DEALLOYED CORE-SHELL FUEL CELL ELECTROCATALYSTS

Peter Strasser¹²

¹Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204 USA
²Institut fuer Chemie, Technische Universitaet Berlin, 10624 Berlin, Germany

ABSTRACT

We review our recent work on dealloyed nanoparticle electrocatalysts and address their synthesis, structural characterization and surface catalytic performance in low-temperature Polymer Electrolyte Membrane fuel cells (PEMFCs). The active form of the catalyst is obtained by voltammetric dealloying of non-noble metal rich Pt alloy precursors. In the dealloying process, the less noble precursor component, here Cu, is selectively removed from the surface of the precursor alloy particles and hence a Pt enriched particle shell is formed. Single fuel cell tests showed that, when used on the cathode of PEMFCs, dealloyed Pt catalysts show reactivities for the oxygen reduction reaction (ORR) which are up to 6 times higher than those of conventional pure Pt fuel cell catalysts. Similarly, the stability of dealloyed nanoparticle catalysts is superior to that of pure Pt particles. X-ray based structural and compositional studies suggested a core–shell particle structure as the active form of the catalyst consisting of a Pt enriched particle shell surrounding a Pt alloy core. At the present time, this catalyst system constitutes one of the most active fuel cell catalyst system reported in the literature.

I. THE CONCEPT OF DEALLOYED NANOPARTICLE CATALYSTS

Despite much recent focus on the development of advanced Li ion batteries for use as power source for short-range inner city transportation
applications, low temperature fuel cells continue to be the solution of choice for medium and long range transportation technologies based on their gravimetric power density as well as the gravimetric energy density of commonly used fuels\textsuperscript{9,8}. Wider use of low-temperature fuel cell technology is hampered by performance, cost, and durability issues associated with materials and components of a single fuel cell. Figure 1 displays a cross section of the layered structure of a low temperature PEMFC showing the anode (left) and cathode (right) gas diffusion layers (GDLs), which sandwich the anode and cathode catalyst layers and the proton exchange membrane. Figure 1 also schematically shows the molecular as well as electrical pathways of hydrogen fuel molecules, oxygen molecules, protons as well as electrons. The overall performance of a PEMFC in terms of its practical cell voltage is limited by kinetic, ohmic, and mass transport processes for low, medium and high current densities, respectively. Of these, the kinetic surface catalytic reactions cause the most severe fuel cell voltage losses.

\[ \text{Anode: } \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \]

\[ \text{Cathode: } \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \]

**Fig. 1:** Cross sectional SEM micrograph through a membrane electrode assembly sandwiched between gas diffusion layers. Reaction processes at anode and cathode, mass and charge flows are indicated (from ref \textsuperscript{36})

In particular, the electrocatalytic Oxygen Reduction Reaction (ORR) at the cathode according to

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad E^0 = +1.23 \text{ V/ RHE} \] (1)

represents the key challenge to improved PEMFCs\textsuperscript{8-10}. In acidic media, Pt catalysts offer the highest catalytic activities which made first unsupported, later high surface area carbon-supported Pt particles the ORR catalyst of
choice\textsuperscript{11, 12}. Figure 2 illustrates the associative (via O\textsubscript{2}H) as well as the dissociative (via O) pathways of reaction (1) from molecular oxygen to water. Key for the catalysis is the chemisorption energy of the adsorbed oxygenated intermediates, such as Pt-O\textsubscript{2}H, Pt-O, and Pt-OH\textsuperscript{13}. On pure Pt, atomic oxygen is bonded too strongly and requires considerable overpotentials to react to Pt-OH. As a result of this, Pt is covered by (hydr)oxide adsorbates near the equilibrium potential of reaction (1). There is a consensus within the fuel cell catalysis community that a moderate reduction of the Pt-O chemisorption energy would result in significant ORR activity increases.

Fig. 2: The mechanism of the electrochemical oxygen reduction reaction on a Pt nanoparticle. Molecular oxygen reacts either in a dissociative or associative pathway. On surfaces which show low oxygen chemisorption energies, hydrogen peroxide formation is possible. Stepwise protonation and reduction results in the formation of adsorbed water molecules. The chemisorption energy of oxygenated intermediates control the rate of the overall reaction (from ref\textsuperscript{36})
Dating back to catalysis research for phosphoric acid fuel cells (PAFCs), many experimental ORR catalysis studies during the 1990s focused on Pt-rich bulk alloys which typically exhibit an intrinsic activity improvement of a factor of 2-3x at 900 mV cell voltage compared to pure Pt.

Later, other promising ORR catalyst concepts emerged. A concise comparative overview of the most promising ORR catalysts is provided by Gasteiger and Markovic. First, Adzic and coworkers reported on a “Pt monolayer catalyst concept”, that is, catalysts that consist of single monolayer of Pt adatoms supported on a non-Pt metal surface, such as Pd. This concept offers first and foremost a tremendous advantage in terms of the Pt dispersion resulting in significant ORR reactivity improvements on a Pt mass basis. However, taking the mass of the supporting noble metal into account as well, these catalysts offer noble metal mass activity improvements comparable to those of uniformly alloyed Pt rich ORR catalysts. Second, research at Argonne National Laboratory reported on “Pt skin electrocatalysts”. Pt Skin catalysts are surface segregated Pt rich alloys where a monolayer of pure Pt forms on top of a non-Pt metal (“M”) enriched second layer, followed by subsequent alloy layers approaching the typical bulk composition Pt35M25. In particular, a pure Pt skin supported on a Pt75Ni25(111) single crystal surface exhibit significantly improved specific, that is, Pt surface area based, ORR activity of up to a factor of 10x compared to the respective pure Pt surface at 900 mV RHE. Nanoparticles exhibiting only Pt75Ni25(111) facets therefore represent a promising high surface area catalyst concept, however, such facet-controlled particles have not been prepared to date. When prepared in a polycrystalline format the ORR activity of Pt-Ni catalysts reduce to levels of 2-3x over pure Pt.

Here, we address a novel catalyst concept referred to as “Dealloyed Pt electrocatalysts”. Dealloying is the selective removal of a less noble component from a bimetallic alloy where the competition of dissolution and surface diffusion give rise to three dimensional metal removal and restructuring inside the bulk of the alloy. Dealloyed Pt catalysts are extremely active materials for the ORR catalysis in terms of their noble-metal mass based ORR activity as well as their intrinsic surface area normalized activity. Dealloyed catalysts lend themselves well for use in high-surface area catalyst formats as used in Membrane Electrode Assemblies (MEAs) of Polymer Electrolyte fuel cells (PEMFCs).
Figure 3 sketches the principle of the dealloying process. A bimetallic alloy precursor consisting of a more noble and a less noble component is rich in the less noble component and undergoes an electrochemical treatment which selectively removes the less noble metal from the surface of the alloy nanoparticle. This is assumed to lead to a Pt enriched surface region (particle shell).

![Diagram of dealloying process](image)

**Fig. 3:** Selective surface dissolution of Cu (dealloying) of a Cu-rich Pt-Cu alloy precursor results in a core-shell particle structure (from ref 36)

In contrast to the “Pt skin” and the “Pt monolayer” catalysts, however, the thickness of the nearly pure Pt shell of the dealloyed particles can be controlled by choice of dealloying conditions. Typically, the Pt shell consists of multiple Pt layers compared to a single Pt monolayer in ‘skin’ and ‘monolayer’ catalysts. This has interesting implications with respect to the mechanistic origin of catalytic reactivity enhancements on dealloyed surfaces. Dealloying processes of bimetallic bulk alloys (macroscopic samples or flat surfaces) have been studied for decades by corrosion scientists, however, the dealloying processes of bimetallic nanoparticle
objects, the controlling factors and the resulting structures have never been studied to date\textsuperscript{54-61}.

Aside from ORR fuel cell catalysis, recent research also revealed that dealloying can be used as a general strategy to modify catalytic reactivity for other reactions such as the Oxygen Evolution reaction (OER) or the Hydrogen Evolution Reaction (HER)\textsuperscript{62}. In this article, we also would like to highlight the fundamental mechanistic and structural aspects of dealloying processes of bimetallic nanoscale objects. Dealloying can be viewed as a novel synthetic strategy for the preparation of nanostructured objects unobtainable by conventional deposition-type syntheses.

2. SYNTHESIS AND CHARACTERIZATION OF ALLOY CATALYST PRECURSORS

Dealloyed Pt ORR electrocatalysts are prepared from bimetallic alloy precursors consisting of Pt and a less noble metal ‘M’. The alloy precursor is generally rich in the less noble component, that is, it exhibits stoichiometries of Pt\textsubscript{x}M\textsubscript{1-x} with x=0.2 – 0.5. The less noble metal M should be miscible with Pt and not segregate into the bulk of the alloy. Copper fulfills this condition well and seems the metal of choice. Selective bulk Cu dissolution (dealloying) from Au-Cu and Pt-Cu has previously been investigated on smooth extended alloy surfaces where it resulted in highly porous Pt surfaces\textsuperscript{54, 58, 63-66}.

The stepwise synthesis of Cu rich precursor materials involves the impregnation of aqueous Cu salt solutions, such as Cu nitrates, onto weighted amounts of highly dispersed carbon-supported Pt nanoparticles. The impregnation is followed by freeze drying, chemical reduction, and thermal alloying of the carbon/ Pt particle / Cu salts composite. Detailed synthesis procedures of Pt-Cu precursor catalysts were reported in references \textsuperscript{38, 40, 44, 46-48, 50}. Surfactants or polymers have also been used to improve the dispersion of the catalyst precursors\textsuperscript{67}, yet the complete removal of the surfactant/polymer has remained a challenge. Freeze drying has been found to result in fine carbon supported catalyst powders which lent themselves well for the preparation of uniform catalyst thin films on polished Glassy Carbon electrode disks.
Figure 4 shows the X-ray diffraction profiles of three Pt$_{25}$Cu$_{75}$ precursor catalysts annealed at 600 °C, 800 °C, and 950 °C. The overall peak profiles suggest the formation of disordered face center cubic (fcc) Pt-Cu alloys with a broad fundamental (111) reflection located at angles in between the fundamental (111) reflections of pure Pt and pure Cu. The peak position of the alloy (111) peak can be related to the Cu content of the alloy using Vegard’s law which holds well for disordered face centered cubic Pt-Cu alloys$^{68,69}$. Figure 4 further suggests that annealing at 600 °C and 800 °C is insufficient to alloy all Cu atoms completely with Pt particles. This is why excess pure Cu phase reflections (sharp reflections) remain visible in the alloy XRD profile; their sharp peak features indicate large-diameter pure Cu particles. The material annealed at 950°C shows some ordering seen by the faint super-lattice peak around 20 – 34°. A more detailed alloy phase analysis is reported for all three temperatures in the last three columns of Table 1$^{48}$. It is seen that the fcc alloy lattice parameters decrease with increasing Cu content (lattice contraction with more Cu according to Vegard’s law), while the alloy uniformity improves for increasing annealing temperatures.

![Fig. 4: X-ray diffraction profiles of carbon-supported Pt$_{25}$Cu$_{75}$ alloy nanoparticle precursor annealed at three different temperatures (from ref. 48)](image-url)
Table 1
Comparison of catalyst synthesis conditions, compositions, catalytic activities, surface areas, and alloy parameters of Pt-Cu precursors and the corresponding dealloyed catalysts. (from ref 48)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Annealing Condition °C/h</th>
<th>Pt mass loading wt%</th>
<th>Nominal Precursor alloying composition at%</th>
<th>Final catalyst composition at%</th>
<th>Pt mass-based current density (900mV) A/mgPt</th>
<th>Specific current density (900mV) µA/cm²</th>
<th>Electrochemical surface area m²/gPt</th>
<th>Bravais lattice of alloy phase</th>
<th>Lattice parameter Å</th>
<th>Precursor alloy phase composition at%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Cu / carbon</td>
<td>600/7</td>
<td>22</td>
<td>25</td>
<td>75 79 21</td>
<td>0.52±0.01</td>
<td>598±22</td>
<td>89</td>
<td>fcc</td>
<td>3.614</td>
<td>0</td>
</tr>
<tr>
<td>Pt-Cu / carbon</td>
<td>600/7</td>
<td>22</td>
<td>25</td>
<td>75 67 33</td>
<td>0.55±0.006</td>
<td>756±9</td>
<td>73</td>
<td>fcc</td>
<td>3.613</td>
<td>0</td>
</tr>
<tr>
<td>Pt-Cu / carbon</td>
<td>950/7</td>
<td>22</td>
<td>25</td>
<td>75 80 20</td>
<td>0.34±0.01</td>
<td>766±10</td>
<td>45</td>
<td>fcc</td>
<td>3.757</td>
<td>46</td>
</tr>
<tr>
<td>Pt / carbon</td>
<td>-</td>
<td>28</td>
<td></td>
<td>100 100 0</td>
<td>0.11±0.01</td>
<td>189±11</td>
<td>77</td>
<td>fcc</td>
<td>3.923</td>
<td>100</td>
</tr>
</tbody>
</table>
To obtain insight in the particle size changes as function of synthesis conditions, Anomalous (or Resonant) Small Angle X-ray Scattering (ASAXS) experiments were performed using the Pt-Cu precursors. SAXS is ideally suited for scattering objects in the 1 – 100 nm range. Performed in the “anomalous” scattering mode, it combines the advantages of diffraction in terms of statistical quality with the power of atom-specific size distributions (see Figure 5). In the anomalous scattering mode, the SAXS profile is measured at two different incident X-ray energies far and near the X-ray absorption edge of a metal of interest; near an absorption edge, the scattering cross section of the respective metal atoms changes strongly; hence, by subtraction the specific contribution of the metal atoms can be isolated.

Figure 6a reports the SAXS profiles of the three carbon-supported Pt25Cu75 alloy nanoparticle electrocatalysts measured at the Pt edge. To obtain these measured scattering curves, the scattering (I-Q) profiles at two different incident energies, E1 and E2, were subtracted from each other. Using the relation

\[ Q \approx \frac{\pi}{d} \]  

the Q range reported in Fig. 6a is estimated to span particle diameters d in the 1.5 – 12 nm range. Larger or smaller objects do not have significant scattering in the chosen Q range. Scattering intensity at large Q is seen to drop in the order 600°C > 800°C > 950°C annealing temperatures. The trends in scattering intensities as function of scattering vector indicate that the particle ensemble annealed at 600°C consists of smaller particles compared to the other two particle ensembles. The measured scattering profiles in Fig. 6a (dashed lines) were fitted using a log-normal particle size distribution function (solid line in Figure 6a)\textsuperscript{70,71}:

\[
P(R) = \exp \left[ -\frac{1}{2} \left( \frac{\ln R}{R_0} \right)^2 \right] \frac{1}{R\sigma\sqrt{2\pi}}
\]

where \( R_0 \) and \( \sigma \) are parameters.

The mean particle diameter \( D_{\text{mean}} \) of the distribution is given by
\[ D_{\text{mean}}(R_0\sigma) = 2R_0 \exp \left( \frac{+\sigma^2}{2} \right), \]

while the variance reads \[ \text{Variance}(R_0\sigma) = R_0^2 \left[ \exp \left( 2\sigma^2 \right) - \exp \left( \sigma^2 \right) \right]^{72}. \]

Table 2 summarizes the fitted mean particle diameters, and Figure 6b shows the resulting size probability distributions for the three nanoparticle catalysts. Fig. 6b also compares the carbon-supported pure Pt precursor which was used as starting material for the synthesis of the Cu rich alloy precursors.

**Fig. 5:** Schematic illustration of element-specific particle size probability distributions \( P(D) \) for Pt atoms and M atoms of a bimetallic Pt-M alloy nanoparticle ensemble with non-uniform composition distribution. Large particles are assumed to be M rich, while small particles are Pt rich. (from ref.40).
Fig. 6: (a) Experimental ASAXS intensity profiles (dashed line) and fits (solid line) for a Pt$_{25}$Cu$_{75}$ alloy nanoparticle precursor prepared at the three different annealing temperatures indicated. (b) Fitted particle size distribution functions (probability distributions) for the Pt-Cu alloy nanoparticle precursor in (a) compared to the pure Pt nanoparticle catalyst used as synthesis starting material. The temperatures indicate the annealing conditions of each catalyst. (from ref$^{40}$)

Table 2
Nanoparticle catalyst compositions, synthesis conditions, alloy phase composition estimates, mean crystallite and mean particle diameter data of Pt$_{25}$Cu$_{75}$ alloy particles as well as the R$^2$ factors of the fittings. (from ref$^{40}$)

<table>
<thead>
<tr>
<th>Overall Catalyst Composition at %</th>
<th>Annealing Temperature °C</th>
<th>XRD Lattice Parameter d (111) Å</th>
<th>Vegard Alloy phase composition at %</th>
<th>XRD Mean Crystallite Size nm</th>
<th>ASAXS Mean particle Diameter nm</th>
<th>Fitting R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt 25 Cu 75</td>
<td>600</td>
<td>2.164</td>
<td>Pt 55 Cu 45</td>
<td>2.82</td>
<td>2.95</td>
<td>0.9839</td>
</tr>
<tr>
<td>Pt 25 Cu 75</td>
<td>800</td>
<td>2.146</td>
<td>Pt 45 Cu 55</td>
<td>4.07</td>
<td>3.51</td>
<td>0.9834</td>
</tr>
<tr>
<td>Pt 25 Cu 75</td>
<td>950</td>
<td>2.141</td>
<td>Pt 40 Cu 60</td>
<td>5.74</td>
<td>4.65</td>
<td>0.9888</td>
</tr>
</tbody>
</table>
The ASAXS measurements of Pt-Cu precursor catalysts directly evidence that an increase in the annealing temperature results in a significant shift of the size distribution toward larger mean diameters. The study also illustrates the power of ASAXS investigations for the characterization of particle size distributions of alloy nanoparticle ensembles. We anticipate that ASAXS in combination with TEM methods will play a much more prominent role in the future for the characterization of particle size and particle composition distribution dynamics. Unlike TEM, SAXS also allows in-situ structural studies of electrocatalyst particles under catalytic conditions. These studies are expected to provide further fundamental insight into the behavior of alloy nanoparticles. First results in this area are forthcoming.

3. CATALYST ACTIVATION AND REACTIVITY FOR THE OXYGEN REDUCTION REACTION (ORR)

The selective dissolution of Cu (de-alloying) is the key process in the formation of the active catalyst. Figure 7 shows the cyclic voltammograms (CVs) during the initial stage of the de-alloying process. The first cycle showed no hydrogen ad- and desorption in the relevant potential window of 0.05 – 0.3 V versus the reversible hydrogen electrode (RHE) consistent with complete Cu surface segregation in Cu-rich Pt alloys. All subsequent electrode potentials are given with respect to RHE. Sweeping anodically, Cu dissolution peaks appeared at 0.3 V and stretch to 0.85 V. On the second cycle, Cu dissolution was limited to regions around 0.3 V and 0.7 V. On the third cycle, the Cu dissolution peaks gradually dropped in intensity, while Hydrogen ad/desorption features in the 0.05 – 0.3 V potential window gradually emerged. After about 200 cycles, the dissolution of Cu was absent resulting in a stable Pt-like CV profile (see inset in Figure 8a). The broad Cu dissolution features during the initial voltammetric scans suggest electrodissolution from a Pt-Cu particle ensemble consisting of a range of different Pt to Cu atomic ratios. While dissolution of Cu atoms embedded in neighboring Cu atoms (pure Cu phases) occurs near the Cu standard potential (+0.34 V), Cu atom dissolution from Pt-Cu alloys or from Pt atoms occurs at much more positive electrode potentials. Dissolution near 0.6-0.7 V is consistent with stripping Cu layers from pure Pt or Pt-rich atomic environments.
Fig. 7: Initial three cyclic voltammetric (CV) profiles (1,2,3) of a Pt_{25}Cu_{75} precursor catalyst (annealed at 600 °C) during electrochemical de-alloying at 100 mV/s. For comparison, the CV of a Pt standard catalyst is shown. (from ref^{48})

The electrocatalytic activity of de-alloyed Pt-Cu catalysts for the ORR was measured by sweep voltammetry in O_{2} saturated HC1O_{4} electrolyte using a Rotating Disk Electrode (Figures 8, 9, and 10). The steep portion of the voltammetric ORR activity profiles of dealloyed Pt_{25}Cu_{75} catalysts (Figure 8a) were shifted to higher potentials indicating increased catalytic activity compared to pure Pt. Figure 8b and 8c show a quantitative comparison of the Pt-mass based activity (units A/mg_{Pt}) and the Pt surface-area based, also referred to as specific, activity (units in µA/cm^{3}_{Pt}) of the de-alloyed Pt-Cu catalysts in the kinetically controlled regime. At 0.9 V electrode potential, the dealloyed Pt_{25}Cu_{75} nanoparticle catalysts, in particular the one annealed at 800 °C outperformed pure Pt particle catalysts by a unprecedented factor of 4-6x. Notably, the electrochemical active surface areas A (ECSAs) (Figure 9c and Table 1) of the three de-alloyed Pt_{25}Cu_{75} catalysts showed no significant increase compared to pure Pt ruling out pure surface area enhancement effects.
Fig. 8: (a) Rotating Disk Electrode (RDE) sweep voltammetry of three dealloyed Pt$_{25}$Cu$_{75}$ catalysts, annealed at 600 °C, 800 °C, and 950 °C compared to pure Pt. Inset: Cyclic voltammograms of the dealloyed catalysts in O$_2$ free electrolyte. (b) and (c) Potential-Activity "Tafel" plots of de-alloyed Pt$_{25}$Cu$_{75}$ catalysts compared to pure Pt: (b) Pt mass based activities $i_m$ (c) Pt surface area based activities, $i_{specific}$. (from ref 48)
Fig. 9: Pt mass based activities $i_m$ at 0.9 V/RHE (a), surface-area specific activities $i_s$ at 0.9V/RHE (b), and electrochemical surface areas (ECSA) (c) of the de-alloyed Pt-Cu catalysts in Figure 8. (from ref 48)

We also studied the effect of the precursor composition on the resulting ORR reactivity after dealloying. Figure 10 summarizes Pt mass based, specific activities and ECSA measurements of dealloyed catalyst as a function of their Pt precursor composition and annealing temperature. Pt mass activities were found to peak for Pt contents of 20-30 at% regardless of annealing temperature. Specific activities are optimal between 20 and 50 at% Pt with precursors annealed at 800 °C performing more active than those annealed at 600 °C. As Figure 10c demonstrates, higher annealing temperature resulted in lower surface area materials throughout.
Fig. 10: Experimental Pt mass based ORR activities $i_m$, specific ORR activities $i_s$, and surface areas of dealloyed Pt-Cu bimetallic alloys as function of precursor composition and annealing temperature / annealing time. Experimental values for pure Pt electrocatalysts are shown as asterisk.

4. THE CORE-SHELL NATURE OF DEALLOYED Pt NANOPARTICLES

In order to gain atomic-level structural and compositional information on the dealloyed active catalysts comparative bulk compositional SEM/EDX analysis (Table 1) and surface compositional XPS analysis were performed before and after dealloying. The study revealed that the Pt$_{25}$Cu$_{75}$ / 600 °C precursor resulted into a an active catalyst phase with overall composition of Pt$_{79}$Cu$_{21}$, while its near surface composition was found to be Pt$_{93}$Cu$_7$. Similar results were obtained for the other two dealloyed Pt$_{25}$Cu$_{75}$ catalysts (Table 1). These findings suggested the formation of a Cu gradient within the dealloyed particles with a Cu rich core and a Pt enriched surface region, as illustrated in
Figure 3. Whether the core-shell structure is the preferred structural type of dealloyed Pt-Cu particles is unclear at present. There is some evidence that for very low Pt precursor content, nanoporous particles rather than core-shell ones are formed\textsuperscript{76}, that is, particles where the Pt and Cu content vary irregularly across individual dealloyed particles\textsuperscript{77,78}.

Table 3
Metal-specific mean 'particle' diameters determined by fitting of subtracted ASAXS scattering profiles at the Pt and Cu edge. (from ref\textsuperscript{40})

<table>
<thead>
<tr>
<th></th>
<th>Mean particle diameter Cu edge nm</th>
<th>Mean particle diameter Pt edge nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As prepared</td>
<td>4.77</td>
<td>4.81</td>
</tr>
<tr>
<td>After electrocatalysis</td>
<td>4.02</td>
<td>4.87</td>
</tr>
</tbody>
</table>

ASAXS measurements of the precursor and the dealloyed catalysts at the Pt and the Cu absorption edge directly revealed the formation of a core-shell structure after dealloying. Figure 11a reports the Cu and Pt specific ASAXS profiles of a Pt\textsubscript{25}Cu\textsubscript{75} / 950 °C catalyst precursor and its dealloyed form\textsuperscript{40}. The corresponding fitted particle size distributions are reported in Fig. 11b. The data shows that the scattering profiles of both the Cu and Pt atoms before electrochemical leaching ("Cu edge" and "Pt edge") almost completely overlap suggesting that the alloy precursor is uniformly alloyed. After dealloying (labels "Pt edge dealloyed" and "Cu edge dealloyed"), the Cu size distribution in Figure 11b is significantly shifted towards smaller values. Table 2 reports the mean particle diameter values of Figure 11b. The difference between the Pt diameter before and after dealloying (4.81 nm and 4.67 nm) is small and may be due to some Pt dissolution. The mean diameter associated with Cu, however, drops significantly from 4.77 nm to 4.02 nm. This suggests that a portion of the Cu atoms were leached out of the initially uniformly alloyed Pt-Cu alloy particles, and now form particle cores with smaller diameters. This is consistent with the structural model of Figure 3: the effective diameter of Cu decreased, because only the core of the particles is participating in the Cu scattering.
Fig. 11: (a) ASAXS scattering profile of a Pt$_{25}$Cu$_{75}$ nanoparticle catalyst prepared at 950°C before and after electrochemical treatment at 1.2 V / RHE for 5 hours in oxygen saturated 0.1 M HClO$_4$ electrolyte. “Cu edge” and “Pt edge” denote atom-specific scattering profiles of the as prepared precursor. “Cu edge
dealloyed” and “Pt edge dealloyed” label the resulting scattering profiles after electrochemical treatment. (from ref 40). (b) Fitted metal-specific particle size distributions of the precursor (“Cu edge” and “Pt edge”) and dealloyed catalyst (“Cu edge dealloyed” and “Pt edge dealloyed”) from Fig 11a. The Cu “particle diameter” is significantly reduced after dealloying suggested the formation of a core–shell structure.

5. MEMBRANE ELECTRODE ASSEMBLY (MEA) IMPLEMENTATION AND SINGLE CELL PERFORMANCE

The practical usefulness of a novel ORR electrocatalyst critically depends on the feasibility to incorporate it into a realistic Membrane Electrode Assembly (MEA) and a single fuel cell for performance and durability studies. Figure 12 schematically illustrates a novel in-situ preparation procedure44,49 of the active dealloyed catalyst phase inside a real single fuel cell cathode. In step 1, the Cu rich alloy precursor is incorporated in the cathode of a fuel cell MEA. In step 2, voltammetric cycling is applied during which Cu atoms dissolve from the cathode catalyst as observed in RDE experiments. The Cu ions migrate and diffuse into the Nafion™ polyelectrolyte and are trapped at negatively charged sulphonic acid groups44. EPMA studies of dealloyed MEAs have confirmed a high Cu ion content in the membrane area adjacent to the cathode layer79. In step 3, the MEA is chemically treated with an inorganic acid. This results in the exchange of Cu ions inside the polyelectrolyte with protons from the liquid acid. After step 3, the catalyst has been converted into its active phase and is ready for use.
Fig. 12: A novel 3 step procedure for in-situ voltammetric dealloying of Cu rich Pt-Cu nanoparticle catalysts inside fuel cell membrane electrode assemblies (MEAs). The top figure illustrates a Membrane-Electro-Assembly of a H\textsubscript{2}/O\textsubscript{2} fuel cells. In-situ formation of the active catalyst phase involves: STEP 1: Cu rich (dark balls) Pt alloy precursors are employed as cathode catalysts. STEP 2: The active phase of the catalysts is formed during a voltammetric dealloying process. STEP 3: Accumulated Cu ions inside the fuel cell membrane or electrode are removed by chemical ion exchange using inorganic acids (from ref 49).

To demonstrate the superior performance of dealloyed Pt cathode catalysts five different dealloyed Pt-Cu alloy nanoparticle catalysts were compared to a state-of-the-art pure Pt catalyst. Table 4 summarizes the synthesis, dealloying conditions and the MEA testing results of the catalysts\textsuperscript{44}. Three Pt\textsubscript{75}Cu\textsubscript{25} precursors, annealed at 600 °C, 800 °C, and 950 °C, were electrochemically dealloyed. Another Pt\textsubscript{75}Cu\textsubscript{25}, prepared at 600 °C, was chemically dealloyed using liquid acid. Since both dealloying procedures resulted in a catalyst composition of about Pt\textsubscript{80}Cu\textsubscript{20} under the chosen conditions, a Pt\textsubscript{80}Cu\textsubscript{20} catalyst was included in the study. Comparison of the dealloyed catalysts with the Pt\textsubscript{80}Cu\textsubscript{20} catalyst serves to directly determine the activity benefits of the dealloying process.
Table 4
Catalyst composition, annealing temperature, dealloying method, electrochemical surface area and activities of dealloyed Pt-Cu bimetallic ORR catalysts in single MEAs (from ref 44).

<table>
<thead>
<tr>
<th>Catalyst comp at%</th>
<th>Annal. Temp, °C</th>
<th>Catalyst dealloying method</th>
<th>ECSA, m²/gPt</th>
<th>Mass activity @ 0.9V-IR free, A/mgPt</th>
<th>Specific activity @ 0.9V-IR free, μA/cm²Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt₄₀Cu₂₀</td>
<td>-</td>
<td>-</td>
<td>63</td>
<td>0.104</td>
<td>166</td>
</tr>
<tr>
<td>Pt₆₀Cu₄₀</td>
<td>600</td>
<td>-</td>
<td>67</td>
<td>0.207</td>
<td>306</td>
</tr>
<tr>
<td>Pt₂₅Cu₷₅</td>
<td>600</td>
<td>Chemical</td>
<td>75</td>
<td>0.374</td>
<td>498</td>
</tr>
<tr>
<td>Pt₂₅Cu₷₅</td>
<td>600</td>
<td>Electro-Chemical</td>
<td>72</td>
<td>0.340</td>
<td>472</td>
</tr>
<tr>
<td>Pt₂₅Cu₷₅</td>
<td>800</td>
<td>Electro-Chemical</td>
<td>48</td>
<td>0.356</td>
<td>739</td>
</tr>
<tr>
<td>Pt₂₅Cu₷₅</td>
<td>950</td>
<td>Electro-Chemical</td>
<td>21</td>
<td>0.413</td>
<td>1964</td>
</tr>
</tbody>
</table>

a 45wt% Pt loading on carbon support (Tanaka Kikinzoku International, Inc.)
b ex-situ catalyst powder acid wash
c in-situ MEA cathode layer voltammetry

The measured PEMFC potential-current (V-I) polarization curves of the catalysts are compared in Figure 13a. It is apparent that high-temperature annealing (950 °C and 800 °C) has a detrimental effect on the performance characteristics outside the kinetic region. This is likely due to a change in carbon structure or change in carbon surface functional groups leading to changes in interaction of the carbon support with water and/or ionomer during the catalyst ink and MEA preparation. The electrochemically and chemically dealloyed Pt₂₅Cu₷₅ catalysts annealed at 600 °C exhibited the most favourable V-I characteristics over the entire current density range at a much reduced Pt loading of only 0.169 mgPt/cm² and 0.11 mgPt/cm² compared to the Pt standard catalyst with 0.313 mgPt/cm².

Figure 13b, c and Table 4 compare the ORR Pt-mass activity and the specific activity of the cathode catalysts in the kinetic regime. As Table 4 shows, the ECSA value, the Pt mass-based and the specific activity of the Pt standard are very consistent with reported state-of-the-art values. The chemically and electrochemically dealloyed MEAs exhibited previously unachieved Pt mass activity improvements of a factor of 3.5x - 4.1x compared to state-of-art Pt cathodes. The observed Pt specific activity was up to twelve times higher than that of the standard Pt. In-situ electrochemically
Dealloyed Pt$_{25}$Cu$_{75}$, prepared at 950 °C exhibited the highest Pt mass activity of 0.41 A/mg$_{Pt}$ and the most favourable specific activity at 0.9 V among the catalysts. The other two electrochemically dealloyed catalysts showed Pt-mass based activities comparable to that of the chemically dealloyed material. The activity of the as-prepared Pt$_{80}$Cu$_{20}$ catalyst exceeded that of Pt by a factor of two, and is thus comparable to other Pt-rich Pt$_{1-x}$M$_x$ (0 < x < 0.25) bimetallic catalyst systems for ORR, such as Pt-Co or Pt-Ni$^{81-88}$ when tested under comparable MEA conditions$^{80}$.

The results reported in Figure 13 demonstrate a significant activity advantage of dealloyed Pt-Cu electrocatalysts for ORR over conventional Pt-rich alloy catalysts and confirm our previous RDE studies. While dealloying of Cu ions into a liquid electrolyte during RDE experiments did not affect the ORR measurements and therefore did not require a removal of Cu ions prior to activity tests, a Cu ion exchange step is crucial for MEA measurements.

Apart from bimetallic systems, the ORR activity of various ternary Pt-Cu-Co alloy nanoparticle catalysts was studied. Voltammetric profiles during the dealloying of the non-noble alloy components were very similar to the binary case. Single cell MEA performance measurements, reported in Table 5, indicated that Cu- and Co rich precursors resulted in dealloyed catalysts with a Pt mass activity benefit of a factor of 4-5x over carbon-supported 30 wt% and a 45 wt% Pt standards$^{49}$. The ternary catalysts were also benchmarked to a dealloyed Pt$_{25}$Co$_{75}$ catalyst in order to show the synergies between Co and Cu. All three ternary alloy catalysts exhibited significantly higher cell potentials over the entire range of current densities. The high current region, where gas and proton transport determine the overall current, shows that the dealloying procedure had no detrimental effect on the transport characteristics of the fuel cell electrodes or membrane. The electrochemical surface areas of the alloy catalysts show that the dealloying of the ternary catalysts resulted in an almost twofold increase in active particle surface area compared to the 45 wt% standard catalyst. While contributing to the improved activity, the surface area change fails to account fully for the observed activity gains.
Fig. 13: (a) Current-voltage characteristics of chemically/electrochemically activated Pt$_{25}$Cu$_{75}$ precursors. Details in reference 44. (b) and (c) ORR activities of dealloyed Pt-Cu cathode electrocatalysts in single MEAs evaluated from 13a: (a) Cell voltage vs. Pt mass based activity (b) Cell Voltage vs. specific activity. Activity rankings are established at 0.9 V cell voltage (horizontal lines). Detailed values are provided in Table 4. All cell potentials are corrected for ohmic losses and H crossover currents. (from ref 44)
Table 5
Alloy composition, electrode Pt loadings, surface areas, and ORR activities at 0.9 V of dealloyed ternary Pt-Cu-Co nanoparticle electrocatalysts in single MEAs..1: 30 wt% Pt; 2: 45 wt% Pt. (from ref 49).

<table>
<thead>
<tr>
<th>Pt Atomic %</th>
<th>Cu Atomic %</th>
<th>Co Atomic %</th>
<th>Cathode Pt loading mgPt cm²</th>
<th>ECSA m²/g</th>
<th>Mass Activity A/mgPt</th>
<th>Specific Activity μA cm⁻³Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>60</td>
<td>20</td>
<td>0.183</td>
<td>112</td>
<td>0.37</td>
<td>337</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>40</td>
<td>0.150</td>
<td>117</td>
<td>0.39</td>
<td>340</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>60</td>
<td>0.150</td>
<td>111</td>
<td>0.49</td>
<td>441</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>75</td>
<td>0.146</td>
<td>70</td>
<td>0.34</td>
<td>491</td>
</tr>
<tr>
<td>100¹</td>
<td>0</td>
<td>0</td>
<td>0.149</td>
<td>79</td>
<td>0.161</td>
<td>209</td>
</tr>
<tr>
<td>100²</td>
<td>0</td>
<td>0</td>
<td>0.313</td>
<td>62</td>
<td>0.102</td>
<td>165</td>
</tr>
</tbody>
</table>

6. STABILITY OF DEALLOYED PT FUEL CELL ELECTROCATALYSTS

Durability is a critical criterion for judging the practical viability of a new ORR catalyst. Due to the relatively high electrode potentials at the cathode, the stability requirements for a ORR fuel cell catalyst are particularly severe. Alloys tend to suffer from non-noble metal leaching over extended periods of time which gradually changes the composition of the catalyst and may affect the surface reactivity in a detrimental way. Alloy particles also change their size during electrocatalytic operation and generally show a severe loss of surface area, and hence activity, over time. We note that in the case of dealloyed Pt-Cu catalysts, initial Cu dissolution is a critical part of the activation of the catalyst and electrode and, hence, is desired. Continued Cu dissolution during fuel cell operation, however, will ultimately result in essentially pure Pt catalysts with reduced cell performance and is therefore undesired. Investigations are under way to determine when desired Cu dissolution turns into undesired detrimental metal dissolution, and whether the catalyst can be held at the point of optimum leaching.⁸⁹

To evaluate catalyst stability at the nanoscale, SAXS techniques, similar to those presented in previous sections, Transmission Electron Microscopy (TEM) or in selected cases X-ray absorption spectroscopy (XAS)⁹⁰-⁹² are
typically used to investigate the dynamics of particle size and composition of particle ensembles\textsuperscript{73} and therefore provide information on the microscopic stability of alloy nanoparticles\textsuperscript{93-95}.

Fuel cell catalyst stability evaluation at the macroscopic scale typically involves monitoring changes in cell current or potential during repeated potential or current cycles. Alternatively, the change in ECSA of the cathode catalyst is monitored as function of time or cycle number. Figure 14 presents the evolution of ECSA of a single fuel cell of dealloyed Pt\textsubscript{25}Cu\textsubscript{75} prepared at the three annealing temperatures over the course of 30,000 potential cycles\textsuperscript{52}. The surface areas were normalized to their initial value to account for differences in initial particle size due to different annealing temperatures. The plot suggests that the dealloyed catalysts annealed at 950 °C and 800 °C exhibit superior stability over pure Pt standards judged from the slope of the ECSA drop. Even though dealloyed Pt\textsubscript{25}Cu\textsubscript{75} / 600 °C shows a rate of ECSA loss comparable to pure Pt, it maintains higher values of normalized ECSA throughout the measurement.

Figure 15 compares the MEA Pt mass based activities, $i_m$, employing dealloyed Pt-Cu cathode catalysts to those of MEA using pure Pt standard catalysts over the kinetic cell potential regime. Initially, the dealloyed Pt\textsubscript{25}Cu\textsubscript{75} / 800 °C catalyst was the most active (see values in Table 6). All three dealloyed Pt catalyst clearly maintain a superior mass activity over the cell potential range considered (open versus solid symbols in Figure 15). The active Pt\textsubscript{25}Cu\textsubscript{75} / 800 °C catalyst exhibits the highest, while the dealloyed Pt\textsubscript{25}Cu\textsubscript{75} / 950 °C catalyst showed the least drop in activity over the voltage cycling stability protocol. After testing, the mass based activity of Pt\textsubscript{25}Cu\textsubscript{75} / 950 °C was still more than 2x that of the 45 wt% Pt standard catalyst (Table 6). All dealloyed ternary catalysts (Table 6) initially exhibited high Pt mass activities over 0.4 A/mg\textsubscript{Pt} in accordance to earlier reports\textsuperscript{49}. Their final Pt mass based activities were comparable to the binary catalysts after the stability protocol\textsuperscript{52}. Taking into account the increase in specific ORR activity over the course of the voltage cycling stability protocol (Table 6), dealloyed Pt\textsubscript{25}Cu\textsubscript{75} / 950 °C and Pt\textsubscript{20}Cu\textsubscript{20}Co\textsubscript{60} / 950 °C were in fact able to retain their kinetic activity advantage relative to pure Pt. This is because their ECSA loss (see Figure 14 in the binary case) is offset by an increase in specific ORR activity, $i_s$, due to particle growth (particle size effect)\textsuperscript{52}. 
Fig. 14: In-situ catalyst stability measurements of dealloyed Pt$_{25}$Cu$_{75}$ cathode catalysts compared to carbon-supported pure Pt standard cathode catalysts in single fuel cell MEAs. The normalized ECSA is plotted the course of 30,000 voltage cycles (0.5 -1.0 V, 100 mV/s). Normalized ECSA values are obtained by normalizing the absolute ECSA values by their initial values at the start of the stability protocol. HSC= high surface area carbon (Ketjen Black), Vul = Vulcan XC 78 carbon. Cell conditions: Anode: H$_2$ Cathode: N$_2$, 100 % relative humidity, 80 C.

7. MECHANISTIC HYPOTHESES IN REGARDS OF DEALLOYED CORE-SHELL NANOPARTICLES

Reactivity in bimetallic systems is controlled by three fundamental effects: ensemble effects, geometric effects, and ligand effects. Ensemble effects arise when dissimilar surface metal atoms, individually or in small groups (ensembles), take on distinct mechanistic functionalities. This was demonstrated for Pd atom pairs on Au for a gas-phase catalytic reaction.$^{96,97}$
Table 6
Catalyst activity parameters in an MEA over the course of 30,000 voltage cycles from 0.5 to 1.0V vs. RHE at 100mVs⁻¹ and 80 °C, with fully saturated pure H₂ (anode) and N₂ (cathode) feeds of 160 ml min⁻¹. (from ref 52).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Annealing Temp [°C]</th>
<th>N-ECSA [%]</th>
<th>$i_m^{0.9V}$ Initial [A/mgₚₜ]</th>
<th>$i_m^{0.9V}$ Final [A/mgₚₜ]</th>
<th>$I_s^{0.9V}$ Initial [µA/cm²ₚₜ]</th>
<th>$I_s^{0.9V}$ Final [µA/cm²ₚₜ]</th>
<th>$I_s^{0.9V}$ 1000 cycles [µA/cm²ₚₜ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt₂₅Cu₇₅</td>
<td>600</td>
<td>35</td>
<td>0.30</td>
<td>0.25</td>
<td>465</td>
<td>1097</td>
<td>21</td>
</tr>
<tr>
<td>Pt₂₅Cu₇₅</td>
<td>800</td>
<td>55</td>
<td>0.53</td>
<td>0.21</td>
<td>1477</td>
<td>1063</td>
<td>-14</td>
</tr>
<tr>
<td>Pt₂₅Cu₇₅</td>
<td>950</td>
<td>73</td>
<td>0.32</td>
<td>0.31</td>
<td>944</td>
<td>1250</td>
<td>10</td>
</tr>
<tr>
<td>Pt₂₀Cu₂₀Co₆₀</td>
<td>600</td>
<td>26</td>
<td>0.49</td>
<td>NA</td>
<td>441</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Pt₂₀Cu₂₀Co₆₀</td>
<td>800</td>
<td>29</td>
<td>0.42</td>
<td>0.23</td>
<td>894</td>
<td>1677</td>
<td>26</td>
</tr>
<tr>
<td>Pt₂₀Cu₂₀Co₆₀</td>
<td>950</td>
<td>49</td>
<td>0.42</td>
<td>0.25</td>
<td>1149</td>
<td>1404</td>
<td>9</td>
</tr>
<tr>
<td>Pt/HSC 30 wt%</td>
<td>–</td>
<td>23</td>
<td>0.21</td>
<td>0.17</td>
<td>290</td>
<td>787</td>
<td>17</td>
</tr>
<tr>
<td>Pt/Vu 45 wt%</td>
<td>–</td>
<td>23</td>
<td>0.16</td>
<td>0.13</td>
<td>279</td>
<td>1056</td>
<td>26</td>
</tr>
</tbody>
</table>
Geometric effects are differences in reactivity based on the atomic arrangement of surface atoms, which give rise to changes in bond energies of intermediates. Distinct crystallographic metal surface planes, for instance, often show widely different catalytic reactivities, seen for instance for electrocatalytic formation of hydrogen monolayers on Pt crystal facets\textsuperscript{34}. Geometric effects may also include compressed or expanded arrangements of surface atoms (surface strain)\textsuperscript{98}. Finally, ligand effects are caused by the atomic neighborhood of two dissimilar surface metal atoms. Ligand effects result in electronic charge transfer between metal atoms, impacting their electronic band structure and, hence, their bond energies to adsorbed reactive intermediates\textsuperscript{99, 100}. As a result of this, ligand effects lead to a stepwise discontinuous modification of surface catalytic reactivity based on the nature of the two metals. Ligand and geometric effects\textsuperscript{31, 34, 97, 100} are strongly convoluted; in some cases, even all three effects\textsuperscript{97} may impact the observed catalytic reactivity.

Our structural and compositional studies of dealloyed Pt-Cu nanoparticles established the existence of a Pt-enriched multilayer surface region (multilayer particle shell) surrounding an Cu-rich alloy particle core (core-shell nanoparticles). This core-shell structure appears to be the active form of the catalyst. We hypothesize that compressive lattice strain in the Pt enriched particle shell (reduced Pt-Pt interatomic distances) is key to understand how the core-shell structure helps accelerate the ORR surface catalysis. Being Cu rich, the alloy particle core has a smaller lattice constant compared to pure Pt. As a result of reduced lattice constants in the core, the Pt-Pt distances in the particle shell are likely to be reduced as well\textsuperscript{101}. This is in accordance with structural studies of pure Pt atomic layers that were epitaxially deposited on Cu(111) single crystal surfaces\textsuperscript{102}. The study showed reduced Pt-Pt atomic distances (compressive strain) across more than 7 atomic Pt layers due to the effect of the underlying Cu(111) lattice constant. The link between strain effects and catalytic surface reactivity is established via the bond energetics of reaction intermediates: DFT computational and experimental studies on extended surfaces suggested\textsuperscript{98, 99, 103-106} that compressively strained surfaces result in reduced adsorbate chemisorption energies which may lead to modified surface catalytic reactivity. In particular, weaker Pt-oxygen surface chemisorption was proposed to improved ORR kinetics\textsuperscript{13} (see Figure 2). Recent unpublished experimental spectroscopic work\textsuperscript{101} on dealloyed Pt-Cu catalysts in fact confirmed that
compressively strained Pt shells lead to a weakening of the Pt-O bond strength, because of a downward shift of the Pt d-band which pulls more of the antibonding character of the oxygen-Pt surface electronic states below the Fermi level.

Fig. 15: Stability measurements of dealloyed Pt$_{25}$Cu$_{75}$ cathode catalysts compared to pure Pt standard cathode catalysts in single fuel cell MEAs. The Pt mass-based activities $i_m$ in the kinetic "Tafel" regime are plotted before and after (marked by *) 30,000 voltage cycles (0.5 -1.0 V, 100 mV/s). HSC = high surface area carbon, Vul = Vulcan XC 78 carbon. Cell conditions: Anode: H$_2$ Cathode: N$_2$, 100 % relative Humidity, 80 C.

There is another interesting aspect in which the modification of surface catalytic reactivity on dealloyed core shell particles differs from reactivity modifications on extended strained metal monolayers$^{106}$. Ligand effects are typically operative over 1-3 atomic layers$^{107,108}$, while geometric effects can affect lattice constants (interatomic distances) across more than 7 atomic layers$^{102}$. Hence, metallic monolayer$^{106}$ or metal skin catalysts show modified surface reactivity due to a convolution of ligand and geometric effects.
Considering that a nearly pure Pt shell extends over several layers \(^{101}\), however, suggest that dealloyed Pt alloy ORR catalysts represent catalysts where predominantly geometric effects are responsible for modifying the surface electrocatalytic ORR reactivity.

An additional unique characteristic of dealloyed core shell nanoparticle catalysts is the fact that the precursor properties as well as the dealloying conditions allow for control of the thickness of the Pt shell. Since the amount of compressive lattice strain of the outermost Pt layer drops as the Pt shell becomes thicker, dealloyed core-shell particles may offer smooth tunability of the experimental ORR reactivity.

8. CONCLUSIONS

We have presented the novel class of dealloyed Pt-Cu alloy nanoparticle electrocatalysts for the electroreduction of oxygen in PEMFC cathodes. The active phase of the Pt-Cu alloy nanoparticle electrocatalysts was prepared by selective dissolution of Cu atoms from nanoparticle precursors. Here, Cu corrosion on the nanoscale had a very beneficial effect on the catalytic performance of the bimetallic particles. Dealloyed Pt-Cu ORR electrocatalysts showed a reactivity improvement of a factor of up to 6x in terms of Pt mass activity compared to a state-of-art Pt cathode catalyst \(^{80}\).

We have also demonstrated the viability of an in-situ voltammetric dealloying procedure to prepare the active catalyst phase inside a real MEA. This catalyst activation procedure by dealloying was shown to lend itself well to the conventional MEA structure of PEMFCs and therefore does not require any significant modification of the state-of-the-art technology.

Surface area measurements after dealloying have ruled out a surface roughening mechanism as the origin for the observed ORR activity enhancements in favor of electronic and/or geometric surface effects. Compositional, structural \(^{40}\) and unpublished microscopic \(^{101}\) analysis points to a core-shell structure of the dealloyed particles. The lattice mismatch between alloy core and Pt shell is hypothesized to result in a reduced Pt-Pt interatomic distance in the top Pt layer of the particle, which, in turn, favourably modified chemisorption energies of reactive intermediates and resulted in improved ORR kinetics.
Future studies will focus on the molecular processes associated with voltammetric dealloying of base metal rich bimetallic alloy nanoparticle precursors. More detailed structural studies are needed to clarify the structural state of the Pt enriched particle shells\(^{40}\). For this purpose, more advanced direct space methods ((S)TEM) and reciprocal space techniques (Small Angle X-ray Scattering) will be utilized.

From a more practical device point of view, the impact of the dealloying procedure on the structure of the membrane-electrode-assembly at the meso- and macro scale (swelling, rupture, deformation, residual metal ion concentration in membrane and anode) has to be investigated in more detail.

A unique feature of the class of dealloyed catalysts is the experimental control over the extent of dealloying (shell thickness) and the alloy core composition (upper limit for strain in the shell). This enables a continuous tuning of catalytic reactivity. Dealloyed catalysts are likely to offer control over the activity of other important electrocatalytic reactions which require modification of adsorption energy of reactive intermediates, such as the electrooxidation of small organic molecules including ethanol, methanol or alike. The noble and the non-noble constituent can be adjusted in the alloy precursor, such that both expansive and compressive strain can be achieved for the purpose of controlled strengthening or weakening surface bonds.

9. ACKNOWLEDGEMENT

This work was supported by the Department of Energy, Office of Basic Energy Sciences (BES), under grant LAB04-20 via a subcontract from Stanford Synchrotron Radiation Laboratory. Partial support by the National Science Foundation, award # 0729722 is gratefully acknowledged. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory (SSRL), a national user facility operated by Stanford University on behalf of the U.S Department of Energy, Office of Basic Energy Sciences. The author gratefully acknowledges support by the cluster of excellence "Unicat" funded by the German National Science Foundation (Deutsche Forschungsgemeinschaft).
REFERENCES


63. Pugh, D. V.; Dursun, A.; Corcoran, S. G., Formation of nanoporous platinum by selective dissolution of Cu from Cu0.75Pt0.25. *J. Mater. Res.* 2003, 18, 216.


83. Koh, S.; Yu, C.; Mani, P.; Srivastava, R.; Strasser, P., Activity of ordered an disordered Pt-Co alloy phases for the electroreduction of


