Supporting Information

Insights into the formation, chemical stability and activity of transient Ni$_y$P@NiOx core-shell heterostructures for the oxygen evolution reaction

Patrick Wilde,‡ Stefan Dieckhöfer,‡ Thomas Quast,‡ Weikai Xiang,^ Anjali Bhatt,‡ Yen-Ting Chen,§ Sabine Seisel,‡ Stefan Barwe,‡ Corina Andronescu,° Tong Li,^ Wolfgang Schuhmann,‡*
Justus Masa‡*

‡ Analytical Chemistry - Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr-Universität Bochum, Universitätsstrasse 150, D-44780 Bochum, Germany

^ Institute for Materials & ZGH, Ruhr-Universität Bochum, Universitätsstrasse 150, D-44801 Bochum, Germany

§ Center for Solvation Science (ZEMOS), Ruhr-Universität Bochum, Universitätsstrasse 150, D-44801 Bochum, Germany

° Chemical Technology III, Faculty of Chemistry and CENIDE (Center for Nanointegration), University Duisburg Essen, Carl-Benz-Strasse 199; D-47057 Duisburg, Germany

* Max Planck Institute for Chemical Energy Conversion, Stiftstrasse 34-36; D-45470 Mülheim an der Ruhr, Germany

Corresponding authors’ *E-Mail: wolfgang.schuhmann@rub.de, justus.masa@rub.de
Experimental Section

Chemicals and materials
Bis(triphenylphosphine)nickel(II) dichloride (synthesis grade), Ni and P powder as well as Nafion 117 (~5% in lower aliphatic alcohols and water) were purchased from Sigma Aldrich. Potassium hydroxide (99.5 %) was purchased from Algin Chemie. Chemicals were used as received.

Methods
Batch 1 of Ni₃P was prepared by thermal decomposition of bis(triphenylphosphine)nickel(II) dichloride ((PPH₃)₂NiCl₂) at a temperature of 400 °C for 2 hours under a N₂ atmosphere containing 10% H₂. Batch 2 of Ni₃P was prepared similarly to Batch 1 but at annealing temperature of 1000 °C, as described previously.¹ The mixture was placed in an ampule, which was evacuated and heated to 1000 °C for 15 h. The material was then allowed to cool down to room temperature. Catalyst ageing and characterization was performed following Scheme S1. Briefly, 300 mg of Ni₃P were suspended in 200 mL of 1 M KOH and stirred continuously at a temperature of 80 °C. 30 mL samples were taken after a period of 1, 6, 12, 24, 72 and 168h. The suspension was then centrifuged at 5000 rpm for 5 minutes and the supernatant was kept for ICP-MS analysis. The catalyst powder was washed multiple times with water until the supernatant showed neutral pH. The sample was then dried at 60 °C for at least 12 hours and kept for further analysis.

Scheme S1. Sample ageing and preparation.
Electrochemical characterization

Electrochemical measurements were performed using an Autolab PGSTAT302N (Metrohm) in a 3 electrode cell setup. A cylindrical Pt mesh counter electrode served as counter electrode, a Ag/AgCl/3 M KCl was used as reference electrode and a glassy carbon rotating disc electrode (RDE) was employed as working electrode \( (A_{\text{electrode}} = 0.1134 \text{ cm}^2) \). The catalyst was deposited on the working electrode by means of drop-coating. The catalyst ink was prepared by 6 min sonication of 1 mg catalyst powder in 200 µL of a mixture of water and ethanol with a 1:1 volume ratio containing 2 vol% Nafion solution. 4.76 µL of the ink were drop-coated on the rotating disc electrode giving a nominal mass loading of 210 µg·mL\(^{-2}\). The electrode was allowed to dry for at least 12 hours in air under ambient conditions before electrochemical measurements were performed. The activity of the catalyst was investigated by RDE measurements with a rotation speed of 1600 rpm. Cyclic voltammograms (CVs) were recorded in 1 M KOH at a scan rate of 10 mV/s. All potentials were converted to the reversible hydrogen electrode (RHE) scale, and corrected for the uncompensated electrolyte resistance according to:

\[
E_{\text{RHE}} = E_{\text{applied}} + E^{\circ}_{\text{Ag/AgCl/3M KCl}} + 0.059 \text{ pH} - iR, \text{ where } pH = 13.78 \text{ and } E^{\circ}_{\text{Ag/AgCl/3M KCl}} = +210 \text{ mV}
\]

Where: \( i = \text{current [A]} \) and \( R = \text{solution resistance [Ω]} \), which was extracted from Nyquist plots of the electrochemical impedance spectroscopy (EIS) data at high frequency. EIS data was recorded in a frequency range of 100 kHz to 0.1 Hz with a perturbation voltage of 10 mV (RMS) at the open circuit potential (OCP).
X-Ray Diffraction (XRD)

X-ray diffraction (XRD) data were obtained using a Panalytical X'PERT Pro MPD X-ray diffractometer (pristine sample) and a Bruker D8 Discover X-ray diffractometer (aged samples) each equipped with a Cu Kα radiation source (λ = 1.5418 Å).

Scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS)

Scanning transmission electron microscopy (STEM) was performed on a JEOL microscope (JEM-2800) with a Schottky-type emission source working at 200 kV. The lattice resolution of the TEM images is 0.09 nm. The point-to-point resolution is 0.20 nm, and 0.14 nm for STEM. The spherical aberration and the chromatic aberration are 0.7 mm and 1.3 mm respectively. Energy dispersive spectroscopy (EDS) mapping was performed with the equipped double SDD detectors, with a solid angle of 0.98 sr with a detection area of 100 mm$^2$. Samples were prepared by drop-coating of catalyst ink onto a carbon coated copper mesh.

Atom probe tomography (APT)

A drop of the diluted nanoparticle dispersions was placed onto a Cu-coated Si flat wafer and subsequently covered by a 150-nm thick protective Cu layer in Leica EM ACE600. Needle-shaped APT specimens were prepared by a site-specific lift-out procedure using a FEI G4 CX focused ion beam (FIB)/scanning electron microscope. The APT experiments were conducted on a CAMECA LEAP 5000 XR instrument at a specimen temperature of 50 K, with a target evaporation rate of 5 ions per 1000 pulses, a pulsing rate of 200 kHz, and laser pulse energy of
50 pJ. The APT data were reconstructed and analysed using the commercial IVAS 3.8.2™ software.

**Inductively coupled plasma – mass spectrometry (ICP-MS)**

ICP MS analysis was performed with an iCAP RQ ICP-MS (Thermo Scientific, Waltham, Massachusetts, USA) employing a TELEDYNE CETAC technologies ASX 560 autosampler. Calibration of elemental concentration was performed with a Q/Qnova calibration solution (Thermo Scientific, Waltham, Massachusetts, USA) in either STD or KED mode with He as collision gas. 300 µL of 69% HNO₃ (ROTIPURAN Supra of Roth) were added to 10 mL of supernatant solution. The solution was measured with a dilution of 1:10. Water was purified using an SG purification system yielding a conductivity of 0.055 µS cm⁻¹.

**X-ray photoelectron spectroscopy (XPS)**

X-Ray photoelectron spectroscopy was performed on an AXIS Nova spectrometer equipped with a monochromatic Al Kα X-ray source (1487 eV, 15 mA emission current). Throughout all measurements, the instrument maintained a pressure around 10⁻⁸ Torr within the sample analysis chamber. Photoelectron collection was done in the fixed transmission mode using a pass energy of 20 eV during region scans. A low-energy electron flood gun was applied for charge neutralization. Calibration of the binding energy scale was conducted by assigning the C 1s peak of adventitious carbon to a value of 284.8 eV.
Brunauer-Emmett-Teller analysis (BET)

N2 adsorption – desorption measurements for determination of the Brunauer-Emmett-Teller (BET) surface area of the catalysts were carried out on a BEL-Mini device supplied by BEL Japan Inc. The samples were first degassed at 250 °C for 4 h before the measurements. The measurements were performed at 77 K. The surface areas were calculated from the linear part of the Brunauer-Emmett-Teller (BET) plots.

![Figure S1](image)

**Figure S1.** Deconvoluted high-resolution P 2p XPS spectra of Ni phosphide samples after different exposure times in 1 M KOH at 80 °C. The spectra for exposure times below 24 h were fitted with two components located at about 133 eV and 130 eV, corresponding to phosphate and phosphide surface species, respectively. Only the 3/2 components from the spin-orbit split doublets were used for calculating the ratios between different Ni and P species present on the sample surface. The last three spectra represent the charge corrected experimental spectra.
Figure S2. Chemical ageing at room temperatures causes a similar behavior compared to samples, which were aged at 80 °C. First anodic linear sweep voltamogram of pristine material, 1 h at 80°C and 3 different ageing times at room temperature. Ageing at room temperature does not allow for the formulation of a trend between the different ageing times due to the subtlety of the changes in comparison to samples aged at 80 °C but it can be clearly seen that a similar loss of activity occurs in comparison to the pristine sample. Similar observations are made with regards to the drastic shrinkage of the Ni(II) to Ni(III) oxidation peak despite the content of Ni remaining unchanged. ICP-MS measurements of the supernatant indicated P-dissolution, with P concentrations increasing from 15,000 ppb (1 h) to 24,000 ppb (168 h). XPS analysis of the aged materials revealed a decreased in P to Ni ratio from 0.17 (1 h) to 0.13 (168 h).

Figure S3. X-ray diffractograms of the pristine (blue), the 1 h (yellow) and the 168 h sample (grey). All diffractograms show diffraction pattern of metallic nickel with the 111 reflection at 44.6°, the 200 reflection at 51.8°, the 220 reflection at 76.3° and the 311 reflection at 92.8°. For better comparison the latter one has been used to normalize all patterns since this peak arises solely from nickel. Besides nickel the sample contains a number of smaller peaks, which positions and intensities agrees well with reference patterns of various Nickel Phosphides, namely Ni₃P, Ni₅P and Ni₁₂P₃. After 168 h aging time new patterns at 33.1°, 38.6°, 59.3° and 62.8° are observed which agree with the 4 most intense reflections of β-Ni(OH)₂ at the 100, 101, 110 and 111 plane, respectively and indicate unambiguously the formation of nickel hydroxide upon aging.
Figure S4. Deconvoluted high-resolution Ni 2p XPS spectra of pristine (a) and 1 h aged (b) Ni phosphide. The spectra were fitted with Gaussian-Lorentzian components representing Ni(0) and Ni(II) species, namely NiO and Ni(OH)$_2$. Broad satellite features were included at the higher binding energy side of the Ni 2p 3/2 branch. Background determination was performed using the Shirley method. Compilation of charge-corrected Ni 2p spectra for different ageing times (c) reveals that ageing in 1 M KOH at 80 °C induces a shift of the main peak accounting for Ni(OH)$_2$ in the pristine sample (a) to lower binding energies. Fitting of the resulting peak (b) shows that the shift is caused by the formation of a NiO species. Superposition of both Ni(II) components results in the peak at 855.4 eV, which remains unchanged throughout the entire ageing process (c), indicating the presence of NiO and Ni(OH)$_2$ in all samples. Ni(0) can only be found in the pristine material.

Figure S5. (a) Enlarged section of the first anodic scan presented in Figure 3a. (b) Reduction peak position in the first cathodic going scan as indicated by the most negative current density. 72 h and 168 h reduction peaks are broadened and hard to distinguish from background current. Increasing ageing time leads to reduction at more cathodic potentials. (c) Enlarged section from (b) as indicated by red dashed box.
Table S1. Tafel plots extracted from the first cathodic-going scan for differently aged samples.

<table>
<thead>
<tr>
<th>Ageing time [h]</th>
<th>Tafel slope [mv·dec⁻¹]</th>
<th>Tafel slope [mv·dec⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pristine</td>
<td>47.4</td>
<td>45.2</td>
</tr>
<tr>
<td>1 h</td>
<td>89.1</td>
<td>57.5</td>
</tr>
<tr>
<td>6 h</td>
<td>100.8</td>
<td>65.2</td>
</tr>
<tr>
<td>12 h</td>
<td>89.8</td>
<td>58.0</td>
</tr>
<tr>
<td>24 h</td>
<td>115.5</td>
<td>133.3</td>
</tr>
<tr>
<td>72 h</td>
<td>119.8</td>
<td>114.8</td>
</tr>
<tr>
<td>168 h</td>
<td>141.8</td>
<td>127.6</td>
</tr>
</tbody>
</table>

Figure S6. Anodic going scans for the aged and pristine sample. First and 25th scan are shown for the pristine sample. 25th cycle is shown for the aged samples. The aged samples never reach the OER current density of the pristine material, not even after 25 cycles of electrochemical activation, indicating irreversible activity loss.
**Figure S7.** High resolution TEM images of the particles aged for 24 hours and 168 hours as shown in Figure 4a and Figure S8d and g. Analysis reveals d-spacings resembling the 012 plane (2.09 Å) and 101 plane (2.41 Å) of NiO. Reference data is taken from pdf-00-044-1159.
Figure S8. EDS elemental maps of submicron particles with Ni (red), P (green) and O (blue) signals including elemental line scans along the respective white dashed arrow for the pristine sample (a-c), the 24 h sample (d-f) as well as the 168 h sample (g-i). Scale bars are 100 nm. Images confirm a native oxide layer in case of the pristine sample, core-shell formation in case of the sample aged for 24 hours and complete particle oxidation for 168 hours with shape identical O and Ni signal.
Figure S9. (a) Size distribution of Batch 1 (blue) and Batch 2 (green) based on SEM analysis. (b) Surface area as determined by BET analysis in m²/g for Batch 1 (blue) and Batch 2 (green).

Figure S10. (a) ICP-MS P concentrations in the supernatant after catalyst ageing in 1 M KOH at 80 °C for different durations in ppb for Batch 2. (b) Ratio of P to Ni signal in XPS spectra for the differently aged samples of Batch 2.
References
