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Supporting Information

Efficient direct seawater electrolysers using selective alkaline NiFe-

LDH as OER catalyst in asymmetric electrolyte feeds

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Experimental measurement:

The electrolyser tests were performed using an in-house bench top setup (See Figure S1). The single electrolyser cell (Hydron Energy) is comprised of stainless-steel endplates, titanium current collector plates with 5 cm² active area and a parallel flow field on the anode and cathode side. The reaction temperature of 50°C generated through heating cartridges mounted on both endplate of the cell and controlled via a temperature controller (CNL). A two channel peristaltic pump (ISMATEC, MCP Process) circulates the electrolyte at 50 rpm representing a flow rate of 100 mL min⁻¹. The electrochemical testing was performed by using a Gamry Reference 3000 potentiostat equipped with a 30K Booster. The gas analysis was conducted by a quadrupole mass spectrometer (Pfeiffer vacuum). Nitrogen gas with a flow rate of 100 ml min⁻¹ was used as a carrier and purging gas on the anode side.



Figure S1: In-house testing set-up. (a) Full in-house bench top testing system equipped with a mass spectrometer, electrolyser cell, potentiostat equipped with a 30 A Booster, a peristaltic pump and mass flow controller. (b) Enlarged section of in-house testing system showing the separated PTFE based electrolyte reservoirs for cathode and anode, the electrolyzer cell, the N_2 carrier gas flow direction and the in-house gas cooling equipment

MEA preparation:

The used MEA consists of an anion exchange membrane Tokuyama A201, 48,47 wt% Pt on carbon black (Elyst Pt50 0380, Umicore) as cathode and synthesized NiFe-LDH as anode catalyst material. AS-4 (Tokuyama) was used as ionomer binder on both sides in a mass ratio of 7:3 (Catalyst:Ionomer). The MEA was prepared via spray coating at 50 °C on a heating plate with vacuum support. The desired catalyst loading was 0.5 mg_{Pt}.cm⁻² for the cathode and 2.0 mg.cm⁻² NiFe-LDH for the anode side.

Cell assembly

The single cell stack was assembled by sandwiching the as prepared dry MEA in between a carbon based GDL (Sigratec BC 25) on the cathode and a gold sputtered (100s, 20mA, both sides) titanium felt (Bekaert, 2GDL6-0,3) under a torque value of 12.5 Nm (See Figure S2).



Figure S2: Assembly of the electrolyser stack. (a) gasket with the endplate equipped with parallel flow channels (b) Au coated Ti-felt is placed on the flow channels for the anode (c) prepared MEA is placed on the PTL (d) Carbon based GDL for the cathode is placed on the catalyst layer (e) for sealing the anode side a gasket is place on the MEA. (f) The endplate is placed on the anode side (g) the screws-nuts are mounted on the screws (h) the screw nuts are lightly fixed by hand and (i) tightened with a torque wrench using 12.5 Nm (h) mounted electrolyser cell

NiFe-LDH Synthesis

Nickel Iron layered double hydroxides (NiFe-LDH) were prepared via a microwave assisted autoclave onepot synthesis route that is described in detail elsewhere.¹ In short, 1200 μ L of 0.6 M Ni(OAc)₂ × 4H₂O (99.998% trace metals basis, Aldrich) and 240 μ L of 0.6 M Fe(NO₃)₃ × 9H₂O (98% trace metals basis, Alfa Aeser) were added to 6 mL DMF and stirred overnight. Afterward, 8 mL ultrapure water (>18 MΩ at room temperature) and 4 mL additional DMF were added to the reaction mixture. The solution was then microwave treated at 120 °C for 60 min and subsequently at 160 °C for 30 min. The final product was collected by centrifuging and subsequently washed using ultrapure water and ethanol.

Physical and Chemical Characterization of NiFe-LDH

In order to verify our NiFe-LDH used in this publication, we conducted ICP and XRD analysis. Further physicochemical characterization and in depth analysis of NiFe-LDH such as transmission electron microscopy (TEM), X-ray absorption spectroscopy (XAS) and extended X-ray absorption fine structure spectroscopy (EXAFS) have been shown by Dresp et al in ref¹.

ICP-OES was used for elemental and compositional analysis using a 715-ES-inductively coupled plasma analysis system with CCD detector (Varian). Prior to detecting, the catalyst materials were dissolved in a mixture of $HNO_3/H_2SO_4/HCl$ in a ratio of 1:1:3.

XRD measurements were carried out to study the crystallinity using a D8 Advance Diffractometer (Bruker) equipped with a Lynx Eye Detector and KFL Cu 2 K X-ray tube. The diffraction profiles were collected between 2θ angles of 10° and 70° with a step size of 0.039°. The divergence slit was set to 6 mm, the anti-scattering grid to 6°, and the Lynx-Iris to 10 mm.



Figure S3: (a) X-ray diffraction pattern of NiFe-LDH and the brucite pattern with the pdf number JCPDS: 00-014-0191¹. (b) Crystal structure of NiFe-LDH with H₂O and Anions in the interlayer to compensate the charge of the layer due to Fe^{3+} incorporated in the neutral Ni(OH)₂ layers. The Nickel and Iron are octahedrally (Oh) surrounded by oxygen atoms. Reprinted with permission from ref¹. Copyright 2018 Wiley-VCH.

Electrochemical measurement protocol – initial performance

All tests shown in Figure 2, S5 and S6 were tested by using a standardized testing sequence of three subsequent polarization curves (I-V curve) as shown in Figure S4. After the first curve, the cell potential was held at 1.7 V_{Cell} for 1.5 h, after the second for 12 h. After each potential the high frequency resistance (HFR) was taken to detect any changes in the cell resistance.



Figure S4: Electrolyser testing sequence for the initial performance test



Figure S5: Three electrolyser polarization curves 1) initial 2) after 1.5 h at 1.7 V_{Cell} 3.) after additional 12 h at 1.7 V_{Cell} with a constant cell potential for 15 min of various electrolyte feeds using an active area of 5 cm² and commercial Pt/C (48,5 wt%) with loading of 0.5 mg_{Pt} cm⁻² as cathode and crystalline Ni_{0.66}Fe_{0.34}-LDH with loading of 2.0 mg_{cat} cm⁻² as anode catalyst.. (a) 0.5 M KOH electrolyte flow at cathode and anode. (b) 0.5 M KOH electrolyte at the cathode and a N₂ stream of 100 ml min⁻¹ at the anode. (c) 0.5 M KOH electrolyte at the cathode and 0.5 M NaCl electrolyte at the cathode and 0.5 M KOH electrolyte at the cathode and 0.5 M KOH



Figure S6: High frequency resistances (HFR) of the electrolyser cell using asymmetrical electrolyte feeds at various potentials. (a) single 0.5 M KOH feed at cathode (b) asymmetrical 0.5 M KOH feed at the cathode and 0.5 M NaCl feed at the anode (c) single 0.5 M NaCl feed at the cathode (d) asymmetrical 0.5 M NaCl feed at the cathode and 0.5 M KOH feed at the anode.



Figure S7: Electrolyser stability test using 0.5 M NaCl at the cathode and a dry anode feed. The active area of 5 cm² is coated with commercial Pt/C (48,5 wt%) (0.5 mg_{Pt} cm⁻²) on the cathode and crystalline Ni_{0.66}Fe_{0.34}-LDH (2.0 mg_{cat} cm⁻²) on the anode. (a) Electrolyser stability with a constant cell potential of 1.7 V_{Cell} for two 12 h periods. (b) Sketch of the cell and electrolyte configuration (c) Subsequent test images of the electrolyte reservoirs of the anode (left) and the cathode (right). The greenish solution represents NiO_x (d) Anode side after the test. The PTL and the catalyst appear black due to oxidation and corrosion

Electrochemical measurement protocol – Selectivity test

The electrochemical tests shown in the selectivity measurements is shown in Figure S4. It consists of a potentiostatic preconditioning until reaching the breaking point, followed by galvanostatic polarization curves and a stability test. The preconditioning starts with a CV ranging from 1.0 V to 1.8 V (100 mV s⁻¹, 10 cycles) to activate the NiFe-LDH on the anode side, followed by a potentiostatic measurement with an applied cell voltage of initial 1.7 V_{Cell} for 1 h, subsequent 1.6 V_{Cell} for 0.5 h and final 1.8 V_{Cell} for 0.5 h. In between each method, a potential controlled electrochemical impedance spectroscopy (PEIS) was conducted in a frequency range of 1 MHz to 10 Hz. The preconditioning step ended with a galvanostatic test using 250 mA for 2h.

The polarization curves were recorded at applied currents of (0.05, 0.1, 0,175, 0,250, 0.375 0.5, 0.75 and 1.0) A. Each current step was held for 15 min. Before and after the polarization curve, a PEIS (before: 1 MHz to 10 Hz at 1.5 V_{Cell} , after: 1 MHz to 1 kHz under 2.5 V_{Cell}) were performed. The stability measurement was recorded at 1.0 A (200 mA cm⁻²) for 12 h. The test ended by a second polarization curve measurement.



Figure S8: Electrolyser testing sequence for selectivity testing. It consists of an extended break-in time and the final measurement of two subsequent polarization curves and a 12 h galvanostatic test at 1.0 A (200 mA cm⁻²)

Faradaic efficiency calculations

Derived from the faraday law (1) and the ideal gas equation (2), we derived a combined equation to calculate the theoretical oxygen evolution flow in V_{O_2} in [m³ s⁻¹] for a 100 % faradaic efficiency.

$$I \cdot t = n \cdot z \cdot F \tag{1}$$

$$p \cdot V = n \cdot R \cdot T \tag{2}$$

$$V_{O_2} = \frac{I \cdot R \cdot T}{z \cdot F \cdot p} \tag{3}$$

in which I represents the applied current in [A], t is the time in [s], n is the amount of substances in [mol], z = 4 represents the electrons transferred per ion, F = 96485.33 s A mol⁻¹ represents the faradaic constant, p = 103000 Pa (determined) is the atmospheric pressure, V is the gas volume in [m³], R = 8.314 kg m² s⁻² mol⁻¹K⁻¹ is the ideal gas constant, T = 299.15 K (determined) is the temperature, and V_{0_2} is the gas evolution rate of O₂ in [m³ s⁻¹].

The obtained flow and the mass flow controlled N₂ flow $V_{N_2} = 100$ ml min⁻¹ were used to obtain the theoretical gas concentrations in [%] for a 100 % faradaic efficiency using equation (4):

$$c_{gas_{theor.}}[\%] = \left(\frac{V_{O_2}}{V_{O_2} + V_{N_2}}\right) \cdot 100$$
(4)

The faradaic efficiency (FE) in [%] was calculated using the theoretical $c_{gas_{theor.}}$ and the nominal measured $c_{gas_{nominal}}$ in equation (5). The nominal gas concentration is the average value of the last 5 min of the 30 min step.

$$FE [\%] = \left(\frac{c_{gas}_{nominal}}{c_{gas}_{theor.}}\right) \cdot 100$$
(5)

Free Chlorine detection

The hypochlorite detection was performed by titration analysis with Iodide explained also in detail elsewhere.² Here, iodometry was conducted by sampling 10 mL of electrolyte at the anode outlet of the cell immediately after the galvanostatic test to an Erlenmeyer flask. 15 mL of 0.5 M KI (Sigma Aldrich > 99.0 % purity) – solution was added. Unless a color change is observed 0.02 M thiosulfate solution was added via a burette until the color changes to a faint yellow. 1 mL of starch solution (Sigma Aldrich) was added resulting in a blue solution. The thiosulfate adding was interrupted until the solution decolorized. The volume of thiosulfate consumed in this titration is recorded and correlates to concentration of hypochlorite at the anode by applying in the following equation:

$$n_{ocl}^{-} = \frac{V_{Thio} \cdot c_{Thio}}{V_{sample}} \cdot V_{total}$$
⁽⁵⁾

 n_{OCl} = Mol of Hypochlorite

 V_{Thio} = consumed volume of thiosulfate

 C_{Thio} = 0.02 M thiosulfate solution

 $V_{Sample} = 10 \text{ mL}$ sample volume

 V_{total} = 400 mL of anolyte in reservoir



Figure S9: Electrolyser O₂ efficiency test using symmetric electrolyte feed with a mixture of 0.5 M NaCl and 0.5 M KOH at cathode and anode. The active area of the electrolyser cell were 5 cm² and commercial Pt/C (48,5 wt%) with loading of 0.5 mg_{Pt} cm⁻² as cathode and Ir-black, Ir /TiO₂ and crystalline Ni_{0.66}Fe_{0.34}-LDH with loading of 2.0 mg_{cat} cm⁻² as anode catalyst was used. The gas evolution was detected by a mass spectrometer in a 100 ml min⁻¹ N₂ flow as carrier gas. (a) Electrochemical sequence for the selectivity measurement related to the MS and recorded cell potential signal with varied constant currents which were held for 15 min using solely Ir/TiO₂ (b) First and second gas concentrations and cell potentials for different catalysts at different currents



Figure S10: Selectivity test applying high current densities for high cell potentials to force OCl⁻ formation using NiFe-LDH as anode catalyst (5 cm² active area) and a symmetric electrolyte feed of mixed 0.5 M NaCl and 0.5 M KOH. The top shows the used electrochemical sequence related to the O_2 signal of the mass spectrometer and the potential of the different currents.

References

- 1. S. Dresp, F. Dionigi, S. Loos, J. Ferreira de Araujo, C. Spöri, M. Gliech, H. Dau and P. Strasser, *Advanced Energy Materials*, 2018, **8**, 1800338.
- 2. F. Dionigi, T. Reier, Z. Pawolek, M. Gliech and P. Strasser, *ChemSusChem*, 2016, **9**, 962-972.