Electronic Supplementary information

Synergism between polydopamine and polyurethane in the synthesis of Ni-Fe alloy monoliths
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Materials and Methods:

Iron (III) chloride hexahydrate (Sigma Aldrich), nickel chloride (Nice Chemicals) and dopamine hydrochloride (Alfa Aesar), ammonium persulfate (Merck), hexamethylene-1, 6-triisocyanate homopolymer (N3300, Bayer), N,N’-dimethylformamide and acetone (Sisco research laboratories) were used as received.

Infrared spectroscopy for the samples was done on a Bruker Tensor 27 FT-IR spectrometer. X-ray diffraction patterns were recorded using a Bruker D8 Advance X-ray diffractometer with a Cu Kα radiation (λ = 1.5418 Å). Surface morphology was studied using Field Emission Scanning Electron Microscope (Zeiss supra 55VP). Cyclic voltammetric experiments were performed on a BASi100 workstation. BET isotherms were obtained using nitrogen adsorption/desorption porosimetry (Quantachrome Autosorb-1 surface area analyser).

Synthesis of Ni-Fe monoliths

In a typical synthetic procedure, Ni-FeOₓ gels were prepared by mixing 1.5 mmoles each of NiCl₂.6H₂O and FeCl₃.6H₂O in 10 mL of N,N’-dimethylformamide (DMF) followed by the addition of 30 mmoles (2.75 mL) of epichlorohydrin. The sol was poured into polypropylene moulds and the gelation time of Ni-FeOₓ gels was found to be 20 minutes. The gels were washed with DMF (3 × 8 h) followed by ethanol washes (3 × 8 h) to remove the unreacted precursors.

Polydopamine was coated on Ni-FeOₓ gels by dipping the wet gels in an ethanolic solution containing 10 mmoles of dopamine hydrochloride and 2 mmoles of ammonium persulfate for 24 h at room temperature [Q. Wei, F. Zhang, J. Li, B. Li and C. Zha, Polym. Chem., 2010, 1, 1430–1433]. The polydopamine coated gels were washed with ethanol and acetone (3 × 8 h) followed by dipping in 0.275g of hexamethylene-1,6-triisocyanate homopolymer (Desmodur N3300 A) dissolved in 10 mL of acetone for 24 hours. The wet gels were dried in an autoclave using scCO₂. The obtained Ni-FeOₓ aerogels were converted to Ni-Fe alloy monoliths by pyrolysis under flowing Ar at 800°C.
**Synthetic Scheme for Ni-Fe alloy monoliths**

1.5 mmoles each of 
NiCl₂.2H₂O and FeCl₃.6H₂O 
in 10 mL DMF

30 mmoles epichlorohydrin 
Gelation time ~30 min

Ni-FeOₓ gels

Dip in 10 mmoles dopamine hydrochloride and 
ammonium persulfate ethanolic solution for 24 h

Ni-FeOₓ@pDA

Dip in 0.275 g of Desmodur N3300 A in 10 mL acetone 
scCO₂ drying

Ni-FeOₓ@pDA-pU 
aerogels

Pyrolysis under Ar @ 800°C

Ni-Fe/C monoliths

**Electrochemical experiments:**

A three-electrode cell with Hg/HgO as reference electrode and a Pt foil as the counter electrode was used. The glassy carbon disk portion of the RRDE was modified with the Ni-Fe-monolithic catalyst and employed for studying the oxygen evolution reaction. 0.1M KOH was used as the supporting electrolyte. Prior to modification, the glassy carbon electrode was well-polished with 1, 0.3 and 0.05 micron sized alumina powder and sonicated for about 5 minutes. A thin film of the Ni-Fe catalyst was prepared in order to perform thin-film hydrodynamic voltammetry, following the method of Behm et al. For this, 5µL Ni-Fe catalyst ink was prepared by sonicating a mixture of 5 mg Ni-Fe catalyst in 1ml of 1% Nafion equivalent to the 80 µg cm⁻² of the catalyst coated on the glassy carbon surface [Note: This Nafion film was soaked in 0.1M NaOH solution to exchange protons with Na⁺ ions]. Voltammetric responses of Ni, Ni-Fe and Fe were recorded in a potential range between 0 to 0.6 V vs. Hg/HgO at a scan rate of 50 mVs⁻¹. For studies on OER electrocatalysis, a potential range of 0 to 0.8 V vs. Hg/HgO and a scan rate of 5 mVs⁻¹ were chosen. All the potential
values are referred against Hg/HgO electrode and water oxidation curves are cited in RHE scale.

**Faradaic efficiency calculation:**

The OER Faradaic efficiency for the Ni-Fe monoliths was determined using RRDE voltammetry based on the reported procedures \[^{83}\]. In order to calculate Faradaic efficiency, one needs to first find the collection efficiency of the ring electrode. RRDE experiments were carried out using a VMP3 multi-channel potentiostat (Biologic Inc), a rotator (MSR), Au Disk-Pt Ring (AFE6R2AUPT), of Pine instruments USA.

**RRDE-Collection Efficiency Calculation:** In a typical RRDE collection experiment, the complete product generated at the disk electrode will not reach the ring electrode. The flow pattern at a rotating electrode generally sweeps anywhere from 20% to 30% of the disk products past the ring electrode. The percentage of material which is collected at the ring electrode is often called the “collection efficiency” of the RRDE. One may empirically measure the collection efficiency of a specific RRDE before using it for any quantitative work. This is normally done using a well-defined electrochemical system such as the ferricyanide-ferrocyanide redox couple. This system can be used to measure stable collection efficiency at rates between 200 and 2500 rpm. The ring collection efficiency was calculated to be 30% (or expressed as 0.3), as measured using a $[\text{Fe(CN)}_6]^{3-/4-}$ redox couple. The ring potential was set at 0.23V vs. Ag/AgCl.

The collection efficiency, $N_{CL}$, calculated from the current response of $K_3\text{Fe(CN)}_6$ (5 mM) in 0.1M KCl was found to be 30 ± 1%. Ar gas was purged into the electrochemical cell for 30 min before the experiment and remained throughout the experiment. 5 μL of the Nafion ink solution containing 5 mg/mL Ni-Fe monolithic catalyst was drop-cast on the Au disk electrode. The Au disk electrode was held at open circuit potential of OER to determine the ring background current, while the Pt ring electrode was held at -0.5 V vs. Hg/HgO. The ring background current was found to be 20 µA. The disk electrode was then subjected to sequential 1 minute current steps at 0.1, 0.2, 0.5 and 1 mA cm\(^{-2}\) at 1600 rpm, while the ring was held constant at -0.5 V vs. Hg/HgO. Faradaic efficiency was calculated based on the ratio of disk and ring currents using the following equation:

$$\varepsilon = \frac{2i_r}{i_d N_{CL}}$$

$i_r$ = Ring current (A); $i_d$ = Disk current (A); $N_{CL}$ = Collection efficiency (%)
$\varepsilon$ = Faradaic efficiency (%)
Turn-over frequency calculation:

The turn-over frequency (TOF) was calculated based on the number of Ni sites in the Ni-Fe monolithic catalyst, according to the procedure followed by A.T.Bell [S2].

\[
\text{TOF}_{\text{max}} = \frac{I \times N_A}{4FN_{\text{atoms}}}
\]

where, \(I\), \(N_A\), \(N_{\text{atoms}}\), \(F\) represent the current obtained at 700 mV, Avogadro number (6.023 \(\times\) 10\(^{23}\) mol\(^{-1}\)), number of atoms on the surface and Faraday constant (96500 C/mol) respectively. \(\text{TOF}_{\text{max}}\) was estimated from the surface area of film and the number of Ni atoms on the surface using a value of 6.4 \(\times\) 10\(^{14}\) Ni atoms per cm\(^2\) area [S2].

The electrochemically active surface area (ECSA) is significant since it’s directly linked to the actual surface involved in the catalytically activity. In the case of Ni surface, determination of active surface area employs the charge (Q) under the CV peak corresponding to Ni (II/III). The ECSA is then calculated from the charge density associated with the formation of 1 monolayer, i.e., equal to 514 \(\mu\)C cm\(^{-2}\) [S3]

\[
\text{ECSA} = \frac{Q}{514 \mu \text{C cm}^{-2}}
\]

\(Q=\) Charge (Coulombs)
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Figure S2: FTIR spectrum of FeO\textsubscript{x}, FeO\textsubscript{x}@pDA and FeO\textsubscript{x}@pDA-pU
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<table>
<thead>
<tr>
<th>Synthesis/materials</th>
<th>$\eta$, mV@ $10$ mA cm$^{-2}$</th>
<th>Tafel slope (mV)</th>
<th>TOF, s$^{-1}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrodeposited Ni-FeO$_x$</td>
<td>~300</td>
<td>~40</td>
<td>87(a)</td>
<td>[S2]</td>
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<tr>
<td>Amorphous Ni-FeO$_x$ nanoparticles</td>
<td>280</td>
<td>32</td>
<td>0.21(b)</td>
<td>[S4]</td>
</tr>
<tr>
<td>Ni-Fe LDH/CNT</td>
<td>300</td>
<td>35</td>
<td>0.56(b)</td>
<td>[S5]</td>
</tr>
<tr>
<td>Ni-FeO$_x$ (solution-cast)</td>
<td>336</td>
<td>30</td>
<td>0.06(b)</td>
<td>[S6]</td>
</tr>
<tr>
<td>Ni-Fe monoliths</td>
<td>375</td>
<td>42</td>
<td>125(a)</td>
<td>this work</td>
</tr>
</tbody>
</table>

(a) TOF$_{\text{max}}$, by taking the measured surface area of a film and calculating the number of Ni atoms at the surface using a value of $6.4 \times 10^{14}$ Ni atoms per cm$^2$ area

(b) Based on the calculation of the number of nickel atoms in the film to be active for OER (TOF$_{\text{min}}$, lower bound), using elemental analysis

§ Note: A value of $\eta = 350$ mV@10 mA cm$^{-2}$ for the electrodeposited NiFeO$_x$ for OER in 1.0M KOH solution has been benchmarked by Jaramillo’s group [C.C.L. McCrory, S. Jung, J.C. Peters, T.F. Jaramillo, J. Am. Chem. Soc., 2013, 135, 16977]. To the knowledge of the authors, no work has been reported for OER using NiFe alloy thus precluding the possibility of its comparison.
Table S2

Determination of TOF for Ni-Fe monolith catalyst for OER

<table>
<thead>
<tr>
<th>Methods</th>
<th>Procedure</th>
<th>Formula</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
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<tr>
<td>Cyclic voltammetry</td>
<td>Calculating the surface area of the film to get the number of Ni atoms of the surface using 6.4×10¹⁴ Ni atoms per cm² area</td>
<td>$i \times \frac{N_A}{4FN_{atoms}}$</td>
<td>125 (TOF_{max})</td>
</tr>
<tr>
<td>RRDE</td>
<td>Calculating the number of moles of active metals drop casted on the electrode</td>
<td>$\frac{i_{ring}}{4 \times F \times N_{CL} \times m}$</td>
<td>1.47</td>
</tr>
</tbody>
</table>

where, $I$, $N_A$, $N_{atoms}$, $F$ represent the current obtained at 700mV, Avogadro number, number of atoms at the surface and Faraday constant respectively. TOF_{max} can be estimated by taking the measured surface area of a film and computing the number of Ni atoms on the surface using a value of 6.4 × 10¹⁴ Ni atoms per cm². $i_{ring}$ = ring current, $N_{CL}$ = collection efficiency of ring electrode and $m$ = number of moles of active metals (drop-cast on the electrode surface).
References