Communication

Ni/Co-based nanosheet arrays for efficient oxygen evolution reaction

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\textbf{A R T I C L E   I N F O}

\textbf{Keywords:}
Oxygen evolution reaction
Electrocatalysis
NiCo nanocomposite
Nanosheet array

\textbf{A B S T R A C T}

Efficient oxygen evolution reaction (OER) catalysts composed of earth-abundant elements are crucial to the development of practical and environmentally friendly water splitting systems. Herein, NiCoO\textsubscript{2}/CoO/Ni\textsubscript{3}N nanosheet arrays (NiCoON NSAs/NF) are fabricated \textit{in situ} on the 3D nickel foam. In the alkaline solution, the NiCoON nanocomposite has excellent catalytic OER properties such as a small overpotential of 247 mV (at 10 mA cm\textsuperscript{-2}) and Tafel slope of 35 mV dec\textsuperscript{-1}, which are better than those of Ni\textsubscript{x}Co\textsubscript{3-x}O\textsubscript{4} and most Ni- and Co-based catalysts. There are more active sites with oxygen vacancies on NiCoON NSAs after the treatment with NH\textsubscript{3} and the face-centered cubic NiCoO\textsubscript{2} enhances the formation of active Ni-Co layered hydroxide/oxyhydroxide species (NiOOH) in comparison with spinal Ni\textsubscript{x}Co\textsubscript{3-x}O\textsubscript{4} during the electrochemical process. In addition, the Ni\textsuperscript{3+}-rich surface together with Co incorporation facilitates the formation of Ni\textsuperscript{3+} creating disordered NiOOH centers [31]. These oxyhydroxides act as active sites for O\textsubscript{2} generation as the highly oxidized metal cations can facilitate the formation of oxyhydroxide species, the key intermediates in the OER process [32]. Catalysts with mixed transition metals have been shown to have better catalytic activity than a single-metal system. Trotzchaud et al. [33] reported that incorporation of iron into Ni(OH)\textsubscript{2}/NiOOH thin films lowered the overpotential of pure NiOOH and binary Ni-Co oxide/NiCo alloy with oxide (CoO-NiO-NiCo) exhibited better catalytic activity in OER than the individual Ni- or Co-based catalysts [34,35]. It is believed that addition of Fe or Co oxide to Ni-based catalysts enriches the Ni\textsuperscript{3+} population on the surface to facilitate the formation of NiOOH and adorption of OH\textsuperscript{−} in an alkaline solution [22]. In addition to the active catalytic sites, electroconductivity is another key factor determining the performance of electrocatalysts [23,36]. The common strategies to improve the conductivity of metal

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https://doi.org/10.1016/j.nanoen.2018.08.010
Received 16 May 2018; Received in revised form 25 July 2018; Accepted 6 August 2018
Available online 07 August 2018
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oxides are: (1) combining oxides with highly conductive materials such as carbon nanotubes, graphene, metallic carbides, and nitrides [37–39] and (2) introducing oxygen vacancies or heteroatom dopants into metal oxides. The latter has been reported to not only augment the conductivity and charge mobility, but also facilitate polaron hopping between adjacent catalytic sites [40–42]. Particularly, nitrogen doping is an efficient way to improve the conductivity by creating a nitrogen-rich surface boasting excellent adsorption of oxygen species and OER performance [43,44].

Although Co incorporation into Ni-based systems has been studied [22,34,45–49], the role of Co in OER catalysis is still controversial and not clearly understood. For instance, Boettcher et al. [48] reported that Co incorporation into NiO lowered the OER performance. The NiO with a rock-salt structure was claimed to be more easily converted in situ to the layered hydroxide/oxyhydroxide phase, whereas the spinel-type structure resulting from Co insertion might inhibit this transformation. On the contrary, Tour et al. [34] reported that nanoporous Ni-rich (10 atom % Co) Ni–Co binary oxides had an enlarged active surface area and reduced charge transfer resistance, which enhanced the catalytic activity in OER in comparison with pure Ni or Co oxide films. Besides, hybrid NiO/Co3O4 nanoparticles prepared on nitrogen-doped carbon (NiO/Co3O4@NC) were shown to have better activity than NiO@NC because of the intimate interaction between Ni and Co through O bridge (Co-O-Ni) at the interface of NiO and Co3O4 [49].

Herein, we present a systematic study on the Co and N doping effects on the structure and electrocatalytic properties of nickel oxide by controlling the Ni:Co ratio and annealing conditions. A porous NiCoO2/CoO/Ni3N nanosheet array (abbreviated as NiCoON NSA) prepared on the 3-dimensional (3D) nickel foam (NiCoON NSAs/NF) is demonstrated to be an active and stable electrocatalyst for OER as manifested by an overpotential of 247 mV at 10 mA cm−2 and Tafel slope of 35 mV dec−1, which are better than those of Ir-based electrocatalysts [48]. Our results reveal the origin of the electrocatalytic activity of the OER catalyst and insights in the design of catalysts based on Ni and other transition metals.

2. Experimental details

2.1. Synthesis of Ni0.5Co2.5O4 NSAs/NF and NiCoON NSAs/NF

The synthesis method was adopted from the reported procedures with slight modification [50]. In the preparation of NiCoO2 NSAs, different ratios of the starting Ni(NO3)2·6H2O to Co(NO3)2·6H2O precursor were mixed with the total concentration kept at 3.93 mmol. 26.25 mmol urea and 10.5 mmol NH4F were added to 70 mL of water and stirred for 1 h at room temperature before transferring to a 100 mL Teflon-lined stainless-steel autoclave. The nickel foam (2 × 3 cm2) was used as the substrate. The autoclave was heated to 100 °C for 8 h to obtain the cobalt-nickel hydroxide precursor. After annealing of the precursor at 350 °C in air for 1 h, NiCoO2/NF with different Ni:Co ratios (n:cm) were obtained. In the preparation of NiCoON(n:cm) NSas/NF, the nickel hydroxide precursor was heated to 300–400 °C under flowing ammonia (NH3, 35 scm) for 3 h followed by cooling in flowing Ar.

2.2. Structural characterization

The morphology and structure of the samples were characterized by field-emission scanning electron microscopy (FE-SEM, JEOL), transmission electron microscopy (TEM, JEOL-2100F equipped with an X-ray energy dispersive spectrometer (EDS)), X-ray diffraction (XRD, X’ Pert PRO PHILIPS with Cu Ka radiation), and Raman scattering spectroscopy. The chemical states were determined by X-ray photoelectron spectroscopy (XPS, AC-2, Riken Keiki).

2.3. Electrochemical characterization

A three-electrode system was adopted in the electrochemical measurement conducted on an electrochemical workstation (CHI760E, Chenhua Shanghai) at room temperature. The nanosheet arrays on the nickel foam (3 × 5 mm2) served as the working electrode (catalyst loading = ca. 0.6 mg cm−2) and the Pt flake and saturated calomel electrode (SCE) were the counter and reference electrodes, respectively. The working electrode was activated by cycling between 0 and 0.6 V (vs. SCE) for ten cycles at a scanning rate of 10 mV s−1 before performing linear sweep voltammetry (LSV). The catalytic OER was evaluated by LSV at a scanning rate of 5 mV s−1 between 1.0 and 1.6 V (vs. reversible hydrogen electrode, RHE). Electrochemical impedance spectroscopy (EIS) was carried out in the frequency range between 100 kHz and 0.01 Hz at 0.55 V (vs. SCE). The polarization curves were iR-compensated according to the equation (Vcalibration = Voriginal − iRsolution resistance, where the solution ohmic drop (Rsolution resistance) was measured from the EIS Nyquist plot). The current-time (i-t) curve and LSV were obtained to assess the stability of the nanosheet arrays and all the electrochemical measurements were performed in 1.0 M KOH.

2.4. Reversible hydrogen electrode calibration

The SCE was calibrated to the RHE with Pt electrodes as both the working and counter electrodes. Using a SCE as the reference electrode, cyclic voltammograms (CVs) were recorded from −1.1 to −0.9 V (vs. SCE) in a high-purity hydrogen saturated electrolyte at a scanning rate of 5 mV s−1 and the CV plots are shown in Fig. S1.

3. Results and discussion

3.1. Morphology

The NiCoON(1:2) NSAs (Ni:Co ratio = 1:2) are fabricated in situ on a 3D nickel foam (NF) via a hydrothermal reaction followed by annealing in ammonia (Scheme 1). Fig. 1a and the inset depict the low and high-magnification SEM images of NiCoON(1:2) NSAs/NF revealing that dense and uniform nanosheets are formed on the Ni foam surface. The morphology of NiCoON(1:2) NSAs/NF is similar to that of NiCoO2 NSAs/NF (Fig. S2) prepared as a control by annealing the hydrothermal product in air.

Scheme 1. Schematic illustration of the synthesis of NiCoON(NiCoO2/CoO/Ni3N) on the NF.
3.2. Crystal structure

Fig. 1b shows the XRD pattern of NiCoON(1:2) NSAs/NF and the diffraction peaks can be indexed to rock-salt NiCoO$_2$ (JCPDS 10-0188), CoO (JCPDS 48-1719), and Ni$_3$N (JCPDS 10-0280) and the strong Ni peaks arise from the substrate. The TEM image in Fig. 1c discloses a rough surface on the NiCoON(1:2) nanosheet, suggesting reduction and partial replacement of O with N during annealing and formation of mesopores with a large surface area.

The high-resolution TEM (HR-TEM) image (Fig. 1d) reveals three distinct species with interplanar distances of 0.244, 0.214, and 0.246 nm attributed to the (111) plane of rock-salt NiCoO$_2$, (002) plane of hexagonal Ni$_3$N, and (111) plane of cubic CoO, respectively, confirming co-existence of NiCoO$_2$, CoO, and Ni$_3$N. The elemental maps obtained by EDS in Fig. S3 show that Ni, Co, O, and N are uniformly distributed in the NiCoON(1:2) nanosheet. The composition and chemical states of the NiCo$_2$O$_4$ and NiCoON(1:2) NSAs are determined by XPS and the spectra and fitted results are presented in Figs. 1e, 1f, and S4. Although the two fitted peaks for Ni 2p$_{3/2}$ (Fig. 1e) indicate the presence of Ni$^{3+}$ (855.5 eV) and Ni$^{2+}$ (853.9 eV) in the NiCo$_2$O$_4$ and NiCoON(1:2) NSAs [22], the calculated Ni$^{3+}$/Ni$^{2+}$ ratio of NiCoON(1:2) (14.2) is larger than that of NiCo$_2$O$_4$ (4.8), indicating that the NiCoON(1:2) NSAs has a Ni$^{3+}$-rich surface. Moreover, the Ni$_3$N peak at 852.4 eV is detected only from the NiCoON(1:2) NSAs [23], providing evidence of partial reduction of Ni$^{2+}$ to Ni$^{1+}$ by ammonia. The N 1s spectrum confirms the presence of Ni$_3$N species on the NiCoON(1:2) NSAs surface (Fig. S4a). The O 1s spectra acquired from both samples exhibit three characteristic peaks corresponding to the oxygen-metal bond (530.1 eV; O1), surface oxygen defect/vacancy species (531.5 eV; O2), and hydroxyl groups or surface-adsorbed oxygen (532.3 eV; O3, Fig. 1f) [51,52]. Comparison of the O2 peaks indicates that the NiCoON(1:2) NSAs contain more oxygen vacancies than NiCo$_2$O$_4$ NSAs. Two Co oxidation states are identified from the NiCo$_2$O$_4$ and NiCoON(1:2) NSAs with the two Co 2p$_{3/2}$ peaks at 780.9 and 779.5 eV corresponding to...
Co\(^{2+}\) and Co\(^{3+}\), respectively (Fig. S4b) [51,53]. The calculated Co\(^{2+}/\)Co\(^{3+}\) ratio of NiCoON(1:2) (9.1) is larger than that of NiCo\(_2\)O\(_4\) (1.6) due to the reducing conditions in the NiCoON(1:2) NSAs synthesis which preferentially favors the formation of species with a smaller valance. Compared with the structure of NiCo\(_2\)O\(_4\) which has the general formula of Co\(^{2+}\)\(_{1-x}\)Co\(^{3+}\)\(_x\)\([\text{Co}_{3+}\text{Ni}_{2+}\)\(_{x}\text{Ni}_{3+}\)\(_{1-x}\)]\(_4\) (0 \leq x \leq 1) [54], the structure of the precursor is believed to be partially destroyed during ammonia annealing and Ni\(^{2+}\) is further reduced to Ni\(^+\) as consistent with the XRD and TEM results.

### 3.3. Electrochemical performance

To evaluate the electrocatalytic OER characteristics of NiCoON(1:2) NSAs/NF, linear sweep voltammetry (LSV) and chronopotentiometry are performed and compared with the results obtained from the two control samples, NiCo\(_2\)O\(_4\) NSAs/NF and NF. Fig. 2a compares the LSV curves obtained at a scanning rate of 5 mV s\(^{-1}\). The pre-OER oxidation peak at a potential range of 1.26–1.37 V (vs. RHE unless stated otherwise) of all the samples is related to oxidation of Ni\(^{2+}\) to Ni\(^{3+}\) [23,55]. At higher potentials, NiCoON(1:2) NSAs/NF shows the smallest OER onset potential with a larger specific current density (j). An overpotential (\(\eta\)) of 247 mV is measured to reach a current density of 10 mA cm\(^{-2}\) and it is less than those of NiCo\(_2\)O\(_4\) NSAs/NF (284 mA cm\(^{-2}\)) and NF (351 mA). The corresponding Tafel plots (\(\eta\) vs. log (j), Fig. 2b) impart more details about the kinetics. NiCoON(1:2) NSAs/NF has the smallest Tafel slope (35 mV dec\(^{-1}\)) than others (45 mV dec\(^{-1}\) for NiCo\(_2\)O\(_4\) NSAs/NF and 75 mV dec\(^{-1}\) for NF) and the overpotential and Tafel slope of NiCoON(1:2) NSAs/NF are among the best compared with other Ni-based electrocatalysts in the literature (Table S1). To investigate the factors leading to the catalytic enhancement, electrochemical impedance spectroscopy (EIS) is carried out. Fig. 2c compares the Nyquist plots acquired from the NF, NiCo\(_2\)O\(_4\) NSAs/NF, and NiCoON(1:2) NSAs/NF. The smallest semi-circle observed from NiCoON(1:2) NSAs/NF indicates the smallest charge transfer resistance (R\(_{ct}\), 4.7 \(\Omega\)) at 1.58 V. Compared with NF and NiCo\(_2\)O\(_4\) NSAs/NF, the solution resistance (R\(_s\)) of NiCoON(1:2) NSAs/NF increases slightly due to larger surface roughness [56]. The areal capacitance of NiCoON(1:2) NSAs/NF (141 mF cm\(^{-2}\)) exceeds those of NiCo\(_2\)O\(_4\) NSAs/NF and NF by 150% and 1800% (Fig. S5). The larger active surface area contributes to the OER rate and NiCoON(1:2) NSAs/NF also exhibits an excellent long-term electrochemical stability. To investigate the corrosion behavior and durability of the samples, different current densities (10, 35, and 55 mA cm\(^{-2}\)) are applied to the NiCoON(1:2) NSAs/NF for a longer time (30 h). As shown in Fig. 2d, the sample is stable even after 30 h at high current densities. The polarization curve also does not show any significant loss in the current density or increase in the overpotential after 1000 continuous potential cycles (inset in Fig. 2d). To evaluate the catalytic efficiency of NiCoON(1:2) NSAs/NF, the amount of oxygen produced by OER electrolysis at 14 mA cm\(^{-2}\) is measured for 90 min and compared with the theoretical values (Fig. S6). The result yields a high faradaic efficiency of 97.8%, indicating that almost all charges are associated with the OER without any other electron pathway or side reaction.

#### 3.3.1. Active sites

The active sites on the transition metal (Ni, Fe, Co)-based OER catalysts in alkaline media have been identified to be oxhydroxides (M-OOH) [10]. With regard to Ni-based catalysts, OER is proposed to proceed in four steps [23]. In brief, surface Ni atoms are first oxidized to NiOOH with sequential oxidation to NiO(OH)\(_2\) and NiOO\(_2\) at higher potentials. Further increase in the potential generates O\(_2\) on NiOO\(_2\) and regenerates NiOOH species. Usually, formation of NiOOH, NiO(OH)\(_2\),
and NiOOH is considered as the OER rate determining steps. To gain insights into the relationship between the material structure and OER activity, the changes on the catalyst surface are monitored by HR-TEM, XPS, and Raman scattering.

Fig. 3a displays the HR-TEM image of the post-OER NiCoON(1:2) in which a 15–20 nm thick amorphous layer is evident along the edge. XPS indicates that the surface layer is composed of oxide and oxyhydroxide species. The two peaks in the Ni 2p_{3/2} spectrum (Fig. 3b) correspond to Ni(OH)₂ (856.0 eV) and NiOOH (857.1 eV) [57] and those in the O 1s spectrum are assigned to oxygen-metal bonds (530.1 eV; O₁), Ni(OH)₂ (531.4 eV), NiOOH (532.0 eV), absorbed oxygen (532.6 eV), and H₂O/O (533.9 eV) [52]. The NiOOH species on the surface of post-OER NiCoON(1:2) NSAs/NF is verified by the Raman spectra in Fig. 3c. After OER, the NiCoO₂ peak at 532 cm⁻¹ split into two peaks at 474 and 554 cm⁻¹ corresponding to NiOOH (32,58). It is clear from the post-OER characterization that the electrocatalytically active species is in situ formed on the NiCoON(1:2) NSAs/NF surface during OER. It is noted that active species (NiOOH) is produced less on the post-OER NiCoO₂ NSAs/NF as revealed by HR-TEM and Raman scattering (Fig. S7). On the other hand, the Co²⁺/Co³⁺ ratio in the post-OER NiCoON (1:2), calculated from XPS data, has decreased to 1.4 (Fig. S8). This ratio is close to that of Co₃O₄ (1.2) [59] or NiCo₂O₄ (1.6), both of which have a spinel structure.

3.3.2. Effects of annealing temperature

The annealing temperature is an important factor affecting the amount of N dopant in the materials and degree of reduction. By adjusting the annealing temperature between 300 and 400 °C under ammonia, the composition of the product can be controlled as shown by the XRD data in Fig. 4a. The XRD patterns of the samples annealed at 300, 350, 380, and 400 °C can be indexed to spinel NiCo₂O₄, NiCoO₂/CoO/Ni₃N composite (NiCoON(1:2)), (Ni, Co)₃N, and NiCo alloy, respectively. The SEM and TEM images of the (Ni, Co)₃N and NiCo alloy NSAs/NF annealed at higher temperatures disclose the porous structures with large surface areas (Fig. S9) and higher conductivity. In the electrocatalytic OER tests shown in Fig. 4b, the sample annealed at 350 °C (NiCoON(1:2)) outperforms the other NiCo bimetallic catalysts indicating that NiCoO₂/CoO/Ni₃N enhances OER catalysis with the aid of the abundant active sites on the surface. It is also noted that the NiCoON(1:2) exhibits a larger background current than others due to the large pseudocapacitive current contribution from NiCoO₂ and CoO, both of which are good capacitors. The sample annealed at 300 °C shows OER characteristics similar to those of spinel NiCoO₂ treated at 350 °C in air due to the similar surface composition and structure.

3.3.3. Effects of Ni to Co ratio

The Ni to Co ratio in the NiCo-based catalysts determines the morphology and catalytic OER properties [34]. To investigate the influence of Co incorporation, a series of NiCo precursors with predetermined Ni:Co ratios are prepared and annealed at 350 °C in ammonia. Formation of uniform nanosheets on the NF is confirmed for the samples of various Ni:Co ratios (Fig. S10). When only Ni is used without Co, Ni₃N/NF nanosheets with a smaller coral moss-like structure result due to the fragile nature of Ni-O bond that easily breaks and combines with N to yield Ni₃N. Meanwhile, when only Co is used in the synthesis, pure CoO/NF is formed with an average nanosheet size of 9.4 µm. As the Ni:Co ratio is changed from 1:3–3:1, the average size of the nanosheets decreases from 6.4 to 2.3 µm. The OER performance of the different morphologies are examined and the results are summarized in Figs. 5a and 5b.

Pre-OER peaks corresponding to M²⁺ (M-OH; M = Ni, Co) to M³⁺ (M-OOH) oxidation are observed in the range of 1.25–1.45 V (inset in Fig. 5a) from all the samples [32,48,55]. As discussed before, the pre-OER peak is closely related to the OER activity. The current intensity or more precisely, the integrated peak area, of the pre-OER peak indicates the amount of active species (M-OOH) on the surface and consequently correlates with the OER efficiency of the catalyst. There is a strong dependence of the pre-OER peak potential on the sample composition. The pre-OER peak of the samples prepared with pure Ni or Co appears at around 1.4 V and shifts to a lower potential when the sample is prepared from the Ni/Co mixture. The pre-OER peak potential versus the ratio shows an inverted volcano shape (inset in Fig. 5a) and the sample with a Ni:Co ratio of 1:2 shows the smallest potential. A similar trend is observed from the overpotentials and Tafel slopes (Fig. 5b). The charge transfer resistance plot versus Ni:Co ratio follows the same trend (Fig. S11), suggesting that the 1:2 ratio of Ni:Co leads to the formation of the optimal NiCoON NSAs/NF composite with the lowest overpotential of 247 mV, the fastest reaction rate of 35 mA dec⁻¹, and the smallest resistance of 4.7 Ω.

To obtain better understanding of the OER characteristics, Raman scattering spectra are acquired from the post-OER different ratio of Ni to Co samples and compared in Fig. 5c. While only a small amount of active species, CoOOH, is detected from the pure Co-based electrode (Raman peak at 505 cm⁻¹), a large amount of another active species, NiOOH, is observed from the pure Ni- and Ni/Co mixture-based catalysts. The pair of dominant peaks at 474 and 554 cm⁻¹ observed from all the Ni-containing samples are ascribed to Ni–O vibration in γ-NiOOH and β-NiOOH, respectively [32,55,60]. Bell’s group [32] attributes the excellent OER activity of Ni(OH)₂ to the phase transformation...
of α-Ni(OH)₂ to β-Ni(OH)₂ phase. They have also reported that β-NiOOH phase has an optimal adsorption energy for atomic oxygen close to that of IrO₂, concluding that the β-NiOOH phase is more active in catalyzing OER than the γ-NiOOH phase. However, further studies have pointed out that the enhanced OER activity of β-NiOOH phase may arise from the Fe impurities (< 1 ppm) in the unpurified KOH electrolyte [61,62]. To rule out this impurity effect, the Fe concentration in our electrolyte is determined by ICP-OES and only 0.035 ppm Fe is detected. Even with further purified electrolyte (0.004 ppm Fe), no significant difference in the OER activity is observed from our samples (Fig. S12), implying that the Fe impurity does not affect our experiments. Interestingly, the relative intensity of the β- and γ-NiOOH peaks varies with the Ni:Co ratio. Similar to the OER activity and Tafel slope (Fig. 5b), the γ-NiOOH to β-NiOOH peak ratio follows the inverted volcano-like trend as the Ni:Co ratio (Fig. 5d), suggesting the Ni:Co ratio plays a critical role in the formation of active sites. Ni and Co apparently facilitate the formation of the active NiOOH phase by modulating the electronic structure to rock-salt NiCoO₂ [48]. The amount of β-NiOOH increases gradually with the Co content and reaches the maximum value at a Ni:Co ratio of 1:2. Incorporation of Co...
facilitates structural transformation of surface Ni atoms from α-Ni(OH)2 to β-Ni(OH)2 [63], which are the pre-oxidation species of α-Ni(OH)2 and β-Ni(OH)2, respectively [32]. However, an excess amount of Co depletes Ni atoms from the surface and mitigates formation of active species. Our results are consistent with previous reports that the OER activity of Ni-based hydroxide is higher than that of Co-based hydroxide due to the weaker Ni–OHad interaction (adsorbed OH species) interaction than Co–OHad interaction [9].

The superior OER performance observed from NiCoON NSAs/NF (Ni:Co = 1:2) can be explained from the following perspectives. Firstly, the rock-salt type NiCoO2 can be easily in situ converted to the layered NiOOH as active catalytic sites for OER and Co enhances the formation of β-NiOOH giving rise to a Ni3++-rich surface [22]. Secondly, the large amount of oxygen vacancies in NiCoOON(1:2) NSAs/NF not only improves the charge mobility, but also lowers the adsorption energy of H2O to further promote OER electrolysis [51,53]. Thirdly, Ni,Ni in NiCoOON(1:2) NSAs improves the conductivity. The higher surface Fermi energy of Ni3N, which is higher than that of oxide, allows electron injection into NiOOH to reduce the overpotential [49,64]. Fourthly, direct growth of NiCoOON(1:2) NSAs on the conductive NF provides an excellent pathway for collection and rapid transfer of electrons.

4. Conclusion

A series of NiCo-based nanosheet arrays prepared using different Ni:Co ratios on nickel foam and containing different Ni:Co compositions on the surface including oxides (spinel type NiCoO2 and rock-salt type NiCoO2), nitrides, and alloy are evaluated as OER electrocatalysts. The oxide/nitride NiCo-based nanosheet arrays exhibit an inverted volcano-like trend in the overpotentials and Tafel slopes for OER when the Co content is increased. Systematic comparison of the catalytic activity, morphology, and composition reveals that the NiCoO2/Co/Ni3N (NiCoOON(1:2)) hybrid structure is a highly efficient OER catalyst and controlled insertion of Co is crucial to the formation of β-NiOOH active species. The NiCoOON(1:2) NSAs delivers the best OER performance such as a small overpotential (247 mV at 10 mA cm−2) and Tafel slope (35 mV dec−1), which outperform those of Ir-based benchmark catalysts reported in the literature. Our results provide direct demonstration and guidelines on how to design and tune the structure and composition of electrocatalysts to obtain the optimal catalytic OER characteristics.

Acknowledgements

The authors thank the financial support from the Innovation and Technology Commission of Hong Kong, Hong Kong Polytechnic University, as well as Hong Kong Research Grants Council (RGC) General Research Funds (GRF) (Nos. 11301215 and 11205617). The TEM experiments were conducted at the Hong Kong Polytechnic University Research Facility in the Materials Characterization and Device Fabrication (UMF)-center for Electron Microscopy. We acknowledge the use of the facilities and engineering support by Dr. Wei Lu.

Appendix A. Supporting information

Supplementary data including SEM images, XRD patterns, Raman spectra, XPS results, and electrochemical plots associated with this article can be found in the online version at doi:

Appendix B. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2018.08.010.

References


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Supporting Information

Ni/Co-Based Nanosheet Arrays for Efficient Oxygen Evolution Reaction

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Fig. S1. Cyclic Voltammograms recorded with a Pt electrode as the working electrode from -1.1 to -0.9 V (SCE as reference electrode, Pt as counter electrode) in 1.0 M KOH at a scanning rate of 5 mV s⁻¹.
Fig. S2. (a) Low- and (b) high-magnification SEM images, (c) XRD pattern of NiCo$_2$O$_4$ NSAs/NF, and (d) HR-TEM images of a NiCo$_2$O$_4$ nanosheet.
Fig. S3. Elemental maps of a NiCoON(1:2) nanosheet.
**Fig. S4.** (a) N 1s and (b) Co 2p XPS spectra of NiCo$_2$O$_4$ (top) and NiCoON (1:2) NSAs/NF (bottom).

**Fig. S5.** Areal capacitance of Ni foam, NiCo$_2$O$_4$, and NiCoON (1:2) NSAs/NF with the current density measured in 1.0 M KOH as a function of scanning rate.
**Fig. S6.** Faradaic efficiency measurement of NiCoON (1:2) NSAs/NF showing the theoretically calculated and experimentally measured O₂ with time at a current density of 14 mA cm⁻².

**Fig. S7.** Co 2p XPS spectra of pre- (lower) and post-OER (upper) NiCoON (1:2) NSAs/NF.
Fig. S8. (a) HR-TEM image a post-OER NiCo$_2$O$_4$ nanosheet. (b) Raman scattering spectra of the pre- and post-OER NiCo$_2$O$_4$.

Fig. S9. SEM images of the samples (Ni:Co=1:2) treated at (a) 380 °C and (b) 400 °C under ammonia. The HR-TEM images (c) and (d) correspond to (a) and (b), respectively.
Fig. S10. SEM images of NiCoON NSAs/NF with various feeding Ni:Co ratios: (a) CoO (0:1), (b) 1:3, (c) 1:2, (d) 1:1, (e) 2:1, (f) 3:1, and g Ni$_3$N (1:0); (h) Plot showing the change in the NiCoON NSAs (a) to (g).
Fig. S11. (a) Nyquist plots and (b) Corresponding charge transfer resistance (CRT) of NiCoON NSAs/NF versus the feeding Ni:Co ratios.

Fig. S12. OER polarization curves of the NiCoON (1:2) in unpurified (black) and purified (red) 1.0 M KOH.
Table S1. Comparison of OER performance of different Co and Ni-based electrocatalysts under alkaline conditions ($\eta$: overpotential at the current density of 10 mA cm$^{-2}$).$^a$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>$\eta$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>CoN</td>
<td>Ni foam</td>
<td>290</td>
<td>70</td>
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<td>NiO/CoN</td>
<td>Carbon fiber papers</td>
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<td>[S2]</td>
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<td>Co$_3$O$_4$/N-rmGO</td>
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<td>Fe$<em>6$Ni$</em>{10}$O$_x$</td>
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<td>48</td>
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<td>Co$_2$B</td>
<td>ITO</td>
<td>380</td>
<td>45</td>
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<td>CTs/Co-S</td>
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<td>72</td>
<td>[S6]</td>
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<td>[S7]</td>
</tr>
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<td>FTO</td>
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<td>Ni$<em>{0.9}$Fe$</em>{0.1}$O$_x$</td>
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<td>Mn$_3$O$_4$/CoSe$_2$</td>
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<td>Co$<em>{0.4}$Fe$</em>{0.6}$Se$_2$</td>
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<td>NiCoON</td>
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<td>This work</td>
</tr>
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</table>

$^a$ rmGO: reduced mildly oxidized graphene oxide; GCE: glass carbon electrode; ITO: Indium tin oxide; FTO: fluorine doped tin oxide; LDHs: layered double hydroxides.
References


