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Electrochemical and Structural Study of a Chemically Dealloyed PtCu Oxygen Reduction Catalyst

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Abstract

A carbon-supported, dealloyed platinum-copper (Pt-Cu) oxygen reduction catalyst was prepared using a multi-step synthetic procedure. Material produced at each step was characterized using high angle annular dark field scanning transmission electron microscopy (HAADF-STEM), electron energy loss spectroscopy (EELS) mapping, x-ray absorption spectroscopy (XAS), x-ray diffraction (XRD), and cyclic voltammetry (CV), and its oxygen reduction reaction (ORR) activity was measured by a thin-film rotating disk electrode (TF-RDE) technique. The initial synthetic step, a co-reduction of metal salts, produced a range of poorly crystalline Pt, Cu, and Pt-Cu alloy nanoparticles that nevertheless exhibited good ORR activity. Annealing this material alloyed the metals and increased particle size and crystallinity. TEM shows the annealed catalyst to include particles of various sizes, large (>25 nm), medium (12–25 nm), and small (<12 nm). Most of the small and medium-sized particles exhibited a partial or complete core-shell (Cu-rich core and Pt shell) structure with the smaller particles typically having more complete shells. The appearance of Pt shells after annealing indicates that they are formed by a thermal diffusion mechanism. Although the specific activity of the catalyst material was more than doubled by annealing, the concomitant decrease in Pt surface area resulted in a drop in its mass activity. Subsequent dealloying of the catalyst by acid treatment to partially remove the copper increased the Pt surface area by changing the morphology of the large and some medium particles to a “Swiss cheese” type structure having many voids. The smaller particles retained their core-shell structure. The specific activity of the catalyst material was little reduced by dealloying, but its mass activity was more than doubled due to the increase in surface area. The possible origins of these results are discussed in this report.

Keywords

Dealloyed catalyst; fuel cell; PtCu catalyst; HAADF STEM; EELS; TEM

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SUPPORTING INFORMATION AVAILABLE. The supporting information contains 1) Catalyst Synthesis, 2) Chemical Characterization using ICP-OES, 3) Structural Analysis and Phase Identification using XRD, 4) Structural and Chemical Analyses using HAADF STEM and EELS Mapping, 5) Structural characterization using XAS, 6) Electrochemical Measurements using RDE, 7) Determination of Pt d-band vacancies from Pt L₂ and L₃ edge XANES, and 4) Structural Characterization using EXAFS. This material is available free of charge via the internet at <http://pubs.acs.org>.

INTRODUCTION

One of the major stumbling blocks to the commercialization of automotive fuel cells is the high cost of the platinum catalysts used. While platinum is used in both the anode and cathode, the cathode requires a substantially higher loading of platinum due to the sluggish kinetics of the oxygen reduction reaction (ORR) that occurs there. As a result, most of the work on Pt thrifting has been focused on improving the catalytic activity of the cathode catalyst. Although research and development over the past twenty years have resulted in significantly decreased platinum loading for both electrodes, recent economic calculations suggest that a further reduction by at least a factor of four must be realized if automotive fuel cells are to become commercially viable^{1,2}.

In general, the key to creating highly active platinum-containing ORR electrocatalysts involves the optimization of the oxygen binding energy. Specifically, the Pt-O bond must be strong enough to adsorb and retain oxygen and the related intermediates (O^{2-} , O_2^{2-} , H_2O_2 etc) during the reaction, but not so strong as to inhibit desorption of the products. This idea is illustrated by the “volcano” plot of ORR activity versus oxygen binding energy calculated by Norskov, et.al.³ In addition, the adsorption of spectator oxygenated species such as Pt-OH_{ads} must be minimized since these can block active sites and thus act as catalyst poisons^{4,5}. Several factors have been reported to affect Pt-O bonding characteristics including, particle size, surface roughness, Pt-Pt bond distance, and electronic (or ligand) effects, especially as they affect d-band population and distribution.

Early efforts to improve ORR activity explored the use of platinum alloys, but the reported activities of these materials are typically only two to three times that of a standard platinum catalyst^{4,6,7}. More recently, several groups have reported promising ORR activities from rather different catalyst systems. These include Pt monolayer catalysts on nanoparticles of other metals or metal combinations^{8,9}, dealloyed Pt alloy nanoparticle catalysts^{10–13}, and a Pt₃Ni (111) single crystal face¹⁴. The approach developed by Strasser and coworkers utilizes a dealloyed Pt-Cu catalyst^{10–13}. According to their findings, a catalyst synthesized from a Pt₂₅Cu₇₅ precursor and annealed at 800°C showed an ORR activity of 0.44 A/mg_{Pt} and 720 μA/cm²_{Pt} at 0.9 V¹¹. Common to all of these promising systems is a reactive Pt surface that is perturbed by a subsurface layer(s) of differing composition or structure. Clearly, subsurface characteristics such as composition, lattice mismatch, and lattice vacancies can affect surface properties such as Pt-Pt distance and electronic structure that are important for ORR activity. Thus to better understand these catalysts, it is important to probe both their surface and near-surface regions.

Early efforts to probe below a catalyst surface were made by Toda and coworkers who prepared unsupported PtM (M = Fe, Co, Ni) alloys by radio frequency magnetron sputtering and evaluated the alloy surfaces with XPS¹⁵. They observed that, after measuring ORR activity in perchloric acid, the catalysts retained their activity despite leaching of the non-noble metal atoms from the surface of the catalysts. The active catalysts were covered by a few monolayers of pure Pt that Toda et al. called a “Pt-skin” electrode. Further insights regarding the mechanism(s) behind the activity enhancements of bimetallic catalysts were recently offered by Stamenkovic and coworkers¹⁴. This group studied a series of ultrahigh-vacuum (UHV) sputtered Pt₃M (M = Ni, Co, Fe, V and Ti) surfaces before and after annealing. Auger electron spectroscopy (AES) and low energy ion scattering (LEIS) techniques showed that after annealing, the surface atomic layer was pure Pt due to surface segregation. They also showed that the formation of this monolayer, which they termed a ‘Pt-skin’ (in contrast to the thicker “Pt-skin” layer of Toda et al.), was compensated for by a depletion of Pt in the next atomic layer and a slight Pt enrichment in the third layer. In the same study it was shown that exposure of the sputtered alloys to ORR cycles,

(0.05V < E < 1.0V) in 0.1M HClO₄, resulted in the dissolution of the non-noble metal atoms from the surface region, leaving behind a disordered layer of pure Pt several atoms thick. This structure, which they refer to as a 'Pt-skeleton' seems to be very similar to Toda et al.'s "Pt-skin". RDE analysis revealed that 'Pt-skin' surfaces gave consistently better ORR performance than the corresponding 'Pt-skeleton' surfaces, particularly when viewed in terms of their specific activities. When these electrocatalytic trends were combined with experimentally determined (using ultraviolet photoemission spectroscopy, UPS) surface electronic structure (d-band centers), it revealed a 'volcano-type' behavior with a Pt_{skin}/Pt₃Co surface having the highest specific activity of 3 times compared to a polycrystalline Pt disk. Refining the Pt "skin" concept, this group recently described a Pt₃Ni (111) single-crystal surface which was found to have the highest specific activity ever reported; about 10-fold more active than a Pt (111) surface. Characterization of this material by AES and LEIS showed the surface atomic layer to be pure platinum, while the second and third layers contained nickel in specific amounts. While the work involving bulk Pt alloys and single crystals is of great interest, actual fuel cell catalysts are more likely to consist of carbon supported metal nanoparticles. For these systems, many of the characterization tools used to study single and polycrystalline samples are ineffective.

All of the above hypotheses and understanding of the catalyst structure and its relationship with specific activity have been derived from electrochemical experiments and indirect characterization techniques. Direct microscopic analysis of these theories has not been reported until recently, when, with the advent of spherical aberration (Cs) corrected TEM/STEM, it has become possible to study the structure of nanoparticle Pt-based fuel cell catalysts from an atomic point of view^{8, 16–19}. A recent study by Shao-Horn *et al.* on PtCo bimetallic catalysts was conducted using Cs-corrected HAADF STEM¹⁸. The random contrast differences in a 'Pt-skeleton' structure were explained as resulting from a combination of Co dissolution during leaching in conjunction with the diffusion of Pt from one atomic column (as viewed in TEM) to another. It was further explained that this phenomenon creates "percolated Pt-rich" (possibly thicker) and Pt-poor (possibly thinner) regions with sizes in the range of 1–2 nm. A further example from Allard *et al.* recently demonstrated the formation of AuPd core-shell type structures via HAADF STEM¹⁹. These particles showed three regions of contrast comprising a dark central core (often faceted), a bright inner shell, and a distinct outer shell. Additional work by the same group has indicated that the surface layer of the nanoparticle contains kinks, terraces, and steps at the sub-angstrom level²⁰, and that adding a second metal induces the formation of such defects.

In the present work we report a simple multistep synthesis technique to produce a highly active PtCu dealloyed ORR catalyst and use HAADF STEM in combination with XRD and XAS to monitor the progression of the catalyst with each step. Correlating this chemical and structural information with electrochemical measurements can provide the basis for understanding the origin(s) of high activity in these catalysts.

EXPERIMENTAL METHODS

Catalyst synthesis and physical characterization

Catalyst synthesis involved three steps: 1) the simultaneous reduction of Pt and Cu chloride salts with hydrazine hydrate to yield carbon-supported metal nanoparticles (referred to as the "as-reduced catalyst"); 2) annealing under a reducing atmosphere (6 hrs at 800°C under 7% H₂) to produce alloy nanoparticles (described herein as the "annealed catalyst"); and 3) chemically dealloying the nanoparticles of the catalyst (2 days in 1M HNO₃) to produce the material referred to below as the "dealloyed catalyst". Dried catalyst powders from each step were examined by XRD, and their metal contents determined using an inductively coupled plasma - optical emission spectrometer (ICP-OES). HAADF STEM and EELS mapping of

the samples were accomplished with a Cs corrected JEOL 2100F TEM/STEM equipped with a Schottky field emission gun (FEG), a CEOS GmbH hexapole aberration corrector, a HAADF detector, and a post-column Gatan 863 GIF Tridiem® detector for EELS analysis. XAS measurements were taken at beamlines X-3B at the National Synchrotron Light Source (Brookhaven National Labs, Upton, NY) and XOR-9BM at the Advanced Photon Source (Argonne National Lab, Argonne, IL). The as-reduced, annealed, and dealloyed materials were probed under *ex situ* conditions at both the Cu K (8979 eV) and Pt L_{2,3} (13273 and 11564 eV) edges. Details of the catalyst synthesis and the various characterization techniques are included in the Supporting Information.

Electrochemical Measurements

Electrochemical measurements of the various catalysts were conducted at room temperature using a TF-RDE method based on one previously reported by Schmidt, et.al.²¹. Catalyst inks were prepared using 0.5 to 1.0 mg catalyst ml⁻¹ in a propanol-water mixture with a small amount of 5wt% Nafion® solution as a binder. Pt loadings on the 5-mm glassy carbon electrode were maintained in the range of 7.8–14.1 µg_{Pt} cm⁻². A reversible hydrogen electrode (RHE) was used as a reference and all electrochemical measurements were taken in 0.1 M HClO₄. All potentials are reported relative to RHE. A detailed description of the method is given in the Supporting Information.

RESULTS AND DISCUSSION

Synthesis and Chemical Characterization

The analyzed metal contents of the prepared materials are presented in Table 1. As expected, both the as-reduced material and the annealed sample were copper-rich, with a Pt-to-Cu molar ratio of 0.3. Upon dealloying, however, a significant fraction of the copper was removed to give a material with a Pt/Cu ratio of 1.8.

Structural and Phase Characterization using XRD

As-reduced Catalyst—The XRD scan of the as-reduced catalyst is displayed in Fig. 1(a). The few sharp 2θ diffraction peaks at 44.3°, 50.5°, 70.4° and 90.0° are indexed to Cu, indicating the presence of large copper crystals. The very broad peaks at 40° (with adjacent shoulder), 68° and 82° are consistent with Pt metal, but their width and ill-defined peak shapes indicate little or poor crystallization. The Pt peak positions are close to the expected values for pure Pt showing no evidence for alloying. A small amount of copper oxide (Cu₂O) was also observed in this sample, seen as the weak peak at 36.5° in Fig. 1(a).

Annealed Catalyst—The XRD data from the annealed sample, along with the overlaid Rietveld refinement results and the corresponding difference plot, are displayed in Fig. 1(b). The strongest peaks are indexed to an FCC structure and are intermediate to those of Pt and Cu. The weak 2θ diffraction peaks at 29°, 34°, and 56° are indexed to an ordered Cu₃Pt (*Pm* $\bar{3}$ *m*) structure. However, the observed relative peak intensities for the weaker reflections are much less than those reported for the ordered Cu₃Pt phase in the ICDD database, suggesting only partial ordering.

Closer examination of the XRD data reveals that the strong reflections are asymmetric. To account for the peak shape and peak intensities, Rietveld structure refinement required two catalyst structures; one a disordered *Fm* $\bar{3}$ *m* structure and the other a partially ordered *Pm* $\bar{3}$ *m* structure. The lattice parameter for the disordered *Fm* $\bar{3}$ *m* structure refined to 3.7458 Å. From Vegard's Law, the composition of the disordered phase is estimated to be Cu₅₈Pt₄₂. Since the angular variation of the peak widths did not follow in accord with the Scherrer equation, the Williamson–Hall method²² was employed and gave an average crystallite size

of 19 nm and an average crystallite strain is estimated to be 1.0%. The lattice parameter for the ordered $Pm\bar{3}m$ structure refined to 3.6924 Å and the composition of the ordered phase is estimated to be Cu₇₅Pt₂₅ from Vegard's Law. The Cu and Pt occupancies on the lattice sites were also refined assuming an overall composition of 25 at % Pt, as estimated from the lattice parameter. Using this approach, the Pt occupancy (n_{Pt}) refined to 0.61 on the (0,0,0) site and 0.13 on the (0,½,½) site. Long range ordering was estimated by comparing the refined occupancy to the occupancies of the fully ordered and completely disordered states giving a long range ordering of 50%. For the ordered $Pm\bar{3}m$ structure the Williamson–Hall model gave an average crystallite size of 21 nm and a crystallite strain of 0.5%. Based upon the refinement results, the mass ratio of the ordered to disordered phases is 1:2.

Dealloyed Catalyst—Figure 1(c) displays the XRD data, Rietveld refinement results, and difference plot from a dealloyed sample. The majority of the diffraction peaks can be indexed to an FCC structure with peak positions intermediate to Pt and Cu. The lack of any weak diffraction peaks at 29°, 34°, and 56° 2θ indicate that the alloy is a disordered PtCu ($Fm\bar{3}m$) structure. The broad diffraction peak at 25° is typical of a poorly graphitized carbon support. To account for the peak shapes accurately, two disordered $Fm\bar{3}m$ structures were used in the Rietveld refinement and a graphite peak and an amorphous profile in the background model were used. The lattice parameters for the two disordered $Fm\bar{3}m$ structures refined to 3.7283 Å and 3.7745 Å. From Vegard's Law, the compositions of the two phases are estimated to be Cu₆₃Pt₃₇ and Cu₄₈Pt₅₂, respectively. Using the Williamson–Hall method, the average crystallite size of Cu₆₃Pt₃₇ was 12 nm, with a crystallite strain of 0.8%, and the average crystallite size of Cu₄₈Pt₅₂ was 5.7 nm with a strain of 1.4%. Based upon the refinement results, the mass ratio of the two ordered phases is 1:1.

Electrochemical Measurements using the Rotating Disk Electrode (RDE)

Figure 2 (a, i–iii) presents 50 mV s^{−1} voltammograms of the PtCu electrocatalysts in N₂-sparged 0.1M HClO₄. For comparison, each of these scans is overlaid with the signal from the Pt/V standard. The Pt/V standard shows the classic features of carbon-supported Pt nanoparticles in acid electrolyte: an H⁺ adsorption/desorption region at < 0.4 V, a smooth double layer at 0.4–0.55 V, and Pt-O(H) formation and reduction features at > 0.55 V. All three of the PtCu catalysts display these features although to differing extents of magnitude and clarity, with the CV for the annealed sample being considerably muted. Compared to the Pt/V standard, the as-reduced and dealloyed catalysts exhibit observable changes in the position of the center of the Pt-O(H) reduction peak at ~ 0.72–0.80 V. The as-reduced catalyst (Fig. 2a,i) shows that Pt-O(H) reduction is delayed by ~40 mV. In contrast, the peak of the dealloyed catalyst (Fig. 2a, iii) is shifted positive of the standard by ~20 mV indicating earlier onset of Pt-O(H) reduction. The resolution of the annealed CV (Fig. 2a,ii) is too poor for an analogous comparison. The shifts in the Pt-O(H) formation and oxidation features appear to correlate with the average particle sizes of the PtCu electrocatalysts. It has previously been shown by Gasteiger *et al.*² that smaller Pt particles tend to shift the Pt-O(H) formation/reduction peaks to slightly negative potentials. On the basis of the XRD analysis (Table 1), this trend holds for the PtCu electrocatalysts. The ECSAs of the electrocatalysts were determined from the charge of the hydrogen adsorption region (0.05–0.4 V) and are displayed in Figure 3. These results also complement the XRD analysis (Table 1); the smallest particles (the as-reduced catalyst) showing the highest ECSA, and the annealed sample (a mixture of ~20 nm diameter PtCu alloys) exhibiting the lowest ECSA.

Figure 2 (b) and (c) compare the current densities collected from rotating film electrodes in O₂-saturated 0.1M HClO₄ at 1600 rpm (2 (b)) with the derived mass transfer-corrected Tafel plots (2 (c)). In order to provide a more meaningful comparison, the Tafel plots were constructed on the basis of specific activity (mA cm_{Pt,real}^{−2}) from the determined ECSAs

(Figure 3). With the exception of the annealed sample, all of the catalysts exhibit clear, singular waves with well-defined limiting currents. The Pt/V standard reveals two Tafel slopes (Fig. 2c) of -55 and -106 mV dec $^{-1}$ at low and high overpotentials, respectively. These dual Tafel slopes have been observed frequently in the literature^{23–25} although their origins are still somewhat controversial. In contrast all three PtCu samples show single Tafel slopes with the as-reduced and dealloyed electrocatalysts at ~ -80 mV decade $^{-1}$, and the annealed sample somewhat higher at -117 mV decade $^{-1}$. It has been well-reported^{23, 25, 26} that PtM alloy electrocatalysts examined via RDE in dilute perchloric acid electrolytes tend to exhibit only single Tafel slopes. Explanations range from electronic modification of the Pt atoms by the alloy atoms or a contraction of the Pt-Pt bonds^{4, 27}, to a bifunctional effect involving surface M atoms or islands neighboring Pt surfaces^{24, 28}, and even a roughening of the Pt surfaces from dissolution of near-surface M atoms which modify OH_{ads} strength and/or increase the active surface area^{27, 29}. It must also be allowed that contaminants have also been shown to result in changes in the Tafel slopes, with chloride^{30–32} and nitrates²³ being examples. All of these effects must be considered as we correlate the structure/property relationships of these electrocatalysts with the ORR activity.

The specific and mass activities of the electrocatalysts are presented in Figure 3. On the basis of the Pt mass activity at 0.90 V, the performances can be ranked as Pt/V < annealed < as-reduced < dealloyed. In particular, the dealloyed electrocatalyst reveals a mass activity 3.5 times greater than the Pt/V standard. However, the specific activity at 0.90 V of the dealloyed catalyst slightly trails that of the annealed sample. Upon comparison of their relative surface areas, it is tempting to fully attribute the difference in mass activity between the annealed and the dealloyed samples to the increased surface area of the dealloyed sample. However, given the heterogeneous nature of the catalyst particles, as shown below, this is probably too simplistic. In order to properly correlate the mass activity increase with structural and electronic parameters, we have applied several methods to probe the atomic structures of these systems.

Structural Characterization using HAADF STEM and EELS Mapping

HAADF STEM imaging shows the mass-thickness contrast of a specimen. The mass-thickness contrast in the HAADF arises from the incoherent (Rutherford) elastic scattering of electrons at high angles ($>5^\circ$). The cross-section for Rutherford scattering is a strong function of the atomic number Z (mass or density, ρ), as well as the thickness of the specimen. Thus this technique is also known as ‘Z-contrast’ imaging³³.

As-reduced Catalyst—Figure 4 shows the HAADF images of the as-reduced catalyst at different magnifications. Figure 4(a) shows a typical low magnification image of the as-reduced catalyst. This non-optimized, internally-synthesized catalyst is not very homogeneous, with some regions showing well-dispersed metal nanoparticles and others containing agglomerates. A closer look at a well-dispersed region is shown in Fig. 4(b). As seen from the image, the morphology and distribution are similar to a typical commercial Pt/V³⁴. Figure 4(b) identifies the presence of many single atoms and atomic clusters on the carbon support (shown by arrows) as well as some individual, single-crystal particles. The single atoms of a higher atomic number element show up in HAADF STEM as single white dots on the carbon support, while a cluster would exhibit an agglomeration of these dots devoid of any periodicity or lattice structure. The numerical average particle size of the crystallites (based on their diameter) is observed to be around 3 nm. This type of cluster formation and their relation to the particle size has been observed recently³⁵. To obtain digital diffraction patterns, Fast Fourier transforms (FFT) of different crystalline particles were conducted using DM. Using the FFTs of the crystallites and Vegard’s law it was calculated that most of the particles are a disordered FCC CuPt7 alloy with crystal symmetry

of $Fm\bar{3}m$. The agglomerated region shown in Fig. 4(c) is composed of small ~ 3 nm particles as indicated by the arrow.

EELS mapping was performed on the agglomerated regions to investigate the locations of both Cu and Pt. Figure 4(d) shows the composite map of the Cu $L_{3,2}$ edge and Pt $N_{3,2}$ edge of the agglomerated catalyst region of Fig. 4(c). Both Cu and Pt are distributed uniformly throughout the agglomerate with some Pt predominance at the edge. Figure 4 (e) shows the EELS spectrum of the Cu L edge from the whole region of the agglomerate shown before. The position and shape of the $L_{3,2}$ lines (white lines) indicate that the Cu has a zero oxidation state³⁶. EELS mapping could not be performed on the non-agglomerated single-crystal particles due to their instability under the electron beam.

Annealed Catalyst—Figure 5(a) shows a low magnification image of the annealed sample. Three distinct particle size regimes were observed. The particle size regimes were 1) *large*: greater than 25 nm (>25 nm), 2) *medium*: 12 nm to 25 nm and 3) *small*: less than 12 nm (<12 nm). The smallest particles seen were ~ 3 nm, although the percentages of them were very small. Figure 5(b) shows a HAADF STEM image of a 100 nm particle, with its corresponding composite EELS Map in the inset. From the map it is evident that both Pt and Cu are present throughout the particle. This suggests the particle is essentially a PtCu alloy. Some local concentration of the Cu is also observed as indicated by the difference in redness of the color map at different regions. Figure 5(c) shows a 30-nm particle and its corresponding composite EELS map. The composite map indicates less homogeneity of Cu within this particle. FFT of the lattice image indicates an ordered Cu-rich Cu_3Pt phase ($Pm\bar{3}m$ symmetry) at the lower part of the particle and a Pt-rich $CuPt_7$ phase ($Fm\bar{3}m$ symmetry) on the upper part of the same particle. On some areas a very thin layer (< 1.1 nm) of Pt is observed. The Cu EELS spectrum collected from the particle showed a zero oxidation state, similar to the as-reduced catalyst.

Figure 5(d) shows high resolution STEM data typical of the medium sized particles (12–25 nm). As demonstrated in Fig. 5(d) and the corresponding FFT, these particles have an ordered structure ($Pm\bar{3}m$ symmetry). Applying Vegard's law gives an estimated alloy composition of 90 at % Cu. The perimeter of the particle appears to show a bright $6 \text{ \AA}$ thick surface layer ($\sim 2\text{--}3$ monolayers) of disordered structure. The increased brightness of the surface layer is consistent with an increased surface concentration of Pt and is corroborated by the Cu and Pt EELS map shown in the Fig. 5(d) inset.

Figures 5(e) and (f) show two typical small particles that are less than 12 nm in diameter. The HAADF STEM image of the particle in 5(e) shows a Pt shell $\sim 5\text{-}\text{\AA}$ thick (~ 2 monolayers) (between black and white arrows). While most of the particles seen in this size regime have a similar Pt shell of $\sim 2\text{--}3$ monolayers, the cores of the particles vary. Some particles show an ordered Cu-rich core as seen in Fig. 5(e) whereas others show a disordered structure. Figure 5(f) exhibits a HAADF STEM image of a particle around 3.5-nm diameter showing an ordered Cu_3Pt ($Pm\bar{3}m$ symmetry) structure.

The Pt shell thickness that is formed during annealing of Pt alloy catalysts has been reported to be ~ 1 monolayer^{10, 37}. As seen earlier, the number of monolayers that are formed during our processing reveals more than 1 monolayer. Moreover, the Pt shell that is formed seems to be a function of the particle size of the catalyst. To ensure that this finding is not an artifact of the EELS mapping resolution, high-resolution EELS line-scans were performed on the annealed catalyst with a point resolution of $\sim 1.1 \text{ \AA}$, which is very close to the probe resolution of the STEM. Figure 6 (a) shows a typical catalyst particle of about 10.6-nm diameter and the corresponding line-scan in the inset. It is evident from the line-scan that the particle has a core-shell structure. Calculation of the shell on either side of the particle

shows that the thicknesses were 0.68 nm and 0.5 nm. These shell thicknesses correspond to ~ 3.1 and 2.3 monolayers, respectively. Line-scans were performed on several particles with different diameters to give Figure 6 (b) which shows a plot of the number of Pt monolayers versus particle diameter. These data suggest that, at least for the Pt-Cu system, annealing can produce Pt shells thicker than a monolayer, and further, that smaller alloy particles more easily develop thicker Pt shells. Shell thicknesses as high as 4 monolayers were observed in some of the small particles.

Dealloyed Catalyst—Figure 7(a) shows low magnification HAADF STEM images of the dealloyed catalyst. The catalyst particles are well distributed on the carbon support and have the same type of particle size distribution (three particle size regimes) as that of the annealed catalyst. A closer look at the particles shows a distinct difference in the particle morphology. Figure 7(b) shows a typical large particle with diameter greater than 25 nm and the inset shows a higher resolution EELS map of the same particle. Crystallographic analysis using FFTs of these structures reveals that their composition is a FCC Pt-rich phase of CuPt_7 . As before, the Cu EELS spectrum from these types of particles indicates that the copper is in the zero valence state.

Figure 7(c) shows a typical catalyst particle between 12 nm and 25 nm diameter. The particle shows random regions of contrasting intensity (random dark and bright regions) as before only more pronounced. The intensity in HAADF images is a product of thickness and the square of the atomic number (Z^2) averaged over the column of atoms along the beam direction. This indicates that the regions of low brightness could be due to a higher Cu content (Cu having lower Z than Pt), or to lower thickness (due to hollow regions) than the surrounding regions. Figure 7 (c) inset shows the composite EELS maps of a typical particle with ‘Swiss-cheese’ structure. It is observed that the Cu distribution in these particles is very inhomogeneous and the darker (black) regions are devoid of both Pt and Cu. It is clear from the composite EELS map that the darker regions in the HAADF intensity are devoid of both Cu and Pt. Most of the particles in this size regime have the ‘Swiss-cheese’ structure. A closer look at the particles reveals the brighter regions to have a crystalline structure as observed from lattice fringes and the FFTs. These regions measured to be $\sim 1\text{--}2$ nm.

Figure 7 (d), (e) and (f) show the HAADF STEM images of small particles (< 12 nm) with different morphologies. Fig. 7 (d) shows a typical particle of ~ 10 nm. This particle has ‘Swiss-cheese’ morphology similar to the particles shown in Fig. 7 (c). Apparently the copper in these particles leached out in the same way as the particles in the larger particle size regime. Figure 7 (e) shows a typical particle of ~ 8 nm diameter. This particle shows core-shell type morphology with a Pt shell approximately 8 Å thick, similar to the annealed particles in Fig. 5. The shell in this particle is indicated by a pair of arrows. The corresponding EELS composite map shown in the inset confirms the core-shell type structure but seems to indicate a greater variation in the thickness of the Pt shell. Most of the particles observed in this size range (6–8 nm) show a core-shell type structure with a disordered core. Figure 7 (f) shows a couple of particles below 5 nm in diameters, which have an ordered structure as seen from the FFT. Disordered particles with Pt shells were also observed in this particle size range. No EELS mapping could be done on these particles, as they were unstable under the electron beam.

Structural Characterization using XAS and XANES

The bulk oxidation states of the Cu and Pt components in the electrocatalysts were determined by examining the X-ray absorption edge (E_0) energies at the Cu K and Pt L_3 edges as shown in Table 2. All of the electrocatalysts revealed an oxidation state of zero except the Cu component of the as-reduced electrocatalyst. Comparison of the energy

(8979.6 eV) with known standards allowed for an estimate of the bulk Cu oxidation state as +0.3.³⁸ The ratios of the component elements were also determined by comparing the edge heights of the normalized XANES spectra. These Pt:Cu ratios were determined to be 0.32, 0.36, and 1.8–2.6 for the as-reduced, annealed, and dealloyed electrocatalysts, respectively (Table 2). These results are in agreement with the ICP-AES results save for the dealloyed sample. It should be noted that the Cu contents of the dealloyed samples were too dilute (Cu K edge heights < 0.2) to be truly confident in the XAS results.

For an initial qualitative analysis, the Cu K and Pt L₃ edge XANES signals were visually examined as shown in Fig 8. For the Cu K edge, a small pre-edge feature at ~0 eV (relative) arises from dipole forbidden ($\Delta l \pm 1$) 1s→3p transitions which arise from mixing of the p and d bands in conductive metals^{39, 40}. The intensity of the pre-edge features can be assigned as: as-reduced < dealloyed < annealed < Cu foil. Coupled with the bulk +0.3 oxidation state revealed by the edge analysis, it is not surprising that the as-reduced sample shows the weakest pre-edge as this indicates a loss of metallic character. As seen in the XRD results, this is likely the result of the presence of a not insignificant amount of Cu₂O.

The region of the scan from ~5–25 eV past E₀ is referred to as the “white line” region. For metals, the shape and magnitude of this region is strongly influenced by band vacancies^{39, 41, 42}. In general, the magnitude of the white line increases when the bands are emptied of electrons (e.g. when the absorbing atom is surrounded by a strong-field ligand such as oxygen). At the Cu K edge, the as-reduced sample exhibits the highest magnitude followed by the dealloyed and annealed samples, respectively. At the Pt L₃ edge, the as-reduced and dealloyed samples are very similar although their white line magnitudes are still appreciably higher than that of the Pt foil reference. Particularly interesting is the shape of the XANES signal for the annealed sample at the Pt L₃ edge. The white line shape is completely distinct from the as-reduced and dealloyed samples.

Integration of the XANES regions of the Pt L₂ and L₃ edge signals allowed for the determination of the Pt d-band vacancies presented in Table 2 (see Supplementary Information and references therein). Increases in the vacancies have been shown to increase as a result of two effects^{27, 43}; a decrease in Pt particle size, or alloying with a transition metal. The bulk fractional occupancy of the mono-disperse Pt/C standard (0.321), with an average grain size of 2.5 nm (XRD), correlates well with previous reports. However, the two dealloyed PtCu catalysts (at 0.305 and 0.306, respectively) are much lower than previously reported for Pt-M alloys^{27, 43}. While the dealloyed catalysts show definitive performance gains over the Pt/C standard (Figure 3), this analysis suggests that the dealloyed catalysts either: 1) consist of comparatively large particles, or 2) are not very well alloyed with Cu, or 3) a combination thereof. Details of the structural characterization using EXAFS are included in the Supporting Information.

Development of catalyst particle structures and their effects on ORR activity

While the intent of the initial co-reduction procedure was to produce alloyed nanoparticles of platinum and copper, the XRD data in Fig. 1(a) show no evidence of appreciable alloying, and the broad platinum peaks indicate poor crystallization of the reduced metal. Inhomogeneities in both size and distribution of the as-reduced particles are seen in the high resolution HAADF STEM images and EELS mapping in Fig. 4, including the presence of single atoms and atomic clusters. EELS mapping of the agglomerated regions in Fig. 4 does indicate an intimate physical mixture of Pt and Cu particles and EXAFS and XANES data show mostly Pt-Pt interactions and metallic Cu in the as-reduced catalyst, consistent with a predominance of separate Pt-bearing and Cu-bearing phases. Thus, while the co-reduction successfully reduced the Pt and Cu salts used, few alloy particles were formed. The Cu single atoms and clusters indicated by high resolution HAADF STEM images would be

expected to form oxides rather easily so it is not surprising that XAS data taken weeks after the synthesis show a higher proportion of copper oxide than the XRD measurements, which were taken within days of the reduction. Although HR STEM and EXAFS showed the presence of some alloyed crystals, the weight percentage of them was very small.

Figure 3 shows both the mass activity and specific activity of the as-reduced catalyst to be about double that of a standard platinum catalyst. This is somewhat surprising since the catalyst particles are clearly not alloyed so there should be little interaction between the Cu and Pt atoms (no “alloy effect”). It has been shown before that both the mass activity and the specific activity of Pt ORR catalysts are a strong function of Pt particle size⁴⁴, with the highest mass activity observed in particles close to 3.5 nm diameter. Since the average particle size (by XRD) of the as-reduced catalyst is around 3 nm, versus 2.5 nm for the Pt standard, this increased particle size might account for the enhanced ORR activity.

Expectations that annealing would increase particle size and crystallinity, and would promote alloy formation were borne out by both XRD and TEM observations. The lone atoms and atomic clusters of the as-reduced samples are no longer seen in micrographs of the annealed material (Fig. 5), and most of the 3-nm particles that dominated the as-reduced samples have disappeared as well. Apparently these moieties are sufficiently mobile under the annealing conditions to migrate and be incorporated into larger crystals due to Ostwald ripening and solid state sintering. A comparison with the as-reduced catalyst (Fig. 4(a)) provides a basis for understanding the origin of the different catalyst particle morphologies in the annealed catalyst. As seen from Fig. 4(a), the as-reduced catalysts had regions of agglomerated particles (both Pt and Cu). During annealing at 800°C, these agglomerates sintered to form the largest catalyst particles (>25 nm). Thus, the final size of these particles reflects the size of the agglomerates in the as-reduced material. In contrast, the small isolated single crystals on the carbon migrated during heating and sintered to form the smaller particles (<12 nm) in the annealed sample. The broad range in particle size of these smaller particles is attributed to differences in the initial local population density of the crystallites and the clusters. XRD indicates a predominance of medium-sized particles (12–25 nm) in the annealed catalyst, with average crystal size estimates of 19 nm and 21 nm for the disordered and ordered crystallites, respectively. The large copper crystals from the as-reduced material disappeared from the XRD data of the annealed material, presumably due to alloying.

In addition to particle growth and improved alloying, the HAADF STEM and EELS mapping images in Figures 5 and 6 suggest that thermal segregation of Pt to the surface of alloy particles during annealing results in the formation of core-shell particles. This process is at least partly analogous to the segregation of a monolayer of Pt to the surface of large crystals of Pt alloys¹⁴, although the present TEM results suggest a 2–3 atomic layer shell rather than a single monolayer. In particular, most of the particles below a certain diameter are found to have a Cu-rich core and a pure Pt shell. For the large particles, the time and temperature used for annealing were apparently not sufficient to complete the movements (diffusion) of the respective Pt and Cu atoms to form a core-shell structure. This resulted in the formation of regular PtCu alloy(s) as shown in the EELS map in Fig. 5(b). Even in the medium particle size regime some of the particles were incompletely covered with a Pt shell, leaving portions of the internal Cu-rich alloy exposed on the surface. However, most of the particles below 8 nm showed complete coverage with a Pt shell, indicating a threshold particle diameter below which annealing at 800°C for an hour will reliably cause the formation of a core-shell structure.

From the activity measurements shown in Fig.3, it is clear that annealing the as-reduced material more than doubled the ORR specific activity of the catalyst, to more than four times

that of the Pt standard catalyst. While an increase in activity would be expected due to the increased alloying, the unusually high activity of the catalyst seems likely to be due at least in part to the core-shell structures noted above, since somewhat similar structures have been found to have high ORR activity^{11, 37, 45}. In these examples, core-shell structures were obtained by chemical or electrochemical dissolution (dealloying) of the non-noble metal in the catalyst nanoparticles to generate a near-surface “shell” of Pt (variously described as “percolated” or “spongy”) on the particles. These type of Pt shell structures are likely similar to the Pt skeleton structure reported by Stamenkovic and coworkers for bulk, polycrystalline Pt alloys Pt₃M (M= Ni, Co, Fe, V, Ti). They found the ORR activity of the various Pt structures increased in the order: polycrystalline Pt < Pt-skeleton < Pt-skin⁴⁶. Since the Pt shells of the nanoparticles in our annealed catalyst are thermally generated, they might be expected to be most similar to a Pt-skin, which is also thermally generated. On the other hand, their multilayer thickness is more similar to of a Pt-skeleton structure, although their structure is not a “percolated” one. In either case, the annealed core-shell particles would be expected to have enhanced ORR activity. Unfortunately, while the expectation of improved activity for the annealed catalyst is fulfilled, its mass activity is rather poor, due to the large reduction of platinum surface area that accompanies particle growth. Specifically, the ECSA decreased to less than a third of its initial value upon annealing.

Upon dealloying the annealed catalyst, the ECSA more than doubled due to a reduction in particle size (XRD) and an increase in surface roughness, while the specific activity was reduced by less than 10%. The net effect was a marked increase in ORR mass activity to 0.34 A/mg Pt, more than triple the activity of the Pt standard, but still less than the ~0.5 A mg_{Pt}⁻¹ reported for catalysts derived from more homogeneous PtCu₃ precursors⁴⁷. XRD confirms that the removal of copper during the de-alloying procedure results in a decrease of crystallite size, and shows that the particles are still comprised of PtCu alloys with crystal structures similar to the annealed sample (although the ordered *Pm3̄m* phase appears to have shifted back to a disordered FCC structure). XRD shows the presence of two disordered FCC phases with average crystallite sizes of 12 nm and 5.7 nm. Inspection of the TEM micrographs in Fig. 7 clearly shows that dealloying of the catalyst changed the morphology of the larger particles from nearly uniformly dense to a ‘Swiss-cheese’ type structure filled with voids. Such an open structure greatly increases the available Pt surface area and may leave regions of Pt skeleton-type structures. Previous works on bimetallic catalysts have reported the presence of such particles^{48–50}. A recent study has explained this morphology by the dissolution of the less noble metal during leaching and the diffusion of Pt atoms from one column to another. Here “column” refers to the column of atoms that appears as each spot in HAADF STEM imaging (a 2D projection of the 3D atomic columns). This creates “percolated Pt-rich” (possibly thicker) and Pt-poor (possibly thinner) regions with sizes in the range of 1–2nm¹⁸

It is likely that the relatively high specific activity of the dealloyed catalyst is due largely to the smaller particles that were able to retain an active Pt shell structure since they are responsible for most of the Pt surface area of the catalyst. Chemical leaching of the medium and a few of the small annealed particles with incomplete Pt shells probably removes virtually all of their Cu through the opening in the shell, causing these particles to have ORR activities similar to Pt. On the other hand, some medium and most small annealed particles with a complete Pt shell (or Pt-skin) apparently retain their shell and an alloy core after dealloying, although in some cases the core shifted from an ordered to a disordered structure. It is not clear whether the retained Pt shell is a ‘skin’ or a ‘skeleton’ structure, but either one is likely to have a high ORR specific activity due to the copper retained within or due to lattice compression, as originally proposed by Strasser. Thus, the rather small decrease in ORR specific activity caused by de-alloying of the catalyst can be attributed to the sum of several effects, including (1) a likely increase in the activity of the large particles

due to the formation of Pt-skeleton structures, (2) a possible decrease in the specific activity of the medium particles with partial Pt shells, and (3) the relatively constant high activity of the small core-shell particles (Pt-skin or Pt-skeleton).

CONCLUSIONS

An active Pt-Cu catalyst with roughly three times the ORR mass activity of a standard platinum catalyst was made by a new synthetic route involving a solution-phase reduction, followed by annealing and chemical dealloying. Almost no alloying between Pt and Cu was observed in the as-reduced catalyst by all characterization techniques. Very small atomic clusters decorated on the carbon support were observed by HAADF STEM, as well as large agglomerates of crystallites. Some of the active, unalloyed copper was found to oxidize in air over time. XRD and XAS both showed the presence of Cu-oxides in the as-reduced catalyst several weeks after synthesis.

The annealing of the as-reduced catalyst resulted in the formation of a heterogeneous catalyst with alloy particle sizes varying from less than 5 nm to more than 50 nm. This range of particle sizes complicated the characterization data analysis and made the correlations drawn between electrochemistry and structural data somewhat inconclusive. Nevertheless, some insights concerning the progression of catalyst activity with each synthetic step were realized during this work. Both STEM and XAS have shown the formation of small and medium particles with ~2–3 monolayers of Pt-shell on a Cu-rich core during high temperature annealing of the as-reduced catalyst. This is an indication that core-shell formation in this system is in part a thermal effect. While the specific activity of the annealed material reported here is good, the mass activity is relatively poor due to low Pt surface area.

Partial removal of the copper by acid leaching and dealloying greatly increased the mass activity of the catalyst; increasing the surface area without much affecting the specific activity of the material. The surface area was increased by reducing particle size and producing a porous ‘Swiss-cheese’ structure in the larger particles. However, both EELS mapping, and XAS indicate the retention of some core-shell type structures in the dealloyed catalyst with similar numbers of Pt monolayers as seen in annealed catalyst particles. Moreover, HAADF STEM indicates that this structure is particularly prevalent in particles less than 8 nm in diameter. This suggests that the Pt-shell developed during the annealing process protects the Cu-rich core from acid treatment and helps maintain particle structure. While the increase in the mass activity with dealloying is surely related to the increase in surface area, it is surprising that the specific activity is largely unaffected by the significant loss of alloyed copper from the catalyst particles. Further work with more homogeneous samples will be required to fully explain this puzzle.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(a) XRD scan from the as reduced catalyst; XRD scan, Rietveld refinement and difference plot of (b) annealed catalyst (inset) showing expanded view of (220) reflection, and (c) de-alloyed catalyst (inset) showing expanded view of (220) reflection.

Figure 2.

(a): Cyclic voltammograms of the carbon-supported PtCu electrocatalysts with a standard Vulcan-supported 46wt% Pt/C (Tanaka) electrocatalyst for comparison, (b) Thin film rotating disk electrode studies of the carbon-supported PtCu electrocatalysts with a standard 46wt% Pt/Vulcan (Tanaka) electrocatalyst for comparison. 1600 rpm anodic ORR curves, (c) the corresponding mass transfer-corrected Tafel plots. Ar-saturated 0.1M HClO₄ at 50 mV s⁻¹. Platinum geometric loadings (μg_{Pt} cm⁻²): 46wt% Pt/V (20), As-reduced (9.4), Annealed (7.8), Dealloyed (14.1)

Figure 3.

Performance and properties of the electrocatalysts determined by rotating disk electrode in Argon-sparged 0.1M HClO_4 . Electrochemical surface area (red, ECSA, $\text{m}^2 \text{g}_{\text{Pt}}^{-1}$ from integrations of the hydrogen adsorption/desorption region), mass activity (green, $\text{A mg}_{\text{Pt}}^{-1}$ at 0.90 V and 1600 rpm, derived from i_k), and specific activity (grey, SA, $\text{mA cm}_{\text{Pt,real}}^{-2}$ at 0.90 V and 1600 rpm). The error bars represent 95% confidence levels.

Figure 4.

(a) Low magnification HAADF STEM image of as-reduced catalyst showing different regions, (b) high magnification image of a well dispersed region, (c) high magnification image showing the formation of clusters (shown by arrows) and some crystallites less than 2 nm diameter (d) EELS compositional map of an agglomerated region (note that the aggregates are made of small crystallites), (e) EELS Cu spectrum showing oxidation state zero (metallic Cu).

Figure 5.

(a) Low magnification HAADF STEM image of annealed catalyst showing different regions; HAADF STEM image of a (b) 100 nm particle (inset) corresponding EELS map, (c) 30 nm particle (inset) corresponding EELS map, (d) a typical medium particle of 12–25 nm diameter, (e) a typical small particle of <12 nm diameter with black and white arrows show basis of estimation of surface Pt layer thickness and (f) a typical particle of ~3.5 nm diameter.

Figure 6.

(a) A typical particle with 10 nm diameter with the corresponding line-scan location (red line) inset: plot showing HAADF and elemental intensities with line position. Blue: HAADF Intensity, Green: Normalized Cu Intensity and Red: Normalized Pt Intensity, (b) plot of calculated monolayers from EELS line-scans with catalyst particle diameter; where, 'n' denotes the number of catalyst particles analyzed in each size regime.

Figure 7.

(a) Low magnification HAADF STEM image of dealloyed catalyst showing different regions; HAADF STEM image of a (b) a typical large particle >25 nm diameter (inset) corresponding EELS map, (c) a typical medium particle of 12–25 nm diameter (inset) corresponding EELS map, (d) high resolution HAADF STEM image of a 10 nm particle showing lattice fringes, (e) a typical small particle of <12 nm diameter (inset) typical EELS map of particles of this size and (f) a typical particle of ~3.5 nm diameter.

Figure 8.

Ex situ (a) Cu K and (b) Pt L₃ edge XANES signals of the PtCu electrocatalysts with representative elemental foils for comparison.

Table 1

Summary of PtCu catalyst Composition, particle size and electrochemical properties

sample	composition		Pt/Cu at. ratio	phases and avg crystallite size (nm) [XRD]	ecsa (m ² /g _{Pt})	mass activity (A/mg _{Pt} at 0.90 V)	specific activity (μA/cm ² -Pt at 0.90 V)
	wt. % Pt	wt. % Cu					
as-reduced	20	20	0.3	Pt, Cu, Cu O	70	0.21	300
annealed				<i>Fm</i> $\bar{3}$ <i>m</i> , Cu ₅₈ Pt ₄₂ (19)			
	22	23	0.3	<i>Pm</i> $\bar{3}$ <i>m</i> , Cu ₇₅ Pt ₂₅ (21)	19	0.14	750
dealloyed				<i>Fm</i> $\bar{3}$ <i>m</i> , Cu ₆₃ Pt ₃₇ (12)			
	29	5.4	1.8	<i>Fm</i> $\bar{3}$ <i>m</i> , Cu ₄₈ Pt ₅₂ (5.7)	50	0.29	580

Table 2

Cu K and Pt L₃ edge k²-weighted EXAFS fit results

As-reduced									
Models: <i>Fm-3mCuPt_{0.5}OFm-3mPt_{0.5}Cu</i>									
Edge	M-M	R (Å)	R _{theory}	N	N _{theory}	E ₀ (eV)	ΔR (Å)	S ₀ ²	r
									(%)
Cu K	Cu-Cu	2.530	2.553	2.3	12	-0.60	0.012	0.929	0.011
									88.9
	Cu-O	1.896	1.848	2.3	4	4.85		0.941	0.007
Pt L	Pt-Pt	2.687	2.743	6.8	10.5	3.49	0.006	0.950	0.010
									99.8
	Pt-Cu	2.604	2.743	1.8	1.5	3.49		0.994	0.012
Annealed									
Model: <i>Fm-3mCu₃Pt</i>									
Edge	M-M	R (Å)	R _{theory}	N	N _{theory}	E ₀ (eV)	ΔR (Å)	S ₀ ²	r
									(%)
Cu K	Cu-Cu	2.578	2.611	6.4	8	2.65	0.115	0.990	0.010
									31.1
	Cu-Pt	2.582	2.611	1.3	4	3.63		0.933	0.005
Pt L	Pt-Pt	2.652	2.611	2.1	4	6.94	0.009	0.939	0.006
									158.8
	Pt-Cu	2.621	2.611	9.0	8	9.04		0.931	0.008
Dealloyed									
Models: <i>Fm-3mCu_{0.5}Pt_{0.5}</i>									
Edge	M-M	R (Å)	R _{theory}	N	N _{theory}	E ₀ (eV)	ΔR (Å)	S ₀ ²	r
									(%)
Cu K	Cu-Cu	2.654	2.671	5.6	6	6.44	0.042	0.945	0.012
									28.7
	Cu-Pt	2.608	2.671	2.8	6	1.25		0.946	0.003
Pt L	Pt-Pt	2.708	2.671	6.3	6	7.65	0.012	0.944	0.008
									192.6
	Pt-Cu	2.656	2.671	2.4	6	7.65		0.931	0.012

Coordination numbers ±20%.

k windows @ Cu K: As-reduced 1.83–15.64 Å⁻¹, Annealed 1.74–16.28, Dealloyed 1.44–12.15, @ Pt L₃: As-reduced 1.72–14.52 Å⁻¹, Annealed 1.53–14.63, Dealloyed 1.99–15.52.

R windows @ Cu K: As-reduced 1.32–3.01 Å, Annealed 1.48–3.28, Dealloyed 1.54–3.31, @ Pt L₃: As-reduced 1.91–3.51 Å, Annealed 1.68–3.51, Dealloyed 1.72–3.5.