Supporting Information

From Bad Electrochemical Practices to an Environmental and Waste Reducing Approach for the Generation of Active Hydrogen Evolving Electrodes

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Syntheses of samples

Synthesis of sample Ni42Pt

Samples with a total geometry of 70 x 10 x 1.5 mm were constructed from 1.5 mm thick Ni42 steel purchased from WST Werkzeug Stahl Center GmbH & Co. KG, D-90587 Veitsbronn-Siegelsdorf, Germany. Pre-treatment: 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.

A three-electrode set-up consisting of a Ni42 steel working electrode (WE), a platinum counter electrode (CE) and a reversible hydrogen electrode (RHE, HydroFlex, Gaskatel Gesellschaft für Gassysteme durch Katalyse und ElektrochemiembH. D-34127 Kassel, Germany) as reference electrode (RE) was used to carry out the first and second activation procedure. An apparent surface area of 2 cm² was defined by an insulating tape (Kapton tape) on the Ni42 steel. A common glass beaker (150
mL) was used as reaction vessel in which the electrolyte consisting of 100 mL of 0.05 M sulfuric acid (Carl Roth GmbH, Karlsruhe, Deutschland) was filled. Constant stirring was applied through a stirring bar (20 X 6 mm); stirring speed (200 r/min). The reference electrode was placed in between the CE and the WE. The distance between RHE and WE was adjusted to 4 mm; the distance between CE and RE was adjusted to 3 mm. A view contact between CE and WE was realized in a way that the RHE was placed around 5 mm higher within the reaction vessel. CV scans according to Figure 2a have been carried out upon cycling of the potential between 0 and -400 mV vs. RHE; the scan speed was set to 5 mV/s. After 100 scans this experiment was stopped. Subsequently afterwards (while completely maintaining the experimental setup) a chronopotentiometry based activation (second activation procedure; See Figure 2b) was performed. The current density was set to 10 mA/cm². After 50000 s the experiment was completed and sample Ni42Pt was taken out of the electrolyte and subsequently rinsed twice with distilled water and dried under air.

Synthesis of sample Ni42SoPt

Samples with a total geometry of 70 x 10 x 1.5 mm were constructed from 1.5 mm thick Ni42 steel purchased from WST Werkzeug Stahl Center GmbH & Co. KG, D-90587 Veitsbronn-Siegelsdorf, Germany. Pre-treatment: 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.

A three-electrode set-up consisting of a Ni42 steel working electrode (WE), a platinum counter electrode (CE) and a reversible hydrogen electrode (RHE, HydroFlex, Gaskatel Gesellschaft für Gassysteme durch Katalyse und ElektrochemiembH. D-34127 Kassel, Germany) as reference electrode was used to carry out the first and second activation procedure. An apparent surface area of 2 cm² was defined by an insulating tape (Kapton tape) on the Ni42 steel. A common glass beaker (150 mL) was
used as reaction vessel in which the electrolyte consisting of 100 mL of 0.05 M sulfuric acid (Carl Roth GmbH, Karlsruhe, Deutschland) was filled. The reference electrode was placed in between the CE and the WE. The distance between RHE and WE was adjusted to 4 mm; the distance between CE and RHE was adjusted to 3 mm. A view contact between CE and WE was realized in a way that the RHE was placed around 5 mm higher within the reaction vessel. The electrolysis setup was placed in an ultrasonic bath (Elmasonic P 30 H; Elma Schmidbauer GmbH, 78224 Singen, Germany). Ultrasonication (80 kHz; 48 W) was applied whilst carrying out CV scans according to Figure 4a. Cycling of the potential between 0 and -400 mV vs. RHE with a scan speed of 5 mV/s was performed. After 65 scans this experiment was interrupted. The platinum electrode was taken out of the electrolyte, cleaned for 60 min in water in an ultrasonic bath (USC300TH, VWR, 64295 Darmstadt, Germany) at 40 kHz; 80 W. The platinum electrode was moved back into the electrochemistry setup and additional 35 CV scans (Ultrasonic assisted activation Step II) were performed. Now, the power of the ultrasonic bath was set to 72 W. As a result, the maximum current density reaches a value of around 45-46 mA/cm². After in total 100 CV scans the ultrasonic assisted activation was completed upon carrying out chronopotentiometry whilst ultrasonication (See Figure S1) while completely maintaining the experimental setup (also the electrolyte was not changed). The current density was adjusted to 10 mA/cm² and the power of the ultrasonic device was put back to 72 W. After 2500 s of chronopotentiometry sample Ni42SoPt was taken out of the electrolyte rinsed with distilled water and dried under air.

**Electrochemical characterization**

A three-electrode set-up was used for all electrochemical measurements. The working electrode (WE) with a total geometry of 70 x 10 x 1.5 mm was constructed from 1.5 mm thick Ni42 steel, on which an apparent surface area of 2 cm² was defined by an insulating tape (Kapton tape). For some measurements a Pt (Pt wire; diameter: 0.5 mm, 6.5 mm length) or a IrO₂–RuO₂ WE have been used. The IrO₂–RuO₂ sample (10 micrometer layer deposited on titanium) with a total geometry of 100 x 100
x 1.5 mm was purchased from Baoji Changli Special Metal Co, Baoji, China. An electrode area of 2 cm² was defined on the plate by Kapton tape. To avoid additional contact resistance the plate was electrically connected using a screw. A platinum wire electrode (4.5 cm geometric area) or a graphite electrode (Hangzhou Guhongni Electronic Co Ltd, Hangzhou, China; rod, 10 mm in diameter, 100 mm in length) was employed as the CE, a reversible hydrogen reference electrode (RHE, HydroFlex, Gaskatel Gesellschaft für Gassysteme durch Katalyse und ElektrochemiembH. D-34127 Kassel, Germany) was utilized as the reference standard, and therefore all voltages were quoted against this reference electrode (RE).

For all measurements the RE was placed between the working electrode and the CE. Sulfuric acid (Carl Roth GmbH, Karlsruhe, Deutschland) in concentrations of 0.05 M and 0.5 M was used as electrolyte (Volume: 80 mL). The distance between the WE and the RE was adjusted to 4 mm and the distance between the RE and the CE was adjusted to 3 mm. For the CV measurements the scan rate was adjusted to 5 mVs⁻¹. Chronopotentiometry measurements were carried out at j=10 mA/cm². 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.

Electrochemical measurements were carried out without any correction of the ohmic voltage drop with one exception: In order to accurately investigate the Tafel behavior, we corrected Ohmic losses manually by subtracting the Ohmic voltage drop from the measured potentials in Figure S2, according to Ohm’s Law and series resistance (Rs). The resistance Rs was determined upon Frequency response analysis measurements carried out in the frequency range of 0.1-50 000 Hz. IR corrected potentials are denoted as E-IR.

**Tafel plots.** Average voltage values for the Tafel plots were derived from 200 second chronopotentiometry measurements at current densities of (-) 8, 10, 15, 20, 30, 40, 60, 80 and 100 mA/cm².
Determination of the double layer capacitance. Voltammetric curves have been derived from the samples in the mere double layer region at various scan rates (Figures S3, S4, S5). No stirring was applied whilst recording the CV scans. Then a plot of the current density in the middle of the potential vs. scan rate is constructed (Figures S6, S7, S8).

**Electrochemically active surface area (ECSA).** Voltammetric curves were derived from the samples in the mere double layer region at various scan rates (Figures S3, S4, S5). Then a plot of the current density in the middle of the potential vs. scan rate was constructed (Figures S6, S7, S8). Under these conditions, that the double layer charging was the only process occurring, this plot was found to be a straight line in the given potential range, the slope of which gave the value of the double layer capacity.

**Determination of Faradaic efficiency for HER** was carried out in close accordance with the procedure described in Popczun *et al.* *J. Am. Chem. Soc.*, 2013, 135, 9267: To quantify the charge to hydrogen formation ratio of the HER, the cathode- and the anode half-cell reactions were separated from each other upon a Nafion® membrane. The distance between RE and WE was adjusted to 1 mm. The distance between RE and CE was ~ 10 mm due to the placement of the membrane in between RE and CE. Hydrogen gas was purged through the cathode half-cell for 3 hours. An inverted solution -containing graduated cylinder was positioned around the working electrode, and the volume of H₂ produced whilst chronopotentiometry at j=10 mA cm⁻² was determined in function of time. The gas amount was compared to the volume calculated from the current passed and the ideal gas law at 293.15 K. The electrode area was 2 cm². Total duration of the measurement: 4000 s. Volume of the electrolysis cell:250 mL. Current: 20 mA. Temperature: 296.15 K. The red line in Figure 5c corresponds to 100% Faradaic efficiency (FE) with a line equation: \( y=0.0025 \times \) with \( y=\)amount of hydrogen (cm³); \( x=\)time (s). The FE determined after 4000 s amounted to 99.9% based on 10.07 mL of produced H₂ (10.08 mL=100%).

**Physical characterization**

**AFM experiments**
AFM measurements were performed in semi-contact mode on a NT-MDT model NTEGRA Probe NanoLaboratory. The V-shaped cantilevers had nominal lengths of 140 mm, force constants of 25–95 N m\(^{-1}\), and a resonance frequency of 242 kHz (within the range of 200–400 kHz). The tip radius was 10 nm. The AFM images were processed by using the software Nova Ppx.

**XPS spectroscopy**

XPS measurements were performed using a PHI 5600ci multitechnique spectrometer equipped with a monochromatic Al K\(\alpha\) 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. The spectrum was fitted with Doniach-Sunjic functions (Figure 6(f)).

**Electron microscopy**

The plane-view SEM images of sample Ni42SoPt were taken using a Zeiss Auriga scanning electron microscope. Cross sectional analysis (vertical plane imaging) of sample Ni42SoPt 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 7 kV for the cross sectional analysis and 3 kV for the plane view analysis. The SEM images were acquired using a secondary electron detector.

**ICP-MS**

The amount of Fe, Ni and Pt dissolved in the electrolyte was determined using a PerkinElmer NexION 2000 inductively coupled plasma mass spectrometer (ICP-MS, PerkinElmer, Inc., Waltham, Massachusetts, USA). Fe and Ni standards (Carl Roth GmbH & Co. Kg, Germany) were prepared at 5, 10, 20 and 50 \(\mu\)g L\(^{-1}\) diluted with a solution of 2\% nitric acid (Merck, Suprapur\textsuperscript{®} HNO\(_3\), 65\%) in ultrapure water (MilliQ, 18.2 M\(\Omega\) cm, TOC < 3 ppb). Pt standard solutions were prepared at 2, 5 and 10 \(\mu\)g L\(^{-1}\) diluted with a 2\% HNO\(_3\) solution. The R-squared values of the calibration curves were over 0.9999 and the background equivalent concentrations (BEC) for \(^{56}\)Fe, \(^{60}\)Ni and \(^{195}\)Pt were 0.5, 0.02 and 0.003 \(\mu\)g L\(^{-1}\).
Collected electrolyte was diluted with a 2% HNO₃ solution to bring the analyte concentrations into the specified calibration ranges. Sample and calibration solutions were spiked with (i) 25 µg L⁻¹ of ⁴⁵Sc internal standard solution for detection of ⁵⁶Fe and ⁶⁰Ni and (ii) 5 µg L⁻¹ ¹¹⁵In internal standard solution for detection of ¹⁹⁵Pt. To attenuate polyatomic interferences (e.g., ⁴⁰Ar₁₆O and ⁵⁶Fe), the detection of ⁵⁶Fe and ⁶⁰Ni was performed in Helium collision mode with kinetic energy discrimination (KED).

| Analyte | Concentration (mg L⁻¹) |
|---------|------------------------|
| Fe      | 12.2                   |
| Ni      | 9.0                    |
| Pt      | 0.2                    |

Regarding the calculation of the amount of Fe, Ni, Pt in the electrolyte (Table 2): The electrolyte was (quantitatively) transferred out of the electrolysis cell to the vessel (used for storage) by rinsing out with the help of distilled water (31 mL). The total volume (of electrolyte + water) amounted to 131 mL and the total amount of Pt in the electrolyte is 26 µg, 1.6 mG [Fe], 1.18 mg [Ni].
Figure S1. Ultrasonic assisted activation step III realized upon chronopotentiometry at a current density of 10 mA/cm$^2$ in 0.05 M sulfuric acid using a platinum counter electrode; Electrode area: 2 cm$^2$.

Figure S2. Tafel plots of samples Ni42, Ni42Pt, Ni42SoPt and Pt based on 200 s chronopotentiometry measurements at current densities of -8, -10, -15, -20, -30, -40, -60, -80, -100 mA/cm$^2$ carried out in 0.5 M sulfuric acid; electrode area: 2 cm$^2$. 
Figure S3. Cyclovoltammetry experiments carried out with sample Ni42 in 0.05 M sulfuric acid at scan rates ranging from 20-140 mV s\(^{-1}\); Electrode area: 2 cm\(^2\).

Figure S4. Cyclovoltammetry experiments carried out with sample Ni42Pt in 0.05 M sulfuric acid at scan rates ranging from 20-150 mV s\(^{-1}\); Electrode area: 2 cm\(^2\).
Figure S5. Cyclovoltammetry experiments carried out with sample Ni42SoPt in 0.05 M sulfuric acid at scan rates ranging from 20-150 mV s\(^{-1}\); Electrode area: 2 cm\(^2\).

Figure S6. Determination of the double layer capacitance of sample Ni42 in 0.05 M sulfuric acid derived from CV scans (potential range: 0.9-1.25 V vs. RHE) with scan rates between 20 and 140 mV/s. A plot of the current density in the middle of the potential (1.075 V vs. RHE) vs. scan rate is shown and the double layer capacitance is taken from the slope (linear fit).
Figure S7. Determination of the double layer capacitance of sample Ni42Pt in 0.05 M sulfuric acid derived from CV scans (potential range: 0.9-1.15 V vs. RHE) with scan rates between 20 and 150 mV/s. A plot of the current density in the middle of the potential (1.025 V vs. RHE) vs. scan rate is shown and the double layer capacitance is taken from the slope (linear fit).

Figure S8. Determination of the double layer capacitance of sample Ni42SoPt in 0.05 M sulfuric acid derived from CV scans (potential range: 0.7-0.85 V vs. RHE) with scan rates between 20 and 150 mV/s. A plot of the current density in the middle of the potential (0.775 V vs. RHE) vs. scan rate is shown and the double layer capacitance is taken from the slope (linear fit).
**Author contribution statement:** L. Ring and H. Schäfer carried out the sample preparations and the electrochemical measurements. B. G. Pollet suggested to add ultrasonication whilst Pt transfer. H. Schäfer wrote the draft of the manuscript. B. G. Pollet and M. Chatenet evaluated, completed the manuscript and brought together with H. Schäfer the manuscript in the final form. B. G. Pollet and M. Chatenet designed some of the electrochemical measurements and some of the ultrasonication assisted synthesis protocols. S. Abbou carried out the ICP MS investigations. A. Gries and M. Huck carried out some of the ECSA measurements and M. Schmidt performed the AFM experiments. K. Küpper performed and evaluated the XPS experiments and wrote the XPS part.