Electrochemical behaviour of addition agents impregnated in cadmium hydroxide electrodes for alkaline batteries

G. Paruthimal Kalaignan *, C. Umaprakatheeswaran, B. Muralidharan, A. Gopalan,
T. Vasudevan

Department of Industrial Chemistry, Alagappa University, Karaikudi 623 003, India

Abstract

The development of electrode additives for the cadmium electrode of the nickel/cadmium battery is aimed mainly at increasing the discharge capacity and minimizing self-discharge. The dissolution and passivation of porous cadmium electrodes containing hydroxide and the relative stability of oxides are of importance in understanding the reversible behaviour of the cadmium electrode. Under standard conditions, the equilibrium potential of $Cd(OH)_2/Cd$ lies above the hydrogen-evolution reaction when the cell is not in use, and the active material of the cadmium electrode undergoes self-reductive dissolution (i.e., loss of active material) accompanied by oxygen evolution. The triangular potential sweep voltammetric technique is used to determine the reversibility of the cadmium electrode in alkaline solution. The role of additives such as $Ni(NO_3)_2$ (0.25–0.1 M) and $FeSO_4$ (0.1–0.4 M), TiO_2 (0.01–0.03 M) and Na_2S (0.01–0.03 M) in $Cd(NO_3)_2$ on the reversibility of the electrode are discussed. The effect of discharge rate on the cyclic efficiency is also investigated. Self-discharge currents are determined by potentiostatic polarization method.

Keywords: Additives; Calcium hydroxide; Alkaline batteries

1. Introduction

The development of electrolyte additives for the cadmium electrode of the nickel/cadmium battery is aimed mainly at increasing the discharge capacity and minimizing self-discharge. The electrochemical behaviour of the cadmium electrode has been the subject of many reviews [1–5]. Nevertheless, research into the electrochemistry of cadmium has been scarce in recent years. The effects of various additives to the electrode and electrolyte have been studied by many authors [6–10]. The influence of the temperature on nickel/cadmium cells has also been investigated [11–13].

The effect of additives on the electrochemical behaviour of the cadmium electrode in alkaline solutions at various temperatures has been reported [14]. The high- and low-rate performance characteristics of the cadmium electrode have been studied as a function of the iron content [15]. Aravamutham et al. [16] evaluated nickel/cadmium cells that used chemically impregnated positive and negative electrodes and found that they maintained good capacity. The dependence of the oxidation/reduction behaviour of the cadmium electrode on the sweep rate has been reported [17]. The batteries

use spongy metal substrates for the cathodes and/or anodes [18]. The negative electrode capacity is 1.7 times that of the positive electrode and this prevents hydrogen evolution during overcharge [19].

In this paper, the triangular potential sweep voltammetric technique is used to determine the reversibility of the cadmium electrode. The role of the additives impregnated into the cadmium hydroxide electrodes is also examined together with the effect of discharge rate on the cyclic efficiency. Self-discharge currents are determined by potentiostatic polarization method.

2. Experimental

2.1. Preparation of sintered nickel electrode

Loose sintered electrodes were prepared from previously reduced INCO nickel 255 powder. The latter was spread over a 10 mesh nickel grid of 0.1 mm thick in a graphite die. The powders were sintered at a temperature of 1123 K in a muffle furnace for about 30 min under a hydrogen atmosphere. The electrode had a geometrical area of 12.5 cm² and a thickness

* Corresponding author.

of 2 mm. Copper rod was welded to the pellet to provide electrical connection.

2.2. Porosity measurement

The porosity of electrode was 75 to 80% and was determined by the xylene impregnation method. The weighed (A g) nickel electrode was kept in xylene below 30 mm mercuric pressure for 1 h in a vacuum flask. The electrode was removed and weighed in air (B g) and in water (C g).

The percentage of porosity is given by:

$$P = \frac{100(B-A)d_w}{(B-C)d_x} \tag{1}$$

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

2.3. Chemical impregnation

The sintered nickel substrate was impregnated under vacuum with 0.7 M $Cd(NO_3)_2 \cdot 4H_2O$ solution in order to decrease the chemical attack of the nitrate solution on the nickel matrix. A small amount of poly(vinyl alcohol) was added to the $Cd(NO_3)_2$ solution. Various addition agents, namely, $FeSO_4$, $Ni(NO_3)_2$, TiO_2 and Na_2S were incorporated along with the cadmium nitrate solution. After vacuum soaking, the plaques were transferred to a polarizing unit where they were cathodically polarized in 6 M KOH solution. The anode was pure nickel mesh. A cathodic current of 40 mA/cm^2 was applied for 30 min using a constant-current regulator. The electrodes were washed free of nitrate ion, kept in double-distilled water for 30 min, and finally dried at 373 K for 30 min. The amount of $Cd(OH)_2$ impregnated into the electrode was determined by the increase in weight. The sequence of impregnation was repeated until there was no appreciable weight gain.

2.4. Triangular potential sweep voltammetry

Triangular potential sweep voltammetric (TPSV) experiments were carried out with a BAS 100 A electrochemical analyser made in the USA. A three-electrode glass cell assembly was used. A sintered cadmium electrode served as the working electrode, platinum foil as the counter electrode and Hg/HgO as the reference electrode. The cadmium electrode was polarized from -0.5 to -1.2 V versus Hg/HgO at different sweep rates from 1 to 5 mV/s. The potential was taken after several experiments in order to get reproducible E–i curves for different sweep rates.

2.5. Potentiostatic polarization

A three-electrode glass cell assembly was used. The working electrode was sintered cadmium, the counter electrode was platinum, and the reference electrode was Hg/HgO. The

cadmium electrode was polarized from -0.5 to -1.2 V versus Hg/HgO.

3. Results and discussion

3.1. Solid cadmium electrode

The electrochemical spectrum of the solid cadmium (geometrical area: 1 cm^2) in 6.0 M KOH solution, in the region -1200 to -600 mV versus Hg/HgO reveals a sharp anodic peak at -875 mV (I) and a broad anodic peak at -820 mV (II) during the forward scan, see Fig. 1. The reverse scan exhibits a broad cathodic peak at -945 mV (III). The anodic peak is attributed to active metal dissolution followed by passivation. The passivation of the electrode is dependent on the diffusion of OH^- ions, through the surface of the developing $Cd(OH)_2$ layer, and is related to the well-known involvement of complex ions in the anodic dissolution process. The appearance of peak potential at -875 mV is due to the formation of CdO and the partial development β-$Cd(OH)_2$, whereas the peak II is due to the formation of β-$Cd(OH)_2$ and the partial formation of γ-$Cd(OH)_2$. The magnitude of the corresponding cathodic peak III indicates significant levels of reduced $Cd(OH)_2$ at completion of the sweep. On repetitive scanning at higher sweep rates, the current flowing under peaks II and III increases with scan number: this suggests that they are conjugated with increase in scan number, the anodic peak potentials shift in the noble (or positive) direction, and the cathodic peak potentials in the active or negative direction. This indicates that the reactions are becoming reversible with subsequent cycling. Concomitantly, the charge under the peaks decreases.
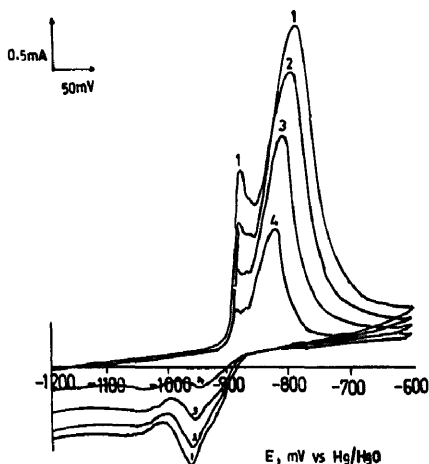

Fig. 1. Typical cyclic voltammogram of cadmium electrode in 6 M KOH at different sweep rates. $E_{\lambda,c} = -1200$ mV; $E_{\lambda,a} = -600$ mV; $\nu = 2, 5, 8, 10$ mV/s. Scan rates, mV/s: (1) 10; (2) 8; (3) 5, and (4) 2.

3.2. Impregnated cadmium hydroxide electrodes

Chemical impregnation of cadmium hydroxide in porous nickel plaque from cadmium nitrate solutions (pH: 2.5–3.5) was carried out. The electrodes were polarized from −0.5 to −1.2 V (versus Hg/HgO) in 6 M KOH solution (Fig. 2). The zero-current crossing potential (ZCC) occurs at −940 mV followed by a sharp anodic peak at −804 mV. The reverse scan revealed a plateau at −900 mV and the cathodic peak at −1131 mV followed by a severe hydrogen evolution at −1.2 V. The charges under the peaks increase with scan number and this suggests that they are couples. The cathodic peak potentials are shifted towards negative values and the anodic peak potentials towards noble values with increase in sweep rates.

The anodic peak at −840 mV indicates the formation of cadmium to $Cd(OH)_2$ and the production of a trace amount of γ-$Cd(OH)_2$ [20] in the reduction process. The plateau commencing at −900 mV is due to the reduction of an 'active' γ-$Cd(OH)_2$. The peak at more higher negative potentials indicates the reduction of β-$Cd(OH)_2$ to cadmium. The reduction is thought to proceed via a low over-potential solid-state mechanism and a high over-potential solution species process [21]. The charge recovered on the cathodic sweep is considerably smaller than that on the previous anodic sweep. This demonstrates the inefficient reduction of $Cd(OH)_2$ on the porous electrode. In the double cathodic reduction, the peaks might be related to the reduction of different types of $Cd(OH)_2$ in the porous electrode. It is possible that the first cathodic peak relates to the reduction of an 'active' γ- or β-$Cd(OH)_2$ that has an inert solubility while the second peak at higher cathodic potentials relates to well-crystallized β-$Cd(OH)_2$ [22].

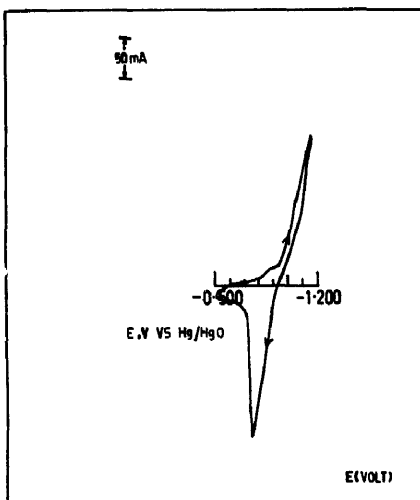Fig. 2. Typical cyclic voltammogram for the impregnated $Cd(OH)_2$ electrode in 6 M KOH. $E_{\lambda,a}$ = −0.5 V; $E_{\lambda,c}$ = −1.2 V; sweep rate = 2 mV/s.

3.3. Application to battery systems

An ideal reversible battery requires the positive and negative electrodes to be electrodes of the same kind [23], i.e., a metal is in contact with its sparingly soluble salt and solution saturated with the salt:

$$O_s + X + ne^- \rightarrow R_s + Y \qquad (2)$$

O_s and R_s are oxidant and reductant present in the solid phase and the species X and Y are species in the electrolyte. The process involves dissolution from kink sites and deposition by nucleation of the active materials in the oxidized and reduced forms of the solid phase. The equilibrium potential of an electrode that sustains the net reaction is determined by the equilibrium activities of the predominant species in the respective phases. 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 for incorporation of the active mass inside the pores of the structure [24]. If the active mass is also a current collector at the electrode, a relatively large IR drop is inevitable. For the cadmium electrode the charge-storage reaction is:

$$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^- \qquad (3)$$

In TPSV studies, the appearance of an anodic peak potential −820 mV and cathodic peak potential −945 mV corresponds to a Cd/Cd(II) redox couple (Fig. 1):

$$[E_p(II) - E_c] - [E_p(I) - E_c] = \Delta E_p \qquad (4)$$

where ΔE_p is a measure of the irreversibility; i.e., the greater the value of ΔE_p the greater the irreversibility of the electrode process. The fact that the electrode potential varies from −1.2 to −0.6 V at different sweep rates corresponds to the discharge of a cadmium electrode at different rates. A lower sweep rate in the TPSV study represents discharging a battery at a low rate by connecting to a load of high impedance and following a single electrode potential with time. In other words, at low sweep rates, the cadmium electrode behaviour is being studied in a TPSV curve near reversible conditions. A high sweep rate corresponds to short circuiting of a battery. Hence, extrapolation of the peak potential separation, ΔE_p, to zero-sweep rate will enable the electrode behaviour to be examined near the reversible potential. An electrode that gives a minimum value at zero-sweep rate will exhibit maximum reversibility and will be a good battery electrode.

3.4. Effect of foreign ions in impregnated cadmium hydroxide electrodes

Electrode preparation details and the amount of active material impregnated into the electrodes are given in Table 1. During the forward scan of nickel co-precipitated with $Cd(OH)_2$ in 6 M KOH solution the zero-current crossing potential occurs at −930 mV followed by a sharp anodic

Table 1
Electrode preparation details

Sample no.	Composition of impregnation solution	Weight of active material impregnated (mg)
1	0.7 M Cd (NO$_3$)$_2$ (blank)	440
2	Blank + 0.25 M Ni(NO$_3$)$_2$	412
3	Blank + 0.50 M Ni(NO$_3$)$_2$	425
4	Blank + 0.75 M Ni(NO$_3$)$_2$	450
5	Blank + 1.00 M Ni(NO$_3$)$_2$	462
6	Blank + 0.01 M TiO$_2$	420
7	Blank + 0.02 M TiO$_2$	442
8	Blank + 0.03 M TiO$_2$	460
9	Blank + 0.10 M FeSO$_4$	422
10	Blank + 0.20 M FeSO$_4$	450
11	Blank + 0.30 M FeSO$_4$	462
12	Blank + 0.40 M FeSO$_4$	490
13	Blank + 0.01 M Na$_2$S	440
14	Blank + 0.02 M Na$_2$S	480
15	Blank + 0.03 M Na$_2$S	492

peak at -770 mV. The reverse scan displays a peak plateau at -908 mV and a cathodic peak at -1130 mV along with hydrogen evolution. Nickel addition favours reversibility, while increasing the sweep rate increases the charges under the peaks. The cathodic peak potentials are shifted towards negative values and the anodic peak potentials towards noble values with increase in sweep rate. Addition of nickel shifted the anodic peak potential to more positive values and this enhances the irreversibility of the cadmium electrode. On the other hand, the addition of nickel enhances the charges under the peak and, in turn, increases the capacity of the cadmium electrode. The addition of a small amount of nickel (< 0.25 M) improves the performance of the cadmium hydroxide electrode.

On the forward scan for TiO$_2$ co-precipitated with Cd(OH)$_2$ in 6 M KOH solution a sharp anodic peak appears at -804 mV. The reverse scan contains a broad cathodic peak at -907 mV and a sharp cathodic peak at -1121 mV, along with hydrogen evolution which favours the reduction of cadmium hydroxide. The addition of TiO$_2$ increases the charges under the cathodic peaks; this assists the reduction of Cd(OH)$_2$ to cadmium. A high concentration of TiO$_2$ (> 0.03 M) enhances the irreversibility of the cadmium electrode, while a low concentration improves the reversibility.

The electrochemical behaviour for iron co-precipitated with Cd(OH)$_2$ in 6 M KOH solution is displayed in Fig. 3. During the forward scan, a broad anodic peak appears at -774 mV, while the reverse scan yields a cathodic peak at -1134 mV, along with hydrogen evolution. The ZCC potential occurs at -1030 mV. Iron addition facilitates oxidation of cadmium to cadmium hydroxide at more negative values. High concentrations of Fe(OH)$_2$ favour the reversibility. The addition of iron increases the charges under the peaks and thus increases the capacity of the Cd(OH)$_2$ electrode.

The electrochemical behaviour for sulfur co-precipitated with Cd(OH)$_2$ in 6 M KOH solution at different scan numbers is given in Fig. 4. During the forward scan, a broad anodic peak appears at -845 mV, while on the reverse scan
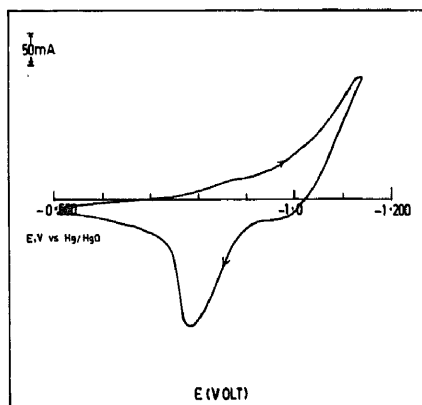
Fig. 3. Typical cyclic voltammogram for iron co-precipitated with Cd(OH)$_2$ from 0.7 M Cd(NO$_3$)$_2$ + 0.3 M FeSO$_4$ in 6 M KOH. $E_{\lambda,a} = -0.5$ V; $E_{\lambda,c} = -1.2$ V; sweep rate = 3 mV/s.
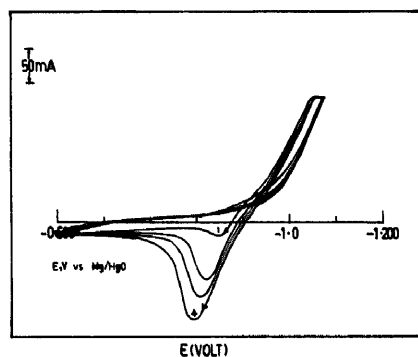
Fig. 4. Typical cyclic voltammogram for sulfur co-precipitated with Cd(OH)$_2$ from 0.7 M Cd(NO$_3$)$_2$ + 0.01 M Na$_2$S in 6 M KOH. $E_{\lambda,a} = -0.5$ V; $E_{\lambda,c} = -1.2$ V; sweep rate = 1 mV/s.

Table 2
Effect of various additives in Cd(OH)$_2$ electrode on the reversibility of charge-storage reaction in 6 M KOH solution

Sample no.	Composition of impregnation solution	ΔE_p at zero-scan rate(mV)
1	0.7 M Cd (NO$_3$)$_2$ (blank)	314
2	Blank + 0.25 M Ni(NO$_3$)$_2$	299
3	Blank + 0.50 M Ni(NO$_3$)$_2$	300
4	Blank + 0.75 M Ni(NO$_3$)$_2$	310
5	Blank + 1.00 M Ni(NO$_3$)$_2$	313
6	Blank + 0.01 M TiO$_2$	276
7	Blank + 0.02 M TiO$_2$	280
8	Blank + 0.03 M TiO$_2$	312
9	Blank + 0.10 M FeSO$_4$	314
10	Blank + 0.20 M FeSO$_4$	305
11	Blank + 0.30 M FeSO$_4$	303
12	Blank + 0.40 M FeSO$_4$	296
13	Blank + 0.01 M Na$_2$S	304
14	Blank + 0.02 M Na$_2$S	284
15	Blank + 0.03 M Na$_2$S	280

a sharp cathodic peak is present at -1084 mV, followed by hydrogen evolution. The presence of sulfur shifts the reduction of Cd(OH)$_2$ to cadmium to a lower negative potential. On repeated cycling, there is an increase in the charges under the anodic peaks and, thereby, an increase in the electrode capacity. The anodic peak potentials move in a noble direction with cycling and, hence, the system becomes more irreversible. Higher concentrations of sulfur improve the reversibility.

Plots of ΔE_p versus sweep rate for various additives are given in Fig. 5. Table 2 represents the effect of various additives to the Cd(OH)$_2$ electrode on the reversibility of charge-storage reaction in 6 M KOH solution. All the addition agents
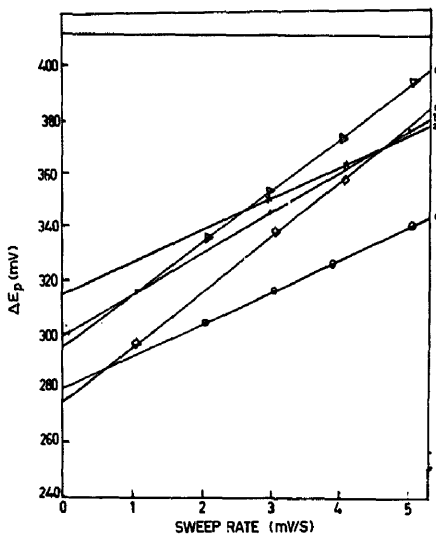
reduce the peak separation, compared with pure Cd(OH)$_2$ electrode and favours reversibility. The ΔE_p value of 314 mV for the Cd(OH)$_2$ electrode was taken as a benchmark. Small additions of Ni(NO$_3$)$_2$ and TiO$_2$ and high additions of FeSO$_4$ and Na$_2$S will improve the reversibility of cadmium electrode in batteries.

3.5. Effect of foreign ions in impregnated cadmium hydroxide electrodes (potentiostatic polarization)

The potentiostatic polarization curve for the impregnated Cd(OH)$_2$ electrode and sulfur co-precipitated with Cd(OH)$_2$ from 0.7 M Cd(NO$_3$)$_2$ + 0.03 M Na$_2$S in 6 M KOH solution are given in Fig. 6. The anodic polarization is greater than the cathodic polarization in all cases. This indicates that both the overall kinetics and the corrosion of the Cd(OH)$_2$ electrode containing various amounts of dopants in 6 M KOH solution are predominantly under anodic control. This obser-
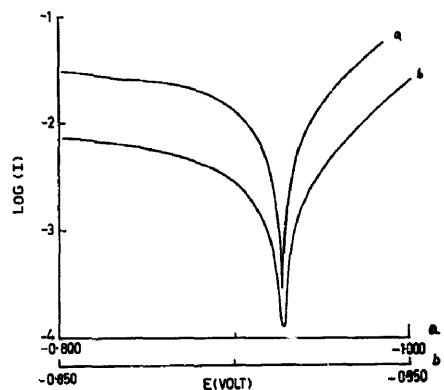
Fig. 5. ΔE_p vs. sweep rate for various additives co-precipitated in Cd(OH)$_2$ electrodes: (a) Cd(OH)$_2$ (blank); (b) blank + 0.25 M Ni(NO$_3$)$_2$; (c) blank + 0.1 M TiO$_2$; (d) blank + 0.4 M FeSO$_4$, and (e) blank + 0.03 M Na$_2$S.

Fig. 6. Potentiostatic polarization curve for the impregnated Cd(OH)$_2$ electrode and sulfur co-precipitated with Cd(OH)$_2$ from 0.7 M Cd(NO$_3$)$_2$ + 0.03 M Na$_2$S in 6 M KOH solution: (a) Cd(OH)$_2$ (blank), and (b) 0.7 M Cd(NO$_3$)$_2$ + 0.03 M Na$_2$S.

Table 3
Parameters derived from potentiostatic polarization studies for various additives co-precipitated in $Cd(OH)_2$ electrodes in 6 M KOH solution

Sample no.	Concentration of impregnation solution	OCV (mV)	E_{corr} (mV)	$I_{corr} \times 10^{-4}$ (A/cm²)	b_a mV/dec	b_c mV/dec
1	0.7 M $Cd(NO_3)_2$ (blank)	−822	−927	5.61	73	57
2	Blank + 0.25 M $Ni(NO_3)_2$	−798	−949	3.94	49	39
3	Blank + 0.50 M $Ni(NO_3)_2$	−797	−948	3.92	48	37
4	Blank + 0.75 M $Ni(NO_3)_2$	−795	−931	2.46	29	21
5	Blank + 1.00 M $Ni(NO_3)_2$	−795	−948	1.73	27	21
6	Blank + 0.01 M TiO_2	−798	−928	3.11	51	30
7	Blank + 0.02 M TiO_2	−798	−958	3.11	52	40
8	Blank + 0.03 M TiO_2	−797	−941	3.09	42	28
9	Blank + 0.10 M $FeSO_4$	−795	−942	3.30	58	40
10	Blank + 0.20 M $FeSO_4$	−794	−907	2.43	43	34
11	Blank + 0.30 M $FeSO_4$	−793	−907	2.25	28	22
12	Blank + 0.40 M $FeSO_4$	−793	−940	1.83	30	21
13	Blank + 0.01 M Na_2S	−796	−935	1.77	34	25
14	Blank + 0.02 M Na_2S	−795	−909	1.63	53	44
15	Blank + 0.03 M Na_2S	−795	−914	0.96	28	20

vation coincides OCV measurements of the $Cd(OH)_2$ electrode in the same electrolyte. For all additives the OCV shifts in a noble direction with increase of additive concentration. There are no abrupt changes in E_{corr} values with the addition of foreign ions. Table 3 shows the parameters derived from potentiostatic polarization studies for various additives co-precipitated in cadmium electrodes in 6 M KOH solution.

All the addition agents decrease the I_{corr} values compared with a pure cadmium hydroxide electrode. In all the cases, the I_{corr} values decrease with increase in additive concentrations.

4. Conclusions

From TPSV studies, the co-precipitation of low concentration of $Ni(NO_3)_2$ or TiO_2, and high concentrations of $FeSO_4$ or Na_2S to impregnated $Cd(OH)_2$ electrode in 6 M KOH solution favours the reversibility and charge-storage reaction of the electrodes.

Potentiostatic polarization studies reveal that all concentrations of the addition agents decrease the I_{corr} values when compared with that of $Cd(OH)_2$ electrode. In all the cases, the I_{corr} value decreases with increase in the additive concentration.

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