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The Effect of Current and Nickel Nitrate Concentration on the Deposition of Nickel Hydroxide Films

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ABSTRACT

An electrochemical quartz crystal nanobalance (EQCN) has been utilized to measure the mass of Ni(OH)₂ films electrochemically deposited from Ni(NO₃)₂ solutions. The objective of this work was to quantify electrochemical deposition as a function of deposition conditions. The changing mass recorded on the EQCN was demonstrated to be the result of Ni(OH)₂ deposition. Deposited mass was observed to increase proportionally with applied charge as suggested by previous investigators. Most significantly, the rate of deposition was found to decrease more than an order of magnitude as the Ni(NO₃)₂ concentration increased from 0.2 to 2.0M. The effect of concentration is shown to be related to Ni(II) concentration as opposed to solution pH or NO₃⁻ concentration. An empirical correlation is given to predict deposition rates in solutions ranging from 0.1 to 3.0M Ni(NO₃)₂ and at current densities ranging from 0.5 to 5.0 mA/cm². The decreased deposition rates in concentrated Ni(NO₃)₂ are attributed to the formation of intermediate species [e.g., NiOH⁺ or Ni₄(OH)₆] which diffuse away from the reaction interface before deposition can occur.

Introduction

Nickel hydroxide is one of the most commonly used active materials for the positive electrode in rechargeable batteries. It has been shown that the electrochemical impregnation of porous nickel plaques produces superior electrodes compared to those made by the conventional loading process (see Gross for a review of electrochemical impregnation¹). The ability to tightly control the operating conditions of the deposition process is one reason for superior performance. In electrochemical impregnation, a nickel plaque is cathodically polarized in a nickel nitrate solution. Nitrate is reduced according to the following reaction²⁻⁴

\[ \text{NO}_3^- + 8\text{H}_2\text{O} + 8e^- \rightarrow 2\text{OH}^- + 2\text{OH}_2^- + 6\text{H}_2\text{O} \]  

Other reactions have been shown to occur, but like the above reaction they also produce OH⁻ ions in approximately a 1:1 ratio of e⁻ to OH⁻. The production of OH⁻ increases the local pH, resulting in the precipitation of Ni(OH)₂.

\[ \text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 \downarrow \]  

where \( \log K_{sp} = -13.79 \).

References

In order to quantify electrochemical impregnation, Ho and Jorne\textsuperscript{6} modeled the impregnation process under various flow configurations. However, since the mechanism for deposition is not well understood, a quantitative relationship between deposition conditions (e.g., current, time, solution composition) and the mass deposited is not available. While numerous investigators have studied plaque impregnation,\textsuperscript{11-14} relatively few have quantified the fundamental deposition chemistry using planar electrodes. Further\textsuperscript{15} studied the kinetics of Ni(OH)\textsubscript{2} formation at the surface of a rotating-disk electrode as a function of current density, solution composition, and the thickness of the diffusion layer. MacArthur\textsuperscript{16} studied the thickness of deposited films as a necessary first step in determining the diffusion coefficient of protons. He used Faraday's law to predict film thickness as a function of current and deposition time, but provided no experimental verification of film thickness other than electrochemical capacity. It will be shown in this study that MacArthur's assumption was good only at low Ni(NO\textsubscript{3})\textsubscript{2} concentrations. At high concentrations, film thickness is overestimated by more than an order of magnitude using Faraday's law. Corrigan et al.\textsuperscript{8,13-16} have correlated various deposition conditions [all in 0.1M Ni(NO\textsubscript{3})\textsubscript{2}] to film thickness on planar electrodes but have not quantitatively related deposition conditions to deposited thickness.

A few researchers have reported on the utilization of the quartz crystal microbalance to study the mass changes in nickel hydroxide films.\textsuperscript{17-19} Of particular interest, Contreras-Torresi et al.\textsuperscript{18} observed that the mass increased approximately linearly with time (up to 250 s) during galvanostatic deposition of a Ni(OH)\textsubscript{2} film at 0.3 mA/cm\textsuperscript{2} from a 0.01M Ni(NO\textsubscript{3})\textsubscript{2} solution. Assuming a ratio of 10 OH\textsuperscript{-}:8 e\textsuperscript{-} in the reduction of NO\textsubscript{3}\textsuperscript{-} (see also Ref. 13-18), they calculated a deposition efficiency equal to 86%.

The objective of this study has been to use the electrochemical quartz crystal nanobalance (EQCN) to quantify the electrochemical deposition of Ni(OH)\textsubscript{2} films as a function of operating conditions (e.g., time, current, solution concentration). The sensitivity of the EQCN is 1 nanogram, allowing precise in situ mass measurements. Quantifying the deposited mass is of interest for several reasons. First, the capacity is needed in order to correlate experimental discharge data with cell discharge models.\textsuperscript{20} Second, accurate determinations of mass, and subsequently film thickness, are needed in order to calculate the diffusion coefficient from electrochemical impedance spectroscopy data.\textsuperscript{21} Finally, our goal has been to better describe the deposition process on planar electrodes so that impregnation of porous plaques may be more thoroughly and fundamentally modeled.  

Experimental

An electrochemical quartz crystal nanobalance (EQCN, Elchema Model EQCN-501) was utilized to make in situ measurements of the mass deposited on a planar gold electrode during chronic chronopotentiometry in nickel nitrate solutions. An illustration of the EQCN cell configuration can be seen in Fig. 1. As shown, the working electrode consists of a quartz crystal with a thin layer of gold sputtered on both sides. The electrode area exposed to solution is 0.2 cm\textsuperscript{2}. The resonant frequency of the EQCN is 1 nanogram, allowing precise in situ mass measurements. Quantifying the deposited mass is of interest for several reasons. First, the capacity is needed in order to correlate experimental discharge data with cell discharge models.\textsuperscript{20} Second, accurate determinations of mass, and subsequently film thickness, are needed in order to calculate the diffusion coefficient from electrochemical impedance spectroscopy data.\textsuperscript{21} Finally, our goal has been to better describe the deposition process on planar electrodes so that impregnation of porous plaques may be more thoroughly and fundamentally modeled.

Depositions were carried out in Ni(NO\textsubscript{3})\textsubscript{2} solutions, whose concentrations ranged from 0.1 to 3.0M at applied current values ranging from 0.01 to 1.0 mA. For solution concentrations below 0.2M Ni(NO\textsubscript{3})\textsubscript{2}, additional NaNO\textsubscript{3} was added such that the NO\textsubscript{3}\textsuperscript{-} concentration was 0.4M. All solutions consisted of 50/50 volume percent (v/v) ethanol and water.\textsuperscript{3,34} All depositions were carried out at room temperature (23 to 35°C) in order that the fundamental deposition chemistry might be more readily understood. The solution pH was found to be a function of Ni(NO\textsubscript{3})\textsubscript{2} concentration, ranging from 2.4 for 2.0M solution to 4.0 for 0.1M solution. In order to determine the effect of pH on deposition rate a solution containing 0.2M Ni(NO\textsubscript{3})\textsubscript{2} was basified to pH 4.0 using concentrated KOH. Depositions were carried out in these solutions at an applied current of 0.5 mA and the data compared to that for the nonacidified or basified solutions. Additional depositions were carried out in solutions saturated in NO\textsubscript{3}\textsuperscript{-} (obtained by adding excess NaNO\textsubscript{3}) to determine the role of NO\textsubscript{3}\textsuperscript{-} in deposition.

Finally, in order to ensure that the EQCN measured Ni(OH)\textsubscript{2} deposition, and not the deposition of metallic Ni, selected films were cycled and discharged in 3% KOH. The cyclic voltammograms were checked for the charge and discharge peaks characteristic of the Ni(OH)\textsubscript{2}/NiOOH system. Further, the discharged capacity was converted to mass via Faraday's law assuring a one-electron transfer.\textsuperscript{2} These were compared to the masses recorded on the EQCN.

Results and Discussion

The cyclic voltammetry behavior of a 30 µg film deposited in the EQCN is illustrated in Fig. 2a (scan rate 10 mAs\textsuperscript{-1}). The characteristic charge and discharge peaks are readily observed indicating the presence of the Ni(OH)\textsubscript{2}/NiOOH couple. The discharge behavior of the film at a constant current of 10 µA is shown in Fig. 2b. The charge passed during the galvanostatic discharge of the film is consistent with a 30 µg film, assuming a one-electron discharge process.\textsuperscript{2} In every case in which a deposited film was cycled and discharged, cyclic voltammograms and charge-discharge times were consistent with the mass determined via the EQCN. The physical appearance of the deposit provided further evidence for the deposition of Ni(OH)\textsubscript{2}. The freshly deposited films were transparent and green, giving the QCN crystal a greenish gold appearance. A Ni deposit would be expected to appear metallic. With charging the films became black, consistent with the formation of NiOOH from Ni(OH)\textsubscript{2}.

A plot of mass vs. time for deposition at 0.2M Ni(NO\textsubscript{3})\textsubscript{2} at applied currents of 0.05, 0.1, 0.25, and 0.5 mA (0.25, 0.5, 1.25, and 2.5 mA/cm\textsuperscript{2}) is shown in Fig. 3. (The mass vs. time curves given in this paper are reproducible within a relative error of 5%.) The mass of the deposit increased linearly with time (with regression values, R\textsuperscript{2}, consistently greater than 0.999) indicating a constant rate of deposition. Lin-
early increasing mass was observed at all deposition conditions with the exception of very low solution concentrations at high currents (e.g., 0.01 M at 0.5 mA). Deposition in dilute Ni(NO₃)₂ solutions is discussed later in this paper. The effect of applied current can also be observed in Fig. 3. Increasing current was observed to increase the deposition rate as indicated by the increasing slopes in the figure.

The effect of applied current is seen more clearly in Fig. 4 which is a plot of deposition rate vs. applied current in 0.2 M Ni(NO₃)₂. The deposition rate increases proportionally with current over two orders of magnitude of current values (0.01 to 1.0 mA).

Note that increasing rate of deposition (slope of the mass-time curve) increases with decreasing Ni(NO₃)₂ concentration. The deposition rates at each concentration are indicated on the figure. Similar behavior (increasing rate with decreasing concentration) was observed at other current values (0.1, 0.25, and 1.0 mA).

In order to separate the effect of Ni(II) and NO₃⁻ at high Ni(NO₃)₂ concentrations, deposition was measured in 0.2 M Ni(NO₃)₂ saturated with NaNO₃. Mass vs. time in a 0.5 mA deposition is compared with that in 2.0 M Ni(NO₃)₂ in Fig. 6. The deposition rate for the solution saturated in NO₃⁻ is approximately 75% of that in 0.2 M Ni(NO₃)₂, indicating that the deposition rate is more dependent on the Ni(II) concentration than on the NO₃⁻ concentration. The 25% decrease in rate resulting from saturated NO₃⁻ may be an ionic strength effect.

The role of solution pH was also considered. Deposited mass was measured in 0.2 M Ni(NO₃)₂, acidified to pH 3.0, 2.5, 2.0, and 1.5 and in 2.0 M Ni(NO₃)₂ basified to pH 4.0.
The effect of pH in 0.2M Ni(NO₃)₂ is shown in Fig. 7. Acidification to pHs of 3.0, 2.5, and 2.0 decreases the deposition rate by less than 10%. Not until the pH was lowered to 1.5 was the deposition rate significantly diminished. However, even at that low pH the deposition rate was nearly an order of magnitude greater than that in 2.0M Ni(NO₃)₂ (in which the pH is approximately 2.4). Regarding the 2.0M Ni(NO₃)₂ solution, increasing the pH to 4.0 did not change the rate of deposition as shown in Fig. 8. Based upon the results shown in Fig. 7 and 8 it can be concluded that the rate of Ni(OH)₂ deposition is nearly independent of pH in the typical pH range of these solutions (pH 2 to 5) and that the concentration effects observed are not the result of pH.

The relationship between deposition rate at an applied current of 0.5 mA and Ni(NO₃)₂ concentration is illustrated in Fig. 9, which plots the deposition rate with respect to the inverse of concentration. It can be seen in Fig. 9 that at low Ni(NO₃)₂ concentrations (0.2 and, especially, 0.1M) nearly 100% of the generated OH⁻ is consumed in the deposition of Ni(OH)₂. However, at higher Ni(NO₃)₂ concentrations the efficiency of OH⁻ utilization decreases dramatically (to less than 20% at solution concentrations greater than 1.0M). Further, at high concentrations the rate of deposition is shown to be linearly related to the inverse of the solution concentration (with a regression value, R², of 0.997). This type of behavior was observed over a range of one order of magnitude of current (0.1 to 1.0 mA).

The data at different applied currents can be normalized by plotting the utilization efficiency of the electrochemically generated OH⁻ vs. inverse concentration as illustrated in Fig. 10. Note that the efficiency of utilization, while increasing slightly with current, is relatively independent of the deposition current. At all currents the utilization is highly inefficient in concentrated solutions and nearly 100% efficient in dilute solutions. It is clear from Fig. 10 that an empirical correlation can be developed to predict the mass of Ni(OH)₂ if the deposition conditions (time, current and solution concentration) are known. Since the data are linearly related to the inverse concentration in concentrated solutions and asymptotically approach 100% utilization of the electrochemically generated OH⁻ in dilute solutions an expression of the following form can be used

\[ y = \left[ y_1(x) \right]^a + \left[ y_2(x) \right]^b \]

where \( y_1(x) \) and \( y_2(x) \) are functions that fit the data at high and low concentrations, respectively, and \( n \) is adjusted to fit the asymptotic region. The slope of the line at the high concentration of solution can be seen in Fig. 9. It should be noted that at low Ni(NO₃)₂ concentrations (0.2 and, especially, 0.1M) nearly 100% of the generated OH⁻ is consumed in the deposition of Ni(OH)₂. However, at higher Ni(NO₃)₂ concentrations the efficiency of OH⁻ utilization decreases dramatically (to less than 20% at solution concentrations greater than 1.0M).

![Fig. 6. A comparison of the mass vs. time for deposition in 0.2M Ni(NO₃)₂, 2.0M Ni(NO₃)₂, and a 0.2M Ni(NO₃)₂ solution saturated with NaNO₃. The deposition rate of the solution saturated with NO₃⁻ is approximately 75% of that in 0.2M Ni(NO₃)₂.](image1)

![Fig. 7. A plot of mass vs. time for deposition in acidified 0.2M Ni(NO₃)₂. Acidification to pHs of 3.0, 2.5, and 2.0 decreases the deposition rate by less than 10%.](image2)

![Fig. 8. A plot of mass vs. time for deposition in basified 2.0M Ni(NO₃)₂. The deposition rate is unchanged at a pH of 4.0.](image3)

![Fig. 9. A plot of deposition rate at 0.5 mA vs. inverse Ni(NO₃)₂ concentration. The horizontal dashed line shows a theoretical deposition rate predicted by Faraday's law. The deposition rate is observed to be both highly inefficient and linearly related to inverse concentration in concentrated solutions.](image4)
concentrations, where \( n \approx 1 \). The correlation experiments reported here were all performed at room temperature (23 to 25°C). Many impregnation recipes suggest elevated temperatures (>50°C). However, at low concentrations, where \( n \approx 1 \), the correlation may hold even at elevated temperatures. Second, Eqs. 5 and 6 have been shown to hold over one order of magnitude of applied current (0.1 to 1.0 mA or 0.5 to 5.0 mA/cm\(^2\)). Third, all depositions were from solutions consisting of a 50/50 v/o mixture of ethanol and water. Finally, the range of concentrations in which Eq. 5 is valid is dependent on the deposition current. At 1.0 and 0.5 mA the correlation is only valid down to 0.1M. However, at 0.1 mA the correlation is valid to 0.02M.

The deposition behavior at 0.1 mA in dilute solutions (<0.02M) is shown in Fig. 12. After a short time, the deposition essentially shuts off, as indicated by the plateau in the mass-time curve. Further, it is shown in Fig. 12 that the mass at which deposition stops off is a strong function of the solution concentration, decreasing with decreasing concentration. Three regions of interest are evident in the mass-time curves. Initially the slopes are identical at all concentrations with the value equivalent to that predicted by Faraday's law (see Eq. 3). Once the initial surface region becomes depleted the rate decreases and becomes limited by the mass transfer of Ni\(^{2+}\) to the reaction interface. Eventually the deposition shuts off as the pH boundary moves away from the electrode surface (because the rate of OH\(^{-}\) generation is faster than its consumption by Ni(OH)\(_2\) deposition) and precipitation occurs in the bulk.

It has been shown above that the increased NO\(_3^-\) concentration and the decreased pH in concentrated Ni(NO\(_3\))\(_2\) solutions are not the primary causes of the inefficient utilization of OH\(^{-}\). The mechanism must therefore be related to the increased Ni(II) concentration in solution. Nickel is well known to complex in aqueous solutions, forming various soluble species (e.g., Ni(OH)\(_2\), Ni(OH)\(_3\), Ni(OH)\(_4\)\(^-\)); Perrin\(^{25}\) demonstrated that Ni\(^{2+}\) is in equilibrium with Ni(OH)\(^+\) in dilute solutions. Other researchers (see references in Baes and Mesmer\(^{25}\)) have shown that the predominant species in more concentrated Ni(II) solutions (>0.015M) is the polymeric Ni\(_2\)(OH)\(_6\)^\(_2\). Equilibrium is given by Eq. 7

\[
4\text{Ni}^{2+} + 4\text{OH}^- \leftrightarrow \text{Ni}_2\text{(OH)}_6^{2+}
\]

where \( K_{eq} = 28.3 \). In the pH range of the bulk Ni(NO\(_3\))\(_2\) solutions used in this study (2.4 to 4.0), Eq. 7 indicates that the concentration of Ni\(_2\)(OH)\(_6\)^\(_2\) is negligible (<10\(^{-14}\)M). However, in the pH range where deposition of Ni(OH)\(_2\) begins (neutral pH; see Eq. 2) the concentration of Ni\(_2\)(OH)\(_6\)^\(_2\) is similar to that of Ni\(^{2+}\). Baes and Mesmer\(^{25}\) conclude that "small amounts of the polynuclear species Ni\(_2\)(OH)\(_6\)^\(_2\) form rapidly at high Ni(II) concentrations (over 0.1M) before precipitation of Ni(OH)\(_2\) occurs.

From the equilibrium expressions given in Eq. 2 and 7 the equilibrium concentration of Ni\(_2\)(OH)\(_6\)^\(_2\) at the pH at which deposition begins can be calculated. The equilibrium constants for Eq. 2 and 7 can be expressed as follows

\[
K_{eq} = c_1c_2^2
\]
If we assume that Ni\(^{++}\) and Ni\(_4\)(OH\(_4\))\(^{4+}\) are the dominant species in solution, the following also holds
\[
K_{sp} = \frac{c_2}{c_1 c_3^2}
\]
\[\text{[9]}\]
where \(c_1\), \(c_2\), and \(c_3\) are the concentrations of Ni\(^{++}\), OH\(^-\), and Ni\(_4\)(OH\(_4\))\(^{4+}\), respectively. Substituting Eq. 8 into 9 yields
\[
c_3 = K_a c_1 c_2^{1/2} = 5.1
\]
\[\text{[10]}\]
If we assume that Ni\(^{++}\) and Ni\(_4\)(OH\(_4\))\(^{4+}\) are the dominant species in solution, the following also holds
\[
c_1 + 4c_3 = c_4
\]
\[\text{[11]}\]
where \(c_4\) is the concentration of Ni(NO\(_3\))\(_2\) added to the solution. Equations 10 and 11 can be solved simultaneously, for each of the solution concentrations used in this study.

Based upon the above discussion, the following two-step deposition mechanism is proposed for high Ni(NO\(_3\))\(_2\) concentrations. First, Ni\(^{++}\) combines with OH\(^-\) to form Ni\(_4\)(OH\(_4\))\(^{4+}\) according to Eq. 7. The Ni\(_4\)(OH\(_4\))\(^{4+}\) then combines with more OH\(^-\) to form deposited Ni(OH)\(_2\), as given in Eq. 12
\[
\text{Ni}_4\text{(OH)}_4\text{O}_4^{4+} + 4\text{OH}^- \rightarrow 4\text{Ni(OH)}_2\downarrow
\]
\[\text{[12]}\]

Depending on the deposition conditions, Ni\(_4\)(OH\(_4\))\(^{4+}\) either reacts with the OH\(^-\) and deposits as Ni(OH)\(_2\), according to Eq. 12, or it diffuses away from the electrode. If there is significant diffusion away from the electrode, deposition rates will be less than that predicted by Faraday's law. Since the concentration of Ni\(_4\)(OH\(_4\))\(^{4+}\) is essentially equal to zero in the acidic environment of the bulk solution, the concentration gradient of Ni\(_4\)(OH\(_4\))\(^{4+}\) is proportional to its concentration near the electrode surface. In concentrated Ni(NO\(_3\))\(_2\) solutions, where the concentration of Ni\(_4\)(OH\(_4\))\(^{4+}\) is high at the electrode (see Table I), the diffusion of Ni\(_4\)(OH\(_4\))\(^{4+}\) away from the electrode will be rapid. This process consumes OH\(^-\) and decreases the efficiency of utilization of electrochemically generated OH\(^-\). Decreasing the concentration of Ni(NO\(_3\))\(_2\) from 1.0 to 0.1 M decreases the concentration of Ni\(_4\)(OH\(_4\))\(^{4+}\) at the electrode surface by a factor of 15 (from 0.20 to 0.013 M) and hence the diffusion of this species. The net result is an increase in the rate of deposition by a factor of 5.

### Conclusions

An electrochemical quartz crystal nanobalance (EQCN) has been utilized to measure the mass of Ni(OH)\(_2\) films electrochemically deposited from Ni(NO\(_3\))\(_2\) solutions. The electrochemical deposition of Ni(OH)\(_2\) has been quantified with respect to deposition time, current, and Ni(NO\(_3\))\(_2\) concentration. The mass changes measured via the EQCN were demonstrated to be the result of Ni(OH)\(_2\) deposition. Cyclic voltammograms of the deposited material showed the characteristic charge and discharge peaks indicating the presence of the Ni(OH)\(_2\)/NiOOH couple while the charge passed in galvanostatic discharges were consistent with the masses determined via the EQCN.

The deposited mass was observed to increase proportionally with both time and current. Most significantly, however, the deposition rate was found to decrease significantly with increasing Ni(NO\(_3\))\(_2\) concentration. At low concentrations (e.g., 0.2 or 0.1 M) it was demonstrated that the utilization efficiency of electrochemically generated OH\(^-\) was nearly 100%. At high concentrations (e.g., 1.0 or 2.0 M) the utilization efficiency of OH\(^-\) was significantly less than 100% (approximately 20% in 1.0 M Ni(NO\(_3\))\(_2\) and linearly related to the inverse Ni(NO\(_3\))\(_2\) concentration. The effect of concentration was shown to be related to Ni as opposed to solution pH or NO\(_3\)\(^-\) concentration. An empirical correlation was obtained which quantified deposition rates in solutions ranging from 0.1 to 3.0 M Ni(NO\(_3\))\(_2\) and at current densities ranging from 0.5 to 5.0 mA/cm\(^2\). The inefficient utilization of OH\(^-\) in concentrated Ni(NO\(_3\))\(_2\) is attributed to the formation of Ni\(_4\)(OH\(_4\))\(^{4+}\) which diffuses away from the reaction interface before deposition occurs.

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### REFERENCES