Polarized Neutron Reflectometry of Metal Consumption and Passive Film Growth on Nickel Exposed to an Alkaline Deuterium Oxide (D$_2$O) Solution

Hung Ha,$^{a,b,*}$ Helmut Fritzseh,$^{a,b}$ Gordon Burton,$^b$ and Jaganathan Ulaganathana

$^a$Canadian Neutron Beam Center, Chalk River, Ontario K0J 1J0, Canada
$^b$Canadian Nuclear Laboratories, Chalk River, Ontario K0J 1J0, Canada

Electrochemical behavior of Ni in an alkaline heavy water electrolyte was studied using cyclic voltammetry and polarized neutron reflectometry. Delays in the hydrogen and oxygen evolution reactions on Ni electrodes and slower kinetics of the reactions in heavy water compared to light water were observed. However, in both 0.01 mol/L NaOH light and heavy water solutions, Ni oxidation and passive film formation occurred at the same potential with similar passive current densities indicating a minor isotope effect of deuterium on passive film growth and formation. Polarized neutron reflectometry detected a passive film growth coefficient of $11.5 \pm 1.1$ Å/V. The Ni consumption coefficient was determined to be $7.3 \pm 1.5$ Å/V. Ni oxidation and passive film growth occurred mostly during the transient period after the applied potential increase but was negligible at the steady state. The electric field strength across the passive film was $8 \times 10^7$ V/cm. The Pilling-Bedworth ratio of the passive film during potentiostatic growth was close to the value of NiO grown on bulk Ni. This work demonstrated the capability of neutron reflectometry in the study of passive films on metals and alloys.

$^*$E-mail: hungharry.ha@cnl.ca

Manuscript submitted June 14, 2017; revised manuscript received September 12, 2017. Published September 21, 2017.

Materials and electrolyte.—Polycrystalline Ni samples for cyclic voltammetry were cut from a 99.98 wt% Ni wire of 1 mm diameter (Goodfellow, Cambridge Limited, Huntingdon, England) and mounted in a cold cure epoxy (System Three, Auburn, WA, USA). Prior to experiments, polycrystalline Ni specimens were ground using silicon carbide paper to a final grit size of 600 to expose a circular cross section of 0.87 cm$^2$ for electrochemical experiments. Nickel thin films for neutron reflectometry were prepared by a Nexedge electron-beam evaporation system (Angstrom, Ontario, Canada) to produce 25 nm thick films on 100 mm diameter x 6 mm thick polished Si (1 1 1) wafers. The chemical composition of the Ni thin films were confirmed by X-ray photoelectron spectroscopy. The Ni thin film specimens were cleaned in ethanol without grinding and were disposed after each experiment.

Heavy water (D$_2$O) of 99.95 wt% was used in this study. The electrolyte was prepared by dissolving NaOH into D$_2$O to make a 0.01 M NaOH solution. The apparent pH of the 0.01 M NaOH (D$_2$O) solution was 12.3, measured using a pH meter calibrated with light water-based pH standard solutions. A solution of 0.01 M NaOH (pH 12) in light water was also prepared using deionized water.

Electrochemical experiments.—Electrochemical experiments were performed in a three electrode cell using a Pt counter electrode and a silver/silver chloride (KCl saturated) reference electrode. Our electrochemical cell for polarized neutron reflectometry experiments did not have the capability to deaerate and all solutions were open to air. All potentials reported in this study are referenced to the silver/silver chloride (KCl saturated) electrode, unless otherwise specified. A Solartron 1287 potentiostat and a Solartron 1255A frequency analyzer were used in all electrochemical experiments.
A cathodic cleaning was performed by applying −1.2 V for 5 minutes before electrochemical measurements. The time and potential used were carefully selected to prevent the thin film specimens from spallation due to hydrogen evolution. Cyclic voltammery was performed on polycrystalline specimens by scanning the potential between −1.0 and +0.65 V at a scan rate of 10 mV/s.

Potentiostatic and electrochemical impedance spectroscopy (EIS) experiments were conducted on the thin film specimens concurrently with polarized neutron reflectometry. After cathodic reduction at −1.2 V, the applied potential was set at −0.8 V for 6 hours followed by EIS measurements at the same potential. Then the applied potential was increased by 0.2 V and the measurement sequence was repeated until the applied potential reached +0.6 V. EIS measurements were performed with a perturbation of 10 mV AC and sweeping frequencies between 100 kHz to 10 mHz.

**Polarized neutron reflectometry (PNR).**—Neutron reflectometry utilizes a highly collimated thermal neutron beam hitting a specimen at a grazing angle, θ (see Fig. 1). The intensity of the reflected and transmitted wave can be described with a neutron spin-dependent index of refraction $n_\pm$, identical to classical optics:45

$$n_\pm = \sqrt{1 - \frac{\lambda^2}{\pi} N (b_{\text{nuc}} \pm b_{\text{mag}})}$$  \hspace{1cm} [1]

where $N$ is the atomic density of the material, $\lambda$ the neutron wavelength, $b_{\text{nuc}}$ and $b_{\text{mag}}$ are the nuclear and magnetic scattering length of the nucleus and atoms, respectively. The product $N-b$ is called the scattering length density (SLD) which is a characteristic of the material. The “+” is used for spin-up neutrons (spin parallel to the external magnetic field $H$ provided by a pair of Helmholtz coils), the “−” is used for spin-down neutrons (spins antiparallel to the external magnetic field). Table 1 summarizes the SLD of the materials in this work.48

It is known that NiO is formed on Ni exposed to air and in aqueous solutions. The use of polarized neutrons increases the difference in the SLD between Ni and NiO (Table 1) compared to unpolarized neutrons, thereby improving the ability to distinguish layers of Ni and NiO in a thin film sample.

Figure 1 shows a schematic of the in-situ PNR experimental setup on the D3 beamline at the National Research Universal (NRU) reactor (Chalk River, Ontario, Canada). More details on the polarized setup on D3 can be found elsewhere.49 The Ni sample was magnetized in a 1000 G magnetic field and was kept in a 56 G magnetic field during the PNR experiment. The magnetic moments of the Ni film in all measurements were approximately 0.48 $\mu_B$/atom which was close to the theoretical value of 0.5 $\mu_B$/atom. The Ni thin film sample was mounted in a three electrode electrochemical cell with a Pt thin film counter electrode and a KCl saturated Ag/AgCl reference electrode. This setup allowed controlling the potential of the sample and performing electrochemical measurements during in-situ PNR experiments. D3 uses a neutron beam with a wavelength of 2.37 Å, an FeCo-Si polarizing supermirror,50 and a Mezei-type spin flipper51 to switch from spin-down to spin-up neutrons. A magnetic guide field parallel to the field of the Helmholtz coils was provided along the neutron path to maintain the polarization of the neutron beam. In this configuration the direction of the neutron spin remained constant after the spin flipper. The polarization of the neutron beam was determined with a Heusler crystal.49 We achieved a flipping ratio, defined as the ratio between the intensity of the spin up and spin down beams, of 20, measured in the straight-through beam. The polarized neutron beam travelled through the Si wafer before it reached the Ni/electrolyte interface at a small grazing angle. The intensity of the specular reflected beam was recorded at different grazing angles $\theta$ and the reflectivity curves were plotted as a function of the scattering vector $Q$ which is related to the incident beam angle and the neutron wavelength by the following expression:52

$$Q = \frac{4\pi}{\lambda} \sin \theta$$  \hspace{1cm} [2]

PNR measurements were performed at each applied potential during the potentiostatic and EIS experiments. There were always two measurements performed at every angle: one with spin-down (R−), and one with spin-up neutrons (R+). The PNR measurements started 3 hours after the applied potential was switched to the set value and each measurement took 90 minutes to complete. The entire in-situ PNR experiments took 4 days. The stability of the experimental setup and the quality of the sample during the experiment was verified by comparing the reflectivity curves at low Q with details discussed in the Results and discussion section. The thickness, roughness, and SLD profile of the layers in the thin film sample were obtained by fitting the spin-down and spin-up reflectivity curves simultaneously to a thin film model using a least squares fit algorithm which includes a recursion algorithm developed by Parratt.53,54

**Figure 1.** A schematic of the in-situ PNR experiment on the D3 beamline at the NRU reactor. The Ni thin film sample, the Pt foil, and the reference electrode were connected to the corresponding terminals of the potentiostat for potential control and electrochemical measurements. The neutron beam travels to the Ni/electrolyte interface through the Si wafer.

**Figure 2.** A schematic of the thin film model used for fitting of the PNR curves measured in air and during potentiostatic experiments in 0.01 M NaOH heavy water solution.

---

**Table 1.** Scattering length and SLD of materials in this study.48

| Material       | Scattering length (fm) | SLD $\times 10^6$ (Å$^{-2}$) |
|----------------|------------------------|-------------------------------|
| H             | −0.3739                | −                              |
| D             | 6.671                  | −                              |
| O             | 5.803                  | −                              |
| H$_2$O        | −1.675                 | −5.6                           |
| D$_2$O        | 19.145                 | 6.39                           |
| Si            | 4.1491                 | 2.07                           |
| SiO$_2$       | 15.7551                | 3.66                           |
| Ni            | 10.3                   | 9.41                           |
| Ni (spin-up)* | 11.88                  | 10.86                          |
| Ni (spin-down)* | 8.69                 | 7.94                           |
| NiO           | 16.103                 | 8.69                           |
| Ni$_3$H$_4$   | 14.428                 | 3.84                           |
| Ni(OH)$_2$    | 35.248                 | 9.19                           |

* Values are for Ni with saturated magnetization.
oxidized in air before the Ni thin film was deposited. The outer layer of the passive film on Ni, which was Ni(OD)$_2$ instead of Ni(OH)$_2$, was not included in the fitting model because such addition did not improve the goodness of the fit. This was attributed to the similarity in the SLDs of NiO and Ni(OD)$_2$. The fitting procedure started with the PNR curve measured in air. In subsequent analysis of the PNR curves measured in D$_2$O solutions, the geometrical and physical parameters of all layers were held fixed except for those of the Ni and NiO. The error of each fitted parameter was determined as the change in the value of that parameter, while keeping the other parameters at their optimized values, which changed the figure of merit by a factor of 2 from the optimized value.

Results and Discussion

**Cyclic voltammetry of polycrystalline Ni.**—Figure 3 shows the voltammograms of the polycrystalline Ni in 0.01 M NaOH light and heavy water solutions. In the first cycle, similar features including two anodic peaks A1 and A2 and one cathodic peak C1 were observed in both voltammograms indicating similar electrochemical behavior of Ni in these solutions. The nature of these anodic and cathodic peaks in alkaline light water environments has been studied by many researchers. The peak A1 has been partially attributed to the oxidation of Ni to Ni(II)$_2$, and also partially attributed to the oxidation of hydrogen that absorbed in the sample during cathodic reduction.17,21,61 The anodic peak A2 and the cathodic peak C1 suggests that the mobility of either or both of Ni$^2+$ and NiO$^-$ ions in the heavy water solution were slower than in the light water solution. This might be attributed to the steric effect on the bond strength between water molecules and between hydrogen and oxygen which play an important role in the transport of hydrated ions in aqueous solutions.58

Compared to the curve in light water solvent, the onset of oxygen evolution in heavy water (region b in Figure 3) was delayed for approximately 100 mV. Similar delay for the onset of deuterium evolution (region c in Figure 3) compared to hydrogen evolution during the downward scan was also observed. Such delays of the oxygen and deuterium evolution was reported for several noble metals including Pt, Au, and Pd.30–32 The difference in the onset potential of oxygen and hydrogen evolution reactions suggests different kinetics and mechanisms of these reactions in light and heavy waters. Three rate determining mechanisms of the hydrogen evolution process has been proposed including the slow discharge mechanism, the electro-chemical desorption mechanism, and the atom recombination mechanism.26,27 Regardless of the exact mechanism, the kinetic ratio of hydrogen and deuterium evolution is dependent on the difference in the heat of activation between proton and deuterium discharge, as well as the surface coverage of the adsorbed reactants at the electrode.26,27 Theoretical calculation indicated that the isotopic ratio of exchange current density for hydrogen and deuterium evolution on metals varies between 2 and 27.26,27 Experimental measurement on Ni determined a value of 3.0$^{+0.08}_{-0.52}$ for the isotopic ratio of exchange current density.26 From the voltammograms in Figure 3, it is evident that the oxygen and deuterium evolution current densities in the heavy water solution was actually half of those in the light water solution, in agreement with previous reports.

In the second cycle of the cyclic voltammetry experiments (Figure 4), the peak A1 was not present in either voltammogram indicating that Ni oxidation was insignificant and the amount of hydrogen/deuteronium absorbed in the sample was negligible. The lack of hydrogen/deuteronium absorption was because the potential was not

**Reactions**

1. $\text{Ni} + 2\text{OH}^- = \text{Ni(OH)}_2 + 2\text{e}^- \quad [3]
2. $\text{Ni} + 2\text{OH}^- = \text{NiO} + \text{H}_2\text{O} + 2\text{e}^- \quad [4]
3. $\text{Ni(OH)}_2 + \text{OH}^- = \text{NiOOH} + \text{H}_2\text{O} + \text{e}^- \quad [5]
4. $\text{Ni} + 2\text{OD}^- = \text{Ni(OD)}_2 + 2\text{e}^- \quad [6]
5. $\text{Ni} + 2\text{OD}^- = \text{NiO} + \text{D}_2\text{O} + 2\text{e}^- \quad [7]
6. $\text{Ni(OD)}_2 + \text{OD}^- = \text{NiOOD} + \text{D}_2\text{O} + \text{e}^- \quad [8]

Figure 3. Cyclic voltammogram (first cycle) of polycrystalline Ni in 0.01 M NaOH light and heavy water solutions. A1 and A2 are oxidation peaks, C1 is a reduction peak. Region a is the passive range, region b is the oxygen evolution range, and region c is the hydrogen evolution range.
The current densities measured during potentiostatic experiments at different applied potentials. (a) $-0.8 \leq E \leq -0.2$ V, (b) $0 \leq E \leq +0.6$ V.

Figure 5. Current density vs. time curves of thin film Ni measured during potentiostatic experiments at different applied potentials. (a) $-0.8 \leq E \leq -0.2$ V, (b) $0 \leq E \leq +0.6$ V.

Figure 4. Cyclic voltammogram (second cycle) of polycrystalline Ni in 0.01 M NaOH light and heavy water solutions. A2 is an oxidation peak. C1 and C2 are reduction peaks. Region a is the passive range. Region b is the oxygen evolution range. Region c is the hydrogen evolution range.

Figure 3. Nyquist plot (Figure 6a) showed a semicircle which can be attributed to a charge transfer process of the oxygen reduction reaction rather than an electronic response from the passive film. This was evident by the cathodic current measured at this potential in Figure 5. Similarly, the EIS spectrum measured at $+0.6$ V was attributed to oxygen evolution which was the dominant reaction to the formation of Ni(OD)$_2$ at this potential. Except for the EIS spectra at $-0.2$ and vicinity of the peak A1, and a passive film was quickly formed on the sample at these holding potentials. Oxygen reduction, however, was the dominant reaction during long term holding at these potentials, resulting in the observed fluctuation in the current density in Figure 5a. The current densities transitioned from cathodic to anodic at a potential between $-0.2$ and 0 V. This is slightly more positive than the open circuit potential of Ni measured to be approximately $-0.25$ V after 1 hour. This drift of the open circuit potential was attributed to the growth of the passive film. At the potentials between $-0.4$ and $+0.4$ V, the anodic current density increased with the applied potential and approached steady state with current densities on the order of 0.01 mA/cm$^2$. At $+0.6$ V, oxygen evolution resulted in an increase in the current density to approximately 10 mA/cm$^2$.

Electrochemical impedance spectroscopy measurements of the Ni thin film in 0.01 M NaOH heavy water solution at applied potentials between $-0.2$ and $+0.6$ V are shown in Figure 6. At $-0.2$ V, the Nyquist plot (Figure 6a) showed a semicircle which can be attributed to a charge transfer process of the oxygen reduction reaction rather than an electronic response from the passive film. This was evident by the cathodic current measured at this potential in Figure 5. Similarly, the EIS spectrum measured at $+0.6$ V was attributed to oxygen evolution which was the dominant reaction to the formation of Ni(OD)$_2$ at this potential. Except for the EIS spectra at $-0.2$ and vicinity of the peak A1, and a passive film was quickly formed on the sample at these holding potentials. Oxygen reduction, however, was the dominant reaction during long term holding at these potentials, resulting in the observed fluctuation in the current density in Figure 5a. The current densities transitioned from cathodic to anodic at a potential between $-0.2$ and 0 V. This is slightly more positive than the open circuit potential of Ni measured to be approximately $-0.25$ V after 1 hour. This drift of the open circuit potential was attributed to the growth of the passive film. At the potentials between $-0.4$ and $+0.4$ V, the anodic current density increased with the applied potential and approached steady state with current densities on the order of 0.01 mA/cm$^2$. At $+0.6$ V, oxygen evolution resulted in an increase in the current density to approximately 10 mA/cm$^2$.

Electrochemical impedance spectroscopy measurements of the Ni thin film in 0.01 M NaOH heavy water solution at applied potentials between $-0.2$ and $+0.6$ V are shown in Figure 6. At $-0.2$ V, the Nyquist plot (Figure 6a) showed a semicircle which can be attributed to a charge transfer process of the oxygen reduction reaction rather than an electronic response from the passive film. This was evident by the cathodic current measured at this potential in Figure 5. Similarly, the EIS spectrum measured at $+0.6$ V was attributed to oxygen evolution which was the dominant reaction to the formation of Ni(OD)$_2$ at this potential. Except for the EIS spectra at $-0.2$ and vicinity of the peak A1, and a passive film was quickly formed on the sample at these holding potentials. Oxygen reduction, however, was the dominant reaction during long term holding at these potentials, resulting in the observed fluctuation in the current density in Figure 5a. The current densities transitioned from cathodic to anodic at a potential between $-0.2$ and 0 V. This is slightly more positive than the open circuit potential of Ni measured to be approximately $-0.25$ V after 1 hour. This drift of the open circuit potential was attributed to the growth of the passive film. At the potentials between $-0.4$ and $+0.4$ V, the anodic current density increased with the applied potential and approached steady state with current densities on the order of 0.01 mA/cm$^2$. At $+0.6$ V, oxygen evolution resulted in an increase in the current density to approximately 10 mA/cm$^2$.
Figure 6. Electrochemical impedance results of thin film Ni in 0.01 M NaOH heavy water solution at potentials between −0.2 and +0.6 V. (a) Nyquist plot and (b, c) Bode plot.

+0.6 V, the EIS spectra at 0, +0.2 and +0.4 V (Figures 6b, 6c) were typical for a capacitance response which was attributed to the passive film. Fitting the EIS spectra to a one time constant electrical circuit returned large uncertainty in the values of the passive film electrical capacitance. However, qualitatively the impedance of the passive film decreased when the applied potential increased from 0 to +0.4 V. This is consistent with the increase in the current density measured in the potentiostatic experiments.

Characterization of the passive film using neutron reflectometry.—Air-formed oxide layer.—Figure 7 shows the PNR curves of the Ni thin film sample in air. The spin-up reflectivity curve was shifted to higher $Q$ compared to that measured with spin-down neutrons as expected due to a higher SLD of spin-up neutrons (see Equation 1). Total reflection was observed in both curves at $Q < 0.02$ Å$^{-1}$. Kiessig fringes, which are the result of interference of neutron beams reflected from the surface and interfaces in the sample, were observed at higher $Q$. Both reflectivity curves were simultaneously fitted to the thin film model depicted in Figure 2 which is comprised of a Si substrate, SiO$_2$, Ni, and NiO. The thickness of the SiO$_2$ layer was determined to be 6 Å. The roughness at the Si/SiO$_2$ and SiO$_2$/Ni interfaces were 4 and 7 Å, respectively. The thicknesses of the Ni and air-formed NiO layers were 244 Å and 12 Å, respectively. This air-formed oxide thickness is close to the value measured by other researchers. The NiO layer can also be seen in the SLD profile as shown in the inset of Figure 7.

Passive film growth in 0.01 M NaOH deuterium oxide solution.—Selected PNR curves of the Ni thin film collected during immersion in 99.95% D$_2$O before cathodic reduction and during potentiostatic experiments are depicted in Figure 8. All reflectivity curves overlapped at $Q < 0.03$ Å$^{-1}$ and the location of the critical edge, at which the reflectivity dropped from total reflection, did not change. These results indicated the stability of the PNR experimental setup and the good quality of the Ni thin film sample during the 4-day period. Changes in the reflectivity curves, however, were detected at $Q > 0.05$ Å$^{-1}$. The difference between the PNR curves measured in 99.95% D$_2$O and in 0.01 M NaOH deuterium oxide solution at −0.8 V was mainly due to the removal of the air-formed oxide layer during cathodic reduction at −1.2 V. The difference between the PNR curves measured at applied potentials from −0.8 to +0.6 V, however, was mainly due to Ni consumption and passive film growth during the potentiostatic experiments in this potential range.
However, in the above potential range, however, yielded large uncertainties. There-

were not able to distinguish the NiO and Ni(OD)\textsubscript{2} layers. However, in a
temporary period after potential switch but were negligible during the longer potentiostatic experiment. A Ni
dissolution rate was also observed to decrease with time following a
logarithmic law.\textsuperscript{47} In the alkaline environment employed in this work,
it is expected that the oxidation rate of passivated Ni in the steady state was even lower.

The potential dependence of the Ni consumption and the passive film growth could be
determined from the slope of the curves in Figure 10. Based on the voltammogram of Ni (Figure 3), three poten-
tial regions were identified including (i) oxidation of Ni to Ni(II) at potentials between \(-0.8\) and \(+0.4\) V (ii) stable passive film between \(-0.4\) and \(+0.2\) V and (iii) oxidation of Ni(II) to Ni(III) above \(+0.2\) V. Linear regression of the thickness vs. potential curves for each of the above potential range, however, yielded large uncertainties. Therefore, average slopes for Ni consumption and passive film growth in the entire potential range between \(-0.8\) and \(+0.4\) V were determined to be \(7.3 \pm 1.5\) and \(11.5 \pm 1.1\) Å/V, respectively. In the current study, we

were not able to distinguish the NiO and Ni(OD)\textsubscript{2} layers. However, in another study of Ni passivity in 0.01 M NaOH light water electrolyte performed in our laboratory (results to be published), the considerable difference in the SLD between NiO and Ni(OH)\textsubscript{2} allowed us to distinguish the two layers in the passive film. It was found that the outer Ni(OH)\textsubscript{2} layer was porous and several nanometer thick. Notably, the potential-dependent coefficients for Ni consumption and NiO growth in the light water solution were similar to those in the current study.

Fitting the experimental data to the thin film model in Figure 2 yielded good fits as can be seen in Figure 9. The results of the fitting are summarized in Table II and in Figure 10. During potentiostatic experiments between \(-0.8\) and \(+0.6\) V, the thickness of the Ni layer decreased from 245 to 234 Å while the thickness of the passive film increased from 12 to 26 Å\textsuperscript{3}. It was demonstrated in our experiment (the data are not shown here) that the reflectivity curves measured at 3 and 5 hours after switching the potential were identical, indicating the thickness of the Ni and NiO layers did not change significantly during this period of time. This signifies that steady state was quickly established after switching the applied potential: Ni oxidation and NiO growth occurred during the transient period after potential switch but were negligible during the longer potentiostatic experiment. A Ni consumption rate of ca. 0.3 Å/h after 10 hour exposure to an acidic solution was reported earlier by our group.\textsuperscript{47} In that paper, the Ni dissolution rate was also observed to decrease with time following a
logarithmic law.\textsuperscript{47} In the alkaline environment employed in this work, it is expected that the oxidation rate of passivated Ni in the steady state was even lower.

In addition, we also observed that the passive current densities in both light and heavy water solutions were almost identical. Based on these, we attributed the observed passive film formed in heavy water to the inner NiO, though the presence of a Ni(OD)\textsubscript{2} layer cannot be discounted.

Metal oxidation and passive film growth are controlled by the interfacial and bulk potential drops which are related to the applied potential by: \textsuperscript{71–73}

\[
E = \vartheta_{Ni/NiO} + \varepsilon L + \vartheta_{NiO/d}
\]  

where \(E\) is the applied potential, \(\vartheta_{Ni/NiO}\) and \(\vartheta_{NiO/d}\) are the interfacial potential drops at the Ni/NiO and NiO/electrolyte interfaces, \(\varepsilon\) is the electric field strength across the passive film, and \(L\) is the thickness of the film. The thinning of Ni was due to the oxidation of Ni at the metal/oxide interface as described by Reactions 6 and 7. Thus, the

Figure 8. Selected polarized neutron reflectivity curves of the Ni thin film measured in 99.95% D\textsubscript{2}O (black dashed curve) and in 0.01 M NaOH heavy water solution at different holding potentials (all other curves).

Figure 9. Experimental and fitted polarized neutron reflectivity curves of the Ni thin film during potentiostatic experiments in 0.01 M NaOH heavy water solution.
The kinetics of Ni thinning could be described by a Butler-Volmer type expression:

\[ i = i^{eq} \left\{ \exp \left[ \frac{nF}{RT} \alpha (\theta_{Ni/NiO} - \theta^{eq}_{Ni/NiO}) \right] - \exp \left[ -\frac{nF}{RT} (1 - \alpha) (\theta_{Ni/NiO} - \theta^{eq}_{Ni/NiO}) \right] \right\} \]  \[ \text{[10]} \]

where \( i^{eq} \) is the overall exchange current density at equilibrium, \( n \) is the number of electrons involved in the reaction (\( n = 2 \)), \( F \) is Faraday’s constant, \( R \) is the universal gas constant, \( T \) is the absolute temperature, \( \alpha \) is the charge transfer coefficient, \( \theta_{Ni/NiO} \) is the potential drop at the Ni/NiO interface, and \( \theta^{eq}_{Ni/NiO} \) is the potential drop at the Ni/NiO interface at equilibrium. Experimental results showed that most of Ni oxidation occurred during the transient period after potential increase and further Ni oxidation was negligible in the steady state as evident from the current density behavior in Figure 5b and by repeated PNR measurements. These results suggest that after the applied potential increased, \( \theta_{Ni/NiO} \) increased from a value close to \( \theta^{eq}_{Ni/NiO} \), but quickly decayed as the passive film thickened and approached a value close to \( \theta^{eq}_{Ni/NiO} \) at the steady state so that the current density calculated by Equation 10 was negligible.

Assuming that at the steady state, the potential drop at the film/electrolyte interface is also constant, differentiating Equation 9 with respect to the distance from the metal/oxide interface yielded the expression for the electric field strength across the passive film as follows:\[ \text{[11]} \]

\[ \varepsilon = -\frac{dE}{dL} \]

From the passive film thickness-potential relationship (Figure 10) the electric field strength across the passive film was approximately \( 8 \times 10^6 \) V/cm. This electric field strength was similar to the value measured on Ni in borate buffer pH 8.4\[18\] and was on the same order of magnitude compared to the electric field strength on other passive materials such as stainless steel\[75,76\], Al alloys\[77,78\], and Ti alloys\[79,80\].

By a simple derivation, the efficiency of the NiO layer growth could be expressed by:

\[ n_{NiO} \cdot \rho_{Ni} \cdot r_{NiO} \cdot M_{Ni} \]

where \( n_{NiO} \) and \( n_{Ni} \) are the number of moles of Ni consumed and NiO formed, respectively, \( \rho \) is the density of the materials (\( \rho_{Ni} = 8.908 \) g/cm\(^3\), \( \rho_{NiO} = 6.67 \) g/cm\(^3\)), \( r_{Ni} \) is the average amount of Ni consumed (\( r_{Ni} = 7.3 \) Å/V), \( r_{NiO} \) is the average amount of NiO growth (\( r_{NiO} = 11.5 \) Å/V), \( M \) is the molecular weight (\( M_{Ni} = 58.69 \) g/mol, \( M_{NiO} = 74.69 \) g/mol). The passive film formation efficiency is calculated using Equation 12 to be 0.94. This calculation suggests that most of Ni consumption resulted in the formation of the passive film.

The changes in the SLD profile of the passive film during potentiostatic experiments are shown in Figure 11. The protective properties of an oxide film could be evaluated from the ratio of the growing oxide volume to the consumed metal volume using the Pilling-Bedworth ratio.\[82\] For oxidation of a Ni thin film, growth of the NiO layer is mainly in the direction perpendicular to the film surface and lateral expansion is negligible, the ratio can be determined from the changes in the location of the metal/oxide and oxide/electrolyte interfaces:

\[ R_{PB} = 1 + \frac{f_o}{f_i} \]

where \( f_o \) is the increase in the distance of the NiO/electrolyte interface with respect to the SiO\(_2\)/Ni interface and \( f_i \) is the decrease in the distance of the NiO/Ni interface with respect to the SiO\(_2\)/Ni interface. The changes in the distances of the interfaces and the corresponding Pilling-Bedworth ratio calculated at different applied potentials are summarized in Table III. The values of \( R_{PB} \) calculated in this study was approximately 1.7, which is in agreement with the Pilling-Bedworth

---

**Table II. Summary of the thickness and roughness of layers in the Ni thin film sample during potentiostatic experiments in 0.01 M NaOH heavy-water solution. The values were obtained by fitting the PNR curves to the thin film model in Figure 2.**

| Potential (V) | Thickness (Å) | Roughness (Å) | Thickness (Å) | Roughness (Å) |
|--------------|--------------|---------------|--------------|---------------|
| Air          | 244 ± 1      | 6 ± 1         | 3 ± 1        | 4 ± 1         |
| −0.8         | 245 ± 1      | 6 ± 1         | 4 ± 1        |
| −0.6         | 243 ± 1      | 6 ± 1         | 4 ± 1        |
| −0.4         | 244 ± 1      | 6 ± 1         | 4 ± 1        |
| −0.2         | 240 ± 1      | 6 ± 1         | 4 ± 1        |
| 0            | 240 ± 1      | 5 ± 1         | 4 ± 1        |
| 0.2          | 237 ± 1      | 5 ± 1         | 4 ± 1        |
| 0.4          | 238 ± 1      | 4 ± 1         | 6 ± 1        |
| 0.6          | 234 ± 1      | 4 ± 1         | 9 ± 1        |

---

**Figure 10.** Change in the thicknesses of the Ni layer and passive film during potentiostatic experiments between −0.8 and +0.6 V in 0.01 M NaOH heavy water solution. The thicknesses of the layers were obtained by fitting the PNR curves to the thin film model in Figure 2b. Symbols are experimental data. Dashed lines are linear regression results.

**Figure 11.** SLD profiles of the Ni thin film sample during potentiostatic experiments in 0.01 M NaOH heavy water solution.
Table III. Summary of the outward ($f_0$) and inward ($f_1$) oxide growth distances, and the Pilling-Bedworth ratios ($R_{PB}$) for the passive film on Ni during potentiostatic experiments in 0.01 M NaOH heavy water solution.

| E (V) | $f_0$ (Å) | $f_1$ (Å) | $R_{PB}$ (calculated) | $R_{PB}$ (referenced) |
|-------|---------|---------|---------------------|------------------|
| -0.6  | 1.3 ± 0.2 | 1.0 ± 0.2 | 1.7 ± 0.2 | 1.7 |
| -0.4  | 1.8 ± 0.2 | 1.5 ± 0.2 | 1.8 ± 0.2 | 1.8 |
| -0.2  | 4.5 ± 0.2 | 3.5 ± 0.2 | 1.7 ± 0.2 | 1.7 |
| 0     | 4.8 ± 0.2 | 4.6 ± 0.2 | 1.9 ± 0.2 | 1.9 |
| 0.2   | 7.4 ± 0.2 | 5.5 ± 0.2 | 1.7 ± 0.2 | 1.7 |
| 0.4   | 7.8 ± 0.2 | 7.7 ± 0.2 | 1.9 ± 0.2 | 1.9 |

The ratio of NiO growth on bulk Ni, suggesting the film potentiostatically grown in 0.01 M NaOH heavy water solution was protective.

Conclusions

The electrochemical behavior of Ni in an alkaline heavy water electrolyte was studied using cyclic voltammetry and polarized neutron reflectometry. Hydrogen and oxygen evolution reactions on Ni in 0.01 M NaOH heavy water solution was delayed by approximately 100 mV compared to those in 0.01 M NaOH light water solution. However, cyclic voltammetry revealed no significant isotope effect on Ni oxidation and passive film formation in heavy water compared to light water. Similar to that in the alkaline light water solution, Ni exhibited a large passive range between −0.8 and +0.4 V followed by oxidation of Ni(II) to Ni(III) at more positive potentials. In-situ polarized neutron reflectivity was able to detect Ni consumption and passive film growth during potentiostatic experiments. Ni consumption and passive film growth occurred mostly during the transient period after the applied potential increase but was negligible at the steady state. Potential-dependent coefficients of Ni consumption and NiO growth were determined to be 7.3 ± 1.5 Å/V and 11.5 ± 1.1 Å/V, respectively, over the potential range between −0.8 and +0.4 V. The electric field strength during film growth was 8 × 10⁻⁶ V/cm. The Pilling-Bedworth ratio of the passive film during potentiostatic growth was close to the value of NiO grown on bulk Ni.

Acknowledgments

The authors thank Dr. Zin Tun (Canadian Neutron Beam Center) for his insights and useful discussion about neutron reflectometry and interpretation of the results. The authors would also like to thank Dr. Brian Ellis and Dr. Jayeshkumar Patel (Canadian Nuclear Laboratories) for their help in the preparation of the Ni thin films.

References

1. D. S. Hall, D. J. Lockwood, C. Bock, and B. R. MacDougall, Proc. R. Soc. A., 471(2174), 20140792 (2015).
2. P. Oliva, J. Leonardi, J. F. Laurent, C. Delmas, J. J. Braconnier, M. Figlarz, F. Fievet, and A. D. Guibert, Journal of Power Sources, 8(2), 229 (1982).
3. J. Scherer, B. M. Ocko, and O. M. Magnussen, Electrochimica Acta, 48(9), 1169 (2003).
4. D. Zulli, V. Maurice, and P. Marcus, Journal of the Electrochemical Society, 147(4), 1393 (2000).
5. H. W. Hoppe and H. H. Strebbow, Surface and interface analysis, 14(3), 121 (1989).
6. B. MacDougall and M. Cohen, Journal of The Electrochemical Society, 121(9), 1152 (1974).
7. B. Payne, M. Biesinger, and N. McIntyre, Journal of Electron Spectroscopy and Related Phenomena, 185(5), 159 (2012).
8. S. Medway, C. Lucas, A. Kowal, R. Nichols, and D. Johnson, Journal of Electron Spectroscopy and Related Phenomena, 587(1), 172 (2006).
9. A. Seyeux, V. Maurice, L. Klein, and P. Marcus, Journal of Solid State Electrochemistry, 9(5), 337 (2005).
10. O. Magnussen, J. Scherer, B. Ocko, and R. Behm, The Journal of Physical Chemistry B, 104(6), 1222 (2000).
11. V. Maurice, L. Klein, and P. Marcus, Surface and interface analysis, 34(1), 139 (2002).
12. N. Kitakatsu, V. Maurice, C. Hinnen, and P. Marcus, Surface science, 407(1-3), 36 (1998).
13. A. Seyeux, V. Maurice, L. Klein, and P. Marcus, Journal of The Electrochemical Society, 153(11), B453 (2006).
14. L. Oblonsky and T. Devine, Journal of the Electrochemical Society, 142(11), 3677 (1995).
15. M. Nakamura, N. Ikemiya, A. Iwasaki, Y. Suzuki, and M. Ito, Journal of Electroanalytical Chemistry, 566(2), 385 (2004).
16. D. S. Hall, D. J. Lockwood, S. Potier, C. Bock, and B. R. MacDougall, The Journal of Physical Chemistry B, 116(25), 6771 (2012).
17. D. S. Hall, C. Bock, and B. R. MacDougall, Journal of The Electrochemical Society, 160(3), F235 (2013).
18. A. K. Covington, R. A. Robinson, and R. G. Bates, The Journal of Physical Chemistry B, 115(12), 3038 (2011).
19. L. T. Devine, H. K. Levermore, and C. Bock, The Journal of Physical Chemistry B, 111(8), 2015 (2007).
20. R. Mesmer and D. Herling, Journal of Solution Chemistry, 7(12), 901 (1978).
21. D. S. Hall, C. Bock, and B. R. MacDougall, Journal of The Electrochemical Society, 117(10), 1270 (1970).
22. J. Noel, D. Shoesmith, and Z. Tun, Journal of The Electrochemical Society, 155(8), C444 (2008).
23. Z. Tun, J. Noel, and D. Shoesmith, Physica C: Condensed Matter, 241, 1107 (1997).
24. Z. Tun, J. Noel, and D. Shoesmith, Journal of The Electrochemical Society, 146(3), 988 (1999).
25. Z. Tun, J. Noel, and D. Shoesmith, Pramana, 71(4), 769 (2008).
26. H. Fritzsche, F. Klose, C. Rehm, Z. Tun, M. Wolff, and B. Hjorvarsson, in Neutron Scattering and Other Nuclear Techniques for Hydrogen in Materials, p. 115, Springer (2016).
27. M. Zveiaie, J. Noel, Z. Tun, and D. Shoesmith, Journal of The Electrochemical Society, 160(9), C414 (2013).
28. H. Ha, H. Fritzsche, G. Burton, and J. Ulaganathan, Journal of The Electrochemical Society, 164(6), C258 (2017).
29. H. Rauch and W. Waschkowski, in Neutron Data Booklet, A.-J. Dianoux and G. Landers, Editors, p. 1-11-1-17, Old City Publishing, Philadelphia, PA (2003).
30. H. Fritzsche, Review of scientific instruments, 76(11), 15104 (2005).
31. E. K. Trost, C. Pappas, T. Keller, and F. Mezei, Physica C: Condensed Matter, 213, 939 (1995).
32. F. Mezei, Zeitschrift für Physik A Hadrons and nuclei, 255(2), 146 (1972).
33. R. Sr. Sherlock-Guzmán, J. R. Vich, and A. J. Arvia, Journal of The Electrochemical Society, 125(10), 1578 (1978).
34. R. Sr. Sherlock-Guzmán, A. Carcea, and R. Newman, Corrosion science, 47(12), 3234 (2005).
35. M. Alsabed, M. Gedei, and G. Jerkiewicz, Electrochemistry, 6(1), 60 (2015).
36. K. Heusler and T. Ohlfska, Science, 101(1-3), 194 (1980).
37. B. MacDougall and M. Cohen, Journal of The Electrochemical Society, 123(2), 191 (1976).
38. B. MacDougall and M. Cohen, Journal of The Electrochemical Society, 123(2), 1783 (1976).
39. J. Ord, J. Clayton, and D. DeSmet, Journal of The Electrochemical Society, 124(11), 1714 (1977).
68. M. E. Tuckerman, D. Marx, and M. Parrinello, Nature, 417(6892), 925 (2002).
69. B. Conway, in Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences, p. 400. The Royal Society; (1958).
70. M. Dmochowska and A. Czerwiński, Journal of Solid State Electrochemistry, 2(1), 16 (1998).
71. C. Chao, L. Lin, and D. Macdonald, Journal of the Electrochemical Society, 128(6), 1187 (1981).
72. M. Momeni and J. Wren, Faraday discussions, 180, 113 (2015).
73. A. Seyeux, V. Maurice, and P. Marcus, Journal of The Electrochemical Society, 160(6), C189 (2013).
74. Y. Xu, M. Wang, and H. Pickering, Journal of the Electrochemical Society, 140(12), 3448 (1993).
75. H. Xu, D. Sun, and H. Yu, Applied Surface Science, 357, 204 (2015).
76. R. Lillard, G. Vasquez, and D. Bahr, Journal of the Electrochemical Society, 158(6), C194 (2011).
77. M. Lohrengel, Materials Science and Engineering: R: Reports, 11(6), 243 (1993).
78. T. Ohtsuka, M. Masuda, and N. Sato, Journal of The Electrochemical Society, 132(4), 787 (1985).
79. W. Nowak and E. Sun, Corrosion science, 43(10), 1817 (2001).
80. R. Bedworth and N. Pilling, J Inst Met, 29(3), 529 (1923).
81. Z. Grzesik, in ASM Handbook Vol 13A - Corrosion: Fundamentals, Testing, and Protection, S. D. Cramer, J. Bernard, and S. Covino, Editors, p. 90, ASM International, Materials Park, OH (2003).