH to $Ni(OH)_2$ and produces higher current output. But in the anodic region the peak appears at higher positive potential along with oxygen evolution and causes the poor charging capability of the electrode. Higher concentrations of thiourea addition favours additives in $Ni(OH)_2$ electrode on the reversibility of charge storage reaction in 6M KOH solution (Table-2). Fig.3 presents the plot of ΔE_p vs sweep rate for various additives co-precipitated in $Ni(OH)_2$ electrodes. Addition of Cu^{2+}, Mg^{2+} and thiourea into the nickel hydroxide electrode reduces the $(\Delta E_p)_{\gamma=0}$ values and favours the reversibility. Under practical conditions $(\Delta E_p)_{\gamma=0}$ value 436mV was taken as reference. Increase of concentrations of all the addition agents increases the reversibility of the nickel hydroxide electrode. The reversible reaction which is responsible for the electrochemical behaviour of nickel hydroxide is

$$Ni_3O_2(OH)_4 + OH^- \rightleftharpoons 3NiOOH + H_2O + e$$

the concentration gradient of water is responsible for the electrochemical activity of nickel hydroxide electrode and at potentials near oxygen evolution, nickel may exist either as $Ni(OH)_4$ or $Ni(OH)_5^-$.

Potentiodynamic polarization measurements

The potentiodynamic polarization curve for the thiourea co-precipitated with $Ni(OH)_2$ in 6M KOH solutions is given in Fig.4. Table-3 shows the parameters derived from potentiodynamic polarization of porous nickel hydroxide electrodes with different co-precipitated additives in 6M KOH solution at a scan rate 1mV/s. For all the additives the open circuit potential (OCP) shifts in a noble direction with increase of

TABLE – 2

Effects of various additives in $Ni(OH)_2$ on the reversibility of charge storage reaction in 6M KOH solution

S.No.	Concentration of impregnation solution	$(\Delta E_p)_{\gamma=0}$ (mV)
1.	3M $Ni(NO_3)_2$ + 0.5M $NaNO_2$ (Blank)	436
2.	Blank + 0.2 M $Cu(NO_3)_2$	402
3.	Blank + 0.4 M $Cu(NO_3)_2$	382
4.	Blank + 0.6 M $Cu(NO_3)_2$	372
5.	Blank + 0.8 M $Cu(NO_3)_2$	364
6.	Blank + 0.1M NH_2CSNH_2	422
7.	Blank + 0.2M NH_2CSNH_2	404
8.	Blank + 0.3M NH_2CSNH_2	377
9.	Blank + 0.4M NH_2CSNH_2	368
10.	Blank + 0.2 M $Mg(NO_3)_2$	430
11.	Blank + 0.4 M $Mg(NO_3)_2$	406
12.	Blank + 0.6 M $Mg(NO_3)_2$	382
13.	Blank + 0.8 M $Mg(NO_3)_2$	376

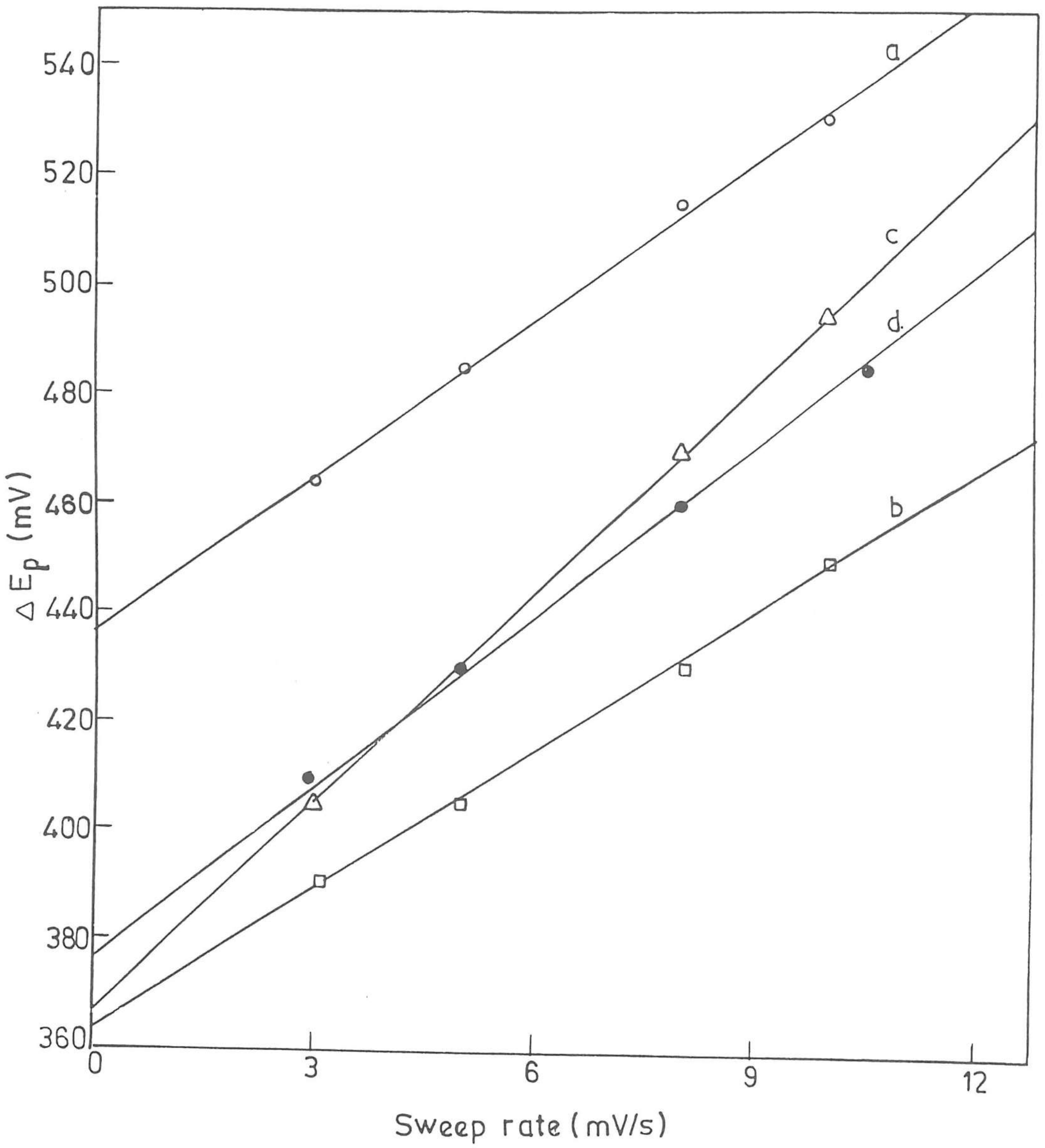

Fig. 3 A plot of ΔEp Vs Sweep rate for various additives co-precipitated in $Ni(OH)_2$ electrodes.

a) $Ni(OH)_2$ (Blank)

b) Blank + Cu^{2+}

c) Blank + Thiourea

d) Blank + Mg^{2+}

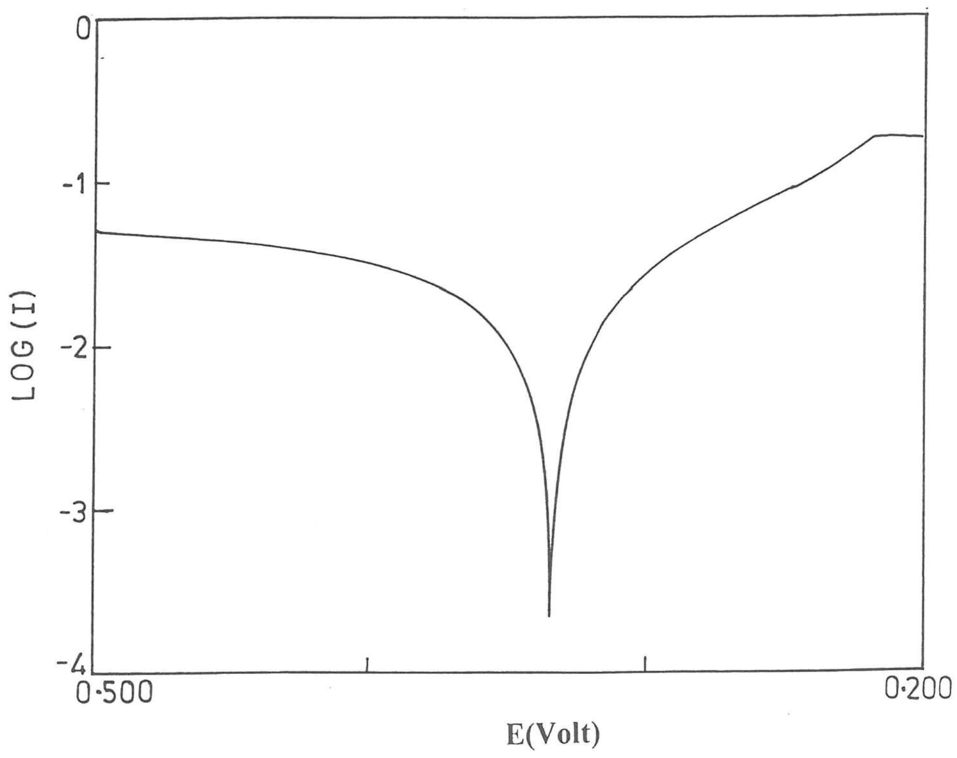

Fig. 4 Potentiodynamic polarisation curve for the Nickel Hydroxide electrode in 6M KOH solution.

TABLE – 3

Parameters derived from potentiodynamic polarization of porous nickel hydroxide electrode with different co-precipitated additives in 6M KOH solution at a scan rate 1mV/s

Concentration of impregnation solution (M)	OCP (mV)	E_{corr} (mV)	i_{corr} (A/cm^2) x 10^{-4}	Tafel slope (mV/decade)		% reduction of i_{corr}
				b_a	b_c	
Blank (B)	466	335	62.10	11.0	13.0	---
B + 0.2 M $Cu(NO_3)_2$	417	228	18.90	28.0	31.0	69.9
B + 0.4 M $Cu(NO_3)_2$	407	237	7.80	11.6	13.3	81.0
B + 0.6 M $Cu(NO_3)_2$	434	153	3.80	18.3	20.0	94.0
B + 0.8 M $Cu(NO_3)_2$	424	155	0.30	25.0	26.0	99.0
B + 0.1 M $(NH_2)_2CS$	367	301	16.00	35.0	37.0	74.0
B + 0.2 M $(NH_2)_2CS$	415	202	6.10	10.0	12.0	90.0
B + 0.3 M $(NH_2)_2CS$	421	228	2.50	56.0	56.0	96.1
B + 0.4 M $(NH_2)_2CS$	419	232	0.80	18.3	18.3	98.7
B + 0.2 M $Mg(NO_3)_2$	427	364	29.70	40.0	46.0	52.0
B + 0.4 M $Mg(NO_3)_2$	468	360	16.50	42.0	52.0	73.0
B + 0.6 M $Mg(NO_3)_2$	439	362	13.70	26.0	46.0	78.0
B + 0.8 M $Mg(NO_3)_2$	436	339	10.60	30.0	40.0	83.0

additive concentration. All the addition agents decrease the i_{corr} values increase with increase in additive concentration. In the case of copper and thiourea additions favour the mixed control reactions but in the case of addition of magnesium shows predominantly under cathodic control reaction. The addition of copper and thiourea shifted the E_{corr} values in the less positive direction while the addition of magnesium in the reverse direction.

Impedance Measurements

The impedance studies for the $Ni(OH)_2$ electrode representing the fully discharged condition of the NiOOH electrode with and without addition were carried out over a base potential of zero volts with super imposition of A.C voltage of amplitude 5mV in the frequency ranges 100MHz to 100KHz. The results are presented in Table-4 and in figs.5 and 6. In most of the cases the Nyquist plots were distorted semi-circles indicating the electrode process to be under charge transfer control. In the case of $Cu(OH)_2$ impregnated electrode, there is a rising portion at the end of the semi-circle indicating the reactions to be partly under diffusion control. In the case of the blank ($Ni(OH)_2$ electrode) the presence of two semi-circles indicates the two stage electrodic process as is reported earlier [17]. It is observed with additives $Cu(OH)_2$ and thiourea , there is decrease in R_t values and increase in capacity values when compared to the blank. The capacity values is in agreement with cyclic voltammetric results, where we find the cathodic charge under repetitive cycles is higher than the blank values confirming the beneficial effect of the additives. However, in the case of $Mg(OH)_2$ additive R_t values have decreased. Such reduction in capacity values are also reflective in cyclic voltammetric studies. The R_t values of the impedance results are to not to be confused with the polarization results of the corrosion studies. Here R_t values corresponds to the electrodic process associated with cathode under fully discharged condition.

TABLE – 4

Parameters derived from impedance measurements for porous nickel hydroxide electrodes with different co-precipitated additives in 6M KOH solution

Electrolyte composition	R_t (ohm)	C_{dl} (F.cm^{-1}) x 10^{-3}
Blank	139.00	1.134
Blank + 0.2 M $Cu(NO_3)_2$	5.63	2.830
Blank + 0.4 M $Cu(NO_3)_2$	10.20	3.830
Blank + 0.6 M $Cu(NO_3)_2$	12.40	4.430
Blank + 0.8 M $Cu(NO_3)_2$	15.68	6.410
Blank + 0.1 M $(NH_2)_2CS$	27.68	1.880
Blank + 0.2 M $(NH_2)_2CS$	22.45	1.720
Blank + 0.3 M $(NH_2)_2CS$	23.60	1.640
Blank + 0.4 M $(NH_2)_2CS$	25.36	1.840
Blank + 0.2 M $Mg(NO_3)_2$	284.00	0.696
Blank + 0.4 M $Mg(NO_3)_2$	423.00	0.470
Blank + 0.6 M $Mg(NO_3)_2$	359.00	0.520
Blank + 0.8 M $Mg(NO_3)_2$	148.00	0.820

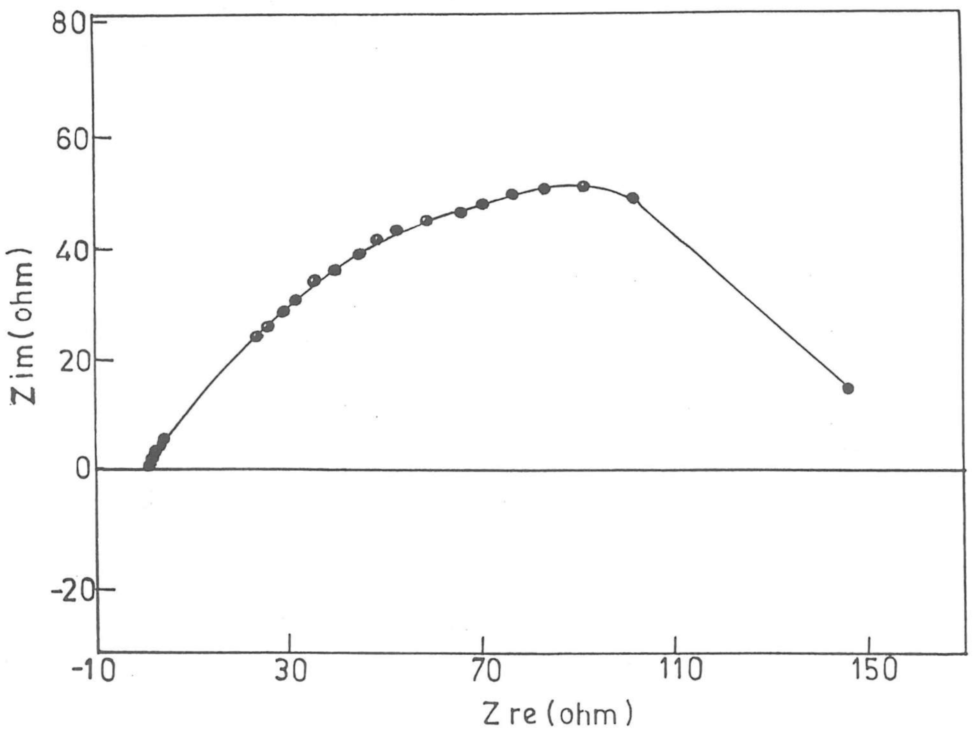

Fig. 5 : Nyquistian plot of porous Nickel Hydroxide electrode in 6M KOH Solution

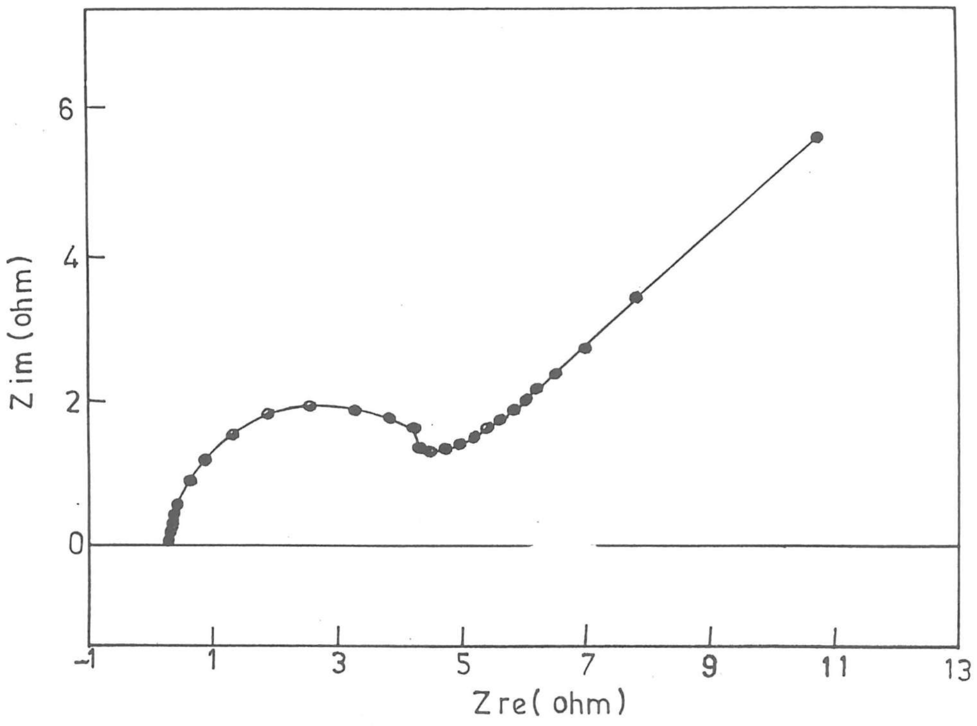

Fig. 6 : Nyquistian plot of porous Nickel Hydroxide electrode with co-precipitated $Cu(OH)_2$ (0.2M) in 6M KOH Solution.

CONCLUSIONS

All the addition agents favours the reversibility of the charge storage reaction of nickel electrode. Increase of concentration of all the ions increases the reversibility of the electrode. In all the cases, percentage reduction of i_{corr} values increase with increase in additive concentration. In the case of copper and thiourea addition increases the capacity values, whereas magnesium decreases. Based on the above results, copper and thiourea co-precipitated with $Ni(OH)_2$ electrode are the best additives.

REFERENCES

1. P.Oliva, J.Leonardi, J.F.Laurent, C.Delmas, J.J.Braconnier, M.Figlarx, F.Fievet and A.De.Guitert, J.Power Sources, 8 (1982)229
2. J.L.Weininger, The Nickel Electrode, Proc.Electrochem. Soc., 82-84 (1982)1
3. D.Tuomi, J.Electrochem. Soc., 122(1965)1
4. A.H.Zimmerman, J.Power Sources, 12(1984)233
5. A.J.Salkind, J.M.C.Breen, R.Freeman and W.A.Parkhurst, Power Sources , 10 (1985)425
6. B.Klapste, K.Micka, J.Mrha and J.Vondrak, J.Power Sources, 8 (1982)351
7. R.D.Armstrong and E.A.Charles, J.Power Sources, 25(1989)89-97
8. M.Abdul Kadir, G.Paruthimal Kalaignan, B.Muralidharan and T.Vasudevan, Bull. of Electrochem., 12(1996)201-205
9. G.Paruthimal Kalaignan, V.S.Muralidharan and K.I.Vasu, Proc. Of 10th Int. Congress on Metallic Corrosion Vol.1, 2.46(1987)615
10. G.Paruthimal Kalaignan, Ph.D. Thesis, Madurai Kamaraj University, Madurai (1988)
11. K.I.Vasu, V.S.Muralidharan, M.Ramakrishnan, G.Paruthimal Kalaignan and N.Jeyalakshmi, J.Power Sources, 28 (1989)409
12. R.Barnard and C.F.Randall, J.Appl.Electrochem., 12(1982)27
13. R.Barnard and C.F.Randall, J.Appl.Electrochem., 13(1983)89
14. R.Barnard and C.F.Randall, J.Appl.Electrochem., 13(1983)97
15. R.Barnard and C.F.Randall, J.Power Sources, 9(1983)185
16. R.Barnard and C.F.Randall, J.Power Sources, 9(1983)185-204
17. R.T.Barton, M.Hughes, S.A.G.R.Karunathilaka, N.A.Hampson, J.Appl.Electrochem., 15(1985)399-404.

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