Chapter-2

ELECTROCHEMICAL SYNTHESIS OF HYDROXIDES AND OXIDES

Abstract

Section-A

Cathodic reduction of aqueous metal nitrate solutions leads to the deposition of micrometer thick coatings of metal hydroxides. Heat treatment of the green hydroxide deposits results in the formation of adherent oxide coatings. In this Section, we discuss the synthesis of a number of oxides such as MgO, Co₃O₄ and RE₂O₃ (RE = Y, Dy, Eu). These oxides as well as their hydroxide precursors belong to different structure types showing that electrochemical deposition is a general method of fabrication of oxide coatings. The distinctive feature of all the precursor coatings is that they are macroporous with pore size in the micrometer range. The pores arise by the truncation of lamellar crystallites. The porosity is morphological rather than structural and is caused by aggressive gas evolution that takes place simultaneously with the deposition process at the cathode. The oxide coatings obtained by the thermal decomposition of the hydroxide precursors are also macroporous. The porosity is conserved as the pore size is larger than the diffusion length at the decomposition temperature.

Section-B

Ni(OH)₂ coatings with different thickness (0.54 nm and 1.2 nm) were electrodeposited on Pt coated quartz crystals from aqueous nickel nitrate solutions. The thickness of the coatings was monitored by using an electrochemical quartz crystal microbalance. The cyclic voltammetry of the as-deposited coatings were studied in a 1 M KOH solution. The $E^\circ$ value estimated by cyclic voltammetry is found to vary with the thickness of the deposit showing the effect of weak van der Waal's interaction on the electronic structure of nickel hydroxide. The results also show that thin coatings are electrochemically more reversible when compared to thick coatings.
Section-A

Electrochemical synthesis of macroporous oxide coatings on stainless steel substrates

2.1 Introduction

While cathodic electrodeposition of elemental metals and alloys from aqueous solutions of metal salts is widely practiced in science and industry, the electrodeposition of metal oxides is less well known. Zhitomirsky\textsuperscript{1} has reviewed the electrodeposition of metal oxides by the cathodic reduction of metal nitrate solutions. A hydrous oxide is generally deposited on the cathode as a micrometer thick X-ray amorphous coating.\textsuperscript{2-4} A brief heat treatment is given to crystallize the oxide.

Switzer\textsuperscript{5-6} has successfully deposited compositionally modulated Pb-Tl-oxide films, with a variable Pb:Tl ratio. The modulation length is in the nanometer range. Synthesis of nanoparticulate CeO\textsubscript{2} as a polycrystalline powder has also been reported by cathodic reduction.\textsuperscript{7}

The importance of oxides arises due to the wide range of electrical, magnetic, optical and other properties exhibited by them, by virtue of which, they find applications as catalysts, sensors, phosphors and optoelectronic devices. For instance, Co\textsubscript{3}O\textsubscript{4} besides being a magnetic material, is used as a catalyst for the evolution and reduction of molecular oxygen\textsuperscript{8} and hydrocarbon oxidation.\textsuperscript{9} It is also used as a material for super capacitor fabrication.\textsuperscript{10} MgO is useful for fixing atmospheric CO\textsubscript{2}\textsuperscript{11} and as a catalyst.\textsuperscript{12} A dense coating of Y\textsubscript{2}O\textsubscript{3} is transparent and can be used as an antireflecting device. It is also doped in Al\textsubscript{2}O\textsubscript{3}-based ceramics to increase the ductility.\textsuperscript{13} Rare earth oxides RE\textsubscript{2}O\textsubscript{3} [RE = Y, Dy, Eu and others] are used as phosphors.\textsuperscript{14} Dy\textsubscript{2}O\textsubscript{3} is a catalyst for the oxidative coupling of methane.\textsuperscript{15}

For these and many other applications, it is essential to obtain transition metal and rare earth oxides in the form of thin/thick films and coatings, as this geometry maximizes material utilization. Further, porous films with pores in the micrometer range, enhance the effective surface area.

Conventionally, oxide coatings are fabricated by such techniques as pulsed laser deposition,\textsuperscript{16} rf sputtering,\textsuperscript{17} ion/electron beam etching or chemical vapor deposition.\textsuperscript{18} These techniques need high vacuum and intense photon/ion/electron beam sources,
making them both capital and energy intensive. The thin films obtained are compact and if the substrate is single crystalline, the film is also single crystalline and oriented. Electrochemical deposition is a soft chemical alternative to these techniques, as the atom source is an aqueous solution, the deposition temperature is close to the ambient (< 100 °C) and the energy source is electric current.

In this section, we report the electrodeposition of a number of oxide coatings. These coatings are porous, with micrometer sized pores. The porosity is not structural, but morphological arising due to aggressive gas evolution that occurs simultaneously with the deposition process.

2.2 Experimental

All hydroxide coatings were made by cathodic reduction of the respective aqueous metal nitrate solutions. Co(NO₃)₂ and Mg(NO₃)₂ were procured from Merck, India and used as such to make standard solutions. Y(NO₃)₃, Dy(NO₃)₃, Eu(NO₃)₃ solutions were made by dissolving the respective metal oxides (S.d. fine Chem., India) in 2 M nitric acid and pH was adjusted to approximately 2 using sodium hydroxide pellets and diluted to the desired molarity. All the solutions were prepared using ion-exchanged Type-I water (Milli-Q Academic water purification system, specific resistance 18.2 megaohm cm).

Stainless steel flags (SS 304, area 4.5 cm²) were used as cathodes and a Pt mesh (28 cm² geometric area) was used as counter electrode. The depositions were carried out galvanostatically (current density 1-5 mA cm⁻²) using a EG&G (PARC) Model Versastat IIA Galvanostat/Potentiostat. The deposition potentials were measured with respect to a saturated calomel electrode.

After deposition, the coatings were rinsed with water and dried at 65 °C. The stainless steel flags were weighed before and after deposition to monitor the mass of the deposit. Using density data, the approximate thickness of the deposit was estimated. Prior to electrodeposition, the stainless steel flags were cleaned with detergent and then electrochemically cleaned by polarizing them anodically (30 s) and then cathodically (30 s) in 1 M KOH solution, and again anodically (30 s) in 1 M HCl acid (current density 20 mA cm⁻²).
The as-prepared coatings were those of the corresponding metal hydroxides. The hydroxides were scraped and subjected to thermogravimetric analysis (TGA) (Metler Toledo TG/sDTA Model 851\textsuperscript{e} driven by Star\textsuperscript{e} software, heating rate 5 °C min\textsuperscript{−1}, ambient air) to determine the decomposition temperature. Freshly prepared hydroxide coatings were then thermally decomposed in a muffle furnace at different temperatures as indicated by the TGA data. In Table 1 are listed the deposition conditions and the decomposition temperatures employed for different oxide coatings. These temperatures were selected to get completely phase formed, crystalline and adherent coatings of metal oxides.

All coatings were characterized by X-ray diffraction by mounting the electrode directly on a Bruker aXS Model D8 Advance powder X-ray diffractometer (Cu Ka source $\lambda = 1.541$ Å). IR spectra were recorded using a Nicolet Model Impact 400D FTIR spectrometer (KBr pellets, resolution 4 cm\textsuperscript{−1}). The particle morphologies were studied using a scanning electron microscope (JEOL Model JSM 6490 LV, operating voltage 15 kV) by mounting a small piece of the coated electrode on conducting carbon tape and sputter coating with Pt to improve conductivity.

### 2.3 Results and Discussion

Cathodic reduction of aqueous metal nitrate solutions leads to an increase in the pH near the working electrode. This is known as electrogeneration of base.\textsuperscript{19} The most important reactions responsible for electrogeneration of base are the nitrate reduction reactions:

\[
\text{NO}_3^- + \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{NO}_2^- + 2 \text{OH}^- \quad E^\circ = 0.01 \text{ V} \tag{1}
\]

\[
\text{NO}_3^- + 7 \text{H}_2\text{O} + 8 \text{e}^- \rightarrow \text{NH}_4^+ + 10 \text{OH}^- \tag{2}
\]

These reactions lead to the formation of metal hydroxides and hydroxynitrate coatings as:

\[
\text{M}^{n+} + n \text{OH}^- \rightarrow \text{M(OH)}_n \downarrow \tag{3}
\]

\[
\text{M}^{n+} + (n-x) \text{OH}^- + x (\text{NO}_3^-) \rightarrow [\text{M(OH)}_{n-x}(\text{NO}_3)_x] \downarrow \tag{4}
\]

Cathodic reduction of aqueous cobalt nitrate solution yields $\alpha$-cobalt hydroxide (see Fig. 2.1a for the PXRD pattern of $\alpha$-cobalt hydroxide). The formation of $\alpha$-cobalt hydroxide
is also reported by Gupta and coworkers,\textsuperscript{20} who electrodeposited the material potentiostatically.

Table 2.1 Synthetic conditions employed for the deposition of different oxide coatings.

<table>
<thead>
<tr>
<th>Bath</th>
<th>Molarity (M)</th>
<th>Current Density (mA/cm(^2))</th>
<th>Cell Potential (V)</th>
<th>Time (Min.)</th>
<th>Mass of Hydroxide Coating* (mg)</th>
<th>Thickness of Oxide Coating (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co(NO(_3))(_2)</td>
<td>0.1</td>
<td>1</td>
<td>-0.81</td>
<td>15</td>
<td>2.7 (2.2)</td>
<td>0.8</td>
</tr>
<tr>
<td>Mg(NO(_3))(_2)</td>
<td>0.1</td>
<td>5</td>
<td>-1.28</td>
<td>30</td>
<td>8.3 (5.7)</td>
<td>3.5</td>
</tr>
<tr>
<td>Y(NO(_3))(_3)</td>
<td>0.01</td>
<td>1</td>
<td>-1.01</td>
<td>30</td>
<td>5.6 (3.7)</td>
<td>1.64</td>
</tr>
<tr>
<td>Dy(NO(_3))(_3)</td>
<td>0.01</td>
<td>1</td>
<td>-0.97</td>
<td>45</td>
<td>8.8 (6.8)</td>
<td>1.93</td>
</tr>
<tr>
<td>Eu(NO(_3))(_3)</td>
<td>0.01</td>
<td>1</td>
<td>-1.04</td>
<td>45</td>
<td>7.4 (5.5)</td>
<td>1.65</td>
</tr>
</tbody>
</table>

*Values in parentheses correspond to the mass of the oxide coatings (mg) obtained by heat treatment at 700°C.
Fig. 2.1 XRD patterns of (a) pristine $\alpha$-Co(OH)$_2$, (b) (a) heat treated at 350°C and (c) (a) heat treated at 700°C. Features marked by the asterisk correspond to stainless steel.
Cathodic reduction of aqueous magnesium nitrate solution yields a thick magnesium hydroxide coating (see Fig. 2.2a). The observed Bragg reflections match with that of the JCPDS (PDF: 7-238) standard.

![XRD patterns](image)

Fig. 2.2 XRD patterns of (a) Mg(OH)\(_2\) and (b) MgO. Features marked by the asterisk correspond to stainless steel.
Cathodic reduction of aqueous solutions of rare earth nitrates yields hydroxy nitrates and X-ray amorphous products (see Fig. 2.3). IR spectra of all these coatings show the OH stretching vibration around 3475 cm\(^{-1}\) and vibrations due to intercalated/adsorbed nitrate around 1385 cm\(^{-1}\) (data not shown). No attempt was made to either synthesize pure metal hydroxides or to further characterize the pristine products.

![XRD Patterns](image)

**Fig. 2.3** XRD patterns of (a) Y(OH)\(_3\), (b) Dy(OH)\(_3\) and (c) Eu(OH)\(_3\).
However on decomposition, all as-prepared coatings yielded oxide products. All the decomposed products were crystalline and characterized by PXRD. The observed Bragg reflections were compared with those reported for the corresponding JCPDS standards. TGA of the pristine cobalt hydroxide yields a decomposition temperature 220°C. The cobalt hydroxide coatings were therefore decomposed at two different temperatures: 350°C and 700°C. Decomposition at these temperatures yields monophasic cobalt oxide, Co₃O₄ [see Fig. 2.1(b,c)]. The observed pattern matches with the standard pattern of Co₃O₄ [PDF: 9-418].

Magnesium hydroxide was decomposed at 700°C; this high temperature was selected to complete the transformation of magnesium hydroxide to magnesium oxide (see Fig. 2.2b). The observed pattern matches with the standard pattern of MgO [PDF: 45-946]. All rare earth hydroxides were decomposed at 700°C to get completely phase formed, crystalline and adherent oxide coatings. Hydroxides of Y, Dy and Eu yield Y₂O₃, Dy₂O₃ and Eu₂O₃ respectively and were characterized by PXRD (see Fig. 2.4). The observed patterns match with the standard patterns of Y₂O₃ [PDF: 25-1200], Dy₂O₃ [PDF: 86-1327] and Eu₂O₃ [PDF: 34-392].

Typical SEM images of the bare stainless steel electrodes after electrochemical cleaning have been published elsewhere. The surface exhibits sub-millimeter scratches. The SEM image of the pristine Co(OH)₂ coating (see Fig. 2.5a) shows that the substrate is fully covered over and has a porous structure. The pores are funnel shaped with the mouth widening towards the outer surface of the coating. The walls of the funnel comprise nanostructured sheets growing outwards from the substrate surface. In earlier papers, the sheet morphology was attributed to the lamellar structure of cobalt hydroxide. Co(OH)₂ comprises a stacking of charge neutral slabs having the composition [Co(OH)₂]. The structure is that of mineral brucite, Mg(OH)₂. The intralayer bonding is strong ionocovalent, while the interlayer bonding is weak van der Waals type. Crystallites of such layered solids are known to grow in the form of platelets. In the present case the sheets fold over themselves to enclose pores.

On decomposition at 350°C, cobalt hydroxide oxidatively decomposes to yield Co₃O₄ as:

\[ 3\text{Co(OH)}_2 + \text{O} \rightarrow \text{Co}_3\text{O}_4 + 3\text{H}_2\text{O} \]  \hspace{1cm} (5)
Fig. 2.4 XRD patterns of (a) Y₂O₃, (b) Dy₂O₃, and (c) Eu₂O₃. Features marked by the asterisk correspond to stainless steel.
Co$_3$O$_4$ crystallizes in the cubic structure, with a rhomboidal morphology. In the present case however, the Co$_3$O$_4$ coating retains the same porous morphology as that of the precursor hydroxide (see Fig. 2.5b). Since Co$_3$O$_4$ is a 3-D structure, the observed sheet-like morphology is not attributable to its crystal structure. The porous morphology is conserved even when the decomposition is carried out at 700°C, although the PXRD pattern shows a narrowing of peaks due to crystal growth and sintering.

The SEM micrographs of the precursor Mg(OH)$_2$ coating and MgO are shown in Fig. 2.6. The film comprises sheets with rounded edges and in this case the sheets grow parallel to the substrate. The sheets are deposited layer over layer. On decomposition, the sheet morphology is conserved, but the loss of 31.3% mass has caused shrinkage of the sheets which are frayed at the edges. Smaller sub-micron pores emerge on the sheets, showing a hierarchy of porosity in the MgO coating. This sheet like morphology is in contrast to the dense morphology observed for MgO, made by other methods.

![SEM images](image_url)

**Fig. 2.5 SEM images of (a) pristine and (b) heat-treated $\alpha$-Co(OH)$_2$.**
Fig. 2.6 SEM images of (a) Mg(OH)$_2$ and (b) MgO.

The SEM micrographs of RE(OH)$_3$ and RE$_2$O$_3$ (RE = Y, Dy) are shown in Fig. 2.7. In this case also the Y(OH)$_3$ coating comprises a porous structure. The pores are funnel shaped with the mouth widening outwards. The pores are formed between adjacent sheets. The sheets are nanostructured. The decomposed product, Y$_2$O$_3$ retains the same morphology. This morphology is different from the morphology of the material, reported by other authors by electrogeneration of base method.$^{25}$ The SEM micrograph of Dy(OH)$_3$ is shown in Fig. 2.7(c). The morphology of this material is similar to the morphology of Y(OH)$_3$. In this case also decomposed product, Dy$_2$O$_3$ conserved the morphology of the precursor, as shown in Fig. 2.7(d). The SEM micrographs of Eu(OH)$_3$ and Eu$_2$O$_3$ are shown in the Fig. 2.8. The hydroxide film comprises stacks of compactly arranged sheets. These compactly arranged bunches of sheets, from different directions meet to form pores, these sheets are nanostructured. The decomposed product, Eu$_2$O$_3$ retains the same morphology. This morphology is similar to that reported for electrodeposited CeO$_2$.$^{26}$ Eu$_2$O$_3$ obtained by the oxidation of a freshly electrodeposited Eu metal coating has a granular morphology.$^{27}$
Fig. 2.7 SEM images of (a, c) RE(OH)₃ and (b, d) RE₂O₃. (a) and (b) correspond to Y, (c) and (d) correspond to Dy.
Fig. 2.8 SEM images of (a, c) Eu(OH)$_3$ and (b, d) Eu$_2$O$_3$. 
The hydroxide precursors as well as the oxides investigated in this study belong to different structure types. While the bivalent hydroxides have a layered structure, the rare earth hydroxides crystallize in the UCl₃ structure, where the atoms are bonded along all the three dimensions. Therefore the origin of lamellar morphology which is seen in all the hydroxide precursors is not structural. These results suggest that the lamellar morphology is characteristic of electrochemical synthesis. This also explains why an oxide such as CeO₂ having the fluorite structure also deposits as a macroporous coating.²⁶ During cathodic reduction, the deposition potentials (see Table 2.1) are high enough to cause the electrolysis of water.

\[ 2 \text{H}_2\text{O} + 2 e^- \rightarrow \text{H}_2 \uparrow + 2 \text{OH}^- \quad E^o = -0.828 \text{ V} \]  \hspace{2cm} (6)

Further, given the acidic pH of the metal nitrate solutions, the hydrogen evolution reaction (HER) also takes place.

\[ 2 \text{H}^+ + 2 e^- \rightarrow \text{H}_2 \uparrow \quad E^o = 0.0 \text{ V} \]  \hspace{2cm} (7)

These reactions in fact contribute in greater measure to electrogeneration of base than even nitrate reduction.²⁸ Gas evolution generates porosity in the coating. This porosity is morphological and the pores are on the micrometer length scale. Thermal treatment causes the hydroxides to decompose to their corresponding oxides. There is a large mass loss during the decomposition. In bulk decomposition reactions, mass loss causes volume shrinkage, elimination of pores and sintering, leading to particles of larger grain size. However in the present case, the lamellar morphology and porosity of the precursor phase is conserved. This is because the length scale of the pores exceeds the diffusion length at the temperature employed. Further, bonding with the substrate might also limit the diffusion length. Thereby although, none of the oxides reported here have a layered structure, all the oxide coatings reported here have a lamellar morphology.

### 2.4 Conclusions

In conclusion, electrochemical synthesis is a general method of fabrication of metal hydroxide/hydroxide-nitrate coatings. These coatings have a porous structure. The micron-sized pores are morphological and are formed by the assembly of lamellar crystallites. The pores are generated an account of aggressive gas evolution during
electrodeposition. During decomposition of the hydroxides into the product oxides, the lamellar morphology of the particles and the pore structure of the coatings is conserved. The pores are retained on decomposition and thermal treatment as the temperature induced diffusion lengths are much smaller than the pore size. Electrosynthesis thus provides a convenient route to the fabrication of macroporous oxide coatings.
References


Section-B

Thicknes dependent cyclic voltammetry study of Ni(OH)$_2$ coatings obtained by electrodeposition

2.5 Introduction

Synthesis of thin, thick films of inorganic materials on variety of substrates finds great importance because of their wide applications. For instance the thin films of Ni(OH)$_2$ and its oxide product find many applications as positive electrodes in alkaline secondary batteries$^1$ and metal hydride batteries,$^2$ sensors for biomolecules,$^3$ super capacitors,$^4$ electrochromic coatings$^5$ and catalysts for the oxidation of alcohols.$^6$

Ni(OH)$_2$ crystallizes in two polymorphic modifications $\beta$ and $\alpha$-Ni(OH)$_2$. $\beta$-Ni(OH)$_2$ is isostuctural with mineral brucite, Mg(OH)$_2$ and $\alpha$-Ni(OH)$_2$ is a hydroxyl deficient phase having the composition Ni(OH)$_{2-x}(A^{n-})_{x/2}\cdot yH_2O$ ($A^{n-} = NO_3^-, CO_3^{2-}, SO_4^{2-}$ and others). The anions are intercalated in the interlayer. In this type of materials the hydroxyl ions are hexagonally close packed and metal ions occupy alternative layers of octahedral sites and bonding within the layer is iono-covalent and the adjacent layers are held together by weak van der Waals forces.$^7$

$\beta$-Ni(OH)$_2$ is a thermodynamically stable form whereas $\alpha$-Ni(OH)$_2$ transforms to $\beta$-Ni(OH)$_2$ in alkaline conditions.$^8$ Several chemical methods have been reported in the literature to stabilize the $\alpha$-Ni(OH)$_2$.$^9$-$^{11}$ The need for stabilizing alpha form arises due to its better electrochemical activity.$^{12}$ There are several reports where they have used electrodeposition technique to synthesize $\alpha$-Ni(OH)$_2$ and it was observed that the electrochemically synthesized product shows better activity than the chemically synthesized form.$^{13}$-$^{16}$ This is because the electrochemically synthesized products are highly disordered and disordered products show better activity than ordered products.$^{17}$

In this Section, we report the electrodeposition of nickel hydroxide coatings with different thickness (0.54 nm and 1.2 nm) on Pt coated quartz crystal from aqueous nickel nitrate solutions. The thickness of the coatings was monitored by using an electrochemical quartz crystal microbalance. The cyclic voltammograms of the as-deposited coatings were studied in 1 M KOH solution. The E° value estimated by cyclic voltammetry is found to vary with the thickness of the deposit showing the effect of weak
van der Waal’s interaction on the electronic structure of nickel hydroxide. The results also show that thin coatings are electrochemically more reversible when compared to thick coatings.

2.6 Experimental

All the Ni(OH)$_2$ coatings were obtained by cathodic reduction of Ni(NO$_3$)$_2$ solution. A platinum coated quartz crystal was used as cathode and platinum wire was used as counter electrode. Prior to electrodeposition, the working electrode was cleaned with dilute nitric acid and washed with water. The depositions were carried out galvanostatically (current 0.1 mA, t 30-60 s) using CHI Model 408A galvanostat/potentiostat. The deposition potential was measured with respect to Ag/AgCl electrode. The thickness of the coatings was controlled by using electrochemical quartz crystal microbalance (Model 400A) in situ. After deposition the coatings were rinsed with water and dried at 65°C. All the solutions used for electrodeposition were prepared using Type-I water (Milli-Q Academic water purification system, specific resistance 18.2 megaohm cm).

Cyclic voltammetry of all the coatings was carried out in 1 M KOH solution in a EQCM cell using a Ag/AgCl reference electrode. All the coatings were characterized using IR spectroscopy (Bruker Alpha-T FTIR spectrometer, diamond crystal ATR mode, resolution 4 cm$^{-1}$, 400-4000 cm$^{-1}$).

2.7 Results and Discussions

The polymorphic modifications of nickel hydroxide can be identified by using IR spectroscopy. The IR spectrum of the as-deposited coating (Fig. 2.9) exhibits a broad band around 3500 cm$^{-1}$ corresponding to hydrogen bonded OH group and absorptions in the 1000-1500 cm$^{-1}$ region corresponding to intercalated NO$_3^{-}$. The absorptions at 640-470 cm$^{-1}$ due to the Ni-O-H bending and Ni-O stretching vibrations provide additional evidence for the formation of nickel hydroxide.

Thickness of the nickel hydroxide coatings were monitored using electrochemical quartz crystal microbalance. The microbalance is based on a quartz crystal wafer, which is sandwiched between two electrodes, used to induce an electric field. Such a field
produces a mechanical oscillation in the bulk of the wafer. Surface reactions involving minor mass changes can cause perturbations of the resonant frequency of the crystal oscillator. As the deposition takes place the vibration frequency decreases (see Fig. 2.10 for a typical frequency Vs time plot). For the deposition of 1.4 ng the change in frequency is 1.0 Hz. By using this relation the weight of the deposit is calculated. Knowing the area of the electrode and density of α-nickel hydroxide, the thickness of the coatings has been estimated.

Fig. 2.9 IR spectra of the as-deposited nickel hydroxide coating.
Fig. 2.10 Change in frequency versus time plot of nickel hydroxide deposition.

The cyclic voltammograms of a coating obtained at 30 second deposition time are shown in Fig. 2.11. The CV of the as-deposited coating was obtained at various scan rates ranging from 20-200 mV/sec. The anodic peaks are due to oxidation of nickel hydroxide to nickel oxyhydroxide. As the scan rate increases, there is a small shift in the peak potentials. The characteristic cyclic voltammetric parameters obtained from Fig. 2.11 are shown in Fig. 2.12 as a function of scan rate.
Fig. 2.11 Cyclic voltammograms of the nickel hydroxide coating obtained at 30 sec deposition time.

Fig. 2.12 Characteristic cyclic voltammetric parameters obtained from Fig. 2.11.
The cyclic voltammograms of the coating obtained at 60 s deposition time are shown in Fig. 2.13. As the scan rate increases, there is a large shift in cathodic (towards negative potential) and anodic (towards positive potential) peak potentials, compared to 30 second coating. The characteristic cyclic voltammetric parameters obtained from Fig. 2.13 are shown in Fig. 2.14 as a function of scan rate.

Fig. 2.13 Cyclic voltammograms of the nickel hydroxide coating obtained at 60 sec deposition time.
Fig. 2.14 Characteristic cyclic voltammetric parameters obtained from Fig. 2.13.

In order to compare the effect of thickness on electronic properties of the nickel hydroxide coatings, the results of the cyclic voltammetric study are listed in Table 2.2. The average peak potential $E_{\text{rev}}$ is taken as an estimate of the reversible potential $E^0$ and the difference in the anodic and cathodic peak potentials, $\Delta E_{a,c}$, is taken as an estimate of the reversibility of the reaction.

The $E_{\text{rev}}$ of nickel hydroxide coating obtained at 30 second deposition time varies from 360 to 382 mV and $\Delta E_{a,c}$ varies from 66 to 104 mV with respect to scan rate. For the coating obtained at 60 second deposition time the variations are from 336 to 354 mV ($E_{\text{rev}}$) and from 95 to 192 mV ($\Delta E_{a,c}$) (Table 2.2) respectively. These observations show that the reversible potential ($E_{\text{rev}}$) of the coating decreases as the thickness of the coating increases and the difference in peak potential ($\Delta E_{a,c}$) increases with increase in the thickness of the coating. These results show that the redox reaction of thin nickel hydroxide coatings are associated with a greater energy and is more reversible in thin (30 second deposition time) films than the thick films (60 second deposition time).
Table 2.2 $E_{rev}$ and $\Delta E_{a,c}$ of nickel hydroxide coatings obtained at different deposition times.

<table>
<thead>
<tr>
<th>Scan rate (mV/Sec)</th>
<th>Deposition Time 30 sec</th>
<th>Deposition Time 60 sec</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{rev} = (Ea+Ec)/2$ (mV)</td>
<td>$\Delta E = Ea-Ec$ (mV)</td>
</tr>
<tr>
<td>20</td>
<td>360.0</td>
<td>66.0</td>
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<tr>
<td>40</td>
<td>365.5</td>
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</tr>
<tr>
<td>200</td>
<td>382.0</td>
<td>104.0</td>
</tr>
</tbody>
</table>
2.8 Conclusions

In this study thin films of nickel hydroxide have been made on Pt electrodes. The two films comprise respectively one layer and two layers of nickel hydroxide. The redox chemistry of nickel hydroxide comprises the reversible oxidation of Ni$^{2+}$ [Ni(OH)$_2$] to Ni$^{3+}$ [NiO(OH)]. The end phases of the redox cycle are isostructural and the redox reaction takes by the topotactic deintercalation of a proton from the interlayer gallery. During this process, a considerable increase in the electronic conductivity of the material is observed. The oxidation process is therefore interpreted in terms of a transfer of an electron from the valence band to the conduction band of nickel hydroxide. In this sense, the $E_{\text{rev}}$ obtained by cyclic voltammetry is interpretable as reflecting the magnitude of the band gap of nickel hydroxide. The two-monolayer film has $E_{\text{rev}}$ nearly 22-28 mV lower than that of the one-monolayer film. This lowering in the $E_{\text{rev}}$ value is consistently seen at all scan rates. This observation is significant, in that the bonding between successive monolayers of nickel hydroxide is weak van der Waals. These observations indicate the effect of weak van der Waal’s interaction on the electronic structure of nickel hydroxide. These conclusions have some conceptual flaws in that the cyclic voltammograms do not reflect a reversible redox chemistry. The observed signals can at best be indicative of a quasi-reversible reaction. There are some pitfalls in equating the measured $E_{\text{rev}}$ with the standard reversible potential, $E^\circ$. 
References