

Supporting Information

Stainless steel made to rust: A robust water-splitting Catalyst with Benchmark Characteristics

Helmut Schäfer*¹, Shamaila Sadaf¹, Lorenz Walder¹, Karsten Kuepper², Stephan Dinklage³, Joachim Wollschläger², Lilli Schneider², Martin Steinhart¹, Jörg Hardege⁴, and Diemo Daum³

¹*Institute of Chemistry of New Materials and Center of Physics and Chemistry of New Materials, Universität Osnabrück, Barbarastrasse 7, 49076 Osnabrück, Germany*

²*Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49076 Osnabrück, Germany*

³*Fakultät Agrarwissenschaften und Landschaftsarchitektur, Labor für Pflanzenernährung und Chemie, Hochschule Osnabrück, Am Krümpel 31, 49090 Osnabrück, Germany*

⁴*School of Biological, Biomedical and Environmental Sciences, University of Hull, Cottingham Road, Hull, HU6 7RX, United Kingdom*

* Corresponding author: helmut.schaefer@uos.de (H. Schäfer)

Determination of Faradaic efficiency (Figure 1c, S3) Faradaic efficiency of OER was calculated by determining the dependence of the oxygen concentration in the electrolyte of the time during chronopotentiometry at constant current in alkaline solution under stirring (300 r/min) using a magnetic stirrer (40 mm stirring bar). The oxygen concentration in the electrolyte was measured with an optical dissolved oxygen (OD) sensor using the so-called fluorescence quenching method (Multi 3420 IDS from WTW, Weilheim, Germany). A four necked 2300 mL glass vessel equipped with WE, RE, CE and OD sensor was used for carrying out the experiment (Figure S3). The Faradaic efficiency of sample Elox300 was determined at current densities of 10 mA/cm² and at 1 mA/cm² in 0.1 M KOH. The electrode geometry was as described in the experimental section page 26-27 main text. The distance between RE and WE was adjusted to 1 mm. Before starting the measurement the electrolyte was filled in the vessel and continuously purged with Argon for 3 hours at a constant flow rate of 0.3 cm³/s till the dissolved oxygen was as low as 0.09 mg/l, 0.22 mg/l respectively. The working compartment was completely sealed with glass stoppers before starting the chronopotentiometry. The values of dissolved oxygen were recorded digitally using the device (Multi 3420 IDS from WTW) which was interfaced to a personal computer. All electrochemical data were recorded digitally using a Potentiostat PGStat 20 from Autolab

(Utrecht, Netherlands) which was interfaced to a personal computer. The results can be taken from Table S2, respectively from Figure 1c (measurement at 10 mA/cm²). The red line in Figure 1c corresponds to 100% Faradaic efficiency with a line equation: $y=0.00054072x + 0.09$ with y =Dissolved oxygen (mg/l); x =time (s).

Determination of Ni, Fe and Cr ions in the electrolyte after long term chronopotentiometry (50000 s at 10 mA/cm² in 0.1 M KOH)

Concentrations of Ni ions, Cr ions and Fe ions in the electrolytes used for long time chronopotentiometry as well as in the rinsing water used to clean the samples after chlorination

were determined as follows. One hundred milliliters of the electrolyte used for the long time chronopotentiometry (or rinsing water) was added to a 250 mL glass beaker. The solution was neutralized under stirring by adding around 105 mL of 0.05 M H₂SO₄ (Merck TitriPur, Merck, Darmstadt, Germany) until pH 4 was reached. The solution was concentrated by heating up to 95 °C until the total volume reached 40 mL. After cooling down 1 g of K₂S₂O₈ (99% purity, VWR, Darmstadt, Germany) was added, and the mixture was again heated to 95 °C for additional 3 min. There was no yellow coloration indicating that Cr₂O₇²⁻ ion was obtained. Detection limit was <2 ppm. Twenty mL of the electrolyte used for the long time chronopotentiometry (or rinsing water) was added to a 100 mL glass beaker (beaker Nr. 1). The solution was neutralized under stirring by adding around 20 mL of 0.1 M HCl (99% purity, VWR, Darmstadt, Germany) until pH 6 was reached. The amount of 10 mL was taken from the solution and filled in a second 100 mL glass beaker (beaker Nr. 2). The solution of beaker Nr. 2 was concentrated upon heating to 95 °C for 30 min until the volume reached 3 mL, and after cooling, 60 mg of potassium ferrocyanide K₄[Fe(CN)₆] (99% purity, Carl Roth, Karlsruhe, Germany) was added. The mixture formed was shaken for 1 min. Neither a precipitation nor a coloration took place showing that neither Fe²⁺ nor Fe³⁺ was present. Detection limit <1 ppm. After 20 min 1 mL of saturated H₂O₂ (30 wt %, VWR, Darmstadt, Germany) was added to the remaining solution (beaker Nr.1), and the solution was concentrated by heating to 95 °C for 30 min until the total volume reached 3 mL. After cooling to room temperature, 1 mL of saturated ammonia (25 wt %, VWR, Darmstadt, Germany) was added (pH 10). No precipitation was formed proving that no iron ions were present. One milliliter of 0.1 M ethanolic disodium bis (dimethylglyoximate) (99% purity, Carl Roth, Karlsruhe, Germany) was added. No red precipitation was formed proving that no nickel ions were present. Detection limit was <1 ppm.

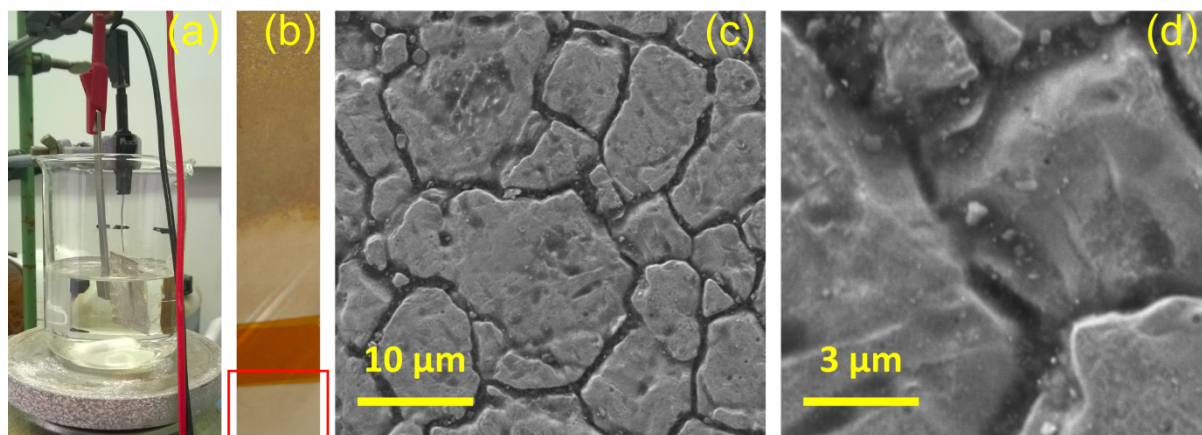


Figure S1. (a) Image of the anodization step performed in 7.2 M NaOH at current density of 1770 mA/cm² (5.2 V, 5.3 A) for 300, respectively 480 min; Area of the electrode immersed into the electrolyte: 3 cm²; Distance between WE and CE: 8 mm. (b) oxidized steel on which an apparent surface area of ~ 1.2-1.7 cm² was defined by an insulating Kapton tape (outlined in red) for conducting electrochemical characterization. SEM images of the electro-oxidized sample recorded at 5000 magnification (c) and at 20000 (d) magnification; accelerating voltage: 5 kV; detector: secondary electron detector.

Sample	Mass (g)
Elox300	11.34143 (11.34147)
Elox480	10.80818 (10.80814)

Table S1. Mass of the samples Elox300 and Elox480 prior to and after (in brackets) chronopotentiometry for 50000 s in 0.1 M in KOH at 10 mA/cm² current density.

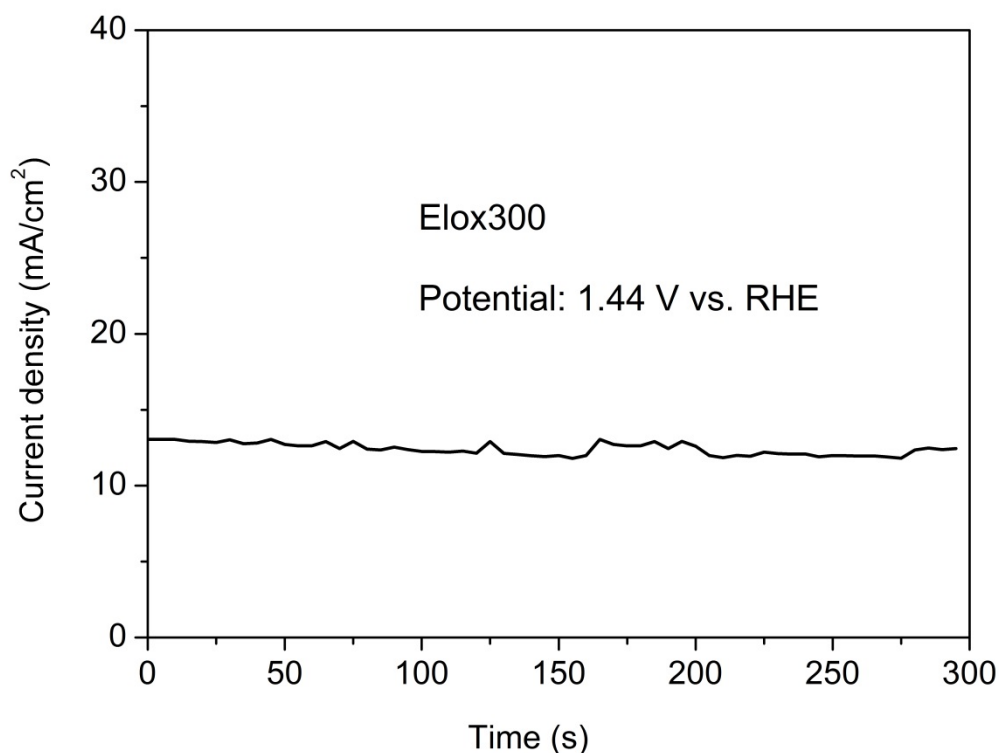


Figure S2. Amperometry plot of sample Elox300 in 1 M KOH. Average current density: 12 mA/cm². Applied potential: 1.44 V vs. RHE. Distance between WE and RE: 1mm. No IR compensation.

Sample	Current density	Amount of 0.1 M KOH	Dissolved oxygen at the beginning (t=0 s)	Runtime	Dissolved oxygen after runtime	Faradaic efficiency after runtime
Elox300	1 mA/cm ²	1.71	0.22 mg/l	60000 s	4.41 mg/l	95.7%
Elox300	10 mA/cm ²	2.31	0.09 mg/l	4000 s	1.33 mg/l	75.5%

Table S2. Determination of the Faradaic efficiency in 0.1 M KOH. The electrode area was 1.5 cm². The distance between WE and RE was adjusted to 1 mm, the distance between CE and RE was ~ 4 mm. The overpotential was 215 mV at 1 mA/cm², 260 mV at 10 mA/cm² respectively.



Figure S3: The set-up used for determining the Faradaic efficiency. Volume of the vessel: 2.3l. Dissolved oxygen was determined with an optical sensor using the fluorescence quenching method (Multi 3420 IDS from WTW, Weilheim, Germany). The Faradaic efficiency of sample Elox300 was determined at current densities of 10 mA/cm² and at 1 mA/cm² at 260, respectively 215 mV overpotential in 0.1 M KOH after 4000 respectively after 60000 s runtime. The results can be taken from Table S2, respectively from Figure 1c (measurement at 10 mA/cm²).

I	II	III	IV	V	VI	VII	IIX
Procedure	Mass loss [mg]	V (NaOH) [ml]	Ion concentration (Electrolyte) [mg/l]	Amount of ions in Electrolyte [mg]	Precipitation on CE [mg]	Σ detected ions [mg]	Σ detected material [mg]
Elox fix 300 (1)	6.15	94.536	5.5 (Fe)	0.52 (Fe)	1.595 (Fe)	2.114 (Fe)	3.8416
			14 (Cr)	1.32 (Cr)	0.026 (Cr)	1.349 (Cr)	
			2.6 (Ni)	0.246 (Ni)	0.132 (Ni)	0.377 (Ni)	
Elox fix 480 (1)	14.346	74.0	13 (Fe)	0.962 (Fe)	7.44 (Fe)	8.402 (Fe)	13.0589
			43 (Cr)	3.182 (Cr)	0.059 (Cr)	3.242 (Cr)	
			12 (Ni)	0.888 (Ni)	0.527 (Ni)	1.415 (Ni)	
Elox fix 480 (2)	17.15	280.0	3.6 (Fe)	1.008 (Fe)	11.57 (Fe)	12.58 (Fe)	14.883
			7.7 (Cr)	2.156 (Cr)	0.019 (Cr)	2.175 (Cr)	
			0.21 (Ni)	0.059 (Ni)	0.069 (Ni)	0.128 (Ni)	
Elox fix 300 (2)	7.7	67.1	21.6 (Fe)	1.45 (Fe)	3.96 (Fe)	5.41 (Fe)	7.64
			28.9 (Cr)	1.94 (Cr)	0.01 (Cr)	1.95 (Cr)	
			0.32 (Ni)	0.021 (Ni)	0.26 (Ni)	0.28 (Ni)	
Elox fix 300 (3)	7.3	81	9.8 (Fe)	0.79 (Fe)	3.85 (Fe)	4.64 (Fe)	6.55
			20.8 (Cr)	1.69 (Cr)	0.018 (Cr)	1.71 (Cr)	
			0.1 (Ni)	0.008 (Ni)	0.19 (Ni)	0.198 (Ni)	

Table S3. Outcome of the AAS analysis. Column II presents the mass loss of the steel sample while carrying out the electro activation procedure. Column III presents the volume of the 7.2 M NaOH electrolyte determined after the electro activation procedure. Column IV: Ion concentration measured in the 7.2 M NaOH after electro activation procedure. Column V: Amount of Fe, Cr and Ni in the 7.2 M NaOH calculated on the basis of the AAS results (column IV). Column VI: Composition of the material deposited on the CE. Column VII: Total amount of detected Fe, Cr, Ni. Column IIX: Total amount of detected material.

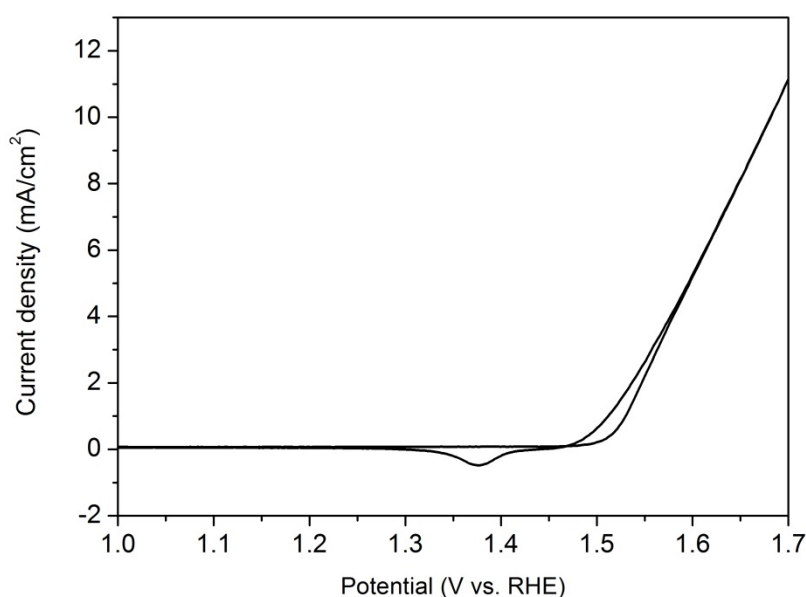


Figure S4. Cyclic voltammogram (voltage against current density (mA/cm^2) scan) of sample EloxCycl measured in 0.1 M KOH. Potential is determined versus reversible hydrogen electrode. Scan rate: 20 mV/s; Step size: 2 mV. No IR compensation was performed.

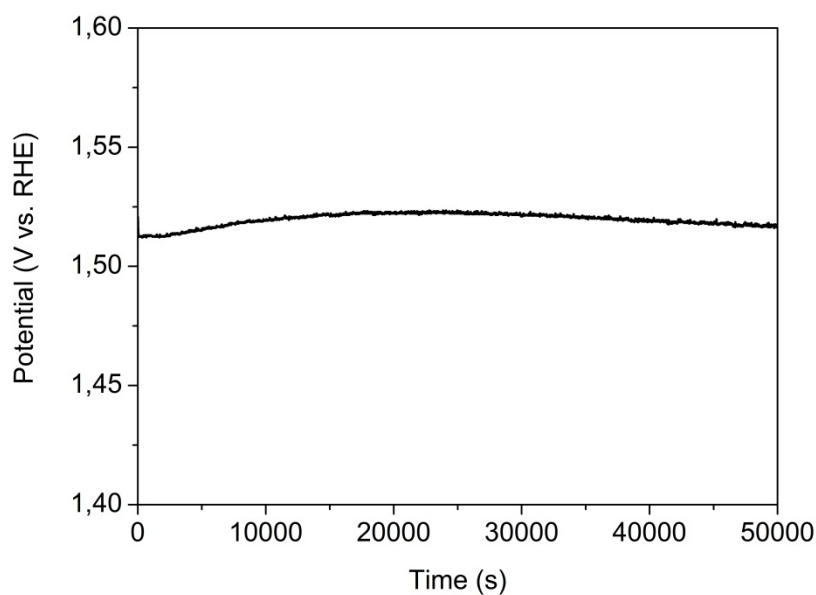


Figure S5. Chronopotentiometry (Potential (V versus reversible hydrogen electrode) against time (s) scan) of sample Elox480 measured in 0.1 M KOH at 10 mA/cm². Average overpotential: 292 mV at 10 mA/cm². Startpotential: 1.513 V vs. RHE (t=90 s); Endpotential: 1.517 V vs. RHE (t=50000 s).

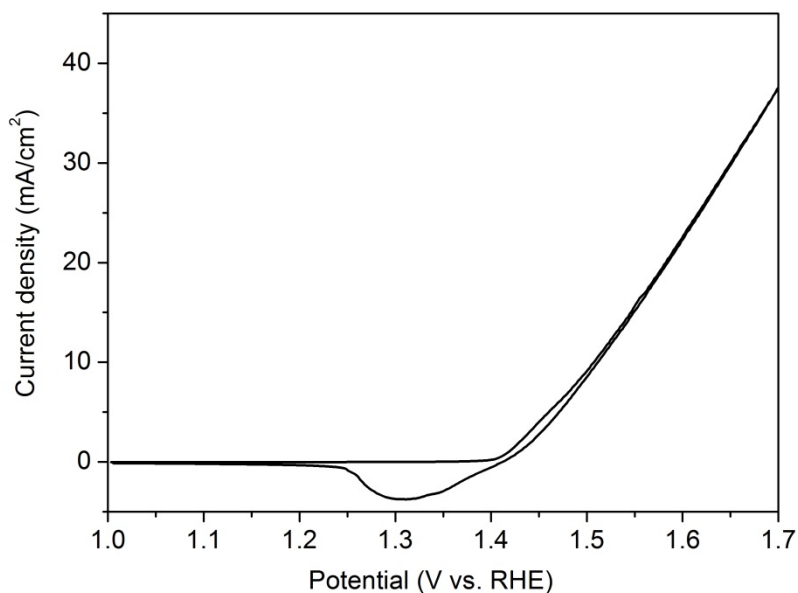


Figure S6. Cyclic voltammogram (voltage against current density (mA/cm²) scan) of sample Elox480 measured in 0.1 M KOH. Potential is determined versus reversible hydrogen electrode. Scan rate: 20 mV/s; Step size: 2 mV. No IR compensation was performed.

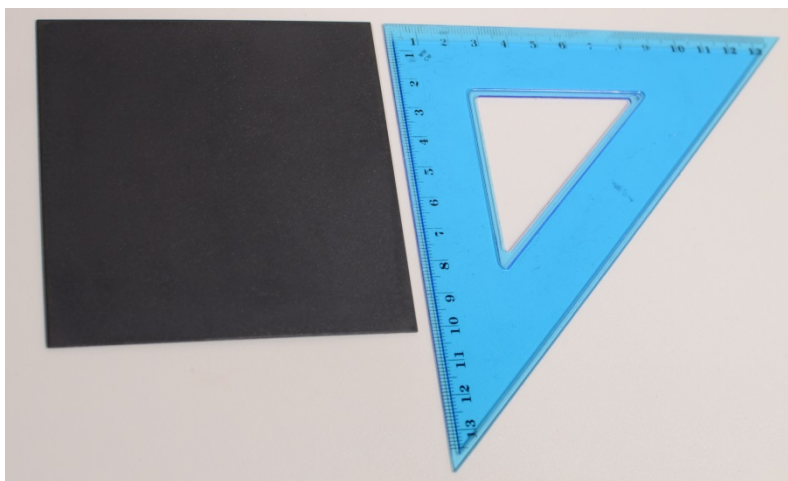


Figure S7: Image of the IrO₂-RuO₂ electrode (IrO₂-RuO₂ coated on titanium) purchased from Baoji Changli Special Metal, Baoji, China. Total geometry 100x100x1.5 mm.

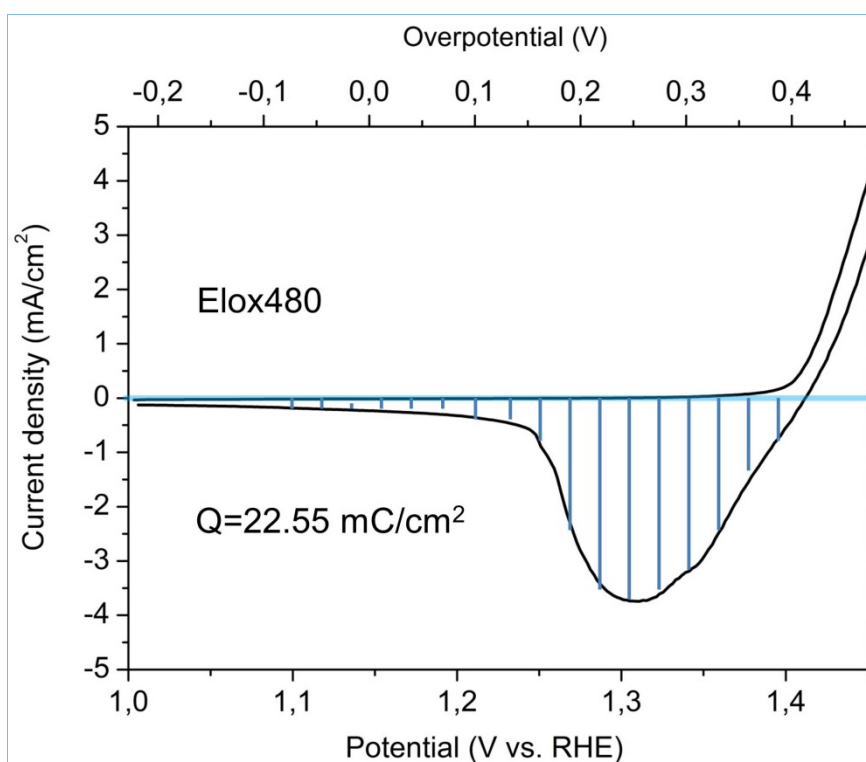


Figure S8. Cyclic voltammogram (Current Density vs. overpotential scan) of sample Elox480 measured in 0.1 M KOH. Determination of the charge capacity Q by integrating the cathodic voltammetric sweep between 1.7 V vs. RHE and 1 V vs. RHE. Q amounted to 22.55 mC cm⁻². Scan rate: 20 mV/s; Step size: 2 mV. No IR compensation was performed.

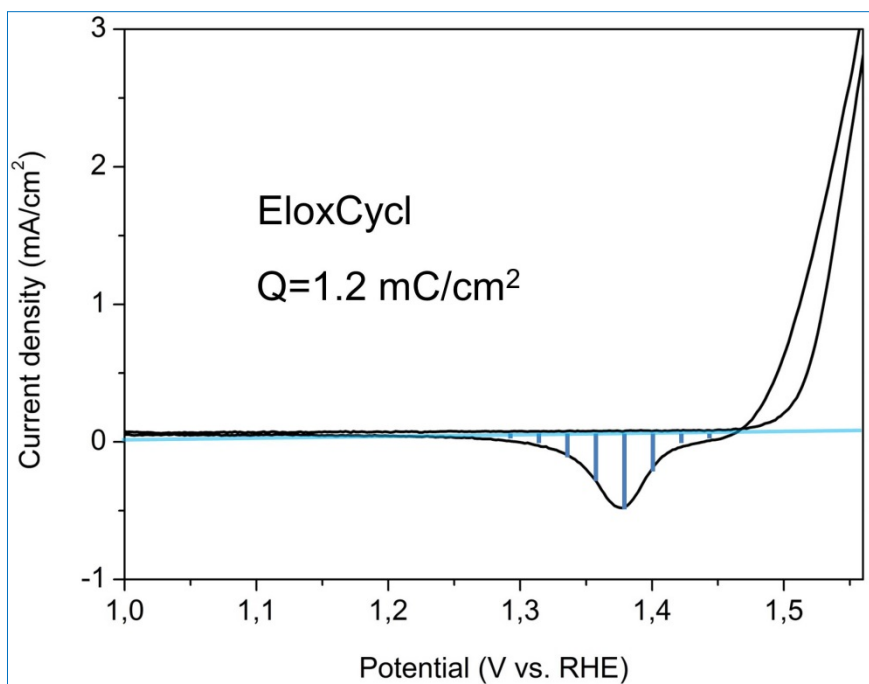


Figure S9. Cyclic voltammogram (Current Density vs. overpotential scan) of sample EloxCycl measured in 0.1 M KOH. Determination of the charge capacity Q by integrating the cathodic voltammetric sweep between 1.7 V vs. RHE and 1 V vs. RHE. Q amounted to 54.80 mC cm^{-2} . Scan rate: 20 mV/s; Step size: 2 mV. No IR compensation was performed.

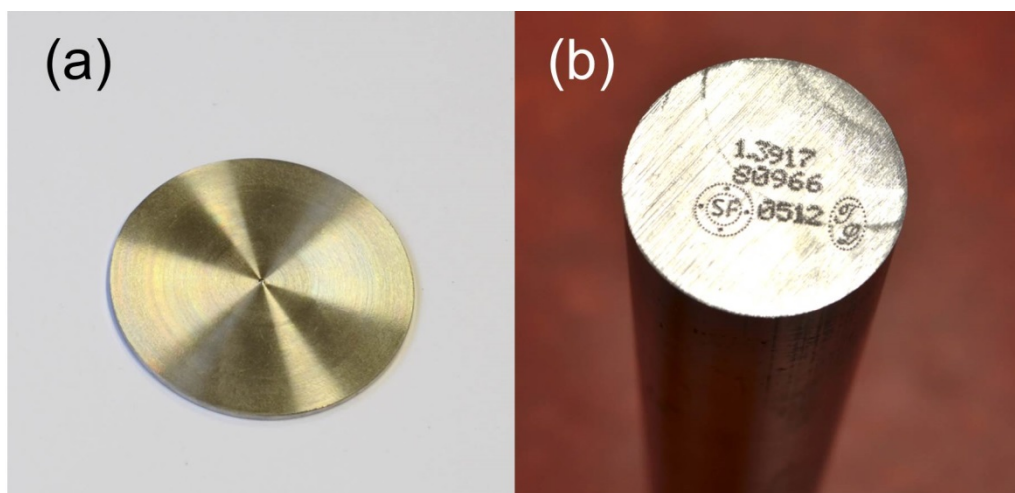


Figure S10: (a) Image of the Ni42 sample, 50 mm in diameter, 1.5 mm in thickness. (b) Image of the certification stamp, stamped on the AISI Ni42 (Faulenbach Schmiedetechnik, Germany; German classification: Werkstoffnummer 1.3917) rod from which the samples were made off.

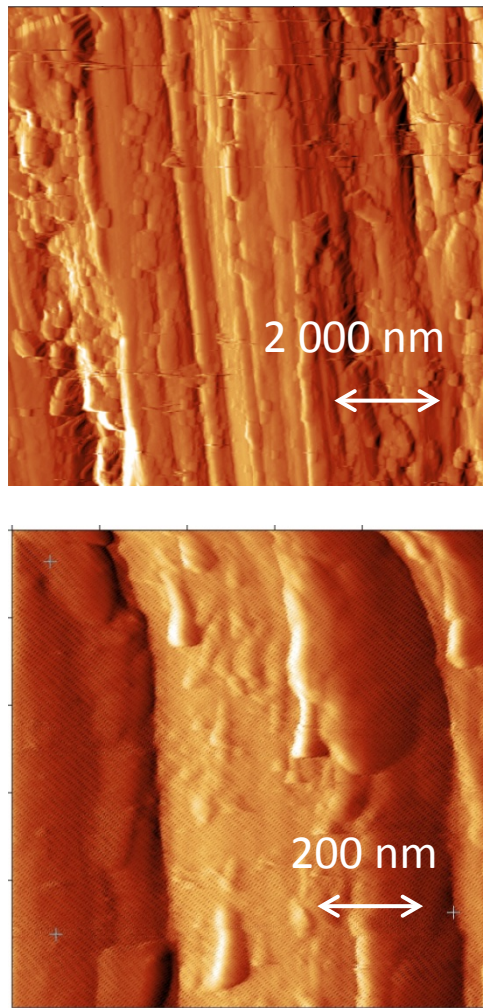


Figure S11. AFM images of the untreated AISI 304 steel sample. : Prior to the AFM experiment the surface of the metal was cleaned intensively with ethanol and polished with grit 600 SiC sanding paper. AFM microscopy measurements were performed in contact mode. The NP-S cantilevers had nominal lengths of $200 \pm 5 \mu\text{m}$; force constant: 0.58 N/m .

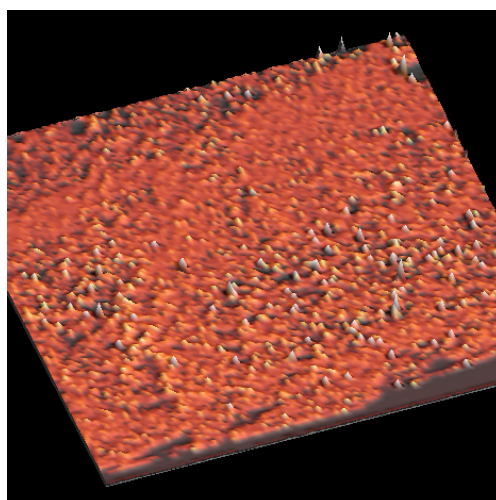
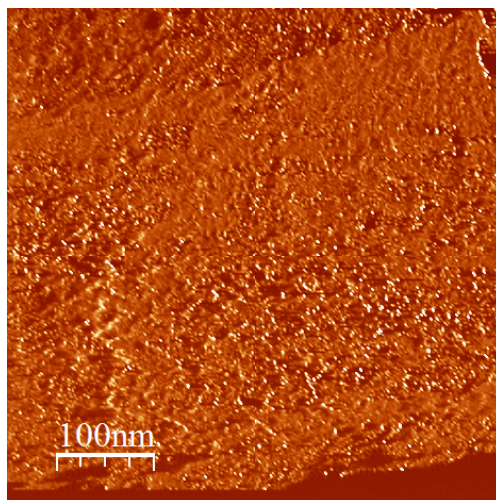


Figure S12. STM images of the untreated AISI 304 steel sample. : Prior to the STM experiment the surface of the metal was cleaned intensively with ethanol and polished with grit 600 SiC sanding paper. Bias voltage: 0.050 V; Tunneling current: 1 nA. The STM tips were cut from 0.25 mm Pt/Ir wire.

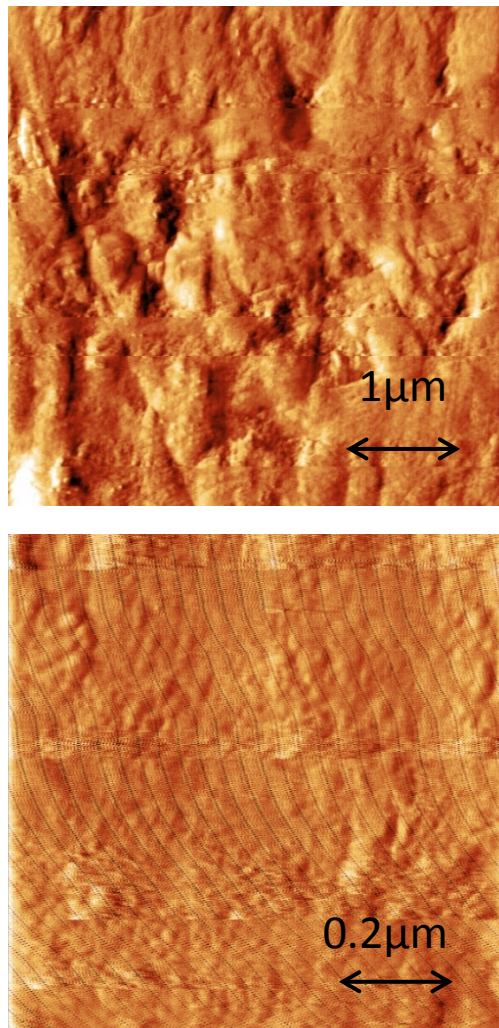


Figure S13. AFM images of sample Elox300. AFM microscopy measurements were performed in contact mode. The NP-S cantilevers had nominal lengths of $200 \pm 5 \mu\text{m}$; force constant: 0.58 N/m .

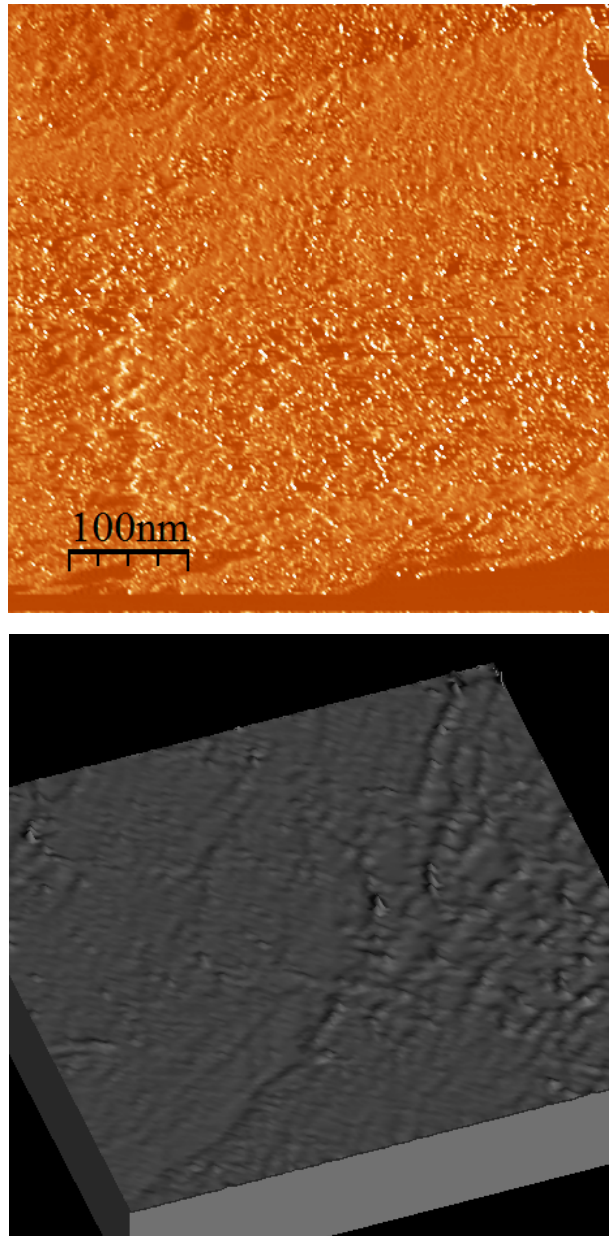


Figure S14. STM images of sample Elox300. Bias voltage: 0.050 V; Tunneling current: 1 nA. The STM tips were cut from 0.25 mm Pt/Ir wire.

