Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Steel-Based Electrocatalysts for Efficient and Durable Oxygen Evolution in Acidic Media

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Sample preparation

Preparation of the sample series Ni42-950,

Samples Ni42 were used as starting material (preparation see experimental part of the main text)

Ni42-950. Prior to each surface modification the surface of the metal was cleaned intensively with ethanol and polished with grit 240 SiC sanding paper. Afterwards the surface was rinsed intensively with deionized water and dried under air for 50 min at room temperature. The samples were heated under air up to 950 °C using a furnace (Fuzhou Wangxiang Goldsmith Products Co., Ltd., Fujian, China) for 12 h. After cooling down to room temperature the sample was rinsed under deionized water for 30 s. In total five samples have been prepared this way (Table 1, column I).

Electrochemical Measurements

A three-electrode set-up was used for all electrochemical measurements. An apparent surface area of 2 cm^2 was defined on the working electrode (WE) by an insulating tape (Kapton tape). The Ir-RuO_2 sample (10 micrometer layer deposited on titanium) with a total geometry of 100x100x1.5 mm was purchased from Baoji Changli Special Metal Co, Baoji, China. An electrode area of 2 cm^2 was defined on the plate by Kapton tape. To avoid additional contact resistance the plate was electrically connected via a screw. A platinum wire electrode (4x5 cm geometric area) was employed as the counter electrode (CE), a reversible hydrogen reference electrode (RHE, HydroFlex, Gaskatel Gesellschaft für Gassysteme durch Katalyse und Elektrochemie mbH. D-34127 Kassel, Germany) was utilized as the reference standard, therefore all voltages are quoted against this reference electrode (RE). For all measurements the RE was placed between the WE and the CE. The measurements were performed in a 0.05 M H_2SO_4 and 0.5 M H_2SO_4 (VWR, Darmstadt, Germany) solution respectively. Measurements were performed at room temperature (295.15 K). The distance between the WE and the RE was adjusted to 1 mm and the distance between the RE and the CE was adjusted to 4-5 mm. Voltage drop compensation was with exception of the measurements shown in Figures 4b, 4c, 6b, 6d realized by 50 % compensation of the solution resistance shown in Table 1 determined upon frequency response analysis measurements. The corrected voltages were denoted as E-IR. All electrochemical data were recorded digitally using a Potentiostat Interface 1000 from Gamry Instruments (Warminster, PA 18974, USA), which was interfaced to a personal computer.

Cyclic Voltammograms (CV) were recorded in 90 mL of electrolyte in a 100 mL glass beaker under stirring (450 r/min) using a magnetic stirrer (21 mm stirring bar). The scan rate was set to 20 mV/s and the step size was 2 mV. The potential was cyclically varied between 1.2 and 1.9 V *vs.* RHE for OER measurements.

Chronopotentiometry scans were conducted at a constant current density of 10 mA/cm^2 in 90 mL of electrolyte for measuring periods < 2000 s, in 800 mL of electrolyte for measuring periods ≥ 10000 s repsectively. The scans were recorded under stirring (450 r/min) using a magnetic stirrer (25 mm stirring bar) for measuring periods < 2000 s, using a magnetic stirrer (40 mm stirring bar) for measuring periods ≥ 10000 s respectively. Before and after carrying out long term chronopotentiometry measurements the weight of the specimen have been determined by using a precise balance (Sartorius 1712, 0.01 mg accuracy).

Tafel plots

Average voltage values for the Tafel plots were derived from 200 second chronopotentiometry scans. The arrangement of RE, WE and CE (taken for recording the chronopontentiometry plots) was as mentioned above (See paragraph *Electrochemical measurements*).

Determination of Faradaic efficiency for OER (Figures 4b, c) was carried out in close accordance with the procedure described in Schäfer *et al.*, *Energy Environ. Sci.*, **2015**, *8,* 2685-2697.

These measurements have been performed with sample Ni42Li205 after 25000 s of chronopentiometry (10 mA/cm^2 current density; pH 1) had been applied this specimen.

Faradaic efficiency of OER was calculated by determining the dependence of the oxygen concentration in the electrolyte during the time of chronopotentiometry at constant current. Experimental details see figure captions of Figures 4b, c. The working compartment was completely sealed with glass stoppers before starting the chronopotentiometry measurement. The results can be taken from Figures 4b, c.

Impedance spectroscopy

Impedance spectroscopy of the samples was conducted under stirring in 0.05 M H_2SO_4 within frequency range 0.1-50469 Hz with an Autolab PGStat 20 potentiostat, controlled by *FRA* Windows software (Frequency Response Analysis for Windows version *4.9.007*). To ensure accurate results more five measurements were made for each sample at defined potential. The reported results in this paper are average ones of the five derived from each sample. The preparation of the electrolyte as well as the electrode geometry can be taken from below (Electrochemical Measurements).

XPS Spectroscopy

XPS measurements were performed using a PHI 5600ci multitechnique spectrometer equipped with a monochromatic Al Kα source with 0.3 eV full width at half-maximum. The overall resolution of the spectrometer is 1.5% of the pass energy of the analyser, 0.45 eV in the present case. The measurements were recorded with the sample at room temperature. No argon etching was applied to the samples.

X-Ray Diffraction

XRD patterns of the oxidized samples were obtained by q/2q scans measured in reflection mode by using a PANalytical X'Pert Pro MRD diffractometer equipped with an Eulerian cradle, which was operated with CuKa radiation at 40 kV and 40 mA.

Electron microscopy

The plane-view SEM images of the samples were taken using a Zeiss Auriga scanning electron microscope. Cross sectional analysis (vertical plane imaging) of samples was realized by a dual beam FIB (focused ion beam)-SEM technique. The SEM images of the cross sections were taken using a Zeiss Auriga scanning electron microscope equipped with a Cobra FIB-column and a Ga ion source using the Feature Milling software module for modeling. The accelerating voltage was adjusted to 20 kV and the SEM images were acquired using a secondary electron- or back scatter detector.

Atomic force microscopy

AFM measurements are done in contact mode on a Quesant Instrument Corp. model Q250 equipment using a tap 150 Al-G type tip. The cantilevers had nominal lengths of 200± 5μm, force constants, 45 Nm^{-1}, resonance frequencies 170 (150–190) range. The tip radius was 10 nm. The AFM images were processed by the free software package Gwydion.

Gas sorption

Gas sorption experiments (adsorption/desorption) were carried out using a Quantachrome Autosorb AS-1C. Physisorption was determined at 77 K and 100 K for N_2 (Linde Gas, purity > 99.999%) with dynamic p_0-determination via a p_0-cell at p = 760 mmHg and an Oxford Instruments cryostat model Optistat MK1 equipped with an Oxford Instruments controller model ITC 503. Analyses and interpretation of data were carried out utilizing the Quantachrome AS1Win software package, version 2.11. Prior to the determinations, the samples were activated at 100 °C and pressures of $1 \cdot 10^{-3}$ mbar for 24h and at $1.5 \cdot 10^{-6}$ mbar for 24h. All samples were treated in the outgas station until outgassing rates were below 3 microns/minute pressure increase and subsequently contacted with He (Linde Gas, purity > 99.999%)

before the analyses were carried out. An equilibration time of 10 min per analysis point was used and ten points were recorded each for adsorption and desorption.

Determination of iron, chromium, molybdenum, manganese, cobalt, nickel, tungsten, titanium, silicon and potassium in the electrolyte used for 50 ks of chronopotentiometry performed at 10 mA/cm2 with samples Ni42; Ni42-950; Ni42Li127; Ni42Li205; Ni42Li300; via ICP-OES (Table S1).

In total three specimen of each sample have been investigated to guarantee meaningful data. The results can be taken from Table S1. The solution samples were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES, iCAP™ 7400 Duo equipped with MiraMist® Teflon nebulizer, Thermo Fisher Scientific Germany BV & Co KG) according DIN EN ISO 11885:2009-09. Concentrations of selected elements were determined at wavelengths of 228.616 nm (Co), 267.716 nm (Cr), 202.030 nm (Mo), 257.610 nm (Mn), 216.556 nm (Ni), 209.860 nm (W), 209.860 nm (Ti) and 212.412 nm (Si) by using the axial view mode, and at wavelengths of 239.562 nm (Fe), 670.784 nm (Li) and 766.490 nm (K) by using the radial view mode. The calibration standards were prepared according the matrix of the analyte solution and contained 0.001, 0.01, 1.0 and 10 mg/l of the selected elements.

Table S1. Outcome of the ICP-OES analysis. Column II presents the mass loss of the steel samples while carrying out chronopotentiometry for 50 ks at 10 mA cm^{-2} in 0.05 M H_2SO_4. Column III presents the volume of the pH 7 corrected 0.1 M K_2HPO_4/KH_2PO_4. Column IV: Ion concentration measured in the electrolyte. Column V: Total amount of detected Co, Cr, Fe, Li, Mo, Mn, Ni, W, Si, Ti, K.

I	II	III	IV			V
Sample	**Total Massloss [mg]**	**V (Electrolyte) [ml]**	**Ion concentration (Electrolyte) [mg/l]**			**Σdetected ions in the electrolyte [mg]**
Ni42	37.07	132.43	0.08 (Co) 0.05 (Cr) 155.05 (Fe)	0.01 (Mo) 2.8 (Mn) 131.62 (Ni)	0 (W) 0.03 (Si)	38.35
Ni42-950	63.8	143.7	0.13 (Co) 0.18 (Cr) 230.06 (Fe)	0.29 (Mo) 7.05 (Mn) 222.02 (Ni)	0.03 (W) 0.11 (Si) 0.02 (Ti)	66.09
Ni42Li127	9.74	47.64	0.04 (Co) 0.04 (Cr) 162.55 (Fe) 0.64 (Li)	0.02 (Mo) 1.15 (Mn) 46.16 (Ni)		10.03
Ni42Li205	4.01	77.1	0.02 (Co) 0.01 (Cr) 33.19 (Fe) 1.97 (Li)	0.02 (Mo) 0.63 (Mn) 28.85 (Ni)		4.98
Ni42Li300	8.04	149.95	0.02 (Co) 0.01 (Cr) 27.85 (Fe) 0.8 (Li)	0.03 (Mo) 0.53 (Mn) 24.33 (Ni)	0 (W) 0 (Si) 0.01 (Ti) 0.26 (K)	8.07

Table S2. Cationic distribution and position of the $2p_{(3/2)}$ main lines of Fe, Ni and C of samples Ni42 and Ni42Li205 derived from the XPS measurements presented in Figure 9.

Element	Ni	Fe	C	Position of the $2p_{(3/2)}$ main lines	
				Fe	Ni
Ni42	26.6%	72.4%	0.57%	711.4 eV	856.0 eV
Ni42Li205	31.89%	68.11%	0%	712.0 eV	855.8 eV (852.4 eV)

Table S3. Weight loss during electro oxidation of Ni42 steel resulting in sample Ni42Li205. Column II: Mass of the steel samples before (in brackets) respectively after carrying out the electro activation procedure. Column III: Mass difference during electro-activation.

Sample	**Mass (g)**	**Mass difference (g)**
Ni42Li205	6.32678 (6.32675)	+0.00003
Ni42Li205	5.98456 (5.98453)	+0.00003
Ni42Li205	6.50043 (6.50038)	-0.00005

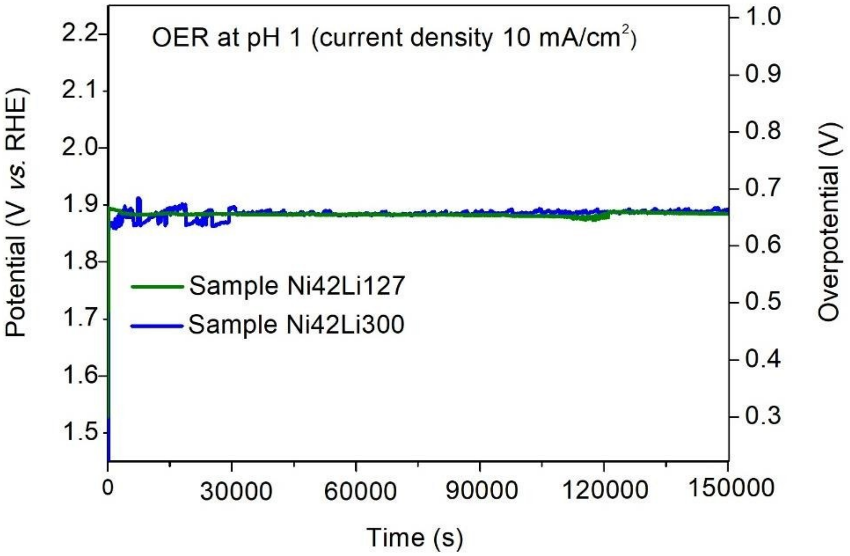


Figure S1. Chronopotentiometry plot (derived from long-term measurement) of samples Ni42Li127 and Ni42Li300 carried out in 0.05 M H2SO4.

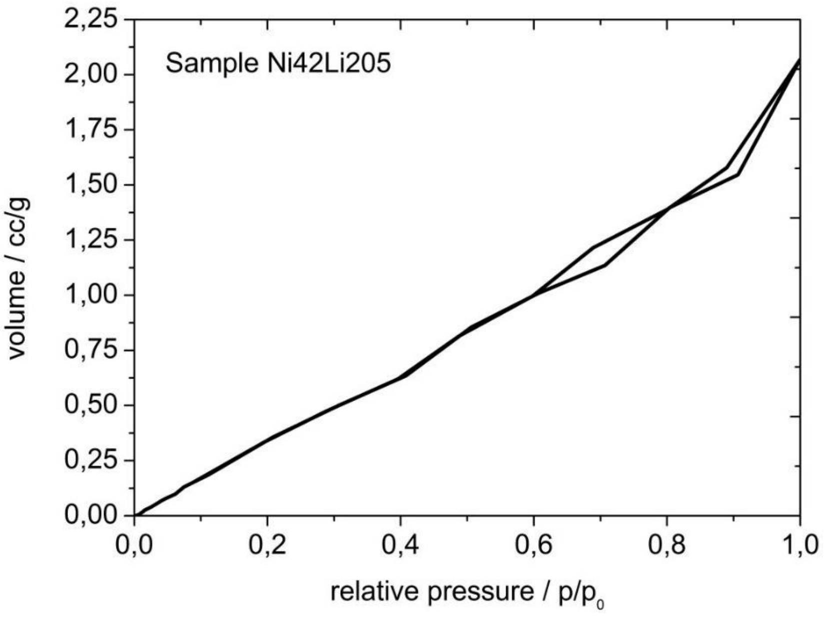
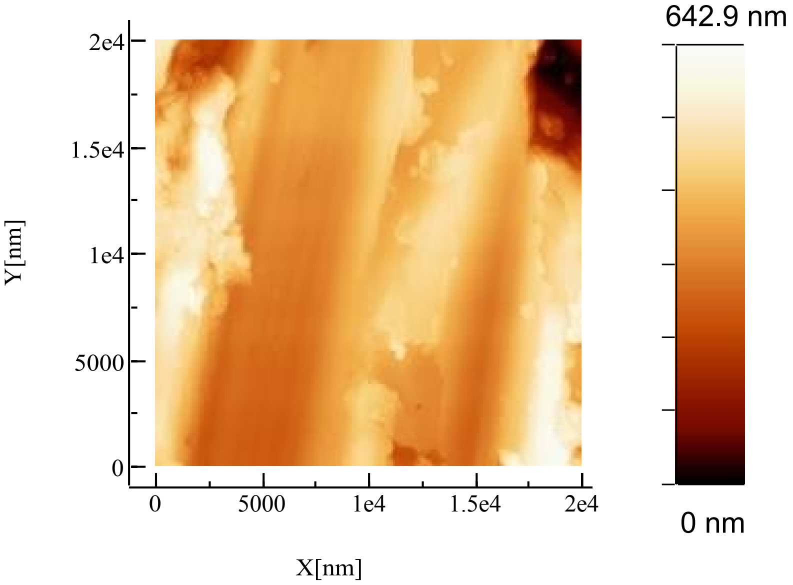
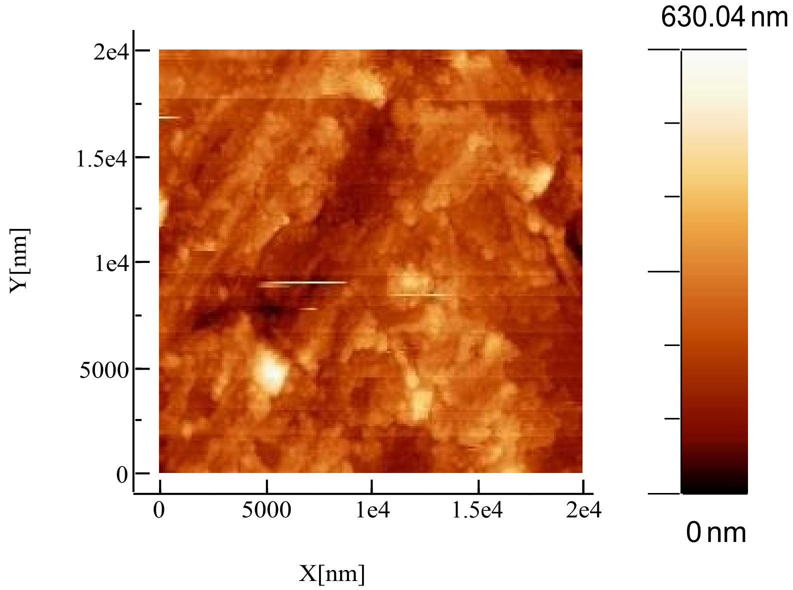


Figure S2. Results from BET measurements. Adsorption/desorption plot of sample Ni42Li205. Sample gas: N2 (77K). Activation was performed by outgassing for 24 h at 100 °C ($1*10^{-6}$ bar) and by 24 h at 100 °C ($1.5*10^{-9}$ bar); Equilibrium time: 10 min.



Sample Ni42
Projected area: 20 µm x 20 µm
Cantilever type: tap 150 Al-G
Roughness average: 75.87 nm
Average height: 390.99 nm



Sample Ni42Li205
Projected area: 20 µm x 20 µm
Cantilever type: tap 150 Al-G
Roughness average: 57.03 nm
Average height: 217.43 nm

Figure S3. Atomic force microscopic experiments carried out with samples Ni42, Ni42Li205 respectively. The measurements were performed in contact mode. The cantilevers had nominal lengths of 200± 5µm; force constant: 0.45 N/m.

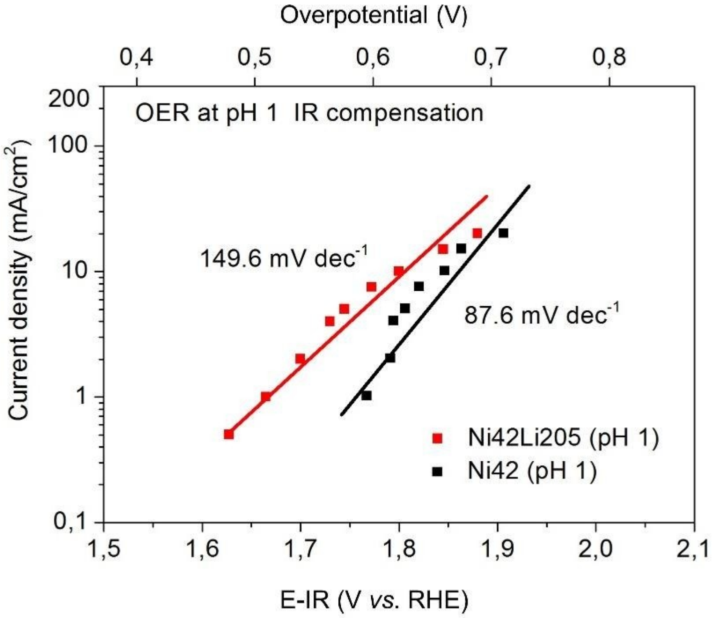


Figure S4. Tafel plots of samples Ni42Li205 and Ni42 determined at pH 1 with correction of the voltage drop. Electrode area of all samples: 2 cm^2. Stirring of the electrolyte was performed for all measurements. Tafel plots are based on averaged values derived from 200 s chronopotentiometry scans.

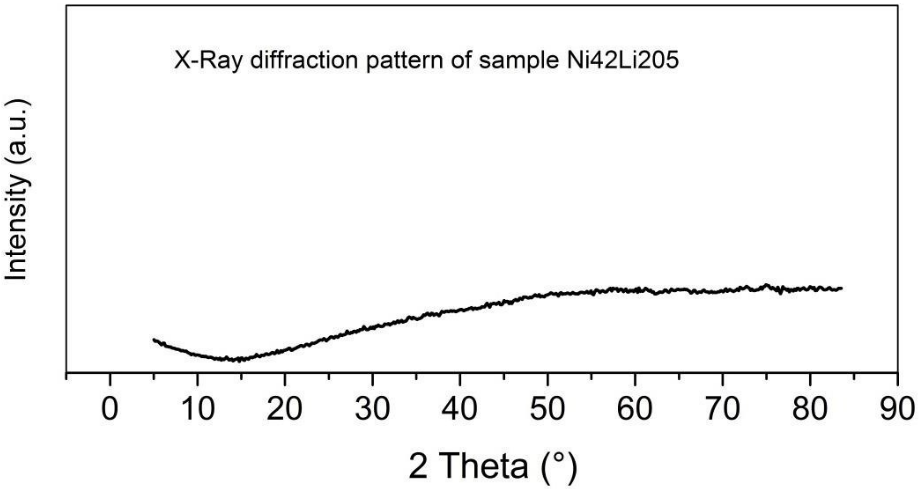


Figure S5. X-Ray Diffraction pattern acquired by a theta/2theta scan in reflection of sample Ni42Li205.