Probing the nanoscale structure of the catalytically active overlayer on Pt alloys with rare earths

Anders F. Pedersen^{a,*}, Elisabeth T. Ulrikkeholm^{a,*}, María Escudero-Escribano^{a,b}, Tobias P. Johansson^a, Paolo Malacrida^a, Christoffer M. Pedersen^a, Martin H. Hansen^c, Kim D. Jensen^a, Jan Rossmeisl^c, Daniel Friebe^d, Anders Nilsson^d, Ib Chorkendorff^a, Ifan E. L. Stephens^{a,e,**}

^aDepartment of Physics, Center for Individual Nanoparticle Functionality, Building 312, Technical University of Denmark, 2800 Lyngby, Denmark

^bDepartment of Chemical Engineering, Shriram Center, 443 Via Ortega, Stanford University, Stanford, CA 94305, USA

^cDepartment of Chemistry, University of Copenhagen, Universitetsparken 5, 2100, Copenhagen, Denmark

^dSLAC National Accelerator Laboratory, 2575 Sand Hill Road, MS31, Menlo Park, CA 94025, USA

^eMassachusetts Institute of Technology, Department of Mechanical Engineering, 77 Massachusetts Avenue, Cambridge, MA 02139 USA

Keywords: Electrocatalysis, Pt-alloys, Pt(111), Oxygen Reduction, Diffraction

***These authors contributed equally to this work.**

****Corresponding author.**

Email address: ifan@fysik.dtu.dk (Ifan E. L. Stephens)

Abstract

Pt_xY and Pt_xGd exhibit exceptionally high activity for oxygen reduction, both in the polycrystalline form and the nanoparticulate form. In order to understand the origin of the enhanced activity of these alloys, we have investigated thin films of these alloys on bulk Pt(111) crystals, *i.e.* Y/Pt(111) and Gd/Pt(111). These surfaces exhibit a 4-fold improvement over Pt(111). We observe the formation of a thick Pt overlayer after the electrochemical measurements, both on Y/Pt(111) and Gd/Pt(111). Using surface sensitive X-ray diffraction we revealed that crystalline closely packed Pt overlayers were formed. The diffraction experiments showed that the strain and crystallinity of the overlayers are strongly dependent on the electrochemical treatment, and in general show lateral compression.

1 Motivation

Polymer electrolyte membrane fuel cells (PEMFCs) are highly promising as a low emission source of power for portable applications, in particular automotive vehicles.[1] However, as a consequence of the slow kinetics of the oxygen reduction reaction (ORR) PEMFCs require a copious amount of Pt to catalyse the reaction. In order for PEMFCs to be scaled up beyond the niche market they occupy today, the amount of Pt needs to be decreased by up to an order of magnitude.[2-4] Arguably the most viable route to achieve this goal is to alloy Pt with other, less noble metals, thus improving the catalytic activity. Most investigations pertaining to Pt ORR alloys over the past two decades have focussed on alloying Pt with late transition metals such as Fe, Co and Ni.[5-9] These catalysts exhibit significant initial improvements in activity over pure Pt, but tend to degrade over time.[10, 11] The cause of the degradation is the leaching out of the less noble solute component into the acidic electrolyte, a process known as dealloying.[12, 13] Recent advances show that the stability of bimetallic Pt catalysts can be enhanced significantly, at least during short term tests.[7, 8, 14, 15] Nonetheless, it still remains to be seen whether these catalysts can survive long term tests in fuel cells.[16]

Earlier studies on Pt and Pt alloys suggest that the active site is located on the closely packed (111) surface.[17-20] According to a model based on density functional theory (DFT) calculations, the catalytic activity for oxygen reduction shows a *Sabatier*-volcano dependence on the binding to the key reaction intermediate, HO^* (where HO^* denotes a hydroxyl group adsorbend on an active site).[21] The optimal catalyst should exhibit moderate binding to HO^* , neither too strong nor too weak, with a binding to HO^* around ~ 0.1 eV weaker than Pt(111). Alloys such as Pt_3Ni or Pt_3Co exhibit improved activity because they exhibit closer to optimal binding of HO^* . [22] The first surface layer of these alloys is composed of pure Pt, as the solute metal will be unstable against dissolution to the electrolyte.[6, 23] Scanning tunnelling microscopy experiments indicated that pure Pt overlayers on acid-leached Pt alloys have smooth (111)-like surfaces.[24] The overlayer exhibits weakened binding to HO^* through ligand or strain effects. Ligand effects are due to the direct interaction of the Pt surface atoms with the underlying atoms of the non-noble metal in the second atomic layer.[25, 26] Similarly, a compressive lateral strain to the surface can also bring about a weakening of the binding of HO^* , by raising the position of the d-band centre relative to the *Fermi* level.[27]

Alloys of Pt and late transition metal have a negligible alloy formation energy.[22] This, in turn causes low bulk diffusion barriers,[28] which could explain their apparent susceptibility to degradation by dealloying.[12, 13, 16] Given these limitations, we embarked on a series of investigations to search for active and stable Pt alloys for the ORR. A DFT-based screening study identified Pt₃Sc and Pt₃Y to be particularly promising candidates.[22] We anticipated that they would have enhanced kinetic stability against dealloying as a result of their highly negative alloying energy, *i.e.* a strong bond between Pt and Sc or Y.

Based on the predictions from DFT, we tested bulk sputter-cleaned polycrystalline electrodes of Pt₃Sc and Pt₃Y in rotating disk electrode (RDE) measurements in 0.1 M HClO₄. Relative to Pt, Pt₃Y exhibited > 6 times improvement in ORR activity over polycrystalline Pt, constituting the most active catalyst ever prepared in this manner[22]. We tested a number of smooth polycrystalline electrodes of Pt rare earth alloys, exhibiting equivalent values of the alloying energy to Pt₃Y, mostly of the Pt₅M composition (where M = Y, Ce, La, Gd).[29, 30] The most active amongst these was Pt₅Gd, which exhibited activity just as high as Pt₃Y.[31] Moreover, we also found that model, mass-selected nanoparticles of Pt_xY and Pt_xGd exhibited an exceptionally high mass activity of up to 3.6 A/mg Pt at 0.9 V with respect to a reversible hydrogen electrode (RHE).[32, 33] During the course of 10,000 cycles between 0.6 and 1.0 V the nanoparticulate catalysts lose around 30 % of their activity. However, most of the activity losses occur between 0 and 1,000 cycles.[33] This suggests that during the first 1,000 cycles, the catalyst reaches a metastable, partially dealloyed state (the thermodynamically stabilised state would be a pure Pt particle with all the rare earth component dissolved into solution).

We initially predicted the high activity of Pt₃Y would be contingent on the formation of a specific structure with a single atom-thick Pt overlayer and at least 25 % Y in the second atomic layer.[22] On the basis that Y is larger than Pt, we expected the overlayer would be under tensile strain. Hence, a thick pure Pt overlayer would bind reaction intermediates stronger than a pure Pt surface, putatively the opposite effect required for an enhancement in ORR activity. Thus, according to our understanding at the time, a ligand effect from subsurface Y was essential to outweigh the effect of the tensile strain imposed onto the surface Pt atoms. Consequently, it came to our surprise to find that X-ray photoelectron spectroscopy (XPS) measurements of the electrodes, performed post-ORR, suggested that

the Pt overlayer was at least 3-4 atoms thick on Pt₃Y [29] and other Pt₅M alloys.[30] We later corroborated our XPS observations with elemental analysis based on transmission electron microscopy on nanoparticulate Pt_xY.[32] The key to understanding our observations came by analysing the bulk structure of the polycrystalline Pt₅M alloys, as deduced from X-ray diffraction (XRD). They form an unusual CaCu₅ structure that accommodates alloy components with different atomic radii in a way that is very different from FCC and HCP alloys, which have uniform bond lengths.[30, 34] Despite the larger size of M, relative to Pt, the closest Pt-Pt nearest neighbour distance in the core is smaller than that of pure Pt.[31] According to our DFT calculations, the 3-4 atom thick Pt overlayer concealing Pt₅M would be equivalent to a compressed closely packed pure Pt overlayer.[31] This notion is also consistent with our extended X-ray absorption fine structure (EXAFS) measurements, which showed that even after exposure to ORR conditions, the nanoparticles of Pt_xY and Pt_xGd remained under compressive strain. Moreover, the surface specific ORR activity showed an exponential dependence on the degree of compressive strain:[32, 33] this is exactly the trend we would expect, should we consider the strain to be imposed from the core on the catalytically active surface atoms.

Despite having established that the catalyst activity was strongly correlated to the bulk lattice strain, the structure of the overlayer remained elusive. To this end, following the precedent set by earlier combined surface science- and electrochemistry studies of Pt-based ORR catalysts,[18, 26, 35-37] we prepared single crystalline surfaces of Pt and rare earths. We were unable to source bulk single crystals of these specific alloys. Instead we formed alloy thin films by vacuum depositing ~200 Å Y or Gd on Pt(111) single crystal substrates. UHV and XRD measurements show that these structures exhibit a in-plane compression of 5 % to 6 %.[38, 39] The Gd/Pt(111) structures exhibit similar structural motifs to those of the CaCu₅ structure we observed in the polycrystalline alloys.[31, 38] The alloy film followed the orientation of the Pt(111) substrate half the time, otherwise it was rotated by 30°. Upon testing the Y/Pt(111) electrode for the ORR, we measured an activity of 7.9 mA cm⁻², representing a 4-fold improvement over Pt(111) at 60 °C.[39] Significant leaching resulted in the formation of a ~1 nm thick Pt overlayer, similar to what we observed on the polycrystalline and nanoparticulate samples. Thus we consider the structures formed in vacuum to be precursors to the active phase.

In this paper, we report the electrochemical activity of Gd/Pt(111) for the ORR. Moreover, we use surface X-ray diffraction[40] to elucidate the strain in the electrochemically formed Pt overlayer on both Y/Pt(111) and Gd/Pt(111). We rationalise our trends with DFT calculations. By doing so we provide a fundamental link between the previously observed bulk strain and the nanoscale surface strain that controls the catalysis of oxygen reduction.

2 Experimental setup

2.1 Sample preparation and characterisation in ultra high vacuum

We have provided a full description of the UHV preparation of Y/Pt(111) and Gd/Pt(111) elsewhere.[38, 39] In brief, the sample preparation and initial characterisation were performed in a UHV chamber with a base pressure of 10^{-10} Torr. The chamber is equipped with standard UHV surface science techniques such as XPS, ion scattering spectroscopy (ISS), low-energy electron diffraction (LEED), and a quadrupole mass spectrometer for temperature programmed desorption (TPD). ISS is performed using He^+ ions accelerated over an acceleration voltage of 1.2 kV. For the XPS experiments the K_α radiation of a Mg anode was used (1253.4 eV).

Non-destructive depth profiles of the surface were made using Angle Resolved XPS (AR-XPS). These experiments were carried out in another UHV chamber, hence the sample was exposed to air prior to these experiments. The electron analyser of this system allows to collect separate XPS signals for different emission angles, and in particular 16 angle intervals between 20 and 80 degrees from the surface normal. After subtraction of a *Shirley* type background and integration of the Pt 4f and Y 3d (or Gd 4d) peak areas, the XPS signals were processed using the simulation tool, ARProcess (Thermo Advantage software), which uses a maximum entropy method combined with a genetic algorithm to define the depth profiles: Emission angles over 65° were omitted to minimise the effects of elastic scattering.

The samples were based on Pt(111) single crystals (MaTecK GmbH, Germany, 5 mm diameter and 3 mm thick). They were mounted with a hairpin shaped tungsten wire onto the feed-through on the manipulator end. The temperature was measured using a type K thermocouple. The samples could be

resistively heated and cooled using liquid nitrogen. The main chamber is equipped with four metal evaporators and a quartz crystal microbalance (QCM), which makes it possible to evaporate metals on the surface of the sample at a well-known evaporation rate. The evaporators were made by cutting flakes of a Gd (Alfa Aesar, 99.9 %, 0.127 mm thick) or Y (Goodfellow, 99.9 %, 0.15 mm thick) foil and attaching them to a coil shaped 0.25 mm 99.95 % tungsten wire. Separate crystals were used for the rotating ring disk electrode measurements and the synchrotron based XRD measurements. However, they were prepared under identical conditions.

2.2 Electrochemical methods

The electrochemical rotating ring disk electrode (RRDE) measurements on Gd/Pt(111), Y/Pt(111) and Pt(111) single crystalline electrodes were performed using RRDE assemblies provided by Pine Instruments Corporation. We used a VMP2 potentiostat (Bio-Logic Instruments), controlled by a computer with EC-Lab software. A standard two-compartment glass cell was used, which was equipped with a water jacket attached to a hot water bath to control the temperature. All glassware was cleaned for 24 h in a “piranha” solution consisting of a 3:1 mixture of 96 % H_2SO_4 and 30 % H_2O_2 , followed by multiple runs of heating (to 85-90 °C) and rinsing with ultrapure water (Millipore Milli-Q, 18.2 M Ω cm, TOC < 5 ppb). All electrochemical experiments were carried out in 0.1 M HClO_4 . The counter electrode (CE) was a Pt wire (Chempur 99.9 %, 0.5 mm diameter) and, the reference electrode (RE), a $\text{Hg}/\text{Hg}_2\text{SO}_4$, K_2SO_4 (0.6 M) (Schott instruments), was separated from the working electrode (WE) compartment by a ceramic frit. All the potentials in the text are referenced to the reversible hydrogen electrode (RHE), and are corrected for Ohmic losses, measured by fitting the high frequency impedance spectra taken typically from 500 kHz to 100 Hz. 0 V vs. RHE was established by performing the hydrogen oxidation and evolution reactions (HOR and HER, respectively) on a Pt electrode by means of cyclic voltammetry (CV) in H_2 -saturated 0.1 M HClO_4 at 50 mV s $^{-1}$ and 1600 rpm. The value for conversion to the RHE was taken as the average intersection with the potential axis of the anodic and cathodic curves. The RRDE was immersed into the electrochemical cell under potential control of ~0.1 V vs. RHE into a N_2 -saturated (N5, Air Products) electrolyte. The ORR activity measurements were conducted in an electrolyte saturated with O_2 (N5, Air Products) at 1600 rpm and 50 mV s $^{-1}$.

Prior to the electrochemical measurements, the Pt(111) single crystal was flame-annealed according to the *Clavilier's* method.[41] Pt(111) was annealed for a few minutes (2-10 min) in the flame of Liquefied Petroleum Gas (LPG) for 5 min and cooled in a reducing 1:1 H₂/Ar atmosphere until room temperature (typically 5 min). The electrode surface was then protected by a droplet of ultrapure water, mounted in RRDE assembly and transferred to the electrochemical cell.

2.3 Synchrotron X-ray diffraction

X-ray diffraction measurements were performed on Gd/Pt(111) and Y/Pt(111) both in the as-prepared state, and after electrochemical conditioning. The X-ray diffraction experiments on the Y/Pt(111) and Gd/Pt(111) single crystalline alloys were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL) at beam lines 1-5 and 7-2. The Y/Pt(111) crystal was measured at BL1-5, which is equipped with a Huber Kappa goniometer (ϕ -axis perpendicular to θ -axis) and a Rayonix MAR345 image plate detector. The Gd/Pt(111) crystal was brought to BL7-2, which has a Huber six-circle (4+2) diffractometer and a Dectris Pilatus 300K pixel detector. Both diffractometer stages were equipped with goniometer heads that allowed the crystal surface normal to be aligned to the ϕ -rotation axis using a laser. All the data were acquired at a fixed incidence angle of 0.2° to maximise surface sensitivity, and the photon energy was set to 11 keV to avoid fluorescence background from Pt. A sketch of the geometry of the scattering experiment is shown in Figure 1. The acquired diffraction data was combined to form a 3 dimensional image of parts of the Q -space, and the intensity was corrected for the *Lorentz* factor, polarisation, and geometrical effects using our own MatLab scripts.

Figure 1: A sketch of the experimental setup used to acquire the X-ray diffraction data using an area detector. During all the experiments the incidence angle was kept at $\Omega=0.2^\circ$ to maximise surface sensitivity. The sample was rotated in steps of 0.2° around the surface normal, and at each step an image was acquired. All the images were combined to form a 3-dimensional representation of the Q -space.

The electrochemical conditioning of the Gd/Pt(111) and the Y/Pt(111) samples was conducted at SSRL. For Gd/Pt(111), we performed 1461 cycles from -0.1 V to 0.8 V and 125 cycles from 0.0 V to 1.00 V, followed by 106 cycles from 0.0 V to 1.1 V and 98 cycles from 0.0 V to 1.20 V *vs.* RHE. The Y/Pt(111) was measured as-prepared, and after 175 cycles from -0.1 V to 0.8 V and 189 cycles from 0.05 V to 1.05 V, followed by 261 cycles from 0.05 to 1.20 V and 202 cycles from 0.05 V to 1.30 V *vs.* RHE. All the diffraction data was acquired *ex-situ*. The electrochemical potential cycling at the synchrotron facility was performed using a standard 3-electrode setup with a Ag/AgCl reference electrode (Innovative Instruments, Inc. LF-1.6, 3.4 M AgCl) and a glassy carbon counter electrode. The two samples were measured at different beam times; two different reference electrodes were used. Due to safety reasons it was not possible to calibrate the RHE scale at the beamtime, as we were unable to saturate our electrolytes with H₂. Following the beamtime, during our analysis of the data, we used the onset of hydrogen evolution to estimate the RHE scale. We came to realise that there was a ~ 0.05 V offset between the onset of hydrogen evolution between the two reference electrodes. Consequently, the potential window for the Y/Pt(111) measurements is offset positively by 0.05 V, relative to Gd/Pt(111)

measurements. The cell is a hanging meniscus type, also described elsewhere.[42] The electrolyte was N₂ saturated 0.1M HClO₄ surrounded by a humidified N₂ atmosphere.

3 Results

3.1 Electrochemical experiments and X-ray photoelectron spectroscopy characterisation

The Gd/Pt(111) and Y/Pt(111) samples were transferred directly from the UHV setup to the electrochemical cell. The samples were exposed to the laboratory air for up to 45 min, whilst it was unmounted from the UHV chamber. The RRDE was immersed into the electrochemical cell under potential control of 0.1 V *vs.* RHE into N₂-saturated 0.1 M HClO₄. CVs between 0.05 and 1.00 V *vs.* RHE at 50 mV s⁻¹ were recorded in N₂-saturated electrolyte. The cycling removes adventitious contamination accumulated on the surface during the transfer from the UHV chamber to the electrochemical cell. Figure 2 shows a negative potential shift for both Gd/Pt(111) and Y/Pt(111) in the H adsorption region (between 0.45 and 0.05 V *vs.* RHE), as well as a positive shift in the OH adsorption region (between 0.55 V and 0.85 V *vs.* RHE), relative to Pt(111). The potential shifts (in absolute values) for both the OH and H adsorption regions, $|\Delta U_{\text{HO}^*/\text{M}/\text{Pt}(111)}| = |U_{\text{HO}^*/\text{Pt}(111)} - U_{\text{OH}^*/\text{M}/\text{Pt}(111)}|$ and $|\Delta U_{\text{H}^*/\text{M}/\text{Pt}(111)}| = |U_{\text{H}^*/\text{Pt}(111)} - U_{\text{H}^*/\text{M}/\text{Pt}(111)}|$, where M is Gd or Y, are shown in Table 1. These values indicate the shift in the potential required to adsorb 1/8, 1/6, 1/4 and 1/3 monolayers (MLs) of OH (HO^{*}) and H (H^{*}), that is 30, 40, 60 and 80 $\mu\text{C cm}^{-2}$ [43]. These shifts are in agreement with a Pt overlayer under compressive strain.[44]

Figure 2: Stable (R)RDE based cyclic voltammograms in N_2 -saturated 0.1 M $HClO_4$ at 50 mV s^{-1} and 23°C of Gd/Pt(111), Y/Pt(111) and Pt(111) electrodes. The sharpness of the butterfly peak at $\sim 0.8 \text{ V}$ in comparison to the literature [45] indicates that the crystal is highly ordered,[46] validating our preparation procedure.

$Q / \mu\text{C cm}^{-2}$	$ \Delta U_{\text{HO}^* \text{ Gd/Pt(111)}} / \text{V}$	$ \Delta U_{\text{H}^* \text{ Gd/Pt(111)}} / \text{V}$	$ \Delta U_{\text{HO}^* \text{ Y/Pt(111)}} / \text{V}$	$ \Delta U_{\text{H}^* \text{ Y/Pt(111)}} / \text{V}$
30	0.107	0.074	0.099	0.054
40	0.104	0.075	0.099	0.057
60	0.110	0.073	0.095	0.050
80	0.136	0.062	0.107	0.036

Table 1: Potential shifts (in absolute values) required to adsorb the charge Q , corresponding to coverages of OH and H adsorption of 1/8, 1/6, 1/4 and 1/3 ML. They have been obtained from the CVs in Figure 2 and shown for Gd/Pt(111) and Y/Pt(111) relative to Pt(111).

Figure 3: (A) Rotating ring disk electrode polarisation curves for the ORR on Gd/Pt(111), Y/Pt(111) and Pt(111). (B) Tafel plots showing the kinetic current density of Gd/Pt(111), Y/Pt(111) and Pt(111) as a function of the potential. The measurements were performed in O_2 -saturated 0.1 M HClO_4 at 50 mV s^{-1} , 1600 rpm and 23 $^\circ\text{C}$.

The oxygen reduction reaction activity of Gd/Pt(111), Y/Pt(111) and Pt(111) electrodes was measured in O₂-saturated 0.1 M HClO₄ once stable CVs in N₂-saturated electrolyte were obtained (see Supplementary Material (S.M.) Figures 1 and 2 for initial and stable CVs). The oxygen reduction values for Pt(111) are marginally higher than other data elsewhere in the literature;[18, 45] we can account for this marginal difference on the basis that we correct our data for Ohmic losses. The kinetic current density, j_k , *i.e.* the current density in the absence of any mass-transfer effects, was calculated by the *Koutecky-Levich* equation, $j_k = (j_l \cdot j) / (j_l - j)$, where j_l is the diffusion limited current density and j the measured current density. The *Tafel* plots (j_k as a function of the potential, U) are shown in Figure 3 for both electrodes. The kinetic current density of Gd/Pt(111) at 0.9 V vs. RHE is $j_{k,\text{Gd/Pt(111)}} = 7.3 \pm 1.4 \text{ mA cm}^{-2}$, exhibiting a 4-fold ORR activity enhancement over Pt(111) ($j_{k,\text{Pt(111)}} = 1.73 \pm 0.07 \text{ mA cm}^{-2}$ at 23 °C). This enhancement is similar to that measured on Y/Pt(111)[39] ($j_{k,\text{Y/Pt(111)}} = 7.9 \text{ mA cm}^{-2}$ at 60 °C), presenting a near 4-fold improvement over Pt(111) as $j_{k,\text{Pt(111)}} = 1.93 \text{ mA cm}^{-2}$ at 60 °C. Moreover, it approaches the improvement of polycrystalline Pt₅Gd and Pt₃Y over polycrystalline Pt.[22, 31]

We performed AR-XPS, before and after the electrochemical testing; from these measurements we produced the depth profiles shown in Figure 4. Consistent with the other alloys tested at our laboratory, including polycrystalline Pt₅Gd,[31] Pt_xY nanoparticles[32] and Y/Pt(111),[39] the thickness of the Pt overlayer has increased significantly to ~10 Å after the electrochemical treatment, suggesting that the Gd has leached out from the surface layer. See S.M. Figure 4 for a depth profile on the Y/Pt(111) crystal after XRD measurements.

Figure 4: AR-XPS depth profiles of the Gd/Pt(111) sample before (solid lines) and after (dashed lines) the electrochemical treatment. These measurements have been performed in another UHV setup, and hence during the transfer the sample has been exposed to atmospheric air prior to these measurements. O and C signals were seen as a result from exposure to air, but have been omitted here for clarity. The depth profile including the surface contamination of O and C may be seen in S.M. Figure 3.

3.2 X-ray diffraction experiments

Figure 5 shows the X-ray diffraction pattern for the Pt_5M alloy phase, as prepared, *i.e.* before electrochemical conditioning. The structure shows an in-plane compression compared to Pt(111), and it has a complicated stacking sequence. One of the most important structural features is the formation of so-called kagomé layers, in which a pure Pt layer is compressed, and forms a (2x2) network of vacancies in order to accommodate a larger Gd atom in the layer above or below. Figure 6 shows a schematic of such a kagomé layer in the CaCu_5 structure; we consider this kagomé layer to be essential for the compression of the Pt-Pt distance relative to Pt(111).[38] We deduced that the red circled spot corresponds to the Pt(111) substrate. For a more convenient description in the context of the Pt(111) surface, the FCC structure of bulk Pt can be represented with a hexagonal unit cell with the unit cell vectors of the lengths $a=b=2.775 \text{ Å}$ parallel to the surface and $c=6.797 \text{ Å}$ for the unit cell vector along

the surface normal, $\alpha=\beta=90^\circ$, and $\gamma=120^\circ$. Using this unit cell, the measured range of Q -space shows diffraction peaks from the Pt(111) substrate with a 3-fold in-plane symmetry at (h,k,l) positions (1,0,1), (1,0,4), and (0,1,2) and 120° rotations thereof; the (0,1,2) reflection appears in Figures 5c, 7c, and 8c. All other peaks originate from the alloy.

Figure 5: Diffraction images of Gd/Pt(111) and Y/Pt(111) taken before electrochemical potential cycling. (a) Gd/Pt(111), $\phi=28^\circ$ - 32° . (b)-(d) Y/Pt(111), (b) $\phi=28^\circ$ - 32° , (c) $\phi=-2^\circ$ - 2° , (d) $\phi=3^\circ$ - 7° . Locations for the overlayer diffraction spots in Figure 7 from the overlayers on the Gd/Pt(111) and Y/Pt(111) before electrochemical potential cycling are indicated by the dashed ellipses (spots not seen here since the thick overlayer has not been formed yet). With the exception of the (0,1,2) peak from the Pt substrate (red circle in (c)), all of the diffraction peaks are from the Pt_5M alloy phase, columns of Bragg peaks indicated by the arrows.

Figure 6: Schematic of the CaCu_5 structure, with Gd atoms shown in red and Pt atoms in grey. (a) shows the bulk structure terminated with the hexagonal layer with a Pt_2Gd stoichiometry, and (b) shows the bulk structure terminated with the pure Pt kagomé layer. The Pt-Pt distances in the kagomé layer is shorter than in bulk Pt, opening up room to accommodate the larger Gd atoms in the layers above and below.

Figure 7: Diffraction measurements of Gd/Pt(111) and Y/Pt(111) after cycling between 0.05 and 1.0 V. The same regions in reciprocal space are shown as in Figure 5. Three weak diffraction spots at $Q_{xy} \approx 2.64 \text{ \AA}^{-1}$ and $Q_z \approx [0.9; 1.8; 3.6] \text{ \AA}^{-1}$ originate from the overlayer, as indicated by the dashed ellipses. The peak indicated by the red circle is from the Pt(111) substrate. All other peaks are from the Pt_5M bulk alloy.

Figure 7 shows the typical diffraction peaks that form on Y/Pt(111) and Gd/Pt(111) post-electrochemical potential cycling. All the features demarcated by the white dashed ellipsoids only appear after electrochemical measurements, suggesting that they are associated with the Pt overlayer; these features resemble those of the host Pt(111) substrate, although they are rotated by 30°; this rotation is identical to the orientation of the close-packed rows of Pt atoms within the kagomé layers of the Pt_5M alloy, as observed with LEED.[38, 39] For each in-plane vector of the overlayer, diffraction spots are

seen at $L=1$, $L=2$, and $L=4$, where the absence of the $L=3$ peaks indicate FCC structure like the Pt(111) substrate, but with two types of domains in the overlayer that are rotated 60° from each other. The image shows the intensity as a function of the in-plane (Q_{xy}) and out-of-plane (Q_z) components of scattering vector Q for the Gd/Pt(111) crystal after initial electrochemical potential cycling. In the figure the overlayer peaks at $Q_{xy} \approx 2.64 \text{ \AA}^{-1}$ and $Q_z \approx [0.9; 1.8; 3.6] \text{ \AA}^{-1}$ are weak and quite broad, especially in the z -direction, indicating that the overlayer is very thin.[47] The other diffraction peaks in the image originate from the Pt₅Gd alloy phase (see Figure 5). Figures 7b and c show the overlayer peaks from the Y/Pt(111) crystal; there are two different sets of overlayer peaks, one set that is rotated 30° from the Pt(111) substrate, and one set that is unrotated from the substrate.

In the second set of electrochemical experiments we cycled Gd/Pt(111) up to 1.20 V *vs.* RHE and Y/Pt(111) up to 1.30 V *vs.* RHE, following which we repeated the diffraction experiments. As shown in Figure 8a, for the Gd/Pt(111) crystal there were no significant changes as only one overlayer was still observed at 30° rotation. In case of the Y/Pt(111) crystal, the overlayer rotated 30° disappeared completely, see Figure 8b, but the unrotated overlayer was still visible, as seen in Figure 8c. Furthermore, a new overlayer seems to appear at $\pm 5^\circ$ rotation from the Pt(111), although very weak; this overlayer feature is shown in Figure 8d. This slightly rotated layer was not visible after the first electrochemical cycling between 0.05 V and 1.0 V, as seen in Figure 7d.

Figure 8: Diffraction measurements of Gd/Pt(111) and Y/Pt(111) after the second electrochemical potential cycling between 0.05 V and 1.2 V. The same regions in reciprocal space are shown as in Figures 5 and 7. The 3 weak spots seen at $Q_{xy} \approx 2.64 \text{ \AA}^{-1}$ and $Q_z \approx [0.9; 1.8; 3.6] \text{ \AA}^{-1}$ are from the overlayer, marked by the dashed ellipses. The remaining peaks are from the Pt_5Gd alloy phase, columns of Bragg peaks indicated by the arrows, except one Pt(111) substrate peak on unrotated overlayer from the Y/Pt(111) crystal, shown by the red circle.

The diffraction pattern of the overlayer suggests that the Pt overlayer has an FCC structure, similar to bulk Pt, albeit with different lattice parameters. By comparing the positions of the overlayer peaks and the Pt(111) substrate peaks, we can determine the strain in both the in-plane and out-of-plane directions. Furthermore, we can estimate the thickness and lateral domain size using *Scherrer's* formula with a shape factor of 0.886.[48] The positions and widths of the overlayer diffraction peaks were determined

by fitting a sum of a 2D Gaussian and Lorentzian, and the resulting structural parameters are shown in Figure 9 and in Table 2. Only the 30° rotated and unrotated layers on the two crystals were fitted. The $\pm 5^\circ$ rotated overlayer was too weak in its diffracted intensity to fit; moreover, upon visual inspection of the diffraction image its structure also appears to be different from the FCC structure that we found on the other overlayers.

To further investigate the structure of the overlayer, we made a number of simulations of the overlayer peaks, considering an FCC and an HCP structure, which differ from each other only in terms of layer stacking. The simulation results in S.M. Figures 5 and 6 show the diffraction patterns from a varying number of atomic layers from 1 to 9. A visual comparison to Figure 7 suggests that the overlayer on Gd/Pt(111) crystal has about 5 atomic layers and the overlayer on the Y/Pt(111) crystal only has 3 layers. This is consistent with the thickness inferred from the peak widths, as well as the AR-XPS results on the polycrystalline samples of same composition. We can also conclude that the structure of the overlayer does not have HCP stacking.

Figure 9: Schematic illustration of a pure Pt overlayers on Pt_5X alloy substrates. (a) A 30° rotated Pt overlayer on Gd/Pt(111). (b) A 30° rotated Pt overlayer on Y/Pt(111). Fitting results for the strain and domain sizes along in-plane (red) and out-of-plane directions (blue) are indicated for the two samples.

Gd/Pt(111) 30°	$U_{max} = 1.00 \text{ V vs. RHE}$	$U_{max} = 1.20 \text{ V vs. RHE}$
Strain xy (%)	-0.31 ± 0.05	-0.07 ± 0.07
Strain z (%)	0.2 ± 0.4	1.1 ± 0.7
d_{xy} (Å)	96 ± 5	105 ± 3
d_z (Å)	10.9 ± 0.3	10.8 ± 0.3
Y/Pt(111) 30°	$U_{max} = 1.05 \text{ V vs. RHE}$	$U_{max} = 1.30 \text{ V vs. RHE}$
Strain xy (%)	-1.4 ± 0.2	-
Strain z (%)	-2.3 ± 0.9	-
d_{xy} (Å)	42 ± 3	-
d_z (Å)	5.1 ± 0.1	-
Y/Pt(111) 0°	$U_{max} = 1.05 \text{ V vs. RHE}$	$U_{max} = 1.30 \text{ V vs. RHE}$
Strain xy (%)	-0.5 ± 0.2	0.2 ± 0.5
Strain z (%)	-3 ± 4	-1.4 ± 2.6
d_{xy} (Å)	61 ± 1	75 ± 5
d_z (Å)	9.7 ± 0.1	16 ± 0.6

Table 2: Fitting results showing the strain and domain sizes of the overlayers on the Gd/Pt(111) and Y/Pt(111) crystal after two different electrochemical treatments.

By estimating the domain size using the Scherrer equation, we implicitly neglect any peak broadening due to microstrain, *i.e.* inhomogeneous interatomic Pt-Pt distance in the overlayer. However, we do anticipate that the localised strain might vary significantly, which could also lead to peak broadening. Even so, we cannot distinguish the two possibilities on the basis of the XRD. Nonetheless, we can calculate a minimum and maximum value of strain. For the Gd/Pt(111) crystal the in-plane strain ranges from -1.39 % to +0.79 % after the first electrochemical cycling between 0.05 V and 1.05 V and -1.06 % to +0.94 % after the second electrochemical cycling between 0.05 V and 1.30 V. For the 30° rotated overlayer on the Y/Pt(111) crystal the in-plane strain ranges from -3.78 % to +1.02 % after the first electrochemical cycling between 0.05 V and 1.05 V; the in-plane strain in the unrotated layer ranges from -2.17 % to +1.20 % after the same treatment. After the second electrochemical cycling between 0.05 V and 1.30 V it ranges from -1.19 % to +1.61 %. These values of strain have been calculated by adding or subtracting half of the peak width at half height (HWHM) to the peak center position.

4. Theoretical Calculations

On a completely homogeneous surface, the difference in OH binding energies on Pt(111) and Gd/Pt(111) can be obtained from the electrochemical experiments, according to equation (1) [26]

$$\Delta E_{\text{Gd/Pt(111)*OH}} - \Delta E_{\text{Pt*OH}} = e(\Delta U_{*OH}) \quad (1)$$

where e is the elemental charge, $\Delta E_{\text{Gd/Pt(111)*OH}}$ and $\Delta E_{\text{Pt*OH}}$ are the OH binding energies on Gd/Pt(111) and Pt(111), respectively. ΔU_{*OH} is the difference in potential of Gd/Pt(111) relative to Pt(111) for adsorbing a fixed amount of charge corresponding to a given coverage of OH. By integrating charge in the cyclic voltammogram shown in Figure 2, we estimate a shift of around 0.1 V in U_{*OH} for Gd/Pt(111), relative to Pt(111) (see Table 1). We can also estimate the change in binding energy for H using a similar relationship

$$\Delta E_{\text{H*Gd/Pt(111)}} - \Delta E_{\text{H*Pt}} = -e(\Delta U_{*H}) \quad (2)$$

where $\Delta E_{\text{H*Gd/Pt(111)}}$ and $\Delta E_{\text{H*Pt}}$ are the binding energies of H on Gd/Pt(111) and Pt(111), respectively, and ΔU_{*H} is the shift in potential at a given coverage of H. The potential shift for hydrogen adsorption is around 0.07 V at 1/4 ML. Based on earlier DFT calculations,[49] the shift in OH binding would correspond to a strain of -3.5 %, whereas the shift in H binding would correspond to a strain of -3.0 %. Both values are significantly greater than the strain we measured in the overlayer. See S.M. Section 4 for more details regarding these calculations.

Figure 10: Oxygen reduction volcano as a function of lateral strain (lower x -axis) and OH binding energy (upper x -axis), relative to Pt(111). The relation between the strain and shift in OH binding energy is based on DFT calculations.[49] The blue dashed line is the thermodynamic Sabatier analysis, representing the upper limit to activity, neglecting additional kinetic barriers.[50] The activity of Y/Pt(111) and Gd/Pt(111) are plotted *versus* their measured strain on the bottom axis (down-triangles with black edge), and *versus* the voltametric shift on the top axis (up-triangles with blue edge). The error bar in the strain corresponds to the microstrain. For comparison, the blue circles represent the activity of the Cu/Pt(111) near surface alloys[26] and the square vacuum annealed Pt₃Ni(111),[18] both plotted as a function of voltammetric shift for OH adsorption, which we assume to be equal to the shift in OH binding. The Gd/Pt(111) activity enhancement is based on several activity measurements of both Gd/Pt(111) and Pt(111) at 23 °C, whereas the Y/Pt(111) activity enhancement is based on a single measurement of Y/Pt(111) and Pt(111) at 60 °C.

5 Discussion

Evidently, for Gd/Pt(111) and Y/Pt(111) a vacuum annealed Pt overlayer structure is not stable when exposed to the electrolyte. This clearly contrasts with the smooth, monolayer-thick annealed Pt overlayers formed on Pt₃Ni(111)[18] and Cu/Pt(111) near-surface alloys,[26] which were stable under ORR conditions. This could partially be due to the increased interactions between adsorbed HO* and O*, and the solute metal in the second surface layer on the rare earth alloys, Y and Gd. Moreover, the greater degree of compressive strain in the bulk of Pt₅Gd and Pt₅Y, relative to those other alloys, could facilitate leaching from the subsurface layer.[39]

Our observation that the Pt overlayer on the dealloyed single crystal surfaces is under compressive strain is consistent with our EXAFS experiments on Pt_xGd and Pt_xY nanoparticles, post-electrochemistry. [32, 33] The mean value of the strain on the overlayer of Gd/Pt(111), at -0.31 %, is very low in comparison to the compression of the nearest-neighbour distance in the bulk of the alloy layer, and at 2.665 Å this is equivalent to 3.9 % compression. Likewise, on the overlayer of the unrotated Y/Pt(111), it is -0.5 %. Based on Table 2, it also seems that the strain is correlated with the thickness of the overlayer. Thus, we can conjecture that the strain relaxes further as the thickness increases. This interpretation is consistent with observations on single crystals based on Cu and Pt.[37, 51] On the other hand, on the Y/Pt(111) overlayer rotated by 30°, the compression is -1.4 %. As we suggested in Section 4, above, the measured strain is lower than we would expect if we were to assume that the shift in the voltammogram is purely due to compressive strain.

Figure 10 shows a volcano plot, where the oxygen reduction activity, relative to Pt(111) is plotted as function of both OH binding energy (upper x -axis), and lateral strain (lower x -axis), by virtue of the linear relationship between OH binding and strain.[49] The open circles represent the activity of the Cu/Pt(111) near-surface alloy[26] and the open square represents that of Pt₃Ni(111),[18] both plotted as a function of the voltammetric shift in OH peak as an estimate of the OH binding energy, equation (1). We have also plotted the thermodynamic Sabatier-volcano[50] (note that the lower magnitude of the experimental enhancement over Pt(111), relative to that predicted by the theoretical thermodynamic Sabatier-volcano, is likely due to kinetic effects[50, 52]). We have located the position of the Gd/Pt(111) points and Y/Pt(111) data points on the x -axis according to (a) the voltammetric shift in OH adsorption,

ΔU_{*OH} , shown as up-triangles with a blue outline, and (b) the measured strain, shown as down-triangles with a black outline. On the basis of the voltammetric shift, and comparing our data to the earlier experimental data on other alloys, the activity of Y/Pt(111) and Gd/Pt(111) is lower than we would expect. [18, 26] On the other hand, comparing the activity with the measured strain in the overlayer, it is evident that the activity of Y/Pt(111) and Gd/Pt(111) is higher than we would expect.

We can account for this offset between our expectations and the actual enhancement on several accounts. The relationship between OH binding energy and voltammetric shift from equation (1) only holds for homogenous surfaces, such as Cu/Pt(111) near-surface alloys[26] and Pt₃Ni(111),[18] as shown on the plot. Although the acid-leached overlayers are crystalline, they are likely to be somewhat heterogeneous. Such heterogeneity is consistent with the large microstrain we estimate in the overlayer on Y/Pt(111) and Gd/Pt(111), represented as error bar in the x -axis on Figure 10. We note that the oxygen reduction activity will be dominated by the sites with the closest to optimum OH binding, whereas the voltammetric shift and the strain in the overlayer are more representative of the entire surface. We also acknowledge that in terms of catalysis, it is the actual surface layer which controls the activity, whereas we are probing the overall strain in the overlayer. Ideally, we would probe the surface layer, post-electrochemistry using UHV based techniques such as LEED[38, 39] or scanning tunnelling microscopy.[53-55] However, our current setup precludes this possibility: the transfer from the electrochemical cell to the UHV chamber through the laboratory air builds up a layer of adventitious contamination. To this end, we are currently in the process of building an electrochemical cell which is directly attached to an UHV chamber. It would be of particular interest to probe whether the oxygen reduction activity might be related to defects such as surface steps[56-58] or surface cavities,[59] in addition to compressive strain.

Finally, it is worth perusing upon the complete relaxation of the strain and loss of order in the overlayer exposed to more positive potentials. This observation explains our data on polycrystalline Pt₅Gd, where upon cycling to 1.2 V, the catalytic activity degraded rapidly.[31] Presumably the cause of this is due to subsurface oxide formation and its subsequent reduction.[60, 61]

6 Conclusion

In summary, we have fabricated Y/Pt(111) and Gd/Pt(111) by vacuum deposition. Subsequent ORR activity measurements show an enhancement over Pt(111) by a factor of 4. The single crystals show overlayers of 3-5 atomic layers upon exposure to electrolyte. We confirm that the overlayers are compressed. Upon electrochemical potential cycling between 0.1 V *vs.* RHE and >1.2 V *vs.* RHE, the strain in the overlayer is strongly reduced, which should result in a significant decrease in ORR activity. Peak broadening suggests that some of the domains may have a distribution of strain; we expect that the most strained regions will dominate the oxygen reduction activity. Future studies in this direction will aim to elucidate the actual structure of the first surface layer.

Acknowledgments

We gratefully acknowledge EU PF7's initiative Fuel Cell and Hydrogen Joint Undertaking's project CathCat (GA 303492), as well as the Strategic Research's project NACORR (12-133817) for funding this work. MEE acknowledges the Danish Council for Independent Research for the Sapere Aude: DFF Research Talent Grant. The use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. We also thank Apurva Mehta and Chad Miller for invaluable assistance with both synchrotron data acquisition and processing. AFP also thanks the Danish Ministry of Higher Education and Science is acknowledged for an EliteForsk travel grant making an extended stay at SLAC possible. Ifan Stephens is the recipient of Peabody Visiting Associate Professorship from the Department of Mechanical Engineering at Massachusetts Institute of Technology.

Vitae

Anders Filsø Pedersen is a PhD student in the group of Professor Ib Chorkendorff and Associate Professor Ifan Stephens at the Department of Physics at the Technical University of Denmark (DTU). His co-supervisor is Professor Andes Nilsson, and he spends most time at the Stanford Linear Accelerator Center National Laboratory at Stanford University in California. His research interest lies in synchrotron research on Pt alloys, as well as oxides for the oxygen evolution reaction. In 2015 he received an EliteForsk travel grant from the Ministry of Higher Education and Science.

Elisabeth Therese Ulrikkeholm is a Post Doc at the Center for individual Nanoparticle Functionality (CINF). The focus of her research is mainly on the behavior of single crystal alloys. She obtained her Masters degree in physics from the Niels Bohr Institute (University of Copenhagen) in 2010. In 2014 she obtained her PhD from the Department of Physics, at the Technical University of Denmark, under the supervision of Professor Ib Chorkendorff.

María Escudero Escribano received her PhD in Chemistry from the Autonomous University of Madrid (2011). In 2012, she joined the Electrocatalysis Group at the Department of Physics at the Technical University of Denmark (DTU), as a postdoctoral researcher. She received several prizes for her work, including the *Suschem Young Chemistry Researcher Award* 2011 and the *Sapere Aude: Research Talent Grant* 2014 (Danish Council for Independent Research). She currently carries out her research at Stanford University and DTU. Her research combines electrochemical techniques with *in situ* X-ray based measurements, spectroscopies and microscopies, in order to investigate problems pertaining to electrochemical energy conversion.

Tobias Johansson researched his PhD at the Center for Individual Nanoparticle Functionality in the Department of Physics at the Technical University of Denmark (DTU) in 2012. The main focus of his PhD thesis was the study of alloy materials as catalysts for the oxygen reduction reaction. He continued his research in catalysis as a postdoctoral researcher at DTU. He combined electrocatalysis, ultra-high vacuum experiments and insight from DFT to elucidate the oxygen reduction reaction, ammonia synthesis and CO electroreduction.

Paolo Malacrida obtained his PhD in Physics at the Technical University of Denmark (DTU) in 2014, under the supervision of Professor Ib Chorkendorff. Both his PhD and his following experience as a postdoctoral researcher in the same group were focused on the study of novel cathode materials for PEMFC. He gained particular experience with the application and development of spectroscopic techniques such as X ray photoelectron spectroscopy, ultraviolet photoelectron spectroscopy and ion scattering spectroscopy applied to electrocatalysts, in particular Pt-based alloys. He is currently employed at Novo Nordisk A/S.

Christoffer Mølleskov Pedersen is an industrial PhD student in the group of Professor Ib Chorkendorff and Associate Professor Ifan Stephens at the Department of Physics at the Technical University of Denmark (DTU), as part of the Industrial PhD Programme of the Danish Council for Technology and Innovation (DCTI). His co-supervisor is Leif H. Christensen from the Danish Technological Institute (DTI). He is developing catalysts for direct methanol fuel cells, specifically for the methanol oxidation and oxygen reduction reaction.

Martin Hangaard Hansen is a PhD student with the Center for Atomic-scale Materials design at the Department of Physics, the Technical University of Denmark (DTU). He obtained his Masters degree in Physics and Nanotechnology from DTU in 2013 under the supervision of Prof. Jan Rossmeisl, with whom he continued as a PhD student. His research is focused on electrocatalysis and new methods for modeling the electrolyte-electrode interface with density functional theory.

Kim Degn Jensen obtained his B.Sc. and M.Sc. in Physics at the Technical University of Denmark (DTU) 2006-2012. He worked at Grundfos Direct Sensors™ from 2012-2015. He is currently pursuing his PhD at DTU Physics, at CINF, under guidance and supervision of Prof. Ib Chorkendorff, Associate Prof. Ifan Stephens and Dr. María Escudero Escribano. His PhD thesis aims to study the oxygen reduction reaction (ORR) electrocatalysis for proton exchange membrane fuel cells. He is currently investigating the ORR activity of model Pt(111) surface and subsurface alloys, as well as the poisoning effect by spectator species such as phosphate anions.

Jan Rossmeisl is Professor of theoretical chemistry at Department of Chemistry and the Nano-Science center at Copenhagen University. Before joining University of Copenhagen in April 2015, Jan was an Associate Professor and group leader for the theoretical catalysis group at Department of Physics at the Technical University of Denmark. Jan holds Masters (2000) and PhD (2004) degrees in physics from the Technical University of Denmark. Since 2007 he has supervised more than 20 PhD students and post doctoral researchers. He is coauthor on more than 110 publications in peer reviewed journals, co-inventor of 4 patents and co-founder of two startup companies. Research interests include: electrocatalysis, energy conversion, atomic scale simulations, rational interface design for catalysis.

Daniel Friebe obtained his PhD in Chemistry at Bonn University in Germany where he used scanning tunneling microscopy to image solid/liquid interfaces with atomic resolution. In 2007, a postdoctoral research fellowship from Alexander von Humboldt Foundation brought him to Anders Nilsson's Surface Science and X-ray Spectroscopy Group at SLAC National Accelerator Laboratory, and he

became Associate Staff Scientist in 2012. His research at SLAC focuses on the development of in situ and operando x-ray spectroscopy and scattering techniques to study catalytic reactions for sustainable energy conversion.

Anders Nilsson received a PhD in physics at Uppsala University, Sweden (1989) in the laboratory created by Kai Siegbahn. He is currently professor in Chemical Physics at Stockholm University and in Photon Science at the SLAC National Accelerator Laboratory and Stanford University. He received the Lindbomska Award at the Swedish Royal Academy of Science, the Royal Oscar Award at Uppsala University in 1994, the Shirley Award in Berkeley 1998, the Humboldt Award for senior scientist in 2010 and was awarded honorable doctor at Denmark's Technical University in 2015. His research interests include synchrotron radiation and x-ray laser spectroscopy and scattering, chemical bonding and reactions on surfaces, ultrafast science heterogeneous catalysis, electrocatalysis in fuel cells, photocatalysis for converting sunlight to fuels, structure of water and aqueous solutions.

Professor Ib Chorkendorff got his PhD in 1985 in experimental surface science from Odense University, Denmark. After working as a post-doc with Prof. John T. Yates Jr. at University of Pittsburgh, USA, he was employed in 1987 at DTU to establish an experimental activity, investigating fundamental aspects of heterogeneous catalysis. In 2005 he established the Center for Individual Nanoparticle Functionality (CINF), and broadened these activities to include technologies for producing solar fuels utilising electro- and photo-catalysis, for finding new and effective materials for improving sustainable energy conversion and environmental protection. Ib Chorkendorff is currently consulting Professor at SUNCAT at Stanford University.

Ifan Stephens leads the Electrocatalysis Group at the Department of Physics at the Technical University of Denmark (DTU). He obtained his PhD in Materials Science at the University of Cambridge. He first joined DTU in 2008 as a postdoctoral researcher and became a member of faculty in 2011. He currently holds the position of Associate Professor. In 2015, he was awarded the Peabody Visiting Associate Professorship by the Department of Mechanical Engineering at the Massachusetts Institute of

Technology. He conducts frontier research into the elucidation and testing of electrocatalytic surfaces. The aim of his investigations is to enable and accelerate the development of electrochemical devices for energy conversion and chemical synthesis.

- [1] O. Groger, H.A. Gasteiger, J.P. Suchsland, *J. Electrochem. Soc.*, 162 (2015) A2605-A2622.
- [2] M.K. Debe, *Nature*, 486 (2012) 43-51.
- [3] H.A. Gasteiger, N.M. Markovic, *Science*, 324 (2009) 48-49.
- [4] F.T. Wagner, B. Lakshmanan, M.F. Mathias, *J. Phys. Chem. Lett.*, 1 (2010) 2204-2219.
- [5] S. Mukerjee, S. Srinivasan, M.P. Soriaga, J. McBreen, *J. Electrochem. Soc.*, 142 (1995) 1409-1422.
- [6] T. Toda, H. Igarashi, H. Uchida, M. Watanabe, *J. Electrochem. Soc.*, 146 (1999) 3750-3756.
- [7] C. Chen, Y.J. Kang, Z.Y. Huo, Z.W. Zhu, W.Y. Huang, H.L.L. Xin, J.D. Snyder, D.G. Li, J.A. Herron, M. Mavrikakis, M.F. Chi, K.L. More, Y.D. Li, N.M. Markovic, G.A. Somorjai, P.D. Yang, V.R. Stamenkovic, *Science*, 343 (2014) 1339-1343.
- [8] B.H. Han, C.E. Carlton, A. Kongkanand, R.S. Kukreja, B.R. Theobald, L. Gan, R. O'Malley, P. Strasser, F.T. Wagner, Y. Shao-Horn, *Energy Environ. Sci.*, 8 (2015) 258-266.
- [9] N. Todoroki, T. Kato, T. Hayashi, S. Takahashi, T. Wadayama, *Acs Catalysis*, 5 (2015) 2209-2212.
- [10] F. Maillard, L. Dubau, J. Durst, M. Chatenet, J. Andre, E. Rossinot, *Electrochemistry Communications*, 12 (2010) 1161-1164.
- [11] F. Hasche, M. Oezaslan, P. Strasser, *J. Electrochem. Soc.*, 159 (2012) B25-B34.
- [12] S. Chen, H.A. Gasteiger, K. Hayakawa, T. Tada, Y. Shao-Horn, *J. Electrochem. Soc.*, 157 (2010) A82-A97.
- [13] K.J.J. Mayrhofer, V. Juhart, K. Hartl, M. Hanzlik, M. Arenz, *Angew. Chem.-Int. Edit.*, 48 (2009) 3529-3531.
- [14] K. Sasaki, H. Naohara, Y.M. Choi, Y. Cai, W.F. Chen, P. Liu, R.R. Adzic, *Nat. Commun.*, 3 (2012).
- [15] X.Q. Huang, Z.P. Zhao, L. Cao, Y. Chen, E.B. Zhu, Z.Y. Lin, M.F. Li, A.M. Yan, A. Zettl, Y.M. Wang, X.F. Duan, T. Mueller, *Y. Huang, Science*, 348 (2015) 1230-1234.
- [16] L. Dubau, M. Lopez-Haro, L. Castanheira, J. Durst, M. Chatenet, P. Bayle-Guillemaud, L. Guetaz, N. Caque, E. Rossinot, F. Maillard, *Appl. Catal. B-Environ.*, 142 (2013) 801-808.
- [17] G.A. Tritsarlis, J. Greeley, J. Rossmeisl, J.K. Nørskov, *Catal. Lett.*, 141 (2011) 909-913.
- [18] V.R. Stamenkovic, B. Fowler, B.S. Mun, G.F. Wang, P.N. Ross, C.A. Lucas, N.M. Markovic, *Science*, 315 (2007) 493-497.
- [19] D.G. Li, C. Wang, D.S. Strmcnik, D.V. Tripkovic, X.L. Sun, Y.J. Kang, M.F. Chi, J.D. Snyder, D. van der Vliet, Y.F. Tsai, V.R. Stamenkovic, S.H. Sun, N.M. Markovic, *Energy Environ. Sci.*, 7 (2014) 4061-4069.
- [20] H. Lv, D. Li, D. Strmcnik, A.P. Paulikas, N.M. Markovic, V.R. Stamenkovic, *Nano Energy*.
- [21] J.K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J.R. Kitchin, T. Bligaard, H. Jonsson, *Journal of Physical Chemistry B*, 108 (2004) 17886-17892.
- [22] J. Greeley, I.E.L. Stephens, A.S. Bondarenko, T.P. Johansson, H.A. Hansen, T.F. Jaramillo, J. Rossmeisl, I. Chorkendorff, J.K. Nørskov, *Nature Chemistry*, 1 (2009) 552-556.
- [23] V.R. Stamenkovic, B.S. Mun, K.J.J. Mayrhofer, P.N. Ross, N.M. Markovic, *J. Am. Chem. Soc.*, 128 (2006) 8813-8819.
- [24] L.J. Wan, T. Moriyama, M. Ito, H. Uchida, M. Watanabe, *Chemical Communications*, (2002) 58-59.
- [25] J.R. Kitchin, J.K. Nørskov, M.A. Barteau, J.G. Chen, *J. Chem. Phys.*, 120 (2004) 10240-10246.
- [26] I.E.L. Stephens, A.S. Bondarenko, F.J. Perez-Alonso, F. Calle-Vallejo, L. Bech, T.P. Johansson, A.K. Jepsen, R. Frydendal, B.P. Knudsen, J. Rossmeisl, I. Chorkendorff, *J. Am. Chem. Soc.*, 133 (2011) 5485-5491.
- [27] M. Mavrikakis, B. Hammer, J.K. Nørskov, *Physical Review Letters*, 81 (1998) 2819-2822.
- [28] U. Grønbjerg Vej-Hansen, J. Rossmeisl, I.E.L. Stephens, J. Schiøtz, *Physical Chemistry Chemical Physics*, accepted (2015).

- [29] I.E.L. Stephens, A.S. Bondarenko, L. Bech, I. Chorkendorff, *Chemcatchem*, 4 (2012) 341-349.
- [30] P. Malacrida, M. Escudero-Escribano, A. Verdaguer-Casadevall, I.E.L. Stephens, I. Chorkendorff, *Journal of Materials Chemistry A*, 2 (2014) 4234-4243.
- [31] M. Escudero-Escribano, A. Verdaguer-Casadevall, P. Malacrida, U. Grønbjerg, B.P. Knudsen, A.K. Jepsen, J. Rossmeisl, I.E.L. Stephens, I. Chorkendorff, *J. Am. Chem. Soc.*, 134 (2012) 16476-16479.
- [32] P. Hernandez-Fernandez, F. Masini, D.N. McCarthy, C.E. Streb, D. Friebe, D. Deiana, P. Malacrida, A. Nierhoff, A. Bodin, A.M. Wise, J.H. Nielsen, T.W. Hansen, A. Nilsson, I.E.L. Stephens, I. Chorkendorff, *Nature Chemistry*, 6 (2014) 732-738.
- [33] A. Velázquez-Palenzuela, F. Masini, A.F. Pedersen, M. Escudero-Escribano, D. Deian, P. Malacrida, T.W. Hansen, D. Friebe, A. Nilsson, I.E.L. Stephens, I. Chorkendorff, *J. Catal.*, *in press* DOI: 10.1016/j.jcat.2014.12.012 (2015).
- [34] W. Bronger, *Journal of the Less-Common Metals*, 12 (1967) 63-&.
- [35] W.P. Zhou, X.F. Yang, M.B. Vukmirovic, B.E. Koel, J. Jiao, G.W. Peng, M. Mavrikakis, R.R. Adzic, *J. Am. Chem. Soc.*, 131 (2009) 12755-12762.
- [36] T. Wadayama, N. Todoroki, Y. Yamada, T. Sugawara, K. Miyamoto, Y. Iijima, *Electrochemistry Communications*, 12 (2010) 1112-1115.
- [37] R. Yang, J. Leisch, P. Strasser, M.F. Toney, *Chem. Mat.*, 22 (2010) 4712-4720.
- [38] E.T. Ulrikkeholm, A.F. Pedersen, U.G. Vej-Hansen, M. Escudero-Escribano, I.E.L. Stephens, A. Mehta, J. Schiøtz, R.K. Feidenhans'l, A. Nilsson, I. Chorkendorff, *Surf. Sci.*, *in press* (2016).
- [39] T.P. Johansson, E.T. Ulrikkeholm, P. Hernandez-Fernandez, M. Escudero-Escribano, P. Malacrida, I.E.L. Stephens, I. Chorkendorff, *Physical Chemistry Chemical Physics*, 16 (2014) 13718-13725.
- [40] Y. Gründer, C.A. Lucas, *Nano Energy*, *in press* (2016).
- [41] J. Clavilier, R. Faure, G. Guinet, R. Durand, *J. Electroanal. Chem.*, 107 (1980) 205-209.
- [42] D. Friebe, D.J. Miller, C.P. O'Grady, T. Anniyev, J. Bargar, U. Bergmann, H. Ogasawara, K.T. Wikfeldt, L.G.M. Pettersson, A. Nilsson, *Physical Chemistry Chemical Physics*, 13 (2011) 262-266.
- [43] N.M. Marković, P.N. Ross, *Surf. Sci. Rep.*, 45 (2002) 117.
- [44] H.E. Hoster, O.B. Alves, M.T.M. Koper, *ChemPhysChem*, 11 (2010) 1518-1524.
- [45] A.M. Gomez-Marin, J.M. Feliu, *Catal. Today*, 244 (2015) 172-176.
- [46] J. Clavilier, A. Rodes, K. Elachi, M.A. Zamakhchari, *Journal De Chimie Physique Et De Physico-Chimie Biologique*, 88 (1991) 1291-1337.
- [47] D.-M. Smilgies, *Journal of Applied Crystallography*, 46 (2013) 286-286.
- [48] D.M. Smilgies, *Journal of Applied Crystallography*, 42 (2009) 1030-1034.
- [49] M. Escudero-Escribano, P. Malacrida, M.H. Hansen, U.G. Vej-Hansen, A. Velazquez-Palenzuela, V. Tripkovic, J. Schiøtz, J. Rossmeisl, I.E.L. Stephens, I. Chorkendorff, *Science*, 352 (2016) 73-76.
- [50] J. Rossmeisl, G.S. Karlberg, T. Jaramillo, J.K. Nørskov, *Faraday Discussions*, 140 (2008) 337-346.
- [51] P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C.F. Yu, Z.C. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M.F. Toney, A. Nilsson, *Nature Chemistry*, 2 (2010) 454-460.
- [52] H.A. Hansen, V. Viswanathan, J.K. Nørskov, *J. Phys. Chem. C*, 118 (2014) 6706-6718.
- [53] A.K. Engstfeld, S. Brimaud, R.J. Behm, *Angew. Chem.-Int. Edit.*, 53 (2014) 12936-12940.
- [54] N. Todoroki, Y. Asakimori, T. Wadayama, *Physical Chemistry Chemical Physics*, 15 (2013) 17771-17774.
- [55] M. Mercer, H. Hoster, *Nano Energy*, accepted (2016).
- [56] A. Kuzume, E. Herrero, J.M. Feliu, *J. Electroanal. Chem.*, 599 (2007) 333-343.
- [57] A. Hitotsuyanagi, M. Nakamura, N. Hoshi, *Electrochimica Acta*, 82 (2012) 512-516.
- [58] K. Kodama, R. Jinnouchi, N. Takahashi, H. Murata, Y. Morimoto, *J. Am. Chem. Soc.*, 138 (2016) 4194-4200.
- [59] F. Calle-Vallejo, J. Tymoczko, V. Colic, Q.H. Vu, M.D. Pohl, K. Morgenstern, D. Loffreda, P. Sautet, W. Schuhmann, A.S. Bandarenka, *Science*, 350 (2015) 185-189.
- [60] H. You, D.J. Zurawski, Z. Nagy, R.M. Yonco, *J. Chem. Phys.*, 100 (1994) 4699-4702.
- [61] M. Wakisaka, S. Asizawa, H. Uchida, M. Watanabe, *Physical Chemistry Chemical Physics*, 12 (2010) 4184-4190.