In Situ Raman Study of Amorphous and Crystalline Ni-Co Alloys for the Alkaline Oxygen Evolution Reaction

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Amorphous Ni\textsubscript{79.2-x}Co\textsubscript{x}Nb\textsubscript{12.5}Y\textsubscript{8.3} (x = 0, 0.5 at.% \%) alloys were synthesized using cryogenic mechanical alloying and evaluated as catalyst for the oxygen evolution reaction (OER) in alkaline media using cyclic voltammetry and Tafel measurements. Electrochemical testing showed that the amorphous alloys possessed lower Tafel values for the OER compared to crystalline Ni and Ni\textsubscript{95}Co\textsubscript{5}. Anodic cycling of amorphous Ni\textsubscript{74.2}Co\textsubscript{5}Nb\textsubscript{12.5}Y\textsubscript{8.3} resulted in a lower onset potential for the OER and decreased Tafel values while no changes were observed for amorphous Ni\textsubscript{79.2}Nb\textsubscript{12.5}Y\textsubscript{8.3} and crystalline Ni\textsubscript{95}Co\textsubscript{5}. Pairing of in situ confocal Raman spectroscopy with anodic cycling showed that the amorphous Ni\textsubscript{74.2}Co\textsubscript{5}Nb\textsubscript{12.5}Y\textsubscript{8.3} alloy formed reversible hydrous Co surface species instead of irreversible CoO\textsubscript{2} typically seen on crystalline Ni-Co alloys in KOH. The formation of hydrous Co surface species upon cycling was also accompanied by increased formation of β-NiOOH leading to enhanced catalytic performance of amorphous Ni\textsubscript{74.2}Co\textsubscript{5}Nb\textsubscript{12.5}Y\textsubscript{8.3} alloy over the amorphous Ni\textsubscript{79.2}Nb\textsubscript{12.5}Y\textsubscript{8.3} and the crystalline counterparts.

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Traditional alkaline water electrolysis has been successful industrially because of the use of low cost, stable, nickel-based electrocatalyst materials. The major drawback to these systems is that they use aqueous KOH as the electrolyte which is not desirable from a corrosion and packaging perspective. The use of novel anion exchange membranes (AEM) in alkaline water electrolyzers is now of particular interest since it eliminates the aqueous KOH electrolyte and can provide enhanced form factors and much higher current densities that rival PEM-based electrolyzers.\textsuperscript{1,4}

Conventional Ni electrocatalysts for the oxygen evolution reaction (OER) still display large overpotentials and slow reaction kinetics.\textsuperscript{5–8} The OER reaction remains the main hindrance for increasing total cell efficiency in water electrolysis.\textsuperscript{5–8} The addition of Co to Ni-based alloys has been noted to increase the activity by stabilizing the β-NiOOH phase over γ-NiOOH, but this often leads to an increase in the oxygen overpotential.\textsuperscript{9,10} The issue of increased overpotential can be mitigated with the use of amorphous structures to reduce the oxygen overpotential with the addition of Co.\textsuperscript{11} This previous research has been limited to planar amorphous metal oxides, which are not ideal for catalysts in AEM water electrolysis.\textsuperscript{11–13}

Effective AEM catalysts should be designed on similar principles as catalysts used in proton exchange membrane (PEM) water electrolyzers. An ideal catalyst should have: a reduced particle size and porous morphology to increase the amount of electrochemically active sites, enhanced gas disengagement, and low charge transfer resistance to reduce the overpotential.\textsuperscript{3} These features are often lacking in amorphous alloys fabricated by planar flow casting which results in smooth surfaces with a low electrochemically active surface area. A potentially attractive alternative production method is mechanical alloying.

Mechanical alloying is a solid-state process that can be used to produce amorphous alloys with high electrochemically active surface area while also facilitating new alloy chemistries by overcoming fabrication difficulties associated with solidification processes.\textsuperscript{14,15} The amorphization process can be further enhanced by using cryogenic temperatures during the mechanical alloying process.\textsuperscript{19}

Experimental

Amorphous Ni\textsubscript{79.2-x}Co\textsubscript{x}Nb\textsubscript{12.5}Y\textsubscript{8.3} (x = 0, 0.5 at.%) alloys were synthesized using mechanical alloying. For mechanical alloying, elemental powders of nickel (99.9 wt\%, −100 mesh), cobalt (99.8 wt\%, −100 mesh), niobium (99.99 wt\%, −325 mesh) and yttrium (99.9 wt\%, −40 mesh) were used as starting material. Powders were packed under an argon atmosphere (99.99% purity, <10 ppm O\textsubscript{2}) in stainless steel vials with two 7 mm diameter stainless steel balls. The ball to powder ratio (BPR) was set at 10:1 for all alloys. A Retsch Cryomill was used to mill the powders at a frequency of 30 Hz for 3, 6, and 12 hr. For cryogenic milling, liquid nitrogen was passed around the vials to ensure they remained at cryogenic temperatures.
The electrolyte was then pre-electrolysed at –1.7 V Hg/HgO for 24 hrs. prepared using AnalaR grade KOH pellets and Type I, 18.2 M H₂O in a 1 M KOH solution deaerated with argon gas. Electrolytes were mechanically alloyed powder (4 mg) with Nafion solution (8 μL) and 825 mV vs. RHE. Static measurements were performed to mirror in situ Raman spectroscopy testing. Working electrodes were prepared by depositing catalysts inks onto a 3 mm diameter glassy carbon electrode polished using 0.05 μm colloidal silica (CH-Instruments). Catalysts inks were prepared by combining mechanically alloyed powder (4 mg) with Nafion solution (8 μL) and isopropanol (200 μL). The ink was sonicated for 10 min and 15 μL was deposited on a glassy carbon electrode rotating at 150 rpm to ensure uniform coating thickness. Experiments were carried out at 30 °C in a 1 M KOH solution deaerated with argon gas. Electrolytes were prepared using Analytical grade KOH pellets and Type I, 18.2 M H₂O. The electrolyte was then pre-electrolysed at –1.7 V Hg/HgO for 24 hrs. prior to testing. Cyclic voltammetry (CV), steady-state potentiostatic, and surface area measurements were performed using a Bio-Logic VSP-300 multichannel potentiostat/galvanostat. Measurements were performed using a static three-electrode set up in a Teflon cell with a Pt mesh as the counter electrode and a Hg/HgO reference electrode filled with 1 M KOH solution (+825 mV vs. RHE). Static measurements were performed to mirror in situ Raman spectroscopy testing. Working electrodes were prepared by depositing catalysts inks onto a 3 mm diameter glassy carbon electrode polished using 0.05 μm colloidal silica (CH-Instruments). Catalysts inks were prepared by combining mechanically alloyed powder (4 mg) with Nafion solution (8 μL) and isopropanol (200 μL). The ink was sonicated for 10 min and 15 μL was deposited on a glassy carbon electrode rotating at 150 rpm to ensure uniform coating thickness. Experiments were carried out at 30 °C in a 1 M KOH solution deaerated with argon gas. Electrolytes were prepared using Analytical grade KOH pellets and Type I, 18.2 M H₂O. The electrolyte was then pre-electrolysed at –1.7 V Hg/HgO for 24 hrs. prior to testing. Cyclic voltammetry (CV) was performed using a scan rate of 50 mV/s between 0.1 and 0.7 V Hg/HgO. Steady-state potentiostatic polarization was performed between 0.3 and 1 V Hg/HgO, while stepping the potential 20 mV and holding for 10 min. Surface area measurements were performed using cyclic voltammetry in the non-faradaic region in accordance with the method outlined by McCreery et al. In situ confocal Raman spectroscopy was employed using a HORIBA iHR320 confocal Raman spectrometer and microscope to monitor the formation and reduction of surface species during potential cycling. Electrochemical measurements were performed using a Bio-Logic SAS SP-50 potentiostat at room temperature in a custom-designed Teflon cell containing 0.1 M KOH solution (pre-electrolysed for 24 hrs. at –1.7 V Hg/HgO) and deaerated with argon gas (99.99%). A schematic cross section view of the custom Raman cell can be seen in Fig. 1. The reduced electrolyte concentration was required because of the quartz window in the in situ Raman spectroscopy cell. A reversible hydrogen electrode (RHE) was used as a reference electrode (~782 mV vs. Hg/HgO). A glassy carbon plate with a geometric surface area of 3 cm² was used as the counter electrode. The working electrodes were prepared by depositing the catalysts ink onto a 9.5 mm diameter glassy carbon disk. Raman spectra were obtained for cyclic voltammetry cycles 5, 10, 20, 50, 75, and 100 using a scan rate of 0.4 mV/s. Other cycles where Raman spectra were not obtained used a scan rate of 50 mV/s to mimic ex situ measurements. The Raman spectra were acquired at 50 mV intervals with each measurements lasting 125 s. Each Raman spectrum is then attributed to an average value over a 50 mV window when cycling. For steady-state potentiostatic measurements, Raman spectra were obtained for each 20 mV step once the current stabilized.

Results and Discussion

Fabrication and structural characterization.—Fig. 2 shows the XRD spectra for Ni₇₄.₂Co₅ Nb₁₂.₅ Y₈.₃ after being cryogenically milled for 3, 6, and 12 hr. The use of cryogenic temperatures was necessary for the amorphization reaction to occur in this alloy system as performing milling at room temperature induced little amorphization even after 12 hr. The alloy milled for 6 hrs. shows a predominantly amorphous structure as evident by the broad peak observed in XRD. Residual trace amounts of Y₂O₃ after 6 hrs. of milling are also observed. Although the yttrium is stored in an argon filled glove box, yttrium has a high affinity for oxygen leading to some oxidation during milling. Prolonged milling for 12 hrs. was noted to cause instability in the amorphous phase allowing some recrystallization to occur. The microstructure of Ni₇₄.₂Co₅ Nb₁₂.₅ Y₈.₃ alloy after 6 hrs. of cryogenic milling was further investigated through imaging and electron diffraction in TEM (Fig. 3). The edges of particles were used for imaging and electron diffraction due to the still relatively large particle size for TEM. Even with thickness variations in the particle, there are no observed crystalline features in the bright field (BF) image. This observation is further validated through SAD patterns, as shown in Fig. 3. The presence of a singular broad ring indicated that the microstructure is amorphous and free of crystalline features. Previous work has shown similar milling behavior was observed for Ni₇₉.₂Nb₁₂.₅ Y₈.₃ with XRD and TEM studies indicating 6 hrs. of cryogenic milling was able to yield an amorphous structure. Crystalline Ni₇₄Co₅ was also prepared through mechanical alloying at room temperature to compare the effect of Co addition in both crystalline and amorphous alloys. The compositions of mechanically alloyed amorphous Ni₇₄.₂Co₅ Nb₁₂.₅ Y₈.₃ (x = 0, 5 at.%) and crystalline Ni₉₀Co₅ were measured using ICP-OES and compared to the nominal composition, shown in Table I. The ICP analysis was shown to be in excellent agreement with the nominal composition, henceforth in the manuscript the nominal composition was used to identify the powders. The excellent correlation also demonstrated that the methodology used to produce the alloys was robust and alloys can be fabricated within ± 1 atomic percent. Through ICP-OES no...
Table I. Nominal and measured (ICP-OES) compositions for mechanically alloyed powders.

| Material (at.%)          | Ni (at.%) | Co (at.%) | Nb (at.%) | Y (at.%) |
|--------------------------|-----------|-----------|-----------|----------|
| Crystalline Ni$_{95}$Co$_5$ | Nominal 95 | 5         |           |          |
|                           | ICP-OES   | 95.1 ± 2.56 | 4.9 ± 0.29 |          |
| Amorphous Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$ | Nominal 79.2 | 12.5 | 8.3 |          |
|                           | ICP-OES   | 81.1 ± 2.39 | 11.1 ± 2.90 | 7.8 ± 1.53 |
| Amorphous Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ | Nominal 74.2 | 5 | 12.5 | 8.3 |
|                           | ICP-OES   | 73.1 ± 2.37 | 5.0 ± 0.27 | 12.4 ± 2.84 |

Figure 3. TEM bright field image of Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ cryogenically milled for 6 hrs. with inset of the corresponding selected area electron diffraction pattern.

Figure 4. SEM images of mechanically alloyed powders before and after electrochemically cycling 220 times in deaerated 1 M KOH at 30°C.

significant impurities were detected within these powders (i.e. Fe < 0.1 at. % was observed).

Fig. 4 shows SEM images comparing morphology and particle size of crystalline Ni$_{95}$Co$_5$ and amorphous Ni$_{79.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ (x = 0, 5 at.%) before and after electrochemical testing. Crystalline Ni$_{95}$Co$_5$ is shown to have much larger particle sizes (43 ± 29 μm) which are more plate-like compared to the amorphous powders (9 ± 5 μm for Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$ and 6 ± 3 μm for Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$). These differences are attributed to amorphous alloys being more brittle and milled under cryogenic temperatures while Ni$_{95}$Co$_5$ was milled at room temperature. No noticeable changes in powder morphology were observed after electrochemical testing for all three alloys. Similarly, XRD showed no discernable differences in structure of the powders after electrochemical testing indicating the amorphous powders are stable electrocatalysts.

**OER activity.**—The OER electrocatalytic performance of amorphous Ni$_{79.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ (x = 0, 5 at.%) powder (6 hrs.) was investigated by performing Tafel measurements using steady-state polarization after anodic cycling. These alloys were chosen for electrochemical studies based on XRD and TEM analysis that confirmed a fully amorphous microstructure. Fig. 5 shows a comparison of Tafel slopes between these alloys and crystalline Ni and Ni$_{95}$Co$_5$ after being anodically cycled 50 times. The Tafel values, along with the OER onset potential (E$_{onset}$) and current density at 600 mV$_{Hg/HgO}$ (j$_{600}$ mV), are shown in Table II. These results demonstrate that the addition of Co to Ni is beneficial for enhancing the OER kinetics in both crystalline and amorphous alloys by reducing the Tafel slope and increasing the current density at a given voltage.

It is also noted in Table II that the addition of Co reduced the onset potential for the OER (E$_{onset}$) for the amorphous alloy but increased it for the crystalline alloy. These results were consistent with previous reports which suggested that this difference in behavior for E$_{onset}$ is due to crystalline NiCo alloys forming non-reversible crystalline Co-based oxides on the surface while amorphous Ni-Co alloys form reversible hydrous Co oxy/hydroxides. Prolonged anodic cycling of crystalline Ni$_{95}$Co$_5$ and amorphous Ni$_{79.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ (x = 0, 5 at.%) further accentuated these differences. Fig. 6 shows CV curves for alloys cycled between 0.1 and 0.7 V$_{Hg/HgO}$ 220 times using a scan rate of 50 mV/s. These alloys exhibited the formation (A$_1$) and reduction (C$_1$) peaks of NiOOH surface species. The crystalline Ni$_{95}$Co$_5$ (Fig. 6a) and amorphous Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$ (Fig. 6b) cathodic peak exhibited splitting into two peaks C$_{1A}$ and C$_{1'}$, which has been previously noted to be the reduction of β-NiOOH and γ-NiOOH, respectively. The presence of cathodic peak splitting indicated
Table II. Tafel slope, onset potential ($E_{\text{onset}}$), and current density ($j \times 10^{-3} \text{mA/cm}^2$) values for the OER of crystalline Ni, Ni$_{95}$Co$_5$, and amorphous Ni$_{79.2}$Co$_{4.8}$Nb$_{12.5}$Y$_{8.3}$ ($x = 0, 5 \text{ at.\%}$) after anodically cycling 50 times with a scan rate of 50 mV/s between 0.1 and 0.7 V$_\text{Hg/HgO}$. Experiments were conducted in deaerated 1 M KOH at 30$^\circ$C and values and errors are based on a minimum of three tests.

| Material                        | Tafel Slope (mV/dec) | $E_{\text{onset}}$ (mV) | $j \times 10^{-3}$ (mA/cm$^2$) |
|---------------------------------|----------------------|--------------------------|-------------------------------|
| Ni                              | 77 ± 1.0             | 541 ± 1.7                | 7.71 ± 1.95                   |
| Ni$_{95}$Co$_5$                 | 51 ± 3.8             | 566 ± 7.8                | 20.2 ± 8.44                   |
| Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$ | 51 ± 2.3             | 548 ± 1.3                | 5.88 ± 1.32                   |
| Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ | 47 ± 4.2             | 518 ± 6.1                | 92.2 ± 12.9                   |

β-NiOOH is not stabilized and was converted to γ-NiOOH which lead to the lack of increased performance in these alloys with cycling. Continued cycling of the crystalline alloy exhibited an anodic peak growing around 0.62 V$_\text{Hg/HgO}$ ($A_2$). This peak was associated with the formation of CoO$_2$ and the absence of a corresponding cathodic peak suggested the oxide was not being fully reduced during cycling. The observation of CoO$_2$ peak appeared to be linked with the formation of γ-NiOOH which suggest that as Co is oxidized to CoO$_2$ it is no longer able to aid in the stabilization of β-NiOOH. In contrast, amorphous Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ (Fig. 6c) did not show a peak at 0.62 V$_\text{Hg/HgO}$. The absence of this peak in the amorphous alloy implied that any Co surface species being formed were subsequently reducible and did not accumulate as a separate phase on the surface, which aided in the stabilization/doping of β-NiOOH.

Fig. 6 shows the current at OER (0.7 V$_\text{Hg/HgO}$) for the crystalline alloy did not increase with potential cycling. The steady current indicated the alloy is not becoming more active with progressive cycling even though the currents associated with the anodic and cathodic peaks continued to increase. Conversely, the amorphous Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ appeared to become more active toward the OER when cycled, in good agreement with other amorphous Ni-based systems shown to produce hydrous oxy/hydroxide surface species. These results suggested that the formation of CoO$_2$ on the surface in the crystalline alloy is ultimately not beneficial for the OER activity. To further confirm this hypothesis, steady-state polarization was conducted after cycling 220 times. Values for the Tafel slope, $E_{\text{onset}}$, and $j \times 10^{-3} \text{mA/cm}^2$ are tabulated in Table III. These results validated the observations seen in CV measurements and show that the speciation of Co is vital for the activation process. Comparing the results from Table III to those seen in Table II for 50 cycles showed no major differences in activity for crystalline Ni$_{95}$Co$_5$ and amorphous Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$. The conversion to γ-NiOOH, and CoO$_2$ surface species for crystalline Ni$_{95}$Co$_5$ dominated the OER given that the NiOOH peaks ($A_1$ and $C_1$) continued to increase in current during cycling. The cycling characteristics of the amorphous Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ did not show any presence of $A_2$ or $C_1$ splitting. The absence of these peaks resulted in the reduction in

![Figure 5](image1.png)  
Figure 5. Comparison of Tafel slopes between Ni powder, crystalline Ni$_{95}$Co$_5$, and amorphous Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$. Samples were anodically cycled 50 times between 0.1 and 0.7 V$_\text{Hg/HgO}$. Experiments were conducted in deaerated 1 M KOH at 30$^\circ$C.

![Figure 6](image2.png)  
Figure 6. Cyclic voltammograms for a) crystalline Ni$_{95}$Co$_5$, b) amorphous Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$, and c) amorphous Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ cycled 220 times between 0.1 and 0.7 V$_\text{Hg/HgO}$ in deaerated 1 M KOH at 30$^\circ$C. Samples were cycled using a scan rate of 50 mV/s.
both Tafel slope (47 to 40 mV/dec) and $E_{\text{onset}}$ (518 vs. 509 mV) values with $j_{600}$ mV increasing more than twofold (92.2 to 209 mA/cm$^2$) when going from 50 cycles to 220 cycles. From Tables II and III it is clear that for a fixed overpotential of 600 mV$_{\text{Hg/HgO}}$: (i) the amorphous Co containing alloy displays a higher current density than the corresponding crystalline alloy, (ii) this effect is enhanced by further cycling (4.5X at 50 cycles, 10.1X at 220 cycles, and (iii) the presence of Co is essential to the catalytic activity toward the OER as the amorphous Co free alloy is not as active, hence both structure and chemistry are critically important.

Another marked difference between amorphous and crystalline CV curves was the amorphous alloys have a slightly more positive A$_1$ peak position which remained constant upon cycling whereas the A$_1$ peak in the crystalline alloy shifted to more positive potentials upon cycling. It is suggested that this difference is a result of amorphous alloys forming hydrous (Ni,Co)OOH while crystalline Ni-Co alloys form NiOOH and CoO$_2$.12,25 Further XPS work is ongoing to confirm the binding shell chemistry.

**In situ confocal Raman spectroscopy characterization.—**In situ confocal Raman spectroscopy was employed to investigate the assumption that the crystalline alloy formed CoO$_2$ and the amorphous alloys formed hydrous (Ni,Co)OOH during potential cycling. The pairing of Raman spectroscopy with CV can provide useful information as to what surface species are being produced and reduced during cycling and the form in which they exist in situ. Fig. 7 demonstrates the ability for Raman spectroscopy to monitor the formation of NiOOH upon the anodic scan (a) and the reduction of NiOOH during the reverse scan (b). The two peaks observed around 460 cm$^{-1}$ and 530 cm$^{-1}$ are attributed to $\delta$ (Ni$^{\text{III}}$ – O) and $\nu$ (Ni$^{\text{III}}$ – O) vibrations respectively.26,27 The broad feature occurring around 1000 cm$^{-1}$ is the formation of NiO$^-$.$^26$

Raman spectra were also generated for Ni powder at cycles 5, 10, 20, 50, 75, and 100 to provide a baseline of peak positions throughout the cycling process as shown in Fig. 8a). With increased cycling, pure Ni was observed to deactivate after cycle 20 and the formation of oxygen on the surface interfered with the Raman signal. Similar experiments were also performed for Co powder (Fig. 8b) which showed peaks at 453, 539, 600, and 670 cm$^{-1}$. The peaks at 453 (E$_g$), 600 (F$_2g$), and 670 (A$_1g$) cm$^{-1}$ have been previously reported to correspond with bare Co with the peak at 539 cm$^{-1}$ (F$_2g$) being attributed to the presence of CoO(OH).27–30 Given that the Co(OH)$_2$ Raman peak position overlaps with the NiOOH peaks, and only a small concentration of the alloys is Co (5 at.%), this peak cannot be easily used to uniquely identify the presence of CoO(OH) over NiO(OH). Instead Yeo and Bell$^28$ reported that anodic polarization of CoO$_x$ from 0 to 0.7 V$_{\text{Hg/HgO}}$ in 0.1 M KOH red-shifts a singular Raman peak from 609 cm$^{-1}$ to 579 cm$^{-1}$ as the oxidation state of Co goes from Co(II) to Co(IV). This red-shift is due to the applied redox potential and has been previously seen in the oxidation of CoO$_x$ in a O$_2$/Ar plasma as the mole fraction of O$_2$ increased.$^{27}$ As such, the presence of a peak in the Raman spectra within the range of 609 to 579 cm$^{-1}$ would suggest Co is present as an oxide rather than as CoO(OH).

Fig. 9 shows a comparison of Raman spectra produced during cycle 100 in the cathodic direction between (a) crystalline Ni$_{95}$Co$_5$, (b) amorphous Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$, and (c) amorphous Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$. The Raman intensities were normalized to the intensity of crystalline Ni$_{95}$Co$_5$ peaks for ease with identification and comparison. Initially, amorphous alloys showed at least 10X lower intensities compared to crystalline Ni$_{95}$Co$_5$ that suggests the surface species of amorphous alloys are more disordered and hydrous in nature compared to those on the crystalline alloy. The most obvious peaks observed are the $\delta$ (Ni$^{\text{III}}$ – O) and $\nu$ (Ni$^{\text{III}}$ – O) Ni peaks. Amorphous Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$ also shows a noticeable peak around 610 cm$^{-1}$ which can be attributed to the $\nu_5$ (Y-O) vibration mode for Y(OH)$_3$ peak.$^{31}$ The presence of Y
surface species was not observed in amorphous Ni74.2Co5Nb12.5Y8.3. The absence of Y Raman peaks in amorphous Ni74.2Co5Nb12.5Y8.3 suggested that Co diffuses to the surface during anodic cycling producing a predominant Ni and Co rich surface. These observations indicate Ni and Co surface species in amorphous Ni74.2Co5Nb12.5Y8.3 are largely responsible for the catalytic activity and correlate with previous XPS depth characterization reports on amorphous Ni-Co alloys.13,14

Due to the low concentration of Co, the CoOx peak is not easily discernable. The CoOx peak position and intensity becomes more apparent when using the Raman spectra from the Ni powder to deconstruct the Ni peaks which is summarized in Table IV. The presence of a CoOx is highlighted using bold text. For amorphous Ni79.2Nb12.5Y8.3 the Y(OH)3 peak is italicized. As noted in Fig. 6a), the CV curve does not show a reduction peak for CoO2, yet the Raman spectra for the crystalline alloy consistently indicated the presence of Co oxides on the surface. By cycle 10 a peak around 590 cm\(^{-1}\) continued to be present for all remaining forward and reverse scans with very little change in Raman peak position. The lack of a change in position verifies that the surface oxide for the crystalline alloy was not being reduced during cycling as changes in Co speciation between Co(II), Co(III), and Co(IV) would have resulted in peak shifts.27

Interestingly the presence of Co oxide was also observed in Fig. 9 for the amorphous Ni74.2Co5Nb12.5Y8.3 at higher potentials even though it was not detected during CV measurements. From 0.5 to 0.6 \(V_{\text{Hg/HgO}}\) the appearance of a peak around 590 cm\(^{-1}\) was observed but subsequently was reduced in the following reverse scan. This phenomenon was observed for each cycle for which Raman spectra were acquired. The formation of Co oxides was noted to correspond with the presence of \(\beta\)-NiOOH over \(\gamma\)-NiOOH. Previous in situ Raman spectroscopy work in 0.1 M KOH has shown the ratio of intensities between the \(\delta\) (Ni\(^{III}\) – O) and \(\nu\) (Ni\(^{III}\) – O) Ni peaks (I\(_{460}/I_{530}\)) can provide insight into which phase is predominant.26,32 These studies have shown that higher ratios are associated with \(\gamma\)-NiOOH due to the disordered structure restricting molecular stretching vibrations (\(\nu\)) and favoring bending ones (\(\delta\)).26,32 Lower intensity ratios refer to \(\beta\)-NiOOH and yield better electrochemical performance.26,32

Table III shows that during potential cycling into the regime of the OER, the I\(_{460}/I_{530}\) ratio decreased for the amorphous and crystalline alloys with amorphous Ni74.2Co5Nb12.5Y8.3 consistently showing the lowest values. Fig. 10 shows a comparison between these crystalline Ni5Co5 and amorphous Ni74.2Co5Nb12.5Y8.3 at 0.6 \(V_{\text{Hg/HgO}}\) during cycle 100. It can be seen that when overlaying the normalized data that the \(\nu\) (Ni\(^{III}\) – O) peak (530 cm\(^{-1}\)) increased for the amorphous Ni74.2Co5Nb12.5Y8.3 indicating the formation of \(\beta\)-NiOOH. These results are consistent with potential cycling and Tafel measurements indicating amorphous materials are more OER active than their crystalline counterparts. Table III also shows that the lowest peak intensity ratios (I\(_{460}/I_{530}\)) were also associated with the presence of a Co oxide peak for Ni74.2Co5Nb12.5Y8.3.

Raman spectra were captured during Tafel measurements using potentiostatic polarization to further investigate the effect of Co on Ni surfaces species during OER. Fig. 11 displays the peak intensity ratio of I\(_{460}/I_{530}\) at select potentials close to the OER during cycle 100 for crystalline Ni5Co5, amorphous Ni79.2Nb12.5Y8.3, and amorphous Ni74.2Co5Nb12.5Y8.3. Observation of CoOx peaks are highlighted in bold text and italics are used to highlight Y(OH)3.

### Table IV. Peak positions (cm\(^{-1}\)) and peak intensity ratio of I\(_{460}/I_{530}\) at select potentials close to the OER during cycle 100 for crystalline Ni5Co5, amorphous Ni79.2Nb12.5Y8.3, and amorphous Ni74.2Co5Nb12.5Y8.3.

| Voltage (V\(_{\text{Hg/HgO}}\)) | Crystalline Ni5Co5 | Amorphous Ni79.2Co5Ni12.5Y8.3 | Amorphous Ni74.2Co5Ni12.5Y8.3 |
|-----------------------------|-------------------|-------------------------------|-------------------------------|
|                             | Peak Positions (cm\(^{-1}\)) | I\(_{460}/I_{530}\) | Peak Positions (cm\(^{-1}\)) | I\(_{460}/I_{530}\) | Peak Positions (cm\(^{-1}\)) | I\(_{460}/I_{530}\) |
| 0.425 (f)                   | 456, 533, 594     | 2.28                          | 453, 525, 607                | 2.38                          | 458, 527                 | 1.99              |
| 0.475 (f)                   | 456, 532, 593     | 2.22                          | 453, 527, 606                | 2.57                          | 457, 529                 | 2.04              |
| 0.525 (f)                   | 457, 532, 594     | 2.15                          | 453, 525, 606                | 2.50                          | 457, 529                 | 2.10              |
| 0.575 (f)                   | 457, 533, 593     | 2.08                          | 452, 523, 610                | 2.13                          | 458, 534, 595           | 1.77              |
| 0.575 (t)                   | 457, 533, 591     | 2.06                          | 452, 525, 606                | 1.99                          | 459, 534, 593           | 1.77              |
| 0.525 (t)                   | 457, 532, 591     | 2.11                          | 451, 525, 606                | 2.03                          | 459, 534, 590           | 1.86              |
| 0.475 (t)                   | 456, 533, 593     | 2.13                          | 453, 526, 607                | 2.22                          | 458, 533, 599           | 2.00              |
| 0.425 (t)                   | 456, 532, 591     | 2.15                          | 454, 525, 608                | 2.48                          | 457, 531                | 2.16              |

(f) refers to forward scan, (t) refers to reverse scan.
Figure 9. In situ Raman spectra acquired for a) crystalline Ni$_{95}$Co$_{5}$, b) amorphous Ni$_{79.2}$Nb$_{12.5}$Y$_{8.3}$, and c) amorphous Ni$_{74.2}$Co$_{5}$Nb$_{12.5}$Y$_{8.3}$ for cycle 100 during the cathodic scan between 0.6 and 0.2 V$\text{Hg/HgO}$ at 0.4 mV/s. Experiments were performed in deaerated 0.1 M KOH at room temperature.

Figure 10. Normalized in situ Raman spectra comparing amorphous Ni$_{74.2}$Co$_{5}$Nb$_{12.5}$Y$_{8.3}$ and crystalline Ni$_{95}$Co$_{5}$ at 0.6 V$\text{Hg/HgO}$ during cycle 100. Experiments were performed in deaerated 0.1 M KOH solution at room temperature.

Figure 11. Peak intensity ratio of Ni $\delta$ and $\nu$ (I$_{460}$/I$_{530}$) vs. voltage during potentiostatic polarization to Tafel regime after anodically cycling 100 times for amorphous Ni$_{74.2}$Co$_{5}$Nb$_{12.5}$Y$_{8.3}$. Dotted line indicates the OER onset potential for Ni$_{74.2}$Co$_{5}$Nb$_{12.5}$Y$_{8.3}$.
and in situ confocal Raman spectroscopy revealed that during anodic cycling amorphous Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$ produced a Ni-Co oxyhydroxide film on the surface which was reversible. Pairing of Tafel measurements and in situ Raman spectroscopy revealed the formation of CoO$_x$ at the onset of OER in crystalline Ni$_{95}$Co$_5$. This phenomena, along with the enhanced reversibility of hydrous surface species, result in the superior cycling and catalytic performance of Ni$_{74.2}$Co$_5$Nb$_{12.5}$Y$_{8.3}$.

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References
1. M. A. Hickner, A. M. Herring, and E. B. Coughlin, J. Polym. Sci. Part B Polym. Phys., 51, 1727 (2013).
2. J. R. Varcoe et al., Energy Environ. Sci., 7, 3135 (2014).
3. S. Marini et al., Electrochim. Acta, 82, 384 (2012).
4. M. K. Cho et al., J. Power Sources, 347, 283 (2017).
5. X. Li, X. Hao, A. Abudula, and G. Guan, J. Mater. Chem. A, 4, 11973 (2016).
6. I. Roger, M. A. Shipman, and M. D. Symes, Nat. Rev. Chem., 1, 1 (2017).
7. F. Le Formul, W. S. Bournèe, M. S. Prévot, and K. Sivula, Chem. Int. J. Chem., 69, 789 (2015).
8. S. Park, Y. Shao, J. Lin, and Y. Wang, Energy Environ. Sci., 5, 9331 (2012).
9. T. N. Lambert et al., Chem. Commun., 51, 9511 (2015).
10. J. Wang et al., Adv. Mater., 28, 215 (2016).
11. R. D. L. Smith, M. S. Prévot, S. Trudel, and C. P. Berlinguette, J. Am. Chem. Soc., 135, 11580 (2013).
12. K. Lian and V. I. Birss, J. Electrochem. Soc., 138, 2877 (1991).
13. K. Lian and S. J. Thorpe, J. Electrochem. Acta, 37, 2029 (1992).
14. A. Budniok and J. Kapka, Electrochim. Acta, 44, 871 (1999).
15. T. Kessler, W. Tiaca, and A. Arvia, J. Appl. Electrochem., 24, 310 (1994).
16. J. J. Podesta et al., Int. J. Hydrogen Energy, 17, 9 (1992).
17. M. H. Enayati and F. A. Mohamed, Int. Mater. Rev., 59, 394 (2014).
18. C. Suryanarayana, Prog. Mater. Sci., 46, 1 (2001).
19. N. Mattern et al., Scr. Mater., 53, 271 (2005).
20. A. Gebert, N. Mattern, U. Kühn, J. Eckert, and L. Schulz, Intermetallics, 15, 1183 (2007).
21. C. C. L. McCrory et al., J. Am. Chem. Soc., 137, 4347 (2015).
22. S. Ghobrial, D. W. Kirk, and S. J. Thorpe, ECS Trans., 85, 107 (2018).
23. D. E. Pissinis, L. E. Sereno, and J. M. Marioli, Open J. Phys. Chem., 2, 23 (2012).
24. S. Yoon, J. Y. Yun, J. H. Lim, and B. Yoo, J. Alloys Compd., 693, 964 (2017).
25. B. S. Yeo and A. T. Bell, J. Phys. Chem. C, 116, 8394 (2012).
26. K. S. Joya and X. Sala, Phys. Chem. Chem. Phys., 17, 21094 (2015).
27. B. S. Yeo and A. T. Bell, J. Am. Chem. Soc., 133, 5587 (2011).
28. C. A. Melendres and S. Xu, J. Electrochemical Soc., 131, 2239 (1984).
29. C. W. Tang, C. B. Wang, and S. H. Chien, Thermochim. Acta, 473, 68 (2008).
30. B. Bozini, E. Tondo, P. Raffa, and M. Boniardi, Trans. Instute Met. Finish., 90, 30 (2012).
31. M. W. Louie and A. T. Bell, J. Am. Chem. Soc., 135, 12329 (2013).
Erratum: In Situ Raman Study of Amorphous and Crystalline Ni-Co Alloys for the Alkaline Oxygen Evolution Reaction [J. Electrochem. Soc., 165, J3122 (2018)]

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The caption for Figure 1 on page J3123 should appear as:

Figure 1. Schematic cross section view of custom Raman cell used to perform in situ Raman spectroscopy studies (courtesy of G. Jerkiewicz and S. Baranton).

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