Supporting Information for

An efficient bifunctional two-component catalyst for Oxygen Reduction and Oxygen Evolution in reversible fuel cells, electrolyzers and rechargeable air electrodes

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Catalyst Preparation

Nickel Iron layered double hydroxides (NiFe-LDH) supported on Vulcan XC72R were prepared via a microwave assisted autoclave one-pot synthesis route (Figure S1). 1200 µl of 0.2 M Ni(OAc)2 x 4 H_2O (Sigma Aldrich, 99.998 % purtity) and 240 µl 0.2 M Fe(NO_3)3 x 9 H_2O (Alfa Aeser, 98 % purity) prepared aqueous precursor solution were added to a 6 mg Vulcan XC72R (Cabot) in 6 ml Dimethylformamid (Sigma Aldrich) dispersion and subsequent stirred for 1 h. Additional 4 ml DMF and 8 ml ultrapure water (18.2 MΩ cm) were added before a two step synthesis microwave treatment (60 min at 120 °C; 30 min at 160° C and) was conducted by using an Anton Paar Monowave 300. The final product was collected by centrifuge, repetitively washing with Ethanol and ultrapure water and lyophilized. All NiFe-LDH/C materials resulted in 37.7 ± 2.1 wt% metals in a Ni/Fe ratio of 3.62 ± 0.03.
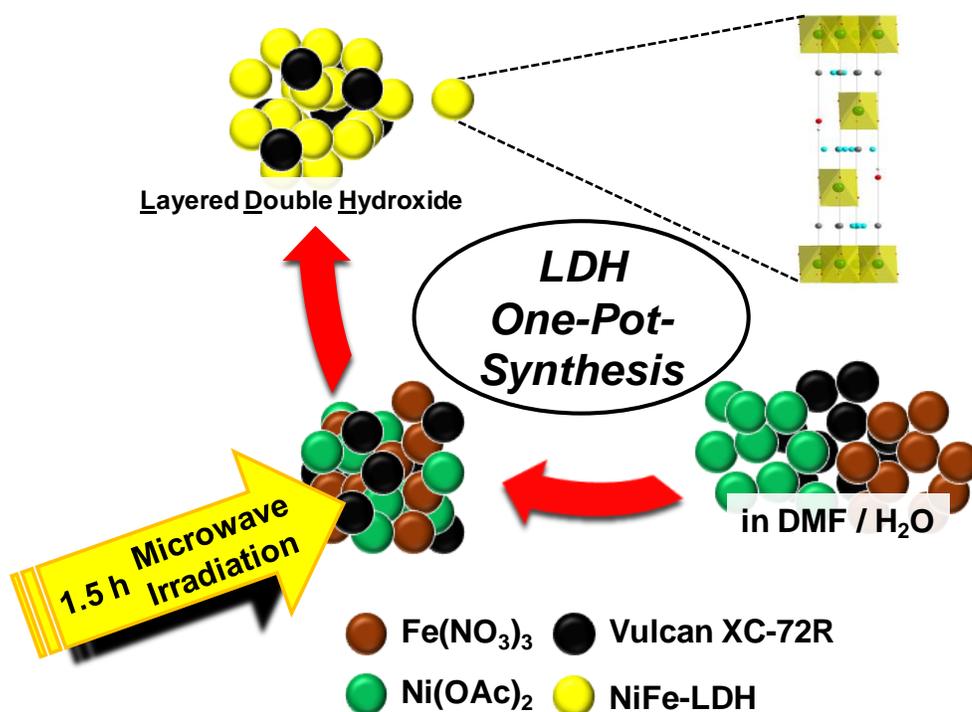

Figure S1: Diagram of one-pot microwave assisted synthesis route

For the Fe/PANI/Ketjen catalyst, Carbon Ketjen was pretreated: As-received commercial carbon support, Ketjen EC 600JC (AkzoNobel) (5 g) was dispersed in 0.5 M HCl (100 ml) for 30 minutes by ultrasonication. The dispersion was kept for 24 h under continuous stirring condition. The pre-leached carbon was collected by filtering, subsequent washing until neutralization and drying overnight at 60 °C

in air. For activation the carbon powder (5 g) was refluxed in concentrated nitric acid (69 wt%, 10ml) at 90 °C for 5 hours. After activation the carbon was washed again until neutralization and dried overnight at 60 °C.

For the final Fe /PANI/Ketjen catalyst, 2 ml aniline (Sigma-Aldrich, > 99.5 % purity) was first dissolved in 250 ml 0.5 M HCl solution. 3 g FeCl3 (anhydrous, Sigma-Aldrich) was added into the solution and kept stirring for 15 min to ensure a total dissolution of aniline and $FeCl_3$. Then, 5 g ammonium peroxydisulfate ((NH4)2S2O8) (Carl Roth, > 98 % purity) was dissolved in 250 ml 0.5 M HCl solution, and added drop wise (30~45 min) to the ice bath cooled dissolution for in situ polymerization of aniline. The polymerization of aniline was indicated by a color change, from initially light blue to a resulting dark blue. The polymer suspension was kept at low temperature until no color change was observed. Then, the pretreated Ketjen (0.4 g) was mixed with Fe/Polyaniline (Fe/PANI) under constant stirring for 48 h at room temperature to achieve uniformly distributed suspension, which was subsequently refluxed for 5 h at 80-90°C. After overnight drying of the mixture at 80-90°C in N_2, a heat treatment was performed at 900 °C for 1 hour in N_2. The remaining excess of Fe was removed by repetitive acid leaching (2M H_2SO_4) under a reflux at 80-90°C for 7-8 h in N2 followed by washing until reaching a pH of 7. The next heat treatment at 900 °C was performed for 3 h in N_2 until the final Fe-N-C product was achieved.
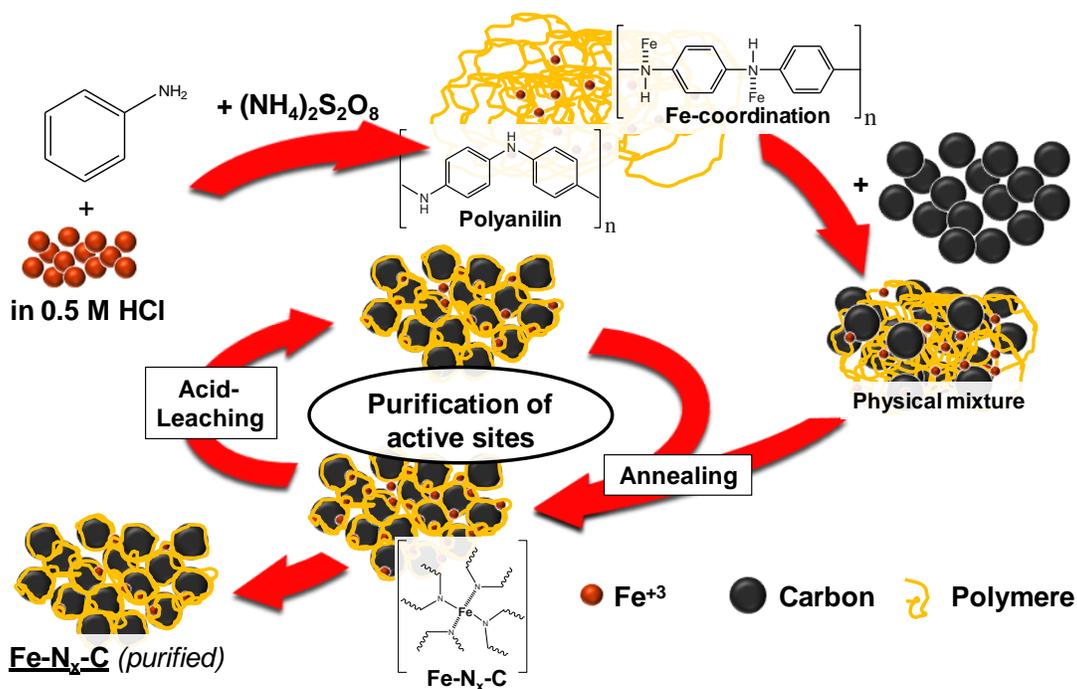

Figure S2: Diagram of synthesis route for preparing Fe in N-doped carbon material

Fabrication of membrane electrode assembly (MEA) and measurement

The membrane electrode assembly (MEA) was prepared by a spray coating technique to obtain a catalyst coated membrane (CCM). Typically, 50 mg catalyst (46.7 wt% Pt/C TKK for the bifunctional Hydrogen electrode), 50 µl ultrapure water (18.2 MΩ cm), 3 ml i-Prop and 460 mg Ionomer (5 wt% AS-4, Tokuyama) were ultrasonicated for 15 min. The membrane (A201, Tokuyama) was fixed on a commercial heatable vacuum table (Carbon and FuelCell) equipped with a dry vacuum pump/compressor (Welch 2511) and a temperature controller (Carbon and FuelCell). Typically, 650 µl of the ink were spray coated on a membrane using 1 bar N_2 stream and a Gun Piece SP-2 spray gun (Rich) equipped with a 0.4 mm tip size to achieve a loading of 0.5 mgPt cm^{-2} for the hydrogen electrode side. To obtain a homogenous 5 cm^2 coating the spraying was conducted in horizontal and subsequent vertical serpentine line and the table temperature was set to 50 °C. A mask was used to protect the protruding part of the membrane and to ensure the optimal vis-à-vis coating. After coating the drying process precedes 10 min. After further 10 min of cooling the mass loading on the membrane was determined. To control the obtained coated catalyst mass the unladen weight were determined before the coating step and compared to the resulted weight.
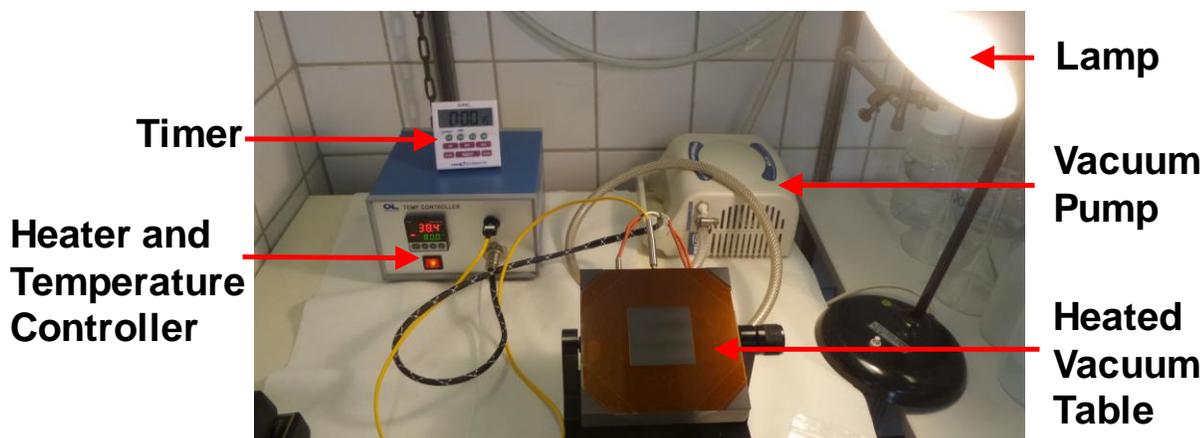

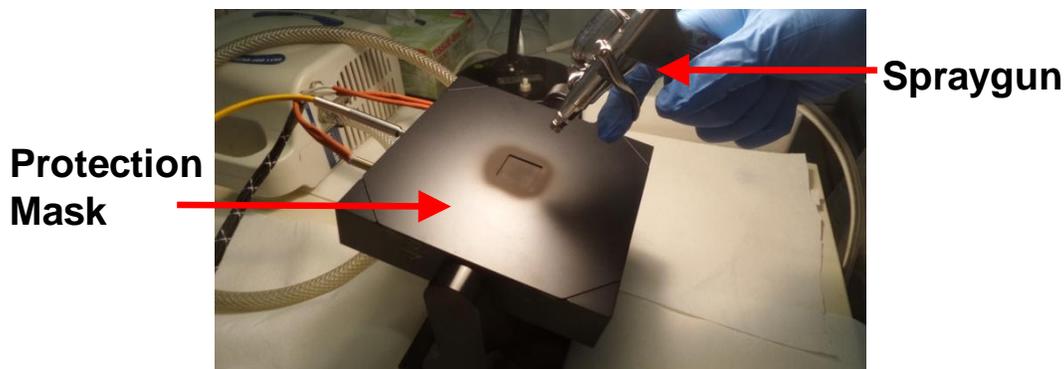**Figure S3:** Membrane coating set up for preparing MEA preparation

Figure S4: Image of the membrane coating

Physical and chemical characterization of the samples

Powder X-ray diffraction **(XRD)** was carried out in locked mode between 10-70 ° and a step size of 0.039° on a Bruker D8 Advance x-ray Powder diffractometer equipped with a Lynx Eye detector and KFL Cu 2K X-ray tube. The divergence slit was set to 6 mm, the antiscattering slit to 6° and the Lynx-Iris to 10 mm. Transmission electron microscopy **(TEM)** and Energy dispersive x-ray spectroscopy **(EDX)** were conducted to study morphology and composition using a Tecnai G2 20 S-TWIN microscope operated at 200 kV, equipped with a GATAN MS794 P CCD-detector. Inductively coupled plasma-optical emission spectroscopy **(ICP-OES)** was used for elemental and compositional analysis using a 715-ES-inductively coupled plasma analysis system (Varian).

Electrochemical characterization

Every given electrochemical potential is given in respect to the reversible hydrogen electrode **(RHE)**. For all rotating disk electrode (RDE) and rotating ring disk electrode (RRDE) measurements, 5 mg catalyst, 960 µl ultrapure water, 250 µl i-Propanol and 40 µl Nafion (5wt %) were ultrasonicated for 15 min. The electrodes were polished initially with 1 µm Alumina (Buehler) on a Nylon pad and subsequently with 0.05 µm Alumina (Buehler) on a microcloth. The residual Alumina was removed by ultra sonicating the electrode in water and acetone. To obtain a catalyst loading of 0.2 mg cm^{-1}, 10 µl of the ink were drop coated on the RDE (0.1963 cm^2 geometrical disk surface area) and 12.60 µl were drop coated on a RRDE (0.2475 cm^2 geometrical disk surface area). All electrochemical measurements were conducted in at

least 15 min deaerated 0.1 M KOH at room temperature and a three electrode measurement set-up using a glass cell equipped with a large surface area Pt counter electrode and a reversible hydrogen electrode (RHE) (HydroFlex) as reference electrode, which is connected to the main compartment of the glass cell via a Luggin capillary. The RDE measurements were performed using a BioLogic SP 200 and the RRDE measurements were carried out using a bipotentiostat BioLogic VSP.

To activate Fe-N-C based materials, the catalyst was cycled between 0.05 – 1.0 V and 100 mV/s in N2 saturated 0.1 M KOH for 20 Cycles until a constant Cyclic Voltammogram (CV) was achieved. The capacitive current was recorded between 0.05 - 1.0 V and 5 mV/s. Impedance measurement (PEIS) between 0.1 Hz – 100 kHz at 1 V was conducted to determine the IR-drop resistance. All measurements are IR-drop corrected.

The activity measurement were conducted in O_2 saturated 0.1 M KOH. The starting ORR activity measurement was carried out by immersing the electrode at 0.05 V and subsequent cycling for one cycle between 0.05 - 1.1 V at 5 mV/s, followed by 20 Cycles at 50 mV/s and ending with 1 Cycle at 5 mV/s. After the ORR measurement the OER activity measurement was performed between 1.0 – 2.0 V in the same way.

Galvanostatic stability measurement was conducted with RDE at 1600 rpm in O_2 saturated 0.1 M KOH by setting alternate 1 h a constant current of 4 mA cm^{-2} for the OER and -3 mA cm^{-2} for ORR.

RRDE measurement was initially performed in N_2 saturated 0.1 M KOH to clean the Platinum surface area of the ring by cycling between 0.05 – 1.4 V for at least 200 Cycles and 100 mV/s until a constant CV was achieved and secondly cleaning the disk surface area by cycling between 0.05 – 1.0 V for 20 Cycles at 100 mV/s followed by determining the capacitive current and the resistance as described previously for the RDE measurement. The bipotentiostat measurement was finally performed in O_2 saturated 0.1M KOH with a scan rate of 5 mV/s and the ring was set to 1.2 V between 0.05 - 1.1 V at different rotation rates.

The collection efficiency was determined by measuring the current of the ring at 1.55 V in N_2 saturated 0.1 M KOH and 0.01 M $K_3[Fe(III)(CN)_6]$ solution by cycling the disk between 0.2 – 1.4 V at 5 mV/s. The ratio between disk current (i_D) and ring current (i_R) at the same potential resulted in the collection efficiency N ~ 0.37:

$$N = -\frac{i_R}{I_D} \tag{S1}$$

The HO$_2^-$ production was calculated by using the following formula:

$$X_{HO_2^-} = -\frac{2i_R/N}{I_D + i_R/N} \tag{S2}$$

And the equation to calculate the **electron transfer** is as follows [1-3]:

$$n = -\frac{4I_D}{I_D + i_R/N} \tag{S3}$$

Where i_r is the measured current of the ring, i_D is the current of the disc and N is the collection efficiency.

The cell measurement was carried out by using a commercial reversible fuel cell assembly (Carbon and FuelCell) consisting of two endplates with gas ports, two current collectors, two bipotential plates (*Carbon plate for bifunctional hydrogen side, gold coated titanium plate for oxygen side*), a gas diffusion layer (GDL-10BC, Sigracet® GDL) and the prepared MEA. The screws were tightened with a torque of 50 kg cm.
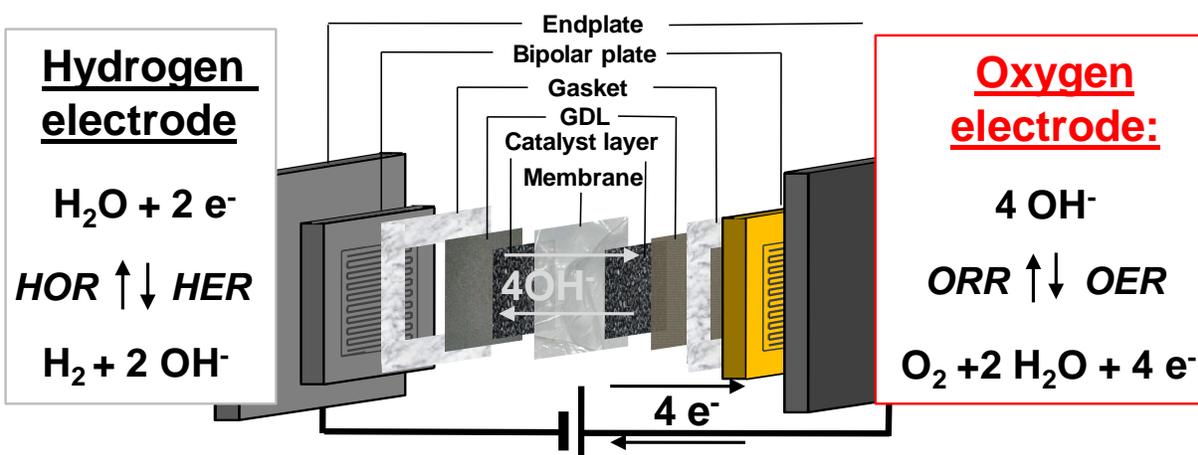

Hydrogen electrode

$H_2O + 2 e^-$

HOR $\uparrow\downarrow$ *HER*

$H_2 + 2 OH^-$

Endplate
Bipolar plate
Gasket
GDL
Catalyst layer
Membrane

$4 OH^-$

$4 e^-$

Oxygen electrode:

$4 OH^-$

ORR $\uparrow\downarrow$ *OER*

$O_2 + 2 H_2O + 4 e^-$

Figure S5: Set-up of reversible electrolyzer cell
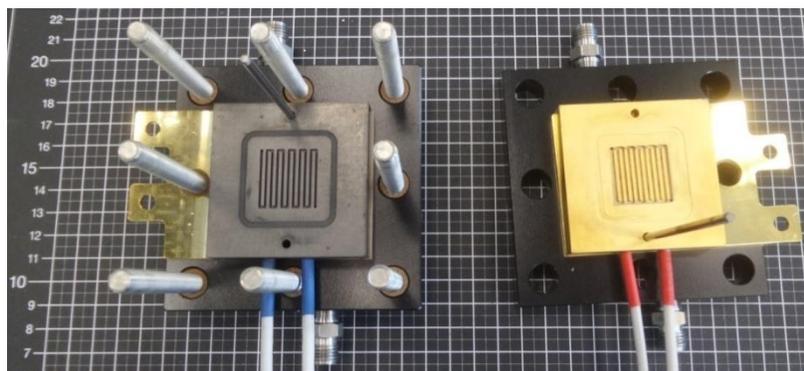

Figure S6: View on the reversible electrolyzer with a carbon based bipolar plate (left) for the bifunctional hydrogen electrode and a gold coated titanium plate (right) for the bifunctional oxygen electrode

At first the reversible electrolyzer cell was tested in a fuel cell mode using a fuel cell test station (Fuel Cell Technologies, Inc.). After a heating procedure and gas purging for 1 h, the VI-curve between 0.35 – 1

V was realized at 50 °C and a gas flow of 200 sccm of H_2 and O_2 was used. Impedanz was recorded after each measurement. For each data point a delay time of 15 s was set. After fuel cell measurement the electrolyzer mode was tested at 50 °C and a flow rate of 0.5 sccm of ultrapure water was set using a Reglo digital MS-2/6 peristalticpump (Ismatec) (Figure S7).
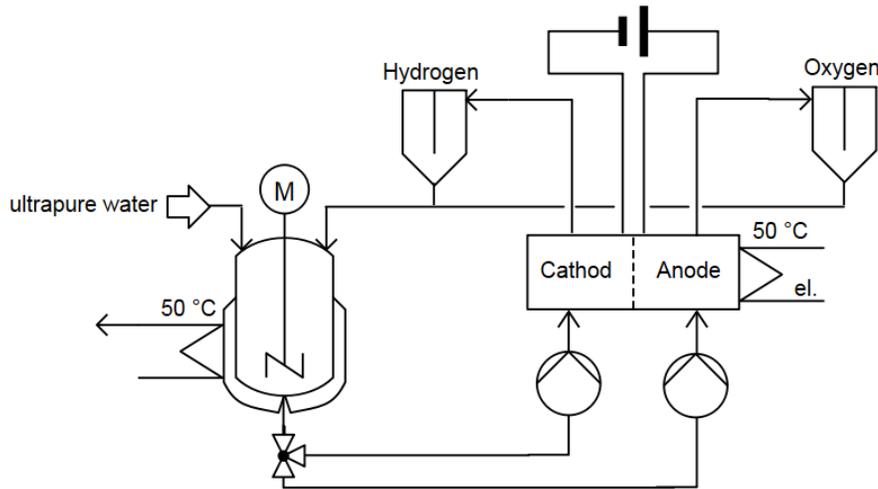
Figure S7: Flowdiagram for Electrolyzer set up

To record the IV-curve a BioLogic SP 200 was used. Each data point was held for 15 s and the last Voltage point was taken. To repeat measuring in fuel cell mode the gases were purged again for at least 1 h at 50 °C to dry the GDL. Afterwards again 3 VI curves were recorded in fuel cell mode.
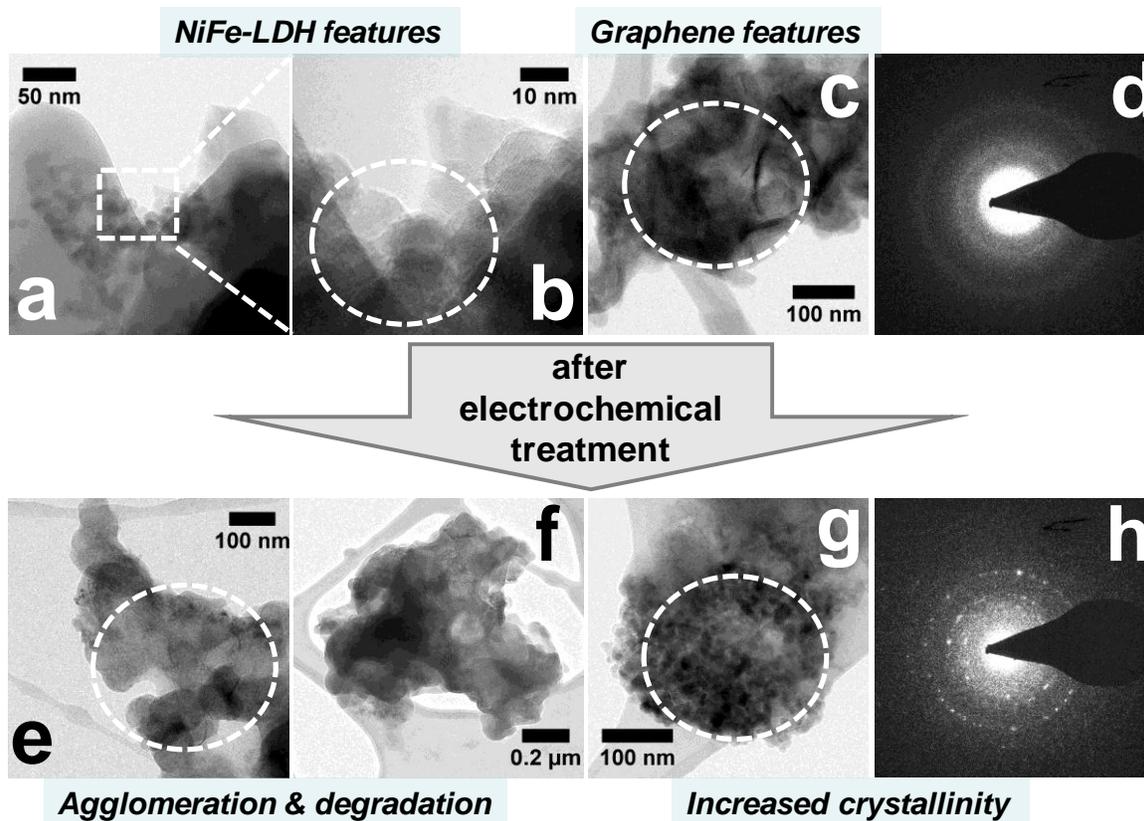
The standard errors (SE) were estimated by determining the value from at least three independent measurements and calculated by using the following formula:

$$SE = \frac{s}{\sqrt{n}} \tag{S4}$$

with

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}} \tag{S5}$$

where **s** is the standard deviation, **n** is the number of measurements, x_i is the value of the i measurement and $\overline{x}$ is the average of the values.

Figure S8: TEM Images of Fe-N-C / NiFe-LDH (3:1) before (a-d) and after (e-h) electrochemical treatment. The SAED spectra (d) and (h) are related to the TEM images (c) and (g). The images are indicating an increased crystallinity nanoparticle formation after electrochemical treatment
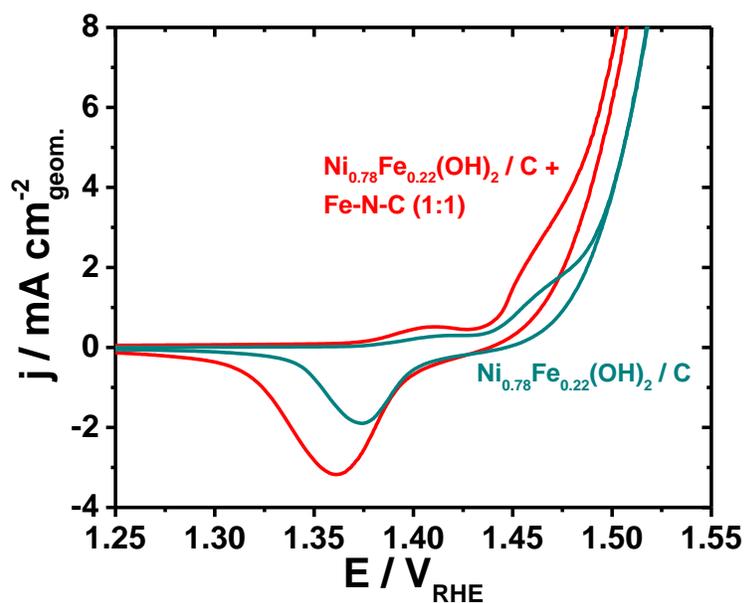
Figure S9: CV of NiFe-LDH and NiFe-LDH + Fe-N-C to 1:1 mixture in O_2 saturated 0.1 M KOH at 50 mV/s . Different size of the $Ni^{2+/3+}$ Redoxpeak may suggest a higher conductivity of the sample or accessibility of the Nickel active sites
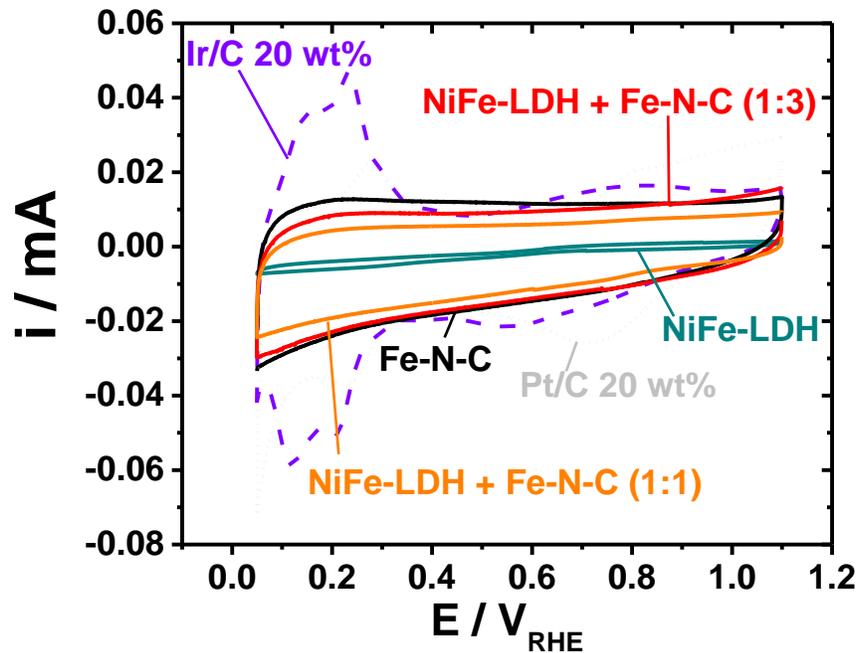

Figure S10: Cyclic voltammogram in N_2 saturated 0.1 M KOH for different catalysts. NiFe-LDH have the shows a CV with the smallest capacitive current
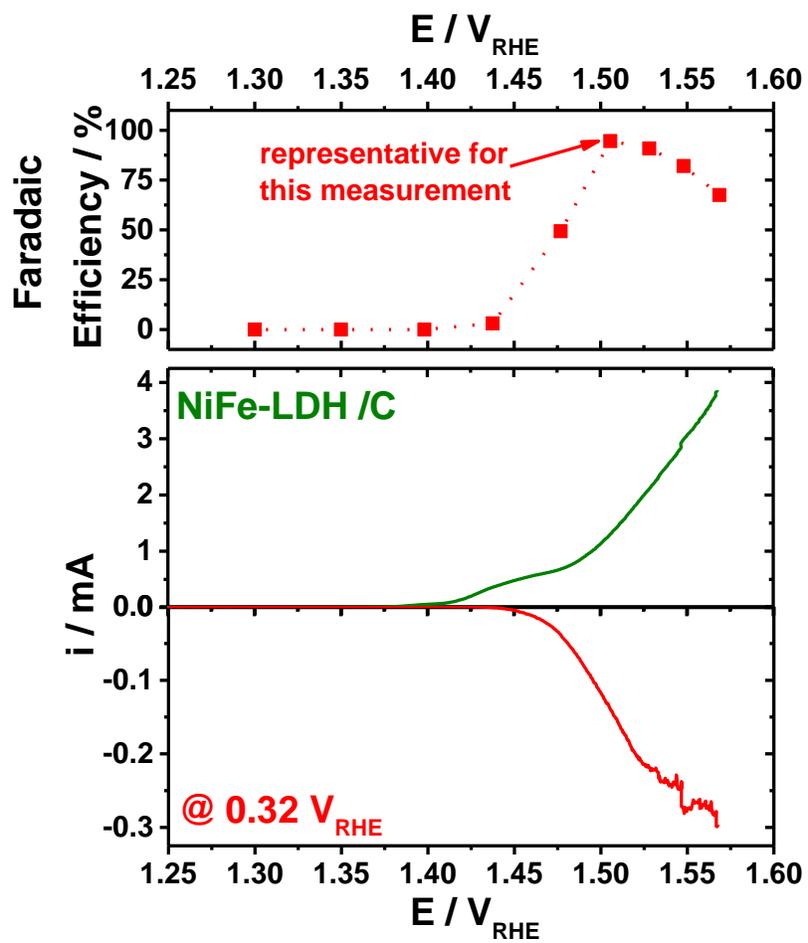
FigureS 11: Faradaic efficiency measurement for Oxygen evolution reactíon
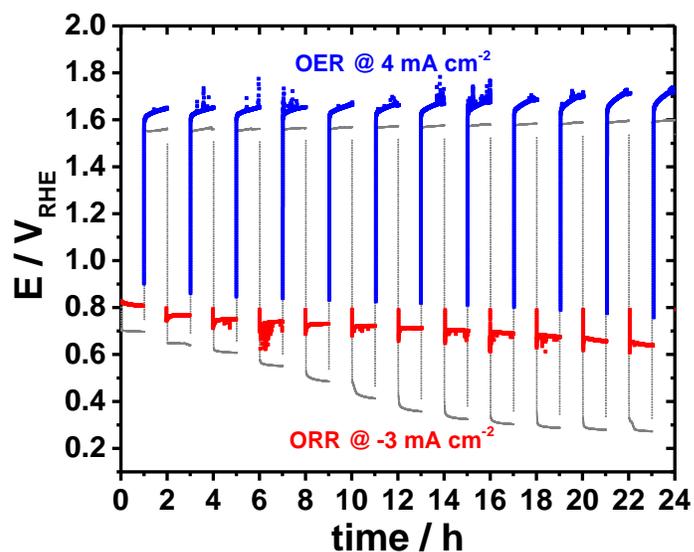
Figure S12: RDE stability measurement over 24 h for Pt/C 20wt% + Ir/C 20 wt% (1:1) mixture (blue @ 4 mA cm^2 and red @ -3 mA cm^2) and NiFe-LDH Fe-N-C (1:3) (grey) in O_2 saturated 0.1 M KOH at 1600 rpm and 0.2 mg cm^{-2} cat loading
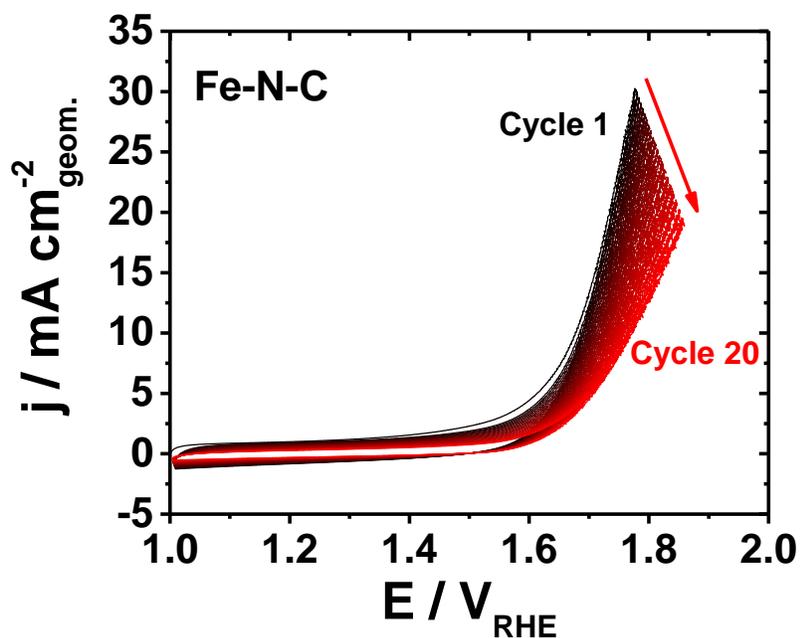
Figure S13: 20 Cycles of Fe-N-C catalyst with 50 mV/s in O_2 saturated 0.1 M KOH. Cycles show the instability of Fe-N-C catalyst during OER potentials. Indicating an oxidation of the catalyst
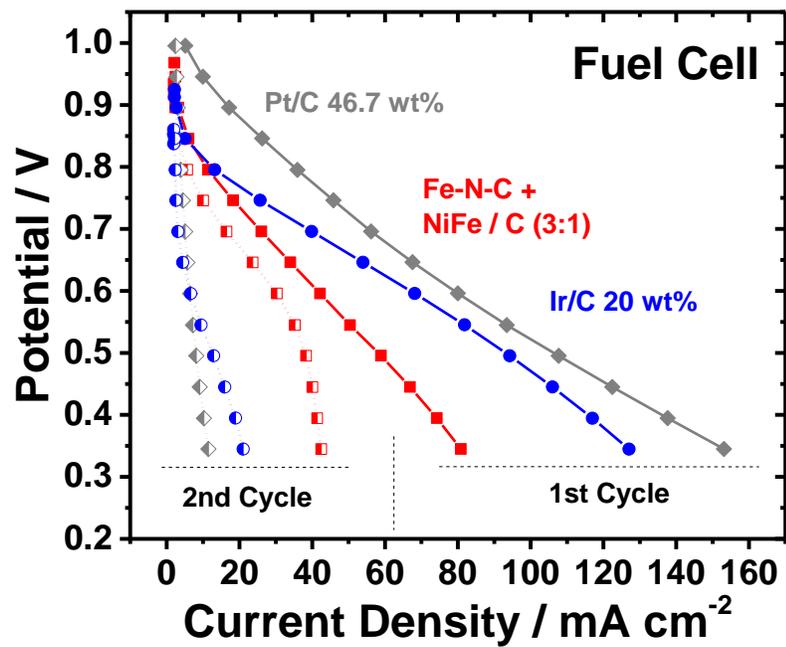
Figure S14: VI-curves for fuel cell testing for different catalysts. The fuel cell activity for the noble materials decreased even more than for the non-noble two component system

Table S1: ORR and OER activities for different catalysts measured in 0.1 M KOH at a rotation rate of 1600 rpm and a catalyst loading of 0.2 mg cm^{-2}.

catalyst	$E_{1/2}$ @ -3 mA cm^{-2} [V]	E @ 10 mA cm^{-2} [V]	ΔE (OER – ORR) [V]	j @ 0.8 V [mA cm^{-2}]	Reference
NiFe-LDH	0.285 ± 0.056	1.550 ± 0.015	1.266 ± 0.071	---	This study
Fe-N-C	0.799 ± 0.009	1.736 ± 0.009	0.937 ± 0.020	3.02 ± 0.218	This study
NiFe-LDH / Fe-N-C (1:1)	0.728 ± 0.034	1.515 ± 0.010	0.786 ± 0.044	1.52 ± 0.219	This study
NiFe-LDH / Fe-N-C (1:3)	0.793 ± 0.003	1.539 ± 0.006	0.747 ± 0.009	3.045 ± 0.071	This study
Pt / C 20 wt%	0.863 ± 0.009	1.901 ± 0.01667	1.038 ± 0.037	5.125 ± 0.125	This study
Ir / C 20 wt%	0.733 ± 0.010	1.586 ± 0.013	0.853 ± 0.023	1.553 ± 0.052	This study
MnOx	0.73	0.54	1.04	-	[4]
Co/N-C-800	0.74	1.599	0.859	-	[5]
Pt/C to BSCF/C = 4:1	0.81	1.61	0.8	-	[6]
Fe3C@NG800-0.2			0.78	-	[7]
/N	0.83 ± 0.01	1.59 ± 0.01	0.76 ± 0.02	-	[8]

Table S2: Obtained loadings for coated Tokuyama A201 membrane

MEA	H$_2$ load. [mg$_{Pt}$ cm^{-2}]	O$_2$ load. [mg$_{cat.}$ cm^{-2}]	j$_{geom.}$ @ 0.8 V [mA cm^{-2}]	j$_{geom.}$ @ 1.53 V [mA cm^{-2}]
Pt/C 46.7 wt% / Pt/C 46.7 wt%	0.51	1.35	34.93	1.45
Pt/C 46.7 wt% / Ir/C 20 wt%	0.47	2.85	12.41	40.04
Pt/C 46.7 wt% / Fe-N-C + NiFe-LDH	0.58	2.50	12.79	25.24

Table S3: Used proportion of mixed catalysts

catalyst	NiFe-LDH [%]	Fe-N-C [%]
NiFe-LDH / Fe-N-C (1:1)	49.9 %	50.1 %
NiFe-LDH / Fe-N-C (1:3)	25,6 %	74,4 %
NiFe-LDH / Fe-N-C (1:3) (MEA)	24.7 %	75.3 %

References

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