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In situ Formation of Nano Ni-Co Oxyhydroxide Enables Water Oxidation Electrocatalysts Durable at High Current Densities

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Abstract. The oxygen evolution reaction (OER) limits the energy efficiency of electrocatalytic systems due to the high overpotential symptomatic of poor reaction kinetics; this problem worsens over time if the performance of the OER electrocatalyst diminishes during operation. Here we report a novel synthesis of nanocrystalline Ni-Co-Se for alkaline OER using ball milling at cryogenic temperature. We discovered that, by anodizing the Ni-Co-Se structure during OER, Se ions leached out of the original structure completely, allowing water molecules to hydrate Ni and Co defective sites, and the nanoparticles to evolve into an active Ni-Co oxyhydroxide. We observe this transformation using operando synchrotron x-ray absorption spectroscopy, with the findings confirmed using density functional theory calculations. The

resulting electrocatalyst exhibited an overpotential of 279 mV at 0.5 A.cm⁻² and 329 mV at 1 A.cm⁻² and sustained performance for 500 hours. This is achieved using low mass loadings (0.36 mg.cm⁻²) of cobalt. Incorporating the electrocatalyst in an anion exchange membrane water electrolyzer yielded a current density of 1 A.cm⁻² at 1.75 V for 95 hours without decay in performance. When we integrated the electrocatalyst into a CO₂-to-ethylene electrolyzer, we achieved a record-setting full cell voltage of 3 V at current density 1 A.cm⁻².

1.1 Introduction

With the large anticipated penetration of low-cost renewable electricity into the power grid comes the need for cost-effective decarbonization strategies combined with large-scale storage. Water splitting and CO₂ reduction (CO₂R) can store electricity in the form of stable chemical bonds in synthetic fuel and chemical feedstocks, mitigating the variability challenge of renewable energy.^[1-3] However, the efficiency of these electrocatalytic systems is limited by the sluggish kinetics and high overpotentials at the anode imposed by the oxygen evolution reaction (OER).^[4] A relatively small selection of OER electrocatalysts meets the requirements needed for industrial electrocatalysis; low OER overpotentials (<300 mV) at high current densities (>500 mA.cm⁻²) for long-term operation (ultimately >60,000 h)^[5]. Identifying durable and efficient OER electrocatalysts is urgently needed to enable large-scale industrial implementation of important electrocatalytic technologies such as water splitting and CO₂R.

To date, benchmark noble electrocatalysts based on RuO_x and IrO_x are considered state-of-the-art OER electrocatalysts in view of their superior performance; unfortunately, their high price and scarcity limit their widespread application. In contrast, earth abundant metal oxides, selenides, nitrides and phosphides derived from the first-row transition metals Ni, Co, and Fe can offer a cheaper alternative for efficient OER electrocatalysts in anion exchange membrane

(AEM) systems, which utilize an alkaline environment that is more compatible with non-noble metal electrocatalysts than an acidic environment.

One of the most efficient non-noble OER electrocatalysts in alkaline systems is Fe doped NiOOH.^[6–8] While a small amount of Fe can boost the OER electrocatalytic activity of NiOOH, it has been reported that, Fe segregates from the Ni-Fe oxyhydroxide lattice to form a secondary FeOOH phase that deactivates the electrocatalyst.^[9] Berlinguette et al. found that at 200 mA.cm⁻² in strong base electrolytes, NiFeO_x OER electrocatalyst had a similar degradation problem as a significant amount of Fe left the structure and diffused to the cathode.^[10] Furthermore, Markovic et al. investigated the activity and stability trends for monometallic oxyhydroxides and observed that Fe is the least stable compared to Ni and Co.^[11] These findings motivate the development of an Fe-free earth abundant OER electrocatalyst that is both active and stable in alkaline conditions.

Among candidates to replace Fe in Ni electrocatalysts, Co is known to lower the OER overpotential and improve electrochemical stability.^[12,13] However, since Co is heavily used in energy applications, especially Li-ion batteries, it is anticipated that it may suffer supply shortages in future.^[14] This mandates the development of methods to reduce Co loadings in energy materials. Here we deploy Se, a chalcogenide, with Ni and Co, to serve as a sacrificial scaffold to enable the efficient activation of small mass loadings of Co in the electrocatalyst during OER. Prior reports have shown that metal selenides are thermodynamically unstable during OER at high pH, resulting in structural changes such as increased nanoporosity, disordering in the lattice, and high density of defective surface sites.^[15–17] We lever these localized structural changes to form, *in situ* amorphous nano Ni-Co oxyhydroxides with high mass and specific activities.

Synthesizing metal chalcogenides has previously proven challenging due to the immiscibility of the constituent elements and the need for high thermal activation temperatures

>500 °C.^[18] We used cryomilling – ball milling at cryogenic temperatures – to synthesize well-mixed Ni-Co-Se electrocatalysts. Milling at such low temperatures provided us with control over a wide compositional range of the compound and enabled the formation of amorphous structures. Amorphous metals have been produced by a variety of methods: atomization, electrodeposition, electroless deposition, planar and flow casting. However, amorphous alloys produced by these methods are limited to a narrow compositional range near low melting point eutectics, unlike cryomilling which can produce a wider range of amorphous phases centered around high melting point intermetallics. Accordingly, targeting Ni-Co-Se compositions with a high melting point favors disordering and the formation of abundant defective and coordinatively unsaturated sites (CUS) that can facilitate the hydration of Ni and Co sites and the formation of oxyhydroxides.^[12,16,19–22] After synthesis, we activated Ni-Co-Se by subjecting it to OER conditions and evaluating its half-cell activity and stability at high current densities >100 mA.cm⁻². The activation process was investigated using operando X-ray absorption spectroscopy (XAS), electron energy-loss spectroscopy (EELS), and density functional theory (DFT) calculations. We find that Se leaches, induces surface reconstruction during OER, and facilitates the hydration of metal centers to form active oxyhydroxides. We study the performance of Ni-Co-Se as OER electrocatalyst with respect to requirements for water splitting and CO₂R in a 5 cm² AEM-based membrane-electrode-assembly (MEA) electrolyzer. We report a full cell voltage delivering 1 A.cm⁻² at 1.75 V for water splitting and 3 V for CO₂R.

1.2 Synthesis and activation of electrocatalysts.

The electrocatalysts were synthesized using a one-pot ball milling process in two steps 1) mechanical alloying at a cryogenic temperature (< -196°C) to produce disordered structures and 2) surfactant-assisted ball milling (SABM) at room temperature to reduce the size of the alloy to nanoparticles (**Figure 1a**). The combination of high-speed mixing (30 Hz, 1800 rpm)

and low temperature (-196 °C) facilitates the formation of nanocrystalline structures centered at high-melting point compositions (see supplementary information for synthesis description).

First, Ni-Se and Co-Se control samples were synthesized to investigate the milling behaviour of Ni and Co with Se and to confirm the formation of metal selenide phases without the need for thermal activation. We observed characteristic XRD peaks of binary metal selenide phases after just 6 hours of cryomilling and no peaks for elemental Ni, Co, or Se, indicative of full incorporation of Se in a mixed Ni-Co selenide structure (**Figures S1 and S2**). Due to the high kinetic energy induced by ball-powder-ball collisions at high speeds, alloying is facilitated by repeated fracture and cold welding of the particles, while crystal defects and the local rise in temperature aids the diffusion of elements in the alloyed structure.^[23] We found that, despite the possibility of particles welding together due to excessive collisions during milling, Se played an important role in stabilizing single phase nanoparticles (<100nm) with Ni and Co (see supplementary information). To reduce Fe contamination from the stainless steel balls and the walls of the vial during milling, we run the mill for a few minutes with the starting precursors to cover all the inside walls of the vial and the surface of the balls with a thick layer of the precursor and prevent direct collision with any Fe. Using inductive coupling plasma atomic emission spectroscopy ICP-AES, we found that the Fe concentration in the catalyst after cryomilling was limited to 0.05 ± 0.03 at. % (see supplementary information for experimental details).

Afterwards, we synthesized Ni-Co-Se compounds centered about two high-melting point compositions: (NiCo)Se and (NiCo)₃Se₄. The particles of Ni-Co-Se compounds had an average size greater than 1 μm and a small surface-to-volume ratio, which is undesirable for electrocatalysis. Therefore, a surfactant was used in the second SABM step to reduce the particle size of the alloyed compounds to 67 nm for (NiCo)₃Se₄ and 37 nm for (NiCo)Se (**Figures 1c, S4, S5, and S6**). The broad diffraction peaks in XRD indicated that nano-sized

crystallites (8.37 nm) were produced after SABM (**Figure 1b**, see supplementary for calculations). Finally, the surfactant was removed from the surface of the alloy after synthesis via washing. After milling, the particles were sonicated for 30 mins in ethanol before centrifuging at 10,000 rpm (11,000 rcf) for 1 h and then the clear solution was washed and replaced with fresh ethanol: this procedure was repeated three times until the nanoparticles precipitated to the bottom of the tube. Thermogravimetric analysis (TGA) was conducted to evaluate the extent of removal of the surfactant species after washing. The uncleaned sample had ~2 wt. % mass loss attributed to the residual surfactant, whereas there was a negligible mass loss (<0.001 wt. %, below the detection limit of the instrument) for the washed particles, indicating the washing step was effective in removing the surfactant (**Figure S7**). In summary, Se played an important role in tailoring the size and crystal structure of the cryomilled alloys. Cryomilling Ni-Co without Se produces large (> 6 μm) crystalline particles which are not amorphized even under prolonged milling times (**Figure S3**).

We then activated (NiCo)Se and (NiCo)₃Se₄ electrochemically by selectively leaching Se out of the nanocrystalline structure (**Figure 2a**). According to the Pourbaix diagram of Se, Se oxidizes to soluble SeO₃²⁻/SeO₄²⁻ at high pH during the OER. The activation process was conducted in 1M of pre-electrolyzed KOH, to purify the electrolyte from Fe ions that could participate in the reaction (**Figure S8**), and initiated by applying a constant current density of 10 mA.cm_{geo}⁻² in a three-electrode cell for 2 hours, a sufficient time to warrant a complete removal of Se.^[15]

Scanning electron microscopy (SEM) images were taken for the as-synthesized (NiCo)₃Se₄ samples before and after activation (**Figure 2b**). Clusters of nanoparticles were observed in the as-synthesized sample and Se accounted for 56 at. % in the structure. After activation, the morphology of the clusters was altered and Se was completely removed (0 at. %, as confirmed by energy dispersive spectroscopy (EDS)), while the atomic ratio between Ni

150 and Co remained unchanged (1:1). TEM and electron energy loss spectroscopy (EELS)
151 mapping were conducted on the as-synthesized (**Figure 2c**) and activated samples (**Figure 2d**).
152 EELS elemental maps showed that Ni, Co, and Se in the as-synthesized $(\text{NiCo})_3\text{Se}_4$ were
153 homogeneously distributed in *ca.* 10 nm nanoparticles. This was also seen by scanning
154 transmission electron microscopy (STEM) and EDS (**Figure S6**). EELS spectra were acquired
155 from the areas indicated in the elemental maps (**Figure S9**). Using EELS $L_{2,3}$ edge position,
156 the oxidation state of Ni and Co in the as-synthesized sample was determined to be 2+ (**Figures**
157 **S10a and S10b**), this, in addition to the lack of O signal inside the particles as shown by the O
158 EELS map (**Figures 2d, S9a**), confirmed that Ni and Co were incorporated in the selenide
159 structure forming Ni-Co-Se. After activation, Se was not detected in the catalyst structure using
160 EELS (**Figures 2c, S10c**), confirming that Se was completely leached out of the structure
161 during electrochemical activation while O was present throughout the particles. The EELS $L_{2,3}$
162 edge position of Ni and Co showed that the oxidation state of both Ni and Co were increased
163 to 3+ after activation (**Figures S10a and S10b**). Furthermore, we conducted inductively
164 coupled plasma atomic emission spectroscopy (ICP-AES) on the catalyst during the first 48
165 hours of the OER (**Figure S11**). We observed that Se dissolved within the first *ca.* 10 mins of
166 the OER confirming EELS and EDS observations. On the other hand, both Ni and Co remained
167 intact in the catalyst as the total ions dissolved amounts were below the background equivalent
168 concentrations (BEC) for Ni (17 ppb) and Co (12 ppb), respectively. XRD and electron
169 diffraction pattern (DP) using TEM were collected after the activation of the sample to
170 investigate the changes in the crystal structure of the catalyst. Both techniques confirmed the
171 change in crystal structure during activation as indicated by the amorphous rings in DP and the
172 lack of diffraction peaks in XRD (**Figures S12 and S13**). Diffraction rings at $2.5\text{\AA}$, $2.1\text{\AA}$,
173 $1.5\text{\AA}$ were clearly observed, corresponding to the (111), (100) and (110) crystal planes of
174 CoO/Co(OH)_2 , Carbon, and Ni(OH)_2 , respectively. ^[24,25]

To characterize the materials further, soft X-ray absorption spectroscopy (sXAS) was conducted to investigate the local chemical and electronic changes to individual Ni, Co and Se atoms after activation. Using a silicon drift detector (SDD), the X-ray absorption near edge structure (XANES) of Se L-edge was obtained. This revealed that Se was incorporated in the dry nanoparticles as selenide (Se^{2-}), and that it departed the structure after activation as indicated by the lack of the Se L-edge signal after 2 h of OER (**Figure 2e**).^[26] The oxidation states of Ni and Co were inspected after activation as shown in XANES of L_3 -edge results (**Figures 2f and 2g**). Two different modes of X-ray detection were used to investigate the oxidation state: fluorescence X-rays using SDD and total electron yield (TEY). The TEY mode is dependent on the conductivity of the surface but is more surface sensitive (<10 nm) compared to SDD (within 100 nm). Using both detection modes allowed us to investigate the changes in oxidation state within the bulk and on the surface of the electrocatalysts before and after activation. The XANES of Ni L_3 -edge of the dry sample revealed that Ni had an oxidation state of 2+ before activation while Co in the as-synthesized sample had a mixed oxidation state of 2+/3+ on the surface implying that Co was in a spinel structure.^[27] The oxidation state of Ni and Co increased to 3+ after activation possibly suggesting the transformation to NiCoOOH .^[28,29] Therefore, we will start describing the catalysts after activation in the following sections as “activated” to reflect the nature of the final structure which is NiCoOOH .

Electrocatalytic performance and stability

The performance of catalysts after activation was evaluated by measuring the overpotential at $10 \text{ mA.cm}_{\text{geo}}^{-2}$ on a glassy carbon electrode as in (**Figure 3a**). The activity of activated $(\text{NiCo})\text{Se}$ and $(\text{NiCo})_3\text{Se}_4$ after SABM (NiCoOOH) improved dramatically due to an increase in the surface-to-volume ratio of the nanoparticles. Alloying Ni and Co in the electrocatalyst lowered the overpotential compared to binary NiSe and CoSe alone by *ca.* 50 mV confirming that Ni and Co have synergistic effects when alloyed together.^[12,30] The best

performance was seen for activated (NiCo)₃Se₄ (NiCoOOH) after SABM with an overpotential of 268±2 mV at 10 mA.cm_{geo}⁻² and a Tafel slope of 42 mV.dec⁻¹ (**Figures S14 and S15 and Table S4**).

To examine the specific catalytic activity, we normalized the current density by the electrochemical surface area (ECSA) using double-layer capacitance measured by cyclic voltammetry (CV) (**Figures S16 and S17**). Activated (NiCo)₃Se₄ (NiCoOOH) demonstrated ECSA current densities 4 times higher than commercial IrO₂ using the same catalyst loading of 0.21 mg.cm⁻² for all electrocatalysts (**Figure 3b**). The turnover frequency (TOF) of the catalyst was calculated as 50.76 x 10⁻³ s⁻¹ per site, considering only Ni and Co as active sites, ca. two folds higher than IrO₂ 28.09 x 10⁻³ per site implying activated (NiCo)₃Se₄ (NiCoOOH) is intrinsically more active.

We then investigated the stability of the catalyst using chronopotentiometry at 10 mA.cm_{geo}⁻² (**Figure S18**). The catalyst maintained a steady overpotential value of 267 mV for 100 h with only 4 mV overpotential increase. At higher current densities and prolonged testing conditions, excessive oxygen bubbling can artificially increase the overpotential by shielding the active sites on the surface and within the pores of the electrocatalyst. Rotating disk electrodes (RDEs) are often used to overcome this problem and improve the detachment of bubbles from the surface of the electrocatalyst and lower mass transport limitations by rotation. However, vigorous rotation for long duration has been reported to affect the binding of the electrocatalyst to the surface of the RDE implying fallacious conclusions about the intrinsic stability of the electrocatalyst.^[31] Therefore, we proposed an alternating current test (ACT) to better assess the intrinsic stability of the electrocatalyst by removing bubbles without mechanical rotation. In ACT, a constant current density of 10 mA.cm_{geo}⁻² was applied to the catalyst for 10 h and then it was allowed to rest at open circuit potential (OCP) for 1 h to release O₂ bubbles on the surface before evaluating the performance using linear sweep voltammetry

(LSV); this resembles one cycle of testing (**Figure 3c**). The potential slowly increased during the first few hours of each cycle because of bubble accumulation on the surface, however, the initial potential was retained in the following cycle suggesting that bubbles were partially or completely released. The test was repeated for 34 cycles (340 hours of operation). After each cycle, the overpotential and Tafel slope were extracted and plotted with respect to time (**Figure 3d**). The electrocatalyst experienced a marginal increase in overpotential (<10 mV) during the entire test while the Tafel slope remained unchanged suggesting that the reaction mechanism was not altered.

The performance of catalyst on nickel foam (NF) was tested at high current densities, the overpotential was 279 mV at $0.5 \text{ A.cm}^{-2}_{\text{geo}}$ and 329 mV at $1 \text{ A.cm}^{-2}_{\text{geo}}$ (**Figure S19**). Next, the stability of the electrocatalyst was evaluated under constant current density (**Figure 3e**). The electrocatalyst had an average potential increase of 0.17 mV.h^{-1} in 500 hours. We compared the performance of activated $(\text{NiCo})_3\text{Se}_4$ (NiCoOOH) with the electrocatalysts from the literature which had demonstrated a durable performance at high current densities $>100 \text{ mA.cm}_{\text{geo}}^{-2}$ (**Table S5**). Our catalyst had the highest mass activities $\text{A.g}_{\text{metal}}^{-1}$ at 1 A.cm^{-2} .

Electronic structure

To investigate the active species during OER and study the dynamics of the electrochemical activation of $(\text{NiCo})_3\text{Se}_4$, in situ XAS on the K-edge of Ni, Co and Se were conducted on the sample at four conditions: dry, OCP, at 1.1 V vs RHE, and during OER at 1.5V vs RHE (**Figure 4**). XANES showed that Se, in the dry sample, was present as a selenide (Se^{2-}) (**Figure 4a**) while Ni had an oxidation state of 2+ and Co had a mixed oxidation state of 2+/3+ suggesting that it exists in a spinel structure (**Figures 4b and 4c**), confirming EELS and sXAS findings. ^[32–34] During OER, Se was oxidized to Se (VI) at 1.5 V as evident by the positive energy shift of the peak at 12,666 eV while the edge position of Ni and Co continuously increased to higher energy values indicating an increase in oxidation state to 3+

during OER.^[35] Extended X-ray absorption fine structure (EXAFS) was conducted to investigate the local structure changes in the vicinity of Ni, Co, and Se atomic sites during OER (**Figures 4d, 4e, and 4f**). A progressive increase in the Se-O peak at 1.7 Å after OCP was observed confirming that Se was leaching out electrochemically as SeO_4^{2-} . In the case of Ni and Co, the as-synthesized sample showed a broad peak centered around *ca.* 2.3 Å and 2.5 Å for Ni and Co, respectively, which corresponds to the single scattering path Ni-Se and Co-Se confirming the local formation of Ni-Co-Se. A FEFF EXAFS fitting was performed to determine the coordination of Ni and Co after cryomilling (**Figure S20**). The coordination of Ni was 3.5 and Co was 3.77 (**Table S6**). Both values are lower than the coordination number of non-defective atoms in tetrahedral and octahedral sites in a Co_2NiSe_4 crystal confirming that the sites are coordinatively unsaturated after synthesis. Once the sample was placed in the electrolyte, a shoulder peak started to emerge at *ca.* 2.0 Å and a new peak at *ca.* 3.0 Å due to the oxidation of Ni and Co and backscattering of Ni-O/Co-O and Ni-Ni/Co-Co in the oxyhydroxides. In the case of Co, there is an additional peak at *ca.* 3.5 Å, a finding we assign to Co occupying an octahedral site in the starting spinel structure.^[36] The Ni-O peak was shifted to the left to 1.88 Å during OER (at 1.5 V) suggesting that Ni oxidized to $\gamma\text{-NiOOH}$.^[37] The Co-O peak at 1.93 Å after the OER confirms the formation of $\gamma\text{-CoOOH}$.^[38] These in situ observations agree with findings from ex situ EELS and sXAS analysis. Finally, XANES spectra were collected for the electrocatalyst after 400 hours of the OER. We found that Ni oxidation state reverted to 2+ after the reaction while Co oxidation maintained a 3+ oxidation state similar to during the OER (**Figure S21**). This indicated that, in contrast with the case of Ni, Co oxidation from 2+ to 3+ is irreversible and that the electrocatalyst is stable after 400 hours of operation.

DFT calculations were used to help in explicating the experimental observations of Se leaching and of surface restructuring to an active oxide layer. Here, OER intermediates were

calculated on the Ni-Se, Ni-Se_{vac}, Ni-Co-Se, and Ni-Co-Se_{vac} (001) and (101) surfaces (see **Figures S22, S23, and S24**). A Se_{vac} (Se vacancy) was used in the model to computationally study the electronic effect of the vacancies, that are left behind in the structure due to Se removal by electrochemical activation, on neighbouring Ni and Co atoms.

Similar results were found for both Miller indices; this discussion shall therefore focus on (101) surfaces and the details of the (001) surface can be found in the Supporting Information. The formation of adsorbed OOH on Ni-Se and Ni-Co-Se was the least enthalpically-favoured reaction step; so, we focus on the structural and electronic aspects for the adsorbed O and OOH. Both Ni-Se and Ni-Co-Se (101) surfaces showed a short interatomic distance of approximately 1.7 Å between a surface Se and the adsorbed O atom (see **Table S7**). The Bader charge analysis shows the Se atom adopted a positive charge as it transferred an electron to the adsorbed O atom (**Figure S25**). The changes to the Se atom's electronic structure closest to the adsorbed O atom on both Ni-Se and Ni-Co-Se (101) surfaces are also confirmed through their projected density of states (**Figure S26**). The Se-O bond formed suggests the possibility of Se leaching as SeO desorption rather than continuing the OER cycle to form adsorbed peroxide on the surface. A comparison between the two processes is justified because the formation of adsorbed OOH on Ni-Se and Ni-Co-Se surfaces represents the potential rate determining step (**Figure 5b**). The enthalpies of both the OOH formation and SeO desorption were computed. As shown in **Figure 5b**, while both processes are enthalpically competitive on the Ni-Se surface, the SeO desorption is not enthalpically favoured on the Ni-Co-Se surface. At a Ni site, the oxygen is also bonded to the nickel; therefore, SeO desorption would disrupt more surface interactions. At a Co site, the loss of a coordinating Se destabilizes the electron hole created by the dopant, Co. Se leaching is not enthalpically favoured over continuing the OER cycle, yet Se leaching has been observed experimentally, from which we propose that it is an entropically driven process.

The Ni-Se_{vac} and Ni-Co-Se_{vac} (101) surfaces were created by removing the Se atom that formed a bond with the adsorbed O atom on the Ni-Se and Ni-Co-Se (101) surfaces, respectively. OER intermediates were calculated again at the same adsorption sites to demonstrate the effects of a Se vacancy. The potential energy differences associated with the potential determining step do not decrease significantly with Co doping or a Se vacancy separately (**Figure 5c and S23**). These surface modifications have the same effect on the Ni-O distances for OER intermediates at a Ni site. The Ni-O distances for OH, O, OOH, and O₂ adsorbed on Ni-Se_{vac} and Ni-Co-Se are between 1.9 and 2.1 Å which is much shorter than the Ni-O distances on Ni-Se, which were all above 3Å. The Ni-O distances for H₂O on each (101) surface investigated were above 3 Å. The corresponding PDOS did not differ from those of the bare surfaces, and this indicates the water molecule does not interact strongly with the surface. Further discussion will be limited to the adsorbed OH, O, OOH, and O₂ species. Like the Ni-Co-Se (101) surface, the Ni-Se_{vac} (101) surface also shows a bond forming between another surface Se and the adsorbed oxygen atom. The Se-O interatomic distance is approximately 1.8 Å, and the Bader charge shows the Se transfer of an electron to the adsorbed O atom on Ni-Se_{vac} (**Figure 5d**). This suggests the Se leaching may continue at a Ni site that has already lost a Se atom, although it will be less enthalpically favoured than the first Se loss because both Ni-Se and Ni-O bonds will be disrupted.

The combination of Co-doping and a Se vacancy on the (101) surface behaves differently from the Ni-Se, Ni-Se_{vac}, and Ni-Co-Se surfaces discussed above. The potential determining step becomes the oxygen molecule desorption. The significantly higher O₂ desorption energy for the Ni-Co-Se_{vac} (101) surface is due to the second oxygen atom also binding to two metal atoms. The desorption from this surface breaks three Ni-O bonds and one Co-O bond, unlike Ni-Se, Ni-Se_{vac}, Ni-Co-Se (101) surfaces where, at most, two metal-oxygen bonds are broken. The greater number of bonds between surface metal atoms and adsorbed

oxygen atoms combined with the high O₂ desorption energy shows that, rather than lose O₂ through desorption, the Ni-Co-Se_{vac} surface forms an active oxide layer.

In addition to the energetic differences, several structural and electronic features distinguish the Ni-Co-Se_{vac} (101) surface from the Ni-Se, Ni-Co-Se, and Ni-Se_{vac} surfaces. The metal-oxygen distances are shorter than those calculated on the Ni-Se, Ni-Co-Se, and Ni-Se_{vac} surfaces. The Ni-O distances on Ni-Co-Se_{vac} for OH, O, OOH, and O₂ are between 1.8 and 1.9 Å, while the Co-O distances are between 1.7 and 1.9 Å (**Tables S7 and S9**). The distances for the Ni and Co sites on Ni-Co-Se_{vac} are consistent with γ -NiOOH^[37], and γ -CoOOH^[38] in agreement with the present EXAFS results and will cycle between these structures and their corresponding hydroxides throughout the OER.^[39,40] The distinction between a Ni and a Co site is lost on the Ni-Co-Se_{vac} (101) surface due to the adsorbed oxygen species filling the Se vacancy and bridging a surface Co and Ni atom. The first adsorbed oxygen species replaces the desorbed Se atom to stabilize the electron hole created by the presence of Co. This simple substitution was not observed on Ni-Se_{vac} and implied the original structure might be more preserved in Ni-Co-Se_{vac} as the surface oxidation progresses. The ratio of the Ni Bader charges for the O, OOH, and O₂ intermediates on the Ni-Co-Se, Ni-Se_{vac}, and Ni-Co-Se_{vac} surfaces compared with the Ni Bader charge on the corresponding bare surfaces show the Ni has been oxidized from Ni⁺² to Ni⁺³. The Ni-Co-Se_{vac} surface differs from the other two surfaces, as a similar analysis shows the Co atom is also oxidized to Co⁺³. Furthermore, an electron transfer from a surface Se on Ni-Co-Se_{vac} was only observed due to the secondary O atom in the OOH intermediate, otherwise, the Se Bader charges remained constant (**Figure 5d**). These electronic differences are confirmed through projected densities of states (**Figure S27**) and agree with the present EELS results.

Our DFT calculations have shown that Se leaching is not an enthalpically favoured process; so, it must be entropically driven. While the Ni-Co-Se, Ni-Se_{vac}, and Ni-Co-Se_{vac}

surface all showed the Ni atom becoming oxidized, the shortest metal-oxygen bonds and Co oxidation were only observed on the Ni-Co-Se_{vac} surface. A surface Se atom only transferred an electron to the second oxygen atom adsorbed on the Ni-Co-Se_{vac} surface contributing to the high energy of the O₂ desorption, thereby energetically favouring the surface restructuring to the active γ -NiCoOOH. The Bader charge analysis and calculated structures agree with the present experimental results. The resulting active surface is therefore NiCoOOH. The good OER activity observed experimentally is an agreement with a recent Shin et al. computational study^[13] which showed that γ -NiOOH doped with Co had the lowest theoretical overpotential, 270 mV, out of a range of transition metal dopants, including Fe.^[41,42] The study predicted that Co when doped with γ -NiOOH can help in the stabilization of the formation of O on the MO bond while the O-O coupling is catalyzed on Ni active sites, making the catalyst a much better OER catalyst than γ -NiOOH.

1.3 AEM water and CO₂R electrolyser

To further evaluate the performance of activated (NiCo)₃Se₄ (NiCoOOH) as an OER electrocatalyst for industrial water splitting and CO₂R, we used a 5 cm² AEM electrolyser with the cathodic reaction supported by Pt/C on carbon paper for hydrogen evolution and Cu on PTFE for CO₂R (**Figures 6a and 6d**). The polarization curves indicated that the catalyst lowered the cell voltage to 2 V at 2 A.cm⁻² for water splitting (**Figure 6b**) and 3 V at 1 A.cm⁻² for CO₂R using 1 M KOH, outperforming IrO₂ (**Figure 6e**). This performance was stable for 95 h at 1 A.cm⁻² for water splitting (**Figure 6c**) and 5 h at 0.5 A.cm⁻² for CO₂R (**Figure 6f**). These results demonstrated the potential of utilizing cryomilled (NiCo)₃Se₄ for industrial applications.

Conclusions

In summary, we reported in this work the synthesis of homogenously dispersed Ni-Co-Se nanocrystals with varying compositions using solid-state cryomilling. Electrochemical

leaching of Se from the structure facilitated the transformation to Ni/Co-oxyhydroxides as validated by DFT, TEM, sXAS, and in situ XAS. The best performing activated (NiCo)₃Se₄ electrocatalyst showed a stable OER performance drawing 0.5 A.cm⁻² at 279 mV, and 1 A.cm⁻² at 329 mV of overpotential for 500 hours in 1M Fe-free KOH. Integrating the electrocatalyst in an AEM electrolyser, we could demonstrate an outstanding water splitting performance delivering 2 A.cm⁻² at 2 V and CO₂R performance of 1 A.cm⁻² at 3 V. The results encourage the utilization of cryomilling and chalcogenides, such as Se, to mass produce efficient earth-abundant electrocatalysts with long-term durability.

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400 **Competing Interests Statement**

401 The authors declare no competing interests

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1.4 References

- [1] P. P. Sharma, X. D. Zhou, *Wiley Interdiscip. Rev. Energy Environ.* **2017**, *6*, DOI 10.1002/wene.239.
- [2] P. De Luna, C. Hahn, D. Higgins, S. A. Jaffer, T. F. Jaramillo, E. H. Sargent, *Science* (80-.). **2019**, *364*, DOI 10.1126/science.aav3506.
- [3] C.-T. Dinh, G. Kibria, A. Seifitokaldani, A. Kiani, O. S. Bushuyev, C. Zou, R. Quintero-Bermudez, E. H. Sargent, T. Burdyny, C. M. Gabardo, J. P. Edwards, Y. Pang, D. Sinton, P. De Luna, *Science* (80-.). **2018**, *360*, 783.
- [4] J. R. SGalán-Mascarós, *ChemElectroChem* **2015**, *2*, 37.
- [5] H. Zhou, F. Yu, Q. Zhu, J. Sun, F. Qin, L. Yu, J. Bao, Y. Yu, S. Chen, Z. Ren, *Energy Environ. Sci.* **2018**, *11*, 2858.
- [6] M. Yu, G. Moon, E. Bill, H. Tüysüz, *ACS Appl. Energy Mater.* **2019**, *2*, 1199.
- [7] M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, *J. Am. Chem. Soc.* **2013**, *135*, 8452.
- [8] C. Liang, P. Zou, A. Nairan, Y. Zhang, J. Liu, K. Liu, S. Hu, F. Kang, H. J. Fan, C. Yang, *Energy Environ. Sci.* **2019**, *13*, DOI 10.1039/c9ee02388g.
- [9] C. Kuai, Z. Xu, C. Xi, A. Hu, Z. Yang, Y. Zhang, C. Sun, L. Li, D. Sokaras, C. Dong, S. Qiao, X. Du, F. Lin, *Nat. Catal.* **2020**, DOI 10.1038/s41929-020-0496-z.
- [10] F. D. Speck, K. E. Dettelbach, R. S. Sherbo, D. A. Salvatore, A. Huang, C. P. Berlinguette, *Chem* **2017**, *2*, 590.
- [11] D. Y. Chung, P. P. Lopes, P. Farinazzo Bergamo Dias Martins, H. He, T. Kawaguchi, P. Zapol, H. You, D. Tripkovic, D. Strmcnik, Y. Zhu, S. Seifert, S. Lee, V. R. Stamenkovic, N. M. Markovic, *Nat. Energy* **2020**, *5*, 222.
- [12] M. Wang, Z. Dang, M. Prato, D. V. Shinde, L. De Trizio, L. Manna, *ACS Appl. Nano Mater.* **2018**, acsanm.8b01418.

428 [13] H. Shin, H. Xiao, W. A. Goddard, *J. Am. Chem. Soc.* **2018**, *140*, 6745.

429 [14] X. Fu, D. N. Beatty, G. G. Gaustad, G. Ceder, R. Roth, R. E. Kirchain, M. Bustamante,
430 C. Babbitt, E. A. Olivetti, *Environ. Sci. Technol.* **2020**, *54*, 2985.

431 [15] W. Li, D. Xiong, X. Gao, L. Liu, *Chem. Commun.* **2019**, 55, 8744.

432 [16] W. Li, X. Gao, D. Xiong, F. Wei, W. G. Song, J. Xu, L. Liu, *Adv. Energy Mater.* **2017**,
433 *7*, 1.

434 [17] R. Gao, G. D. Li, J. Hu, Y. Wu, X. Lian, D. Wang, X. Zou, *Catal. Sci. Technol.* **2016**,
435 *6*, 8268.

436 [18] M. Cui, C. Yang, B. Li, Q. Dong, M. Wu, S. Hwang, H. Xie, X. Wang, G. Wang, L.
437 Hu, *Adv. Energy Mater.* **2021**, *11*, 1.

438 [19] L. Schultz, *Mater. Sci. Eng.* **1988**, *97*, 15.

439 [20] W. L. Johnson, *Prog. Mater. Sci.* **1986**, *30*, 81.

440 [21] K. B. Dhanalakshmi, S. Latha, S. Anandan, P. Maruthamuthu, *Int. J. Hydrogen Energy*
441 **2001**, *26*, 669.

442 [22] K. Fan, H. Zou, Y. Lu, H. Chen, F. Li, J. Liu, L. Sun, L. Tong, M. F. Toney, M. Sui, J.
443 Yu, *ACS Nano* **2018**, *12*, 12369.

444 [23] C. Suryanarayana, *Mechanical Alloying And Milling*, CRC Press, 2004, **2004**.

445 [24] D. Zheng, M. Li, Y. Li, C. Qin, Y. Wang, Z. Wang, *Beilstein J. Nanotechnol.* **2019**, *9*,
446 281.

447 [25] W. Shi, F. Guo, C. Zhu, H. Wang, H. Li, H. Huang, Y. Liu, Z. Kang, *J. Mater. Chem.*
448 *A* **2017**, *5*, 19800.

449 [26] B. Akabayov, C. J. Doonan, I. J. Pickering, G. N. George, I. Sagi, *J. Synchrotron*
450 *Radiat.* **2005**, *12*, 392.

451 [27] Y. Liang, Y. Li, H. Wang, J. Zhou, J. Wang, T. Regier, H. Dai, *Nat. Mater.* **2011**, *10*,
452 780.

453 [28] D. Meyers, S. Mukherjee, J. G. Cheng, S. Middey, J. S. Zhou, J. B. Goodenough, B. A.
454 Gray, J. W. Freeland, T. Saha-Dasgupta, J. Chakhalian, *Sci. Rep.* **2013**, 3, 3.

455 [29] M. Al Samarai, A. W. Hahn, A. Beheshti Askari, Y. T. Cui, K. Yamazoe, J. Miyawaki,
456 Y. Harada, O. Rüdiger, S. Debeer, *ACS Appl. Mater. Interfaces* **2019**, 11, 38595.

457 [30] C. Xiao, X. Lu, C. Zhao, *Chem. Commun.* **2014**, 50, 10122.

458 [31] H. A. El-Sayed, A. Weiß, L. F. Olbrich, G. P. Putro, H. A. Gasteiger, *J. Electrochem.*
459 *Soc.* **2019**, 166, F458.

460 [32] B. G. Amin, A. T. Swesi, J. Masud, M. Nath, *Chem. Commun.* **2017**, 53, 5412.

461 [33] P. F. Wang, Y. J. Guo, H. Duan, T. T. Zuo, E. Hu, K. Attenkofer, H. Li, X. S. Zhao, Y.
462 X. Yin, X. Yu, Y. G. Guo, *ACS Energy Lett.* **2017**, 2, 2715.

463 [34] B. Das, M. V Reddy, B. V. R. Chowdari, **2013**, 1961.

464 [35] S. R. Mellsop, A. Gardiner, B. Johannessen, A. T. Marshall, *Electrochim. Acta* **2015**,
465 168, 356.

466 [36] H. Y. Wang, Y. Y. Hsu, R. Chen, T. S. Chan, H. M. Chen, B. Liu, *Adv. Energy Mater.*
467 **2015**, 5, 1.

468 [37] D. Friebe, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, M. Wise, M. Cheng, D.
469 Sokaras, T. Weng, R. Alonso-mori, R. C. Davis, J. R. Bargar, J. K. Nørskov, A.
470 Nilsson, A. T. Bell, *J. Am. Chem. Soc* **2015**, 137, 1305.

471 [38] J. Huang, J. Chen, T. Yao, J. He, S. Jiang, Z. Sun, Q. Liu, W. Cheng, F. Hu, Y. Jiang,
472 Z. Pan, S. Wei, *Angew. Chemie - Int. Ed.* **2015**, 54, 8722.

473 [39] C. Marini, B. Joseph, S. Caramazza, F. Capitani, M. Bendele, I. Kantor, P. Lotti, O.
474 Mathon, S. Pascarelli, P. Postorino, *High Press. Res.* **2017**, 37, 1.

475 [40] D. Totir, Y. Mo, S. Kim, M. R. Antonio, D. A. Scherson, *J. Electrochem. Soc.* **2000**,
476 147, 4594.

477 [41] J. Zaffran, M. C. Toroker, *ChemistrySelect* **2016**, 1, 911.

478 [42] F. Costanzo, *Phys. Chem. Chem. Phys.* **2016**, *18*, 7490.

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Figure 1. Schematic illustration of the two-step synthesis process a) step 1: milling at a cryogenic temperature $-196\text{ }^{\circ}\text{C}$ to alloy elements, step 2: milling in wet environment using surfactant to reduce the size of the alloyed particles. b) XRD of $(\text{NiCo})\text{Se}$ and $(\text{NiCo})_3\text{Se}_4$ after 6 hours of cryomilling and 10 hours of SABM. c) Particle size distribution for $(\text{NiCo})\text{Se}$ and $(\text{NiCo})_3\text{Se}_4$ after SABM for 10 hours followed by centrifuging at 6000 rpm for 1 hour.

Figure 2. a) A schematic of the activation process for Ni-Co-Se alloys. b) BSE-SEM images and c) and d) TEM images of the $(\text{NiCo})_3\text{Se}_4$ catalyst at 0 h (dry) and after 2 h of activation at $10 \text{ mA}\cdot\text{cm}^{-2}$ (post). The elemental content of the catalyst is shown in the inset tables. Soft X-ray L-edge XANES of e) Se using SDD, f) Ni and g) Co using TEY and SDD.

Figure 3. a) iR-corrected polarization curves on glassy carbon electrode with a loading of 0.21 mg.cm⁻². b) Specific activity of activated (NiCo)₃Se₄ and (NiCo)Se compared to IrO₂, normalized by ECSA at 300 mV overpotential (left axis) and normalized by geometric area (right axis). The roughness factor (RF) value for each catalyst is noted at the top of the bar. c) Activated (NiCo)₃Se₄ NP was deposited on carbon paper and tested using alternating stability test. Inset is a schematic illustration of O₂ bubble accumulation on the surface of the electrocatalyst during oxidation. d) The change in key electrochemical parameters every 10 hours during the alternating stability test. e) Activated (NiCo)₃Se₄ was deposited on Nickel foam and tested for long term stability at high current densities.

All tests were conducted in 1M Fe-free KOH electrolyte.

Figure 4. In situ XANES K-edge of a) Se, b) Ni, and c) Co of $(\text{NiCo})_3\text{Se}_4$ during OER. In situ EXAFS radial distribution function of d) Se, e) Ni, and f) Co of $(\text{NiCo})_3\text{Se}_4$ during OER. Interatomic distances noted in the figures are phase corrected using 0.5 Å shift. All tests were done in 1M KOH.

Figure 5. (a) OER mechanism on the NiSe (101) surface, the Se vacancy is highlighted in magenta, Co doping sites are given in green, and Ni and Se are shown in blue and yellow, respectively. (b) Comparing the energies of OOH formation and SeO desorption on (001) and (101) surfaces. (c) The potential energy of reaction for Ni-Se, Ni-Sevac, Ni-Co-Se, and Ni-Co-Sevac (101) surfaces (d) Bader charge of Ni, Se, and Co atoms for Ni-Se, Ni-Sevac, Ni-Co-Se and Ni-Co-Sevac (101) surfaces.

Figure 6. **a)** Schematic diagram of AEM water splitting **b)** Polarization curve and **c)** Chronopotentiometry test using 0.2 mg_{Pt}.cm⁻² Pt/C on carbon paper for HER and 2 mg.cm⁻² Activated (NiCo)₃Se₄ on Nickel foam for OER. **d)** Schematic diagram of CO₂ reduction. **e)** Polarization curve and **f)** Chronopotentiometry test using 1 mg.cm⁻² Cu on PTFE for CO₂R and 2 mg.cm⁻² activated (NiCo)₃Se₄ on Nickel foam for OER compared to commercial IrO₂.