Cyclic voltammetric studies of electrodeposited solid solution and composite oxide/hydroxide electrodes in 1 M KOH: the $Co(OH)_2$–$Ni(OH)_2$–MnO_2 system

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Abstract

Solid solutions of the type $Ni_{1-x}Co_x(OH)_2$ ($x=0.1$ to 0.9) obtained by cathodic deposition from a mixed nitrate bath show a redox behaviour that is completely different to that of the pure components. The solid solution obtained from a bath containing a Ni/Co ratio of 40/60 exhibits the lowest E_{rev} and the smallest difference between the anodic and cathodic peak potentials (0.03 V). This is indicative of the high reversibility achieved at this composition. A layer-by-layer deposited composite electrode $Pt/Ni(OH)_2/MnO_2$ shows the migration of the active nickel oxide species from the inner layer to the surface and a marked lowering in the E_{rev} of the nickel hydroxide reaction. By contrast, the cobalt counterpart of this electrode does not show any of these interesting features. The Pt/ $MnO_2/Ni(OH)_2$ electrode does not hold much promise as it exhibits a markedly reduced reversibility of the nickel hydroxide reaction. In the cobalt counterpart $Pt/MnO_2/Co(OH)_2$, MnO_2 profoundly affects the reactions of cobalt hydroxide: first anodic reaction is suppressed and the second anodic reaction is less reversible. These observations suggest that there is a common chemical reaction mechanism for all oxide electrodes in alkaline media.

Introduction

Nickel hydroxide, $Ni(OH)_2$, [1, 2] and manganese dioxide, MnO_2, [3] have been extensively used as oxide electrode materials in alkaline batteries, while the possibility of using cobalt hydroxide, $Co(OH)_2$, [4] as a charge-storage material has been increasingly considered [5]. In an earlier paper [6], we have examined the electrode reactions of all of these three electrode materials and have proposed a common reaction scheme that involves a two-electron change to explain the electrode reactions of all oxide electrodes in alkaline media as:

$$M^{II}(OH)_2 \underset{(d)}{\overset{(a)}{\rightleftharpoons}} H^{III}MO_2 \underset{(c)}{\overset{(b)}{\rightleftharpoons}} M^{IV}O_2 \qquad (1)$$

While MnO_2 executes step (c) irreversibly, $Co(OH)_2$ has been found to execute step (a) irreversibly and steps (b) and (c) quasi-reversibly. $Ni(OH)_2$ comes closest to the ideal electrode model and undergoes a 1.67 electron change reversibly [7]. In a logical extension of this work, we now report our investigations on the solid solutions and composites of $Ni(OH)_2$, $Co(OH)_2$ and MnO_2. The motivation for the present study has been to find further evidence for the validity of the above common reaction scheme. If this reaction scheme is indeed valid, then each of these materials should

interact significantly with the others and the solid-solution/composite electrodes should exhibit altered electrochemical activity compared with the pure components. We have also been interested in determining whether these alterations are beneficial to battery performance.

To date, there have been several reports in the literature on the study of coprecipitated metal hydroxides. Cardoba et al. [8] have studied more than eight solid solutions of the hydroxides of Mn, Fe, Co, Ni, and Ag. These authors found that while the hydroxides of Co and Ni interact strongly with one another, those of Co and Mn do not interact at all; other pairs show moderate interaction. Belanger and Laperriere [9] have suggested the formation of a ternary Mn–Ni oxide in a composite electrode of MnO_2 and $Ni(OH)_2$. The largest number of studies has been devoted to the Co–Ni system. In small proportions (5 to 10 mol%), Co has been found to improve the mechanical [10], chemical [11] and electrochemical [12] properties of $Ni(OH)_2$. Recently, doping of Co in $Ni(OH)_2$ in the 20 to 55 mol% range has been found [13, 14] to lend structural stability to $Ni(OH)_2$.

The work reported here, while confirming some of the earlier observations, also brings to light certain new observations. Chief among these is the strong perturbation that MnO_2 imposes on the reactions of $Co(OH)_2$ and the diffusion of the reactive nickel oxide species through MnO_2 layers in composite electrodes. These results, taken together with the strong interaction observed between $Co(OH)_2$ and $Ni(OH)_2$ in solid solution electrodes, further strengthens the validity of the common reaction scheme proposed for oxide electrodes in alkaline media. A knowledge of this mechanism is bound to stimulate a search for new candidate materials for charge-storage applications.

Experimental

Film preparation

Thin films of $Ni(OH)_2$ and $Co(OH)_2$ were deposited in a one-step synthesis by cathodic reduction of their respective nitrates (0.1 M solution) on a Pt flag electrode (1.5 cm^2 area) in an undivided cell. A Pt wire was used as a counter electrode. Prior to deposition, the Pt flag was degreased with detergent and alternately washed in concentrated HNO_3 and distilled water. It was then electrochemically cleaned as described elsewhere [15]. The deposition was carried out at a current density of 1 mA cm^{-2}.

Cathodic reduction of a manganese nitrate solution yields $Mn(OH)_2$, which darkens rapidly to give γ-Mn_2O_3. Therefore, MnO_2 was deposited anodically from a 0.1 M manganese nitrate solution. The cathodic and anodic reactions have been described by Switzer [16].

Solid solutions of the type $M_{1-x}M'_x(OH)_2$ were deposited from mixed nitrate solutions containing M and M' ions in the required proportions. All concentrations are expressed as mol%. Solid solutions could only be obtained in the M = Ni and M' = Co system over the entire range of compositions. For this system, it is assumed that the film composition is equal to the bath composition [10]. Nevertheless, since small differences arising from the difference in solubility products are expected, all compositions expressed in this paper refer more accurately to the bath composition than to the film compositions.

With the Co–Mn and Ni–Mn systems, composite electrodes were prepared by sequential cathodic deposition of $Ni(OH)_2$ followed by anodic deposition of MnO_2. The same procedure was used for $Co(OH)_2$. These electrodes are represented as

Pt/M(OH)$_2$(M = Ni, Co)/MnO$_2$. For the reverse sequence of deposition, the electrodes are represented as Pt/MnO$_2$/M(OH)$_2$ (M = Co, Ni). The composition of the composite electrodes was varied by changing the deposition times of the layers.

Cyclic voltammetry

All cyclic voltammetric studies were carried out using a Princeton Applied Research Model 362 scanning potentiostat/galvanostat that was connected to a Riken Denshi Model F5C *x-y* recorder. The freshly-prepared film was immersed in a plastic tank containing 50 ml of 1 M KOH. A Pt flag was used as a counter electrode. All potentials were measured with respect to a Hg/HgO (1 M KOH) reference electrode. For each system, the switching potentials were chosen so as to monitor all the redox reactions occurring in the region between the gas evolution potentials. The scan rate was 10 mV s^{-1}. The first scan and, sometimes, several successive scans were recorded for each film. At least two fresh films were studied under each set of experimental conditions in order to verify the reproducibility of the film behaviour.

Results and discussion

Co–Ni system: cathodic coprecipitation

Figure 1 shows the cyclic voltammograms of pure Ni(OH)$_2$ (curve 1), pure Co(OH)$_2$ (curve 11), and the solid solutions Ni$_{1-x}$Co$_x$(OH)$_2$ (curves 2–10). Pure Ni(OH)$_2$ displays only one anodic and one cathodic peak [1], while pure Co(OH)$_2$ exhibits two anodic peaks and one cathodic peak [6]. The peak positions are listed in Table 1. The average between the anodic and cathodic peak potentials can be taken as an estimate of E_{rev} while the difference between the anodic and cathodic peak potentials, $\Delta E_{a,c}$, can be used as an index of reversibility of the redox reaction [15].

When Co(OH)$_2$ is coprecipitated with Ni(OH)$_2$ in proportions varying from 10 to 60 mol%, the cyclic voltammograms exhibit only one anodic and one cathodic peak similar to that for pure Ni(OH)$_2$, but the peaks are shifted to more negative potentials. The anodic peak is shifted by more than 300 mV; the E_{rev} is shifted by 280 mV. The coulombic efficiency, estimated as the ratio of cathodic to anodic peak currents, falls drastically from over 50% for pure Ni(OH)$_2$ to below 20%, even with incorporation of 10% Co.

When the proportion of Co is increased beyond 60%, the cyclic voltammogram begins to display the features that are typical for pure Co(OH)$_2$, but all the peaks are shifted to more negative potentials. At 70% Co, the cyclic voltammogram begins to shift in a positive direction back to that of pure Co(OH)$_2$.

Electrosynthesized nickel hydroxide adopts the highly hydrated and disordered α-Ni(OH)$_2$ phase [17]. The latter is electrochemically more active compared with the chemically prepared β-Ni(OH)$_2$ phase and has a higher coulombic efficiency. Electrosynthesized cobalt hydroxide, on the other hand, goes into the β-Co(OH)$_2$ phase and the corresponding α-phase is known to be highly unstable [18]. The sudden fall in the coulombic efficiency of the nickel hydroxide reaction upon incorporation of Co indicates that all the solid solutions in this system adopt the β rather than the α-structure, even for Ni-rich compositions. This is confirmed by X-ray diffraction data, which show that even for 20% Co incorporation, the *c*-axis is reduced from 8 to 4.7 Å. This observation is somewhat disappointing and is at variance with the results of Faure *et al.* [13, 14] who have stabilized the α-phase of Ni(OH)$_2$ with 20% Co incorporation. This difference in results highlights the superiority of the novel synthetic method employed by Faure *et al.* [13] over the routine electrosynthetic technique [19].
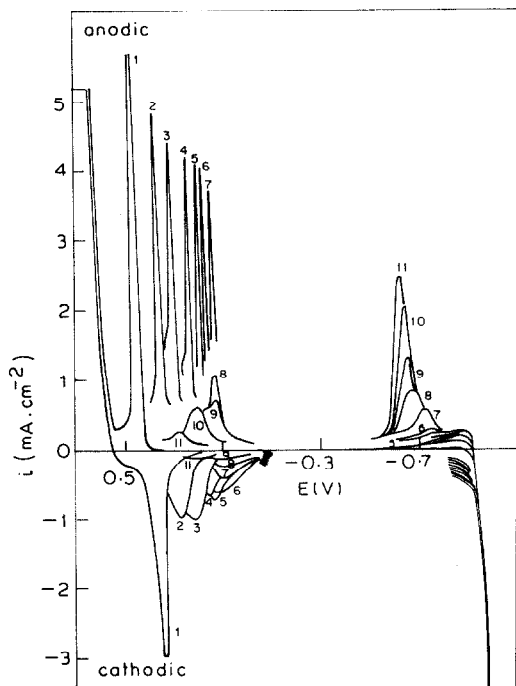
Fig. 1. Cyclic voltammograms of thin films of (curve 1) pure $Ni(OH)_2$; (curve 11) pure $Co(OH)_2$, and (curves 2–10) codeposited solid solutions $Ni_{1-x}Co_x(OH)_2$ ($x = 0.1$ to 0.9). For clarity, only the peaks are shown.

The cathodic shift of E_{rev} is a favourable characteristic and suggests that the solid-solution electrode can be charged at a much lower potential than either of the pure electrodes. The $\Delta E_{a,c}$ is a minimum (0.03 V) at 60% Co (see Table 1) and illustrates the high reversibility achieved at this concentration. This is almost the theoretical limit for a reversible reaction that involves a two-electron change and, therefore, represents a substantial improvement over pure $Ni(OH)_2$ whose $\Delta E_{a,c}$ is > 0.1 V [15]. Such findings further substantiate the common chemical model [6].

Ni–Mn and Co–Mn systems: cathodic coprecipitation

Figure 2 presents the cyclic voltammograms of thin film electrodes, obtained by coprecipitation from mixed Ni–Mn and Co–Mn nitrate baths, as a function of Mn concentration. Even at a low Mn composition (namely, 8 mol%), the electrochemical activity of $Ni(OH)_2$ is lost. At a lower Mn concentration, the cyclic voltammogram is similar in position and coulombic efficiency to pure $Ni(OH)_2$. Only the total intensity declines, and this demonstrates a lower charge capacity. The same is true for the Co–Mn codeposited electrodes. The loss of electrochemical activity could be due to formation of γ-Mn_2O_3 which, by virtue of a dissimilar structure and high stability, does not interact with either $Ni(OH)_2$ or $Co(OH)_2$. Therefore, in order to test the veracity of the proposed model, MnO_2 was deposited anodically to examine the degree of interaction with nickel and cobalt hydroxides. These layer-by-layer deposited electrodes are termed composite electrodes.

TABLE 1

Results of cyclic voltammetry measurements on films of $Ni_{1-x}Co_x$ $(OH)_2$

x	Peak potentials[a]		E_{rev} (V)	$\Delta E_{a,c}$ (V)	Coulombic efficiency (%)
	Anodic	Cathodic			
0.0	0.46	0.36	0.41	0.10	52
0.1	0.36	0.28	0.32	0.08	20
0.2	0.31	0.24	0.27	0.07	20
0.3	0.25	0.16	0.21	0.09	20
0.4	0.23	0.16	0.19	0.07	19
0.5	0.20	0.15	0.18	0.05	11
0.6	0.17	0.14	0.16	0.03	10
0.7	0.16 −0.65	0.13	0.15	0.03	17
0.8	0.16 −0.67	0.11	0.14	0.05	25
1.0	0.28 −0.64	0.15	0.21	0.13	60

[a]All potentials have been expressed in V with respect to a Hg/HgO (1 M KOH) reference electrode.
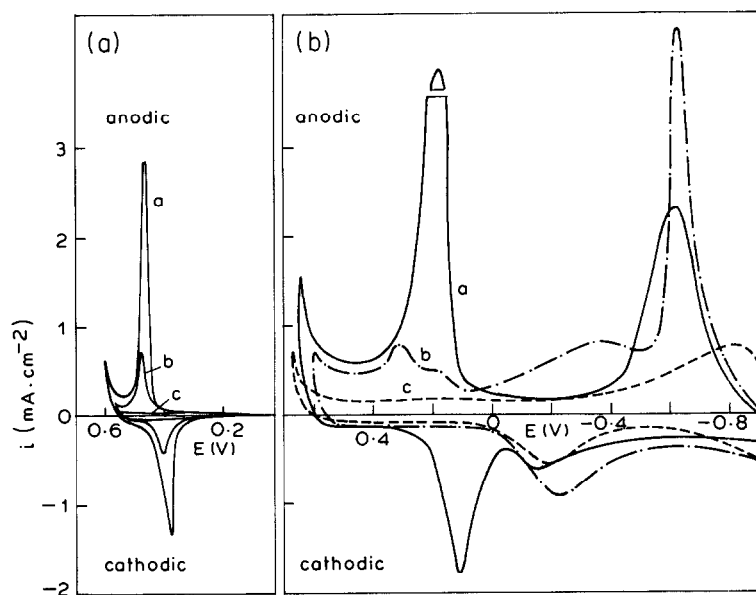

Fig. 2. (a) Cyclic voltammogram of a hydroxide film coprecipitated from a mixed Ni–Mn nitrate bath containing: (curve a) 0, (curve b) 5 and (curve c) 8 mol% Mn, respectively; (b) cyclic voltammogram of hydroxide film coprecipitated from a mixed Co–Mn nitrate bath containing: (curve a) 0, (curve b) 10 and (curve c) 20 mol% Mn, respectively.

Composite electrodes: Ni–Mn system

Figure 3(a) gives the cyclic voltammograms of the Pt/MnO$_2$/Ni(OH)$_2$ composite electrode, where MnO$_2$ is the inner layer. Features due to both the components can be seen in the composite electrode, but the peaks associated with the nickel hydroxide reaction are shifted substantially when compared with those for a pure Ni(OH)$_2$ electrode. The anodic peak is shifted in a positive direction by 0.06 V and the cathodic peak is shifted towards the negative direction by 0.04 V. The increased $\Delta E_{a,c}$ (see Table 2) is not a beneficial influence. In addition, repeated cycling causes these peaks to lose intensity rapidly, i.e., there is loss of electrochemical activity. Our observation is different from that of Belanger and Laperriere [9] who report a negative shift of the peaks due to nickel hydroxide.

When the sequence of deposition is reversed and Ni(OH)$_2$ is made the inner layer, the voltammograms shown in Fig. 3(b) are obtained. During the first few cycles, no peaks are observed due to Ni(OH)$_2$. On repeated cycling, however, there is a
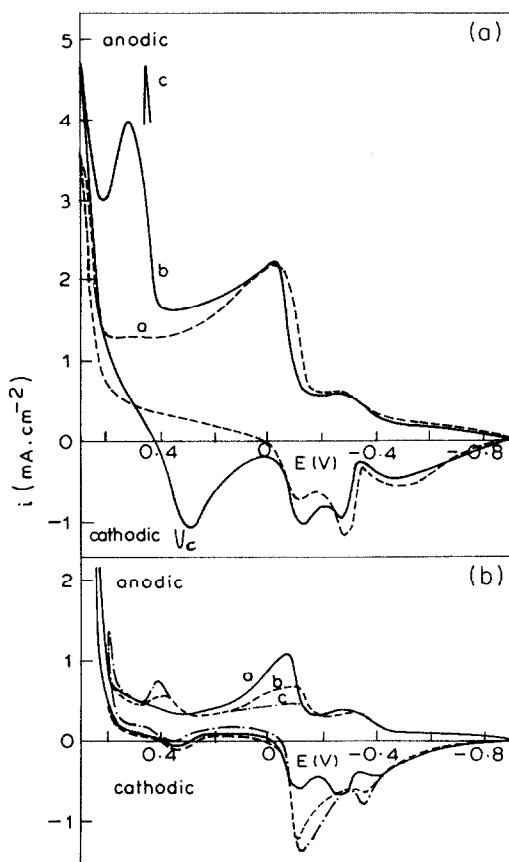

Fig. 3. (a) Cyclic voltammograms for (curve a) pure MnO$_2$ film compared with (curve b) that of the composite electrode Pt/MnO$_2$/Ni(OH)$_2$ (deposition times: MnO$_2$, 10 s; Ni(OH)$_2$, 5 s). Features of a pure Ni(OH)$_2$ electrode are marked c; (b) cyclic voltammogram of Pt/Ni(OH)$_2$/MnO$_2$ (deposition times: Ni(OH)$_2$, 30 s; MnO$_2$, 15 s) composite electrode; cycles 1, 5, and 10 are represented as curves a, b and c, respectively.

TABLE 2

Results of cyclic voltammetry measurements on composite electrodes

Electrode	Peak potentials[a]		E_{rev} (V)	$\Delta E_{a,c}$ (V)
	Anodic	Cathodic		
$Pt/MnO_2/Ni(OH)_2$	0.52	0.34	0.43	0.18
$Pt/Ni(OH)_2/MnO_2$	0.42	0.37	0.39	0.05
$Pt/MnO_2/Co(OH)_2$	0.29	0.10	0.19	0.19
$Pt/Co(OH)_2/MnO_2$				

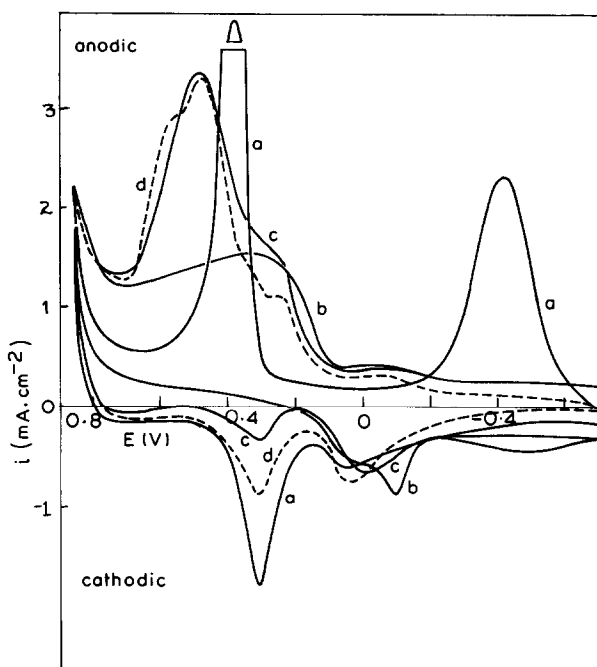[a]All potentials have been expressed in V with respect to a Hg/HgO (1 M KOH) reference electrode.

Fig. 4. Cyclic voltammogram of (curve a) pure $Co(OH)_2$ film compared with a $Pt/MnO_2/Co(OH)_2$ composite. Deposition times: MnO_2, 30 s; (curve b) $Co(OH)_2$, 7 s, (curve c) 15 s, and (curve d) 30 s.

growth in the peaks due to $Ni(OH)_2$. In the 10th cycle, clear peaks due nickel hydroxide can be discerned. These are shifted in a negative direction and the $\Delta E_{a,c}$ is also reduced compared with the value for a pure $Ni(OH)_2$ electrode (see Table 2). It is evident that the active nickel hydroxide species diffuses to the surface from the inner layer; the peak shifts suggest that it interacts with the outer MnO_2 layer as proposed by Belanger and Laperriere [9]. The nature of the interaction can be elicited only by a detailed solid-state approach to the problem.

Composite electrodes: Co–Mn system

The cyclic voltammograms of the composite $Pt/MnO_2/Co(OH)_2$ electrode, together with those of the pure constituents, are given in Fig. 4. Pure $Co(OH)_2$ shows two anodic peaks (curve a), the first is the irreversible oxidation of Co(II) to Co(III), the second is the quasi-reversible oxidation of Co(III) to Co(IV). When deposited on a layer of MnO_2, thin films (curve b) show no peaks at all. As the $Co(OH)_2$ layer is made thicker (curves c and d), the quasi-reversible reaction is observed, but the first anodic reaction is completely absent. This composite deserves further investigation as it appears to eliminate the troublesome irreversible reaction of $Co(OH)_2$.

When $Co(OH)_2$ is made the inner layer, no cobalt hydroxide reactions are observed, even on repeated cycling. This behaviour differs from that for the Ni counterpart.

Conclusions

1. Solid-solution electrodes of $Ni(OH)_2$ and $Co(OH)_2$ exhibit a lower E_{rev} and greater reversible characteristics compared with the parent materials. Especially promising is the electrode obtained from a bath containing a Ni/Co ratio of 40/60. Coprecipitation with $Mn(OH)_2$, however, does not affect the electrode reactions of either nickel or cobalt hydroxides.

2. In layer-by-layer deposited composite electrodes, MnO_2 affects substantially the redox reactions of nickel, as well as cobalt hydroxides. These effects are dependent upon whether MnO_2 is the inner or the outer layer.

3. The strong interaction observed between the components of the $Co(OH)_2$–$Ni(OH)_2$–MnO_2 system suggests that all these three electrode materials have a common electrode reaction mechanism.

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