Supplementary Information

Disclosing Pt-Bimetallic Alloy Nanoparticle Surface Lattice Distortion with Electrochemical Probes

Raphaël Chattot ^{1, 2, *}, Isaac Martens ², Marion Scohy ¹, Juan Herranz ³, Jakub Drnec ², Frédéric Maillard ¹ and Laetitia Dubau ^{1, *}

¹ Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP Institute of Engineering Univ. Grenoble Alpes), LEPMI, 38000 Grenoble, France

² ESRF-The European Synchrotron, ID31 Beamline, 38043 Grenoble, France

³ Electrochemistry Laboratory, Paul Scherrer Institut, 5232 Villigen, Switzerland

*e-mail: (RC) raphael.chattot@grenoble-inp.org ; (LD) laetitia.dubau@lepmi.grenoble-inp.fr

This Supplementary Information file includes:

Experimental Details

Supplementary Equations S1 to S3

Supplementary Figure S1 to S9

Supplementary Tables S1 to S3

References

Experimental details

Reference Electrocatalysts

A Pt/C catalyst with a Pt weight fraction (wt. %) of 20 % was purchased from Tanaka Kikinzoku Kogyo (TKK) and used as reference material for rotating disk electrode (RDE) experiments without any treatment. For the fuel cell tests, 5 cm² commercial custom membrane electrodes assemblies (MEAs) were purchased from Fuel Cells Etc. The anode/cathode was based on 40/60 wt. % Pt/C (0.3/0.5 mg_{Pt} cm⁻², respectively) coated on a gas diffusion layer (GDL-CT) sandwiching a Nafion[®] 115 (Dupont) membrane. Also, a commercial PtNi/C catalyst with a Pt wt. % of 27 % was purchased from Umicore for home-made MEA manufacturing.

Materials Synthesis

The preparation routes for all the electrocatalysts used in this study are reported in the following references: Sphere PtNi ¹, Cube PtNi/C ², Cube Pt/C ², Octahedron PtNi/C ², Hollow PtNi/C ³, Aerogel PtNi ⁴, Sponge PtNi/C ⁵ or in the Supplementary Information of Ref. ⁶.

Electron Microscopy (STEM/X-EDS)

The STEM/X-EDS elemental maps were acquired using a JEOL 2100F microscope operated at 200 kV and equipped with a retractable large angle Silicon Drift Detector (SDD) Centurio detector. The X-EDS spectra were recorded at different magnifications by scanning the beam in a square region of various sizes. The quantitative analyses were performed on Pt L and Ni K lines using the K-factors provided by the JEOL software.

Estimation of the Surface Distortion (SD) descriptor

The SD descriptor values were determined by a combination of Rietveld refinement of high energy synchrotron WAXS patterns collected at the ID31 beamline of the European Synchrotron Radiation Facility (ESRF, Grenoble, France) and chemical composition measurements from STEM/X-EDS experiments. The high energy X-ray radiations (60-78 keV during various experiments) were focused on the catalyst powders contained in a 1 mm diameter Kapton[®] capillary, and the scattered signal was

collected using a Dectris Pilatus CdTe 2M detector. The energy, detector distance and tilts were calibrated using a standard CeO₂ powder and the 2D diffraction patterns were reduced to 1D curves using the pyFAI software package ⁷. Rietveld refinements of the WAXS patterns were performed to extract the crystallite size, lattice parameter and microstrain ⁸ using the *Fm3m* structure of Pt metal and the Fullprof software. The instrumental resolution function was determined by the refinement of a CeO₂ standard sample. As formerly introduced and extensively explained in Ref. ⁶, the surface distortion values were obtained by correcting the bulk microstrain values from both the crystallite size and the bulk chemical disorder. Briefly, the size effect was corrected using the proportion of surface atoms *D* (%) derived from the XRD crystallite size and the mathematical model of Montejano-Carrizales *et al.* ^{9,10} for cuboctahedral nanoparticles, whereas the bulk chemical disorder was subtracted from a former experimental microstrain-composition relationship *f*(%Ni) ⁶, using the equation:

$$SD = \frac{\text{microstrain} - f(\%\text{Ni})}{D}$$
 Eq. S1

Where:

$$f(x) = -2.2 * 10^{-3} * x^{3} + 0.16 * x^{2} - x$$
 Eq. S2

And %Ni is estimated from combined Vegard's law and STEM/X-EDS analysis.

Acidic Treatment

The catalytic powder was dispersed in 1 M H₂SO₄ under room conditions, and stirred for 22 h. The powder was then recovered by filtration, copiously rinsed with 18.2 M Ω cm deionized water and dried for 45 min. at *T* = 110 °C.

Rotating Disk Electrode (RDE) Electrochemical Characterizations

The following electrochemical protocol is largely inspired from the work of Shinozaki and co-workers, who reported the appropriate experimental practices toward more reproducible and accurate RDE measurements on Pt-based electrocatalysts ^{11,12}.

The electrocatalytic inks were prepared by mixing 10 mg of Pt/C or PtNi/C catalyst powder (Pt weight fraction ~ 20 wt. %), 54 μ L of 5 wt. % Nafion[®] solution (Electrochem. Inc.), 1446 μ L of isopropanol and 3.6 mL (18.2 M Ω cm) of deionized water. After sonication for 15 min., 10 μ L of the suspension were pipetted and dried onto a 0.196 cm² glassy carbon disk, using the rotational drying technique ¹³ for better catalytic thin film uniformity and experiment reproducibility.

Electrochemical Setup:

An Autolab PGSTAT302N potentiostat and a custom-made four-electrode electrochemical cell thermostated at T = 25 °C were used. The electrolyte (0.1 M HClO₄) was daily prepared using Milli-Q water and HClO₄ 96 wt. % (Suprapur[®], Merck). The counter-electrode was a Pt grid and the reference electrode a commercial reversible hydrogen electrode (RHE) (Hydroflex, Gaskatel GmbH) connected to the cell via a Luggin capillary. The accuracy of the commercial RHE potential was checked each experiment day with a homemade RHE. A Pt wire connected to the reference electrode by a capacitive bridge was used to filter the high frequency electrical noise.

To investigate the effect of anion adsorption, the 0.1 M perchloric acid electrolyte was replaced by 0.1 M sulphuric acid (Suprapur[®], Merck) or 0.1 M methanesulfonic acid (\geq 70%, Roth).

Catalyst Conditioning/Activation:

Prior to CO_{ads} stripping or ORR measurements, the potential of the working electrode was swept 50 times at 500 mV s⁻¹ then 3 times at 20 mV s⁻¹ between 0.05 V and 1.23 V *vs.* RHE under Ar-saturated 0.1 M HClO₄ solution (Ar >99.999 %, Messer).

CO_{ads} Stripping Experiments:

A monolayer of CO_{ads} was adsorbed on the electrocatalyst surface by bubbling CO gas (> 99.997 %, Messer) in the electrolyte for 6 minutes while keeping the electrode potential at E = 0.1 V vs. RHE, purging with Ar for 20 min. while remaining at the same potential, and finally stripping off (electrooxidizing) this CO_{ads} layer by recording 3 cyclic voltammograms between 0.05 V and 1.23 V vs. RHE at 20 mV s⁻¹. The electrical charge required to electrooxidize the CO_{ads} monolayer provided the

electrochemically active surface area (ECSA) assuming a conversion factor of 420 μ C per cm² of Pt. The cyclic voltammograms were recorded with dynamic Ohmic drop compensation (90 % of the value measured by electrochemical impedance spectroscopy).

Oxygen Reduction Reaction (ORR) Activity Measurement

The electrocatalytic activity for the ORR was measured in O_2 -saturated 0.1 M HClO₄ solution ($O_2 >$ 99.99 %, Messer) using cyclic voltammetry between 0.20 and 1.05 V *vs.* RHE at a potential sweep rate of 5 mV s⁻¹ and at different rotational speeds in the order: 400 (2 consecutive measurements), 900, 1600, 2500 and 400 rpm again. The kinetic current for the ORR was measured at E = 0.95 V *vs.* RHE on the 1600 rpm positive-going potential scan after correction of Ohmic drop and O_2 diffusion in solution (Koutecky-Levich equation):

$$I_k = \frac{I * I_{lim}}{I_{lim} - I}$$
 Eq. S3

Where I is the measured current, I_k is the kinetic current and I_{lim} is the diffusion-limited current

Single Crystals

The Pt(111) single crystal was provided by Surface Preparation Laboratory (purity 99.9995 %, oriented to <0.1°, cylinder with a diameter of 10 mm and a height of 3 mm) and the Pt(100) single crystal was provided by MaTecK (purity 99.999%, oriented to <0.1°, cylinders with a diameter of 5 mm and a height of 4 mm). The single crystals were prepared by annealing in a butane flame at *ca*. 1000°C, cooled in an argon + 5% hydrogen (Ar + 5 % H₂) mixture and protected by a water droplet saturated with this gas mixture before each experiment. The electrode was then transferred to the electrochemical cell and put in contact with the solution under potential control, at *E* = +0.8 V *vs*. RHE. The same activation, base CVs and CO stripping procedures as those applied in RDE measurements were used, except for the replacement of the upper potential vertex of 1.23 V *vs*. RHE by 0.95 V *vs*. RHE to preserve the surfaces structure.

Bulk Pt-poly

A bulk, polycrystalline and 'ball' terminated Pt wire was used as the working electrode for dedicated measurements. The wire was cleaned with a butane flame and electrochemically characterized as for the RDE datapoints.

MEAs Preparation

Catalyst inks targeting a 1.1 carbon to Nafion[®] mass ratio and *ca*. 2 mg_{Pt}.mL⁻¹ were prepared by mixing the appropriate amounts of catalyst powder, 5 wt. % Nafion[®] solution and 8 wt. % aqueous isopropanol solution. After ultrasonication for 30 min. the ink was sprayed on a Nafion[®] 115 membrane side using a frame to confine the coating to the active cell area of 5 cm², hold the membrane and keep the temperature at 80 °C for fast ink drying. Then, the as-prepared catalyst coated membranes (CCMs) were hot-pressed at 140 °C and 4 bars for 3 min. with a gas diffusion layer (GDL 25 BC, Sigracet) and a commercial gas diffusion electrode (GDE, Johnson Matthey, 0.4 mg_{Pt}.cm⁻² HISPEC 9100 Pt/C on Sigracet GDL 25 BC) on the cathode and anode side, respectively. The final cathode catalyst loading was measured by the weight variation before and after the spraying process *via* a microbalance, and was comprised between *ca*. 0.5 – 0.7 mg_{Pt}.cm⁻² for all the 'in house' MEAs investigated.

Fuel Cell Measurements

PEM fuel cell measurements were conducted in a dedicated single 5 cm² cell, controlled by a test station (FCS-4M-100W, LeanCat Fuel Cell) and a Biologic SP-400 potentiostat. Since we aimed at comparing the chemisorption properties of the materials by varying the nature of the electrolyte, the fuel cell tests protocol was adapted to minimize damages caused to the catalysts and to approach the RDE conditions. The cell was operated at 25 °C under H₂/N₂, the flow rate was set to 100/450 sccm at the anode/cathode respectively with a back pressure of 0.5 bar and the relative humidity adjusted to 100 %. Conditioning of the MEA was done like in RDE configuration *i.e.* by cycling 50 times the cathode potential between 0.05 V and 1.23 V vs. the anode potential (that can be considered as a RHE in these conditions) at 500 mV s⁻¹, then 3 times at 20 mV s⁻¹ within the same potential range. For the in situ CO_{ads} stripping

experiments, N_2 was replaced by CO during *ca*. 5 min, then, 20 min. after N_2 was reintroduced, we recorded 3 cyclic voltammograms between 0.05 V and 1.23 V *vs*. RHE at 20 mV s⁻¹.

Estimation of the $Q_{\rm CO}/2Q_{\rm H}$ Ratio

In both solid and liquid electrolyte, the $Q_{\rm H}$ values were extracted by subtracting the second cycle of a $\rm CO_{ads}$ stripping experiment from the first. By doing so, a better correction of the pseudocapacitive current related to the high-surface area carbon support ¹⁴ was achieved (see $\rm CO_{ads}$ stripping curves examples in **Supplementary Figure S1**).



Supplementary Figure S1. Typical CO_{ads} stripping curves measured for a) the Pt/C TKK and b) Pt/C Fuel Cells Etc. reference catalysts in liquid and solid electrolyte, respectively. In both cases, T = 25 °C, the sweep rate is 20 mV s⁻¹ and the Ohmic-drop was compensated in a dynamic manner (90 % of the measured value). The liquid electrolyte is 0.1 M HClO₄, and the fuel cell is operated at 100% humidification rate.

Despite using this procedure, some artifacts at high potential (long tail in the CO_{ads} monolayer electrooxidation peak, see **Supplementary Figure S2** and **Supplementary Figure S3**), that can hardly be attributed to electroxidation of CO molecules but most probably to the re-oxidation of oxygen-

containing groups of the carbon support after their full reduction during the CO adsorption and purging steps performed at E = 0.1 V vs. RHE. Interestingly, this phenomenon was less pronounced for structurally-disordered catalysts which were acid treated (22 h in 1 M H₂SO₄) and for unsupported catalysts (see in **Supplementary Figure S2** and **Supplementary Figure S3**).



Supplementary Figure S2. Examples of background-subtracted CO_{ads} stripping curves for a) Sphere PtNi/C, b) Cube PtNi/C and c) Octahedron PtNi/C catalysts. The curves are recorded in 0.1 M HClO₄ at T = 25 °C and the sweep rate is 20 mV s⁻¹. The regions considered for both Q_{CO} and Q_H charges are coloured. The red lines show typical extra baseline corrections applied to avoid artifacts related to oxide formation.

Consequently, an arbitrary baseline was further subtracted from the background (cycle 2) corrected CO_{ads} stripping curve. This arbitrary baseline included the onset of the CO_{ads} oxidation peaks but not the high potential extra-peak tail (see **Supplementary Figure S2** and **Supplementary Figure S3**).



Supplementary Figure S3. Examples of background-subtracted CO_{ads} stripping curves for a) Hollow PtNi/C, b) Aerogel PtNi and c) Sponge PtNi/C catalysts. The curves are recorded in 0.1 M HClO₄ at T = 25 °C and the sweep rate is 20 mV s⁻¹. The regions considered for both Q_{CO} and Q_H charges are coloured. The red lines show typical extra baseline corrections applied to avoid the various oxide formation artifacts.

Finally, in the <u>only</u> case of Octahedron PtNi/C, Ni_{ads} stripping was observed at low potential. These solvated Ni cations species are believed to originate from the dissolution of pure Ni nanoparticles found in this catalyst after synthesis as reported elsewhere ¹⁵ during catalyst activation. Their

adsorption/desorption from the surface when exposed to low potential induces a very characteristic peak at low potential on the first CO_{ads} stripping scan as shown in **Supplementary Figure S4.a**. Consequently, by bubbling CO at E = 0.4 V vs. RHE, and while sweeping (and holding) down to E = 0.1 V vs. RHE, the preferential CO adsorption was ensured and the adsorption of Ni cations disabled (modified CO introduction protocol in **Supplementary Figure S4.b**).



Supplementary Figure S4. Typical CO_{ads} stripping (with or without undesired Ni_{ads} stripping) curves measured for the Octahedron PtNi/C in liquid electrolyte using a) the usual CO_{ads} stripping protocol and b) the modified CO introduction. In both cases, T = 25 °C, the sweep rate is 20 mV s⁻¹ and the Ohmic-drop was compensated in a dynamic manner (90 % of the measured value). The liquid electrolyte is 0.1 M HClO₄.

Note however that this modified CO introduction protocol did not solve the issue in the fuel cell environment, and the correction for this peak was done manually with an extra baseline subtraction.

Investigation on Possible Anion Adsorption Effect on the Q_{CO}/2Q_H Ratio

An important factor to consider for the transposition of our results to the fuel cell solid electrolyte is a possible effect of anion adsorption. Indeed, the weakly-adsorbing liquid electrolyte used for RDE experiment (0.1 M perchloric acid, HClO₄) is likely to be contaminated by inorganic impurities such as strongly-adsorbing chloride (Cl⁻) anions. In solid Nafion[®] electrolyte, the sulfonate anions (SO₃⁻) are adsorbed much more strongly than perchlorate (ClO₄⁻) anions, thus possibly leading to changes of the $Q_{CO}/2Q_{H}$ charge ratio. To investigate whether the $Q_{CO}/2Q_{H}$ ratio depends on the nature of the anion, we performed base and CO_{ads} stripping experiments in 0.1 M HClO₄, 0.1 M sulphuric acid (H₂SO₄) and 0.1 M methanesulfonic acid (CH₄O₃S) on the Hollow PtNi/C electrocatalyst.

The base and CO_{ads} stripping voltammograms displayed in **Supplementary Figure S5** shows only minor differences. It can be noted than the hydrogen adsorption/desorption features are more pronounced in 0.1 M sulphuric acid compared to 0.1 M methanesulfonic acid, the latter being close to what is observed in 0.1 M perchloric acid.



Supplementary Figure S5. CO_{ads} stripping curves (first and second cycles in solid and dashed lines, respectively) for the Hollow PtNi/C catalyst measured in 0.1 M perchloric acid (black), 0.1 M sulphuric acid (orange) and 0.1 M methanesulfonic acid (red) electrolyte. The curves are recorded at T = 25 °C and the sweep rate is 20 mV s⁻¹.

Nevertheless, the $Q_{CO}/2Q_H$ charge ratios for the Hollow PtNi/C electrocatalyst are 0.86, 0.86 and 0.84 in 0.1 M perchloric acid, sulfuric acid and methanesulfonic acid, respectively (see **Supplementary**

Figure S6), suggesting no influence of the anions. Consequently, it is no surprise that the structural-electrochemical trend determined in liquid electrolyte is still valid in solid Nafion[®] electrolyte (Figure 3).



Supplementary Figure S6. Background-subtracted CO_{ads} stripping voltammograms for the Hollow PtNi/C catalyst in a) 0.1 M perchloric acid, b) 0.1 M sulphuric acid and c) 0.1 M methanesulfonic acid. The curves are recorded at T = 25 °C and the sweep rate is 20 mV s⁻¹. The regions considered for both Q_{CO} and Q_H charges are coloured. The red lines show typical extra baseline corrections applied to avoid artifacts arising from oxide formation.



Supplementary Figure S7. Cyclic voltammograms of a) Pt/C TKK, b) Hollow PtNi/C and c) Sponge PtNi/C before and after CO exposure. The superposition of the curves suggests no surface reconstruction upon CO exposure. The curves are recorded in 0.1 M HClO₄, at T = 25 °C and the sweep rate is 20 mV s⁻¹.



Supplementary Figure S8. Extended $Q_{CO}/2Q_H$ – Surface distortion trend. Data of acid-treated (22 h in 1 M H₂SO₄ at room temperature) preferentially shaped nanoparticles was added (-AT). The plot shows that the increased surface distortion values induced by the acidic treatment and measured by advanced physical method can be probed by the $Q_{CO}/2Q_H$ ratio. Dashed lines serve as guides to the eye.



Supplementary Figure S9. Relation between the $Q_{CO}/2Q_H$ ratio and the ORR specific activity. In *a*), the ORR activity follows a 'reverse' volcano-type curve with the $Q_{CO}/2Q_H$ ratio. Each branch is composed of either structurally-ordered or structurally-disordered materials only. In *b*), the limitations of the $Q_{CO}/2Q_H$ ratio as an ORR activity predictor is evidenced by showing that an intermediate surface state can exist (i.e., a distorted surface that may still benefits from residual strain, ligand or ensemble effect(s)).

Supplementary Table S1. Structural and chemical properties of the different electrocatalysts used in this study. The Ni content was obtained by X-EDS, the particle size (diameter) by TEM on more than 200 particles, the crystallite size and Surface Distortion descriptor by Rietveld refinement of WAXS patterns as introduced in Ref⁶.

Electrocatalysts	Ni Content	Particle Size	Crystallite Size	Surface Distortion
	(at.%)	(nm)	(nm)	(%)
Pt/C TKK	0	2 ± 0.5	1.3 ± 0.2	0.0
Cube Pt/C	0	12.8 ± 2.2	9.5 ± 0.2	1.6 ± 0.1
Sphere PtNi/C	56 ± 1	9.3 ± 0.8	8.6 ± 0.4	0.1 ± 0.1
Sphere PtNi/C-AT	34 ± 1	$\sim 9.3^{\circ}$	11.6 ± 1.8	5.1 ± 1
Umicore PtNi/C	19 ± 5	3.9 ± 1.3	3.3 ± 0.2	1.4 ± 0.3
Cube PtNi/C	25 ± 2	10 ± 1.8	12.9 ± 0.6	0.0 ± 1.0
Cube PtNi/C-AT	11 ± 1	$\sim 10^{\circ}$	10.1 ± 0.2	0.8 ± 0.2
Octahedron PtNi/C	31 ± 1	8.3 ± 1	9.2 ± 0.3	0.0 ± 0.5
Octahedron PtNi/C-AT	19 ± 1	$\sim 8.3^{\circ}$	8.3 ± 0.4	0.8 ± 0.6
A-Pt/C	0	3.4 ± 1.1	7.4 ± 0.6	$4\;.0\pm0.2$
A-PtNi/C	10 ± 4	2.4 ± 0.5	4 ± 0.5	2.7 ± 0.4
Hollow PtNi/C	11 ± 3	11.4 ± 2 $^{\rm a}$	3.3 ± 0.5	4.8 ± 0.4
Aerogel PtNi	17 ± 2	$5.6\pm1.2~^{\text{b}}$	4.8 ± 0.6	7.0 ± 0.6
Sponge PtNi/C	16 ± 1	$61\pm21~^{\rm a}$	4.5 ± 0.9	7.6 ± 1.4

^a Refers to the size of the aggregates

^b Refers to the thickness of the chains

° No significant nanoparticle size change observed after acidic treatment

	$Q_{CO}/2Q_H$	SA 0.95
Electrocatalysts		$(\mu A cm_{Pt}^{-2})$
Sphere PtNi/C	0.96 ± 0.02	207 ± 45
Sphere PtNi/C-AT	0.88 ± 0.03	147.5 ± 5
Umicore PtNi/C	0.98 ± 0.01	60 ± 6
Cube PtNi/C	1.00 ± 0.06	274 ± 46
Cube PtNi/C-AT	0.93 ± 0.04	124 ± 6
Octahedron PtNi/C	1.04 ± 0.01	567 ± 118
Octahedron PtNi/C-AT	0.92 ± 0.04	275 ± 53
Hollow PtNi/C	0.84 ± 0.01	176 ± 10
Aerogel PtNi	0.83 ± 0.03	202 ± 29
Sponge PtNi/C	0.79 ± 0.02	317 ± 11
Pt/C TKK	0.97 ± 0.02	27 ± 4
A-Pt/C	0.88 ± 0.02	53 ± 5
A-PtNi/C	0.90 ± 0.03	76 ± 1
Cube Pt/C	0.92	97 ± 30

Supplementary Table S2. ORR specific activity (SA_{0.95}) measured at E = 0.95 V vs. RHE after Ohmic drop and mass transport correction and $Q_{CO}/2Q_H$ ratio for the electrocatalysts used in this study. The measurements were performed using a rotating disk electrode set-up.

Supplementary Table S3. $Q_{CO}/2Q_H$ ratio and surface distortion descriptor values for the electrocatalysts used in this study. The measurements were performed using in PEM fuel cell configuration. The surface distortion descriptor was calculated as described in Ref⁶

Electrocatalysts	Q со/2 Q _H	Surface Distortion (%)
Umicore PtNi/C	1.05	1.4 ± 0.3
Octahedron PtNi/C	0.97	0.4 ± 0.3
Hollow PtNi/C	0.89	4.8 ± 0.4
Aerogel PtNi	0.81	7.3 ± 0.3
Sponge PtNi/C	0.85	8.2 ± 1.5
Pt/C Fuel Cells Etc	1.03	0.6 ± 0.3

References

- Gan, L.; Rudi, S.; Cui, C.; Heggen, M.; Strasser, P. Size-Controlled Synthesis of Sub-10 Nm PtNi₃ Alloy Nanoparticles and Their Unusual Volcano-Shaped Size Effect on ORR Electrocatalysis. *Small* 2016, *12* (23), 3189–3196.
- (2) Zhang, J.; Yang, H.; Fang, J.; Zou, S. Synthesis and Oxygen Reduction Activity of Shape-Controlled Pt₃Ni Nanopolyhedra. *Nano Lett.* **2010**, *10*, 638–644.
- (3) Bae, S. J.; Yoo, S. J.; Lim, Y.; Kim, S.; Lim, Y.; Choi, J.; Nahm, K. S.; Hwang, S. J.; Lim, T.-H.; Kim, S.-K.; et al. Facile Preparation of Carbon-Supported PtNi Hollow Nanoparticles with High Electrochemical Performance. *J. Mater. Chem.* **2012**, *22* (18), 8820.
- Henning, S.; Kühn, L.; Herranz, J.; Durst, J.; Binninger, T.; Nachtegaal, M.; Werheid, M.; Liu, W.; Adam, M.; Kaskel, S.; et al. Pt-Ni Aerogels as Unsupported Electrocatalysts for the Oxygen Reduction Reaction. *J. Electrochem. Soc.* 2016, *163* (9), F998–F1003.
- (5) Chattot, R.; Asset, T.; Bordet, P.; Drnec, J.; Dubau, L.; Maillard, F. Beyond Strain and Ligand Effects: Microstrain-Induced Enhancement of the Oxygen Reduction Reaction Kinetics on Various PtNi/C Nanostructures. ACS Catal. 2017, 7, 398–408.
- (6) Chattot, R.; Bacq, O. Le; Beermann, V.; Kühl, S.; Herranz, J.; Henning, S.; Kühn, L.; Asset, T.; Guétaz, L.; Renou, G.; et al. Surface Distortion as a Unifying Concept and Descriptor in Oxygen Reduction Reaction Electrocatalysis. *Nat. Mater.* **2018**, *17* (9), 827–833.
- (7) Ashiotis, G.; Deschildre, A.; Nawaz, Z.; Wright, J. P.; Karkoulis, D.; Picca, F. E.; Kieffer, J. The Fast Azimuthal Integration Python Library: PyFAI. *J. Appl. Crystallogr.* **2015**, *48*, 510–519.
- (8) Rodríguez-Carvajal, J. Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction. *Phys. B Condens. Matter* **1993**, *192*, 55–69.
- (9) Montejano-Carrizales, J. M.; Morán-López, J. L. Geometrical Characteristics of Compact Nanoclusters. *Nanostructured Mater.* **1992**, *1* (5), 397–409.
- (10) Montejano-Carrizales, J. M.; Aguilera-Granja, F.; Morán-López, J. L. Direct Enumeration of the Geometrical Characteristics of Clusters. *Nanostructured Mater.* **1997**, *8* (3), 269–287.
- (11) Shinozaki, K.; Zack, J. W.; Richards, R. M.; Pivovar, B. S.; Kocha, S. S. Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilizing Rotating Disk Electrode Technique: I. Impact of Impurities, Measurement Protocols and Applied Corrections. J. Electrochem. Soc. 2015, 162 (10), F1144–F1158.
- (12) Shinozaki, K.; Zack, J. W.; Richards, R. M.; Pivovar, B. S.; Kocha, S. S. Oxygen Reduction Reaction Measurements on Platinum Electrocatalysts Utilizing Rotating Disk Electrode Technique: II. Influence of Ink Formulation, Catalyst Layer Uniformity and Thickness. J. Electrochem. Soc. 2015, 162 (12), F1384–F1396.
- (13) Garsany, Y.; Singer, I. L.; Swider-Lyons, K. E. Impact of Film Drying Procedures on RDE Characterization of Pt/VC Electrocatalysts. *J. Electrocanal. Chem.* **2011**, *662* (2), 396–406.
- (14) Schulenburg, H.; Durst, J.; Müller, E.; Wokaun, A.; Scherer, G. G. Real Surface Area Measurements of Pt₃Co/C Catalysts. *J. Electroanal. Chem.* **2010**, *642* (1), 52–60.
- (15) Beermann, V.; Gocyla, M.; Kühl, S.; Padgett, E.; Schmies, H.; Goerlin, M.; Erini, N.; Shviro, M.; Heggen, M.; Dunin-Borkowski, R. E.; et al. Tuning the Electrocatalytic Oxygen Reduction Reaction Activity and Stability of Shape-Controlled Pt-Ni Nanoparticles by Thermal Annealing -Elucidating the Surface Atomic Structural and Compositional Changes. J. Am. Chem. Soc. 2017, 139 (46), 16536–16547.