# Activation of Nanoparticle Pt-Ru Fuel Cell Catalysts by Heat Treatment: A <sup>195</sup>Pt NMR and Electrochemical Study

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<sup>195</sup>Pt NMR spectroscopic and electrochemical measurements were carried out on commercial Pt-Ru alloy nanoparticle samples to investigate the effect of high-temperature annealing in different vacuum/gas-phase environments. Samples annealed at 220 °C in Ar gas, or in a vacuum, did not show any demonstrable change in catalytic activity vs electrochemically reduced, room-temperature samples. In contrast, annealing at 220  $^{\circ}$ C in H<sub>2</sub> gas led to a 3-fold increase in reactivity toward methanol oxidation (per surface site). NMR experiments show that annealing at 220 °C (in both Ar and H<sub>2</sub>) leads to a slight reduction in the Fermi level local density of states (E<sub>F</sub>-LDOS) at the Pt sites, which we attribute to surface enrichment of Ru. This electronic effect alone, however, appears to be too small to account for the increase in the catalytic activity observed for the H-treated catalyst. By comparing the electrochemical and NMR data of the H- and Ar-treated samples, we conclude that annealing at 220 °C in the hydrogen atmosphere reduces surface Ru oxides into metallic Ru, and consequently, the presence of metallic Ru and its enrichment on the surface are essential for the enhanced catalytic activity. In contrast, heat treatment at 600 °C in both vacuum and argon atmosphere increases the particle size and reduces the amount of platinum on the nanoparticle surface, thereby increasing the surface Ru content beyond the optimum surface composition values. This causes a large reduction in catalytic activity. Our results suggest that optimizing the amount of surface Ru by heat treatment at temperatures near 200 °C, in a hydrogen atmosphere, can be utilized to produce Pt-Ru alloy nanoparticles with high methanol oxidation activity. Finally, our NMR and electrochemical data, taken together with the lattice parameter measurements, lead to a novel model of Pt-Ru alloy nanoparticles having a Ru-rich core and a Pt-Ru alloy overlayer.

## Introduction

Investigating Pt-based nanoparticles and optimizing their catalytic activity are important themes in contemporary fuel cell science.<sup>1</sup> One area that has received particular attention concerns nanoparticle modifications to reduce the CO poisoning effect, which deteriorates catalytic performance of Pt surfaces in direct methanol oxidation fuel cells (DMFCs). Alloys of Pt, in general, show improved CO tolerance when compared to pure Pt,<sup>2,3</sup> and among the various bimetallic catalyst systems, Pt-Ru has shown the best CO tolerance. The improved CO tolerance of Pt-Ru bimetallic catalysts is generally described by either the bifunctional mechanism,<sup>4,5</sup> in which surface Ru provides oxygencontaining species to help oxidize the adsorbed CO, the ligand field effect,<sup>6</sup> which supports the idea of weakened CO chemisorption due to the interaction of Ru with Pt, or to both effects. Because heterogeneous catalysis is a surface property, the composition of a nanoparticle catalyst surface is critical in determining its reactivity, so studying CO tolerance and methanol oxidation at various surface compositions can be expected to help provide a better understanding of DMFC catalysis. For example, the CO tolerance of the bimetallic catalytic surfaces produced by spontaneous deposition of Ru

onto commercial Pt-black is a sensitive function of the surface Ru packing density<sup>7,8</sup> and reaches a peak at a surface Ru packing density of 0.4-0.5, encouraging the use of this approach in the development of novel fuel cell catalysts.

Combining electrochemical nuclear magnetic resonance (EC NMR) with conventional electrochemical methods has emerged as a powerful approach with which to obtain structural and electronic level information about nanoparticle catalyst surfaces.<sup>9–11</sup> Both sides of the electrochemical interface (i.e., the substrate and the adsorbate) can be probed by EC NMR, and by applying phenomenological models<sup>12</sup> one can derive good estimates of the Fermi level local density of states (E<sub>F</sub>-LDOS). The E<sub>F</sub>-LDOS can then be used to investigate alloying processes as well as the chemisorption of simple molecules. EC NMR can also provide detailed insights into the nature of the chemisorption bond as well as the surface dynamics of adsorbed molecules.<sup>13</sup> Here, we use the EC NMR approach, together with conventional electrochemistry, to investigate how heat treatment of commercial Pt-Ru alloy nanoparticles affects DMFC activity. A previous NMR study<sup>14</sup> has shown that the surfaces of commercial Pt-Ru alloy nanoparticles are enriched with Pt. Also, structural investigations<sup>15</sup> have shown that progressive heating of these materials up to 400 °C increases the lattice parameter, possibly due to the incorporation of more Ru into

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#### NMR of Pt-Ru catalysts

the surface alloy layer, while further heating (to 600 °C) results in a precipitous drop in the lattice parameter due to the migration of Pt atoms to the interior of the nanoparticles. Here, we have carried out heat treatments at temperatures below 400 °C (viz., 220 °C, in Ar and H<sub>2</sub> atmospheres) and above 400 °C (viz., 600 °C, in Ar atmosphere and in vacuo) to study the effects of the treatments on the composition, structural, and catalytic activities of Pt–Ru. Transmission electron microscopy (TEM), electrochemical and EC NMR measurements have been carried out on these heat-treated samples. Our results extend those reported previously<sup>14</sup> and indicate that heat treatments can result in major changes in particle size, surface composition, and catalytic activity, as well as in NMR properties, and clearly demonstrate that even simple thermal treatments can result in significant increases in the catalyst performance.

#### **Experimental Section**

Pt-Ru nanoparticle catalysts with a nominal atomic ratio of 1:1 were purchased from Alfa Aesar (Ward Hill, Massachusetts). Heat treatment at 220 °C was performed either under constant H<sub>2</sub> or Ar flow for 24 h, and these two samples will be referred to as PtRu-220H and PtRu-220Ar, respectively. For the 600 °C treatment, the as-received sample was sealed either in an evacuated quartz tube or one filled with Ar gas and heated in a furnace at 600 °C for 6 h. Both of these samples had identical morphology and very similar electrochemical and NMR properties. The results reported here are for the vacuum-annealed sample, denoted as PtRu-600. The compositions of these samples were determined using inductively coupled plasma (ICP) analysis. Electrochemical measurements were performed in a conventional three-electrode cell with a Pt gauze counter electrode and a 3 M Ag/AgCl reference. The working electrode of the cell was a 10-mm-diameter Au disk with typically 0.4 mg of the catalyst physisorbed on the surface.<sup>7</sup> H<sub>2</sub>SO<sub>4</sub> (0.1 M) was used as the electrolyte for electrochemical measurements, and all electrode potentials were converted to the reversible hydrogen electrode (RHE) scale. The catalyst samples were electrochemically cleaned by holding the electrode potential at 0.21 V, with a Pt boat working electrode to hold the nanoparticles. These samples, together with a part of the electrolyte, were then transferred to NMR tubes and flame sealed.<sup>14</sup> A small portion of the catalyst samples was left in the electrochemical cell to carry out the electrochemical measurements. For CO stripping measurements, CO was adsorbed onto the nanoparticle surfaces by bubbling CO gas into the electrochemical cell, held at 0.05 V. After 40 min adsorption, the remaining CO in solution was removed by purging with ultrapure Ar (S. J. Smith Welding Supply), and the stripping voltammogram was recorded. Details of the NMR measurements, which were made at 8.45 T, have been reported previously.<sup>14</sup>

## **Results and Discussion**

The sample used in this study was a commercial 1:1 Pt–Ru alloy nanoparticle catalyst (PtRu), electrochemically cleaned to remove Pt surface oxides. The average particle diameter was 2.7 nm.<sup>14</sup> The <sup>195</sup>Pt NMR spectrum of this catalyst shown in Figure 1A, is completely different from that of the electrochemically cleaned Pt-black (Figure 1B). The <sup>195</sup>Pt NMR spectra of Pt-black,<sup>11</sup> or supported Pt nanoparticles,<sup>16</sup> are usually very broad, extending from ~1.090 to ~1.140 G/kHz because of the spatial variation in the E<sub>F</sub>-LDOS. Surface Pt atoms resonate around 1.10 G/kHz, while atoms in the interior of the particles have their responses shifted toward higher field/frequency ratios, approaching 1.138 G/kHz,<sup>17</sup> the value found for bulk Pt metal.



Figure 1. Point-by-point <sup>195</sup>Pt NMR spectra of: (A) electrochemically cleaned PtRu and (B) Pt-black (from ref 14).



**Figure 2.** Magnetization recovery curves and  $T_1$  values obtained at the surface peak positions for: (A) Pt-black, (B) PtRu, and (C) PtRu-600, all at 80 K.

 TABLE 1: <sup>195</sup>Pt NMR Parameters for Pt-Black and PtRu

sample	Pt-black	PtRu	PtRu-220H	PtRu-220Ar	PtRu-600
center of gravity (G/kHz)	1.1215	1.1055	1.1040	1.1040	1.1186
$T_1T \text{ (ms K)}$	$24\pm2$	$90\pm4$	$109\pm 6$	$106\pm 6$	$38\pm2$

However, the NMR spectrum of clean PtRu (Figure 1A) consists of a single, symmetric Gaussian peak, centered at ~1.106 G/kHz and extending only from 1.095 to 1.115 G/kHz.14 This result indicates that there is a major decrease in the average EF-LDOS at the Pt sites in these alloy nanoparticles as compared to either Pt-black or supported Pt catalysts.<sup>17</sup> These effects are also reflected in the large increase in the spin-lattice relaxation times  $(T_1)$ , (Figure 2) and the Korringa product,  $T_1T$  (Table 1), again as compared to Pt-black. Specifically,  $T_1T$  increases from 24  $(\pm 2)$  ms K in Pt-black to 90  $(\pm 3)$  ms K in PtRu. The peak observed in the PtRu spectrum is closer to the surface peak (1.100 G/kHz) than it is to the bulk Pt NMR peak (1.138 G/kHz), which supports the idea that more Pt atoms reside in the surface layers of Pt-Ru alloy nanoparticles, consistent with conclusions drawn from spin-spin relaxation measurements<sup>14</sup> and comparisons with the NMR results for other Pt alloy nanoparticles, such as Pt-Pd18 and Pt-Rh.19

On thermal treatment, there are major changes in the morphology (Figure 3), electrochemical behavior (Figure 4), catalytic activity (Figure 5 and Table 2), and <sup>195</sup>Pt NMR spectra (Figure 6) and relaxation behavior (Table 1), and in some cases, the effects are large. ICP analysis shows that the bulk composition of PtRu is unaffected by the heat treatments at 220 °C (Table 3). In general, annealing leads to an increase in particle size, as revealed by the TEM images shown in Figure 3. Catalyst heated at 600 °C has a much larger increase in average particle size ( $d \sim 10-16$  nm) as compared to those heated at 220 °C (d



Figure 3. TEM images of: (A) PtRu, (B) PtRu-220, and (C), PtRu-600. The particle diameters increased to 5-7 nm and 10-16 nm for PtRu-220 and PtRu-600, respectively.



Figure 4. Cyclic voltammograms of: (A) PtRu, (B) PtRu-220H, (C) PtRu-600, and (D) Pt nanoparticles with 66% surface Ru coverage, prepared by spontaneous deposition (scan rate = 5 mV/sec, electrolyte =  $0.1 \text{ M H}_2\text{SO}_4$ ). CV of PtRu-220Ar (not shown) is also similar to (B).



**Figure 5.** (A) Comparison of methanol oxidation reactivity for as-received and annealed Pt-Ru alloy nanoparticles. Oxidation at 0.4 V vs RHE in 0.5 M H<sub>2</sub>SO<sub>4</sub>. (B) CO tolerance measured via the CO stripping CVs of Pt-Ru alloy nanoparticles. CO was adsorbed by bubbling CO gas at 0.05 V vs RHE followed by Ar bubbling. Scan rate: 5 mV/sec; electrolyte = 0.1 M H<sub>2</sub>SO<sub>4</sub>.

 $\sim 5-7$  nm). Changes in surface composition due to annealing can be clearly seen from the cyclic voltammograms (CV) shown in Figure 4. The pair of sharp peaks observed near 0.03 and 0.10 V in PtRu-600 have been repeatedly observed in Ruenriched Pt surfaces and in clean Ru surfaces.<sup>7,20</sup> For comparison, the CV of a Pt–Ru sample prepared by spontaneous deposition of Ru on pure Pt nanoparticle is also shown in Figure

4. This sample is known to have 66% Ru on the Pt surface.<sup>7</sup> The similarity of the CV suggests that the surfaces of the heat-treated samples have higher Ru levels than do the as-received PtRu samples. The reactivity of these heat-treated samples toward methanol oxidation was then tested via 10-h chrono-amperometry. Figure 5A compares the reactivities of heat treated samples with those of the as-received sample. All the current

 TABLE 2: The Effect of Heat Treatment on Pt-Ru Alloy Nanoparticles

sample	Pt-Ru	PtRu-220H	PtRu-600
dispersion (calculated) <sup><math>a</math></sup> (m <sup>2</sup> /g)	43	20	10
dispersion (from CV) (m <sup>2</sup> /g)	45	18	13
<i>j</i> at 10 h, $\mu$ A/cm <sup>2</sup>	2.1	5.9	1.7
<i>j</i> at 10 h, µA/mg	1.2	1.7	0.35

<sup>*a*</sup> Calculated assuming the lattice parameter a = 0.39 nm, radius d = 0.14 nm, and Pt sites density  $\Gamma = 1.3 \times 10^{15}$  atom/cm<sup>2</sup>.



**Figure 6.** <sup>195</sup>Pt NMR spectra obtained at 80 K, of: (A) PtRu-220Ar; (B) PtRu-220H; (C) PtRu-600, and (D) PtRu.

TABLE 3: ICP Analysis of Pt-Ru Alloy Nanoparticles

	Pt	Ru	Pt	Ru
sample	(wt %)	(wt %)	(atom %)	(atom %)
Pt-Ru (1:1) (theoretical)	65.9	34.1	50	50
Pt-Ru	66.0	34.0	50.2	49.8
PtRu-220H	65.8	34.2	49.9	50.1

densities are normalized to the electrochemically active surface areas measured from CO stripping. PtRu-220Ar has approximately the same reactivity as does the as-received sample, but PtRu-220H has a much higher reactivity than do the other samples, indicating that this heat treatment leads to an improved surface composition for methanol oxidation. PtRu-600 shows a much lower reactivity than does the as-received sample, suggesting that there are not enough Pt sites for methanol adsorption due to a large increase in surface Ru.

CO tolerance measurements obtained through the CO stripping voltammograms for all four samples are shown in Figure 5B. All the CVs are normalized according to the CO stripping charge. The CO stripping peak of the as-received sample is positioned at 0.49 V. The CV of PtRu-220Ar is unshifted with respect to the as-received sample, but shows a lower CO oxidation current density. For PtRu-220H, the CV peak is negatively shifted (by 40 mV), becomes narrow, and shows an increase in the oxidation current. The CV of PtRu-600 has a slight negative shift, but the CO oxidation current density is reduced considerably, and the peak becomes broad vs PtRu-220H. A similar trend in position and width of the CO stripping peak has been observed previously in Pt nanoparticles with increasing amount of surface Ru,<sup>20</sup> where it was observed that CO tolerance reached its maximum around a Ru coverage of 0.4-0.6 and the peak width was smallest in that composition range. Once the amount of Ru exceeds the optimum range, the CO stripping peak shifts in the positive direction and it becomes wider. The larger area obtained for the CO stripping CV of PtRu-220H implies that the catalyst obtained by modifying the surface Pt/Ru ratio is capable of oxidizing more methanol molecules per unit area. That is, heat treatment in  $H_2$  results in a considerable increase in catalyst activity. But why is this?

In earlier work, it has been shown that the addition of Ru to Pt decreases the Pt metal surface and CO  $2\pi^*$  E<sub>F</sub>-LDOS, resulting in a reduction of the bond strength between CO and Pt.8,14 The <sup>195</sup>Pt NMR data presented below provide a more quantitative analysis of these electronic level alterations of the catalyst surfaces as a result of annealing. The 195Pt NMR spectra of all the four samples are shown in Figure 6, and the center of gravity and the Korringa product  $(T_1T)$  results obtained at the peak position are shown in Table 1. The NMR spectrum of PtRu-600 shows marked differences to that of the as-received PtRu sample. In particular, the single-Gaussian peak obtained for the <sup>195</sup>Pt NMR spectrum of PtRu is not observed with PtRu-600. The PtRu-600 spectrum is clearly much broader, and there is a large shift in its center of gravity toward that of bulk Pt, indicating that Pt atoms are now dispersed into many layers of the nanoparticles. In addition,  $T_1T$  measured at the peak position is very close to the value found for Pt-black, measured at the bulk position.<sup>14</sup> These results indicate that a considerable fraction of the Pt atoms in PtRu-600 have migrated into the inner regions of the nanoparticle, resulting in higher levels of surface Ru. The decrease in the catalytic activity of this sample (Figure 5A) is, therefore, mostly likely due to the reduction of the number of Pt atoms on the surface. In contrast, the <sup>195</sup>Pt NMR spectra of both PtRu-220Ar and PtRu-220H maintain a single-Gaussian line shape similar to that of the as-received sample, indicating that Pt atoms reside predominantly on the surface layers, even after annealing at 220 °C. Although the center of gravity of the NMR peak shows only a slight shift as compared to the asreceived sample, the Korringa product is, however, larger than that of the as-received sample, implying that there is indeed a reduction in the E<sub>F</sub>-LDOS at the Pt atoms. In earlier NMR work on similar systems, a significant reduction in the surface E<sub>F</sub>-LDOS due to the presence of Ru was observed, both by <sup>195</sup>Pt and <sup>13</sup>C NMR.<sup>8,14</sup> Increasing the amount of Ru on the surface of Pt-black by spontaneous deposition was also shown to reduce the surface E<sub>F</sub>-LDOS.<sup>8</sup> This electronic alteration was suggested to be the basis for the ligand field contribution to the "Ru enhancement" seen in Ru-modified Pt catalysts toward the electro-oxidation of methanol. Therefore, the decrease in the E<sub>F</sub>-LDOS in the Pt-Ru alloy due to the heat treatment at 220 °C is also likely because of an increase in the surface Ru content. This result supports the previous proposal, obtained from electrochemical measurement, that the amount of surface Ru increases due to the heat treatment. For PtRu-220Ar, however, this increase in surface Ru does not lead to an increase in its catalytic activity due, we believe, to the presence of Ru in the oxide form on the catalyst surface. In the case of PtRu-220H, however, annealing in H<sub>2</sub> reduces the surface Ru oxide into metallic Ru. Indeed, even in the case of Pt-Ru catalysts in which Ru is spontaneously deposited on Pt-black, it has been found to be necessary to reduce the precursors deposited on the Pt surface to a metallic form to achieve high catalytic activity.7 X-ray photoelectron investigations have also shown that the presence of metallic Ru is a prerequisite for effective methanol oxidation electrocatalysis.<sup>21</sup> From Table 1, it can be seen that the increase in the Korringa constant (i.e., reduction in the E<sub>F</sub>-LDOS) of the Pt atoms in PtRu-220Ar and PtRu-220H is nearly the same. Because the reduction in E<sub>F</sub>-LDOS seen for the 220 °C annealing alone cannot account for the



Figure 7. A schematic representation of Pt–Ru nanoparticle composition and its variation due to heat treatment.

increased reactivity of PtRu-220H, the present study suggests that the more efficient bifunctional path could be the deciding factor in increasing the reactivity.<sup>21,22</sup>

Table 2 summarizes the effect of heat treatment on the alloy nanoparticles. The heat treatment increases the average particle sizes, leading to a reduction in dispersion and active surface area. Particle size effects on reactivity have consistently been observed in Pt and Pt–Ru nanoparticle catalysts, and the general trend is that CO tolerance and reactivity per surface area increases with particle size. The compromise between higher dispersion and better specific reactivity generally results in an optimum size of  $\sim 3$  nm. However, in the present case, the reactivity enhancement obtained for the PtRu-220H sample surpasses the particle size effect, resulting in an increase in the overall reactivity per gram of catalyst.

The results we have described above are consistent with X-ray diffraction data obtained on these same samples. The lattice parameter of as-received Johnson Matthey Pt-Ru (the same sample used for the NMR investigations) was determined by total pattern fitting to be 3.882 Å, close to the 3.862 Å measured on thermodynamic Pt-Ru 1:1 made by arc melting.<sup>15</sup> On progressive heating (up to 400 °C), there was an increase in the lattice parameter, together with the formation of some hexagonal Ru. This Ru is thought to come from the fcc PtRu lattice, and this Ru depletion (from the core) is responsible for the increased Pt/Ru ratio on the surface of the catalysts heattreated at 220 °C. On further heating (to 600 °C), there was a rapid decrease in the lattice parameter. This corresponds to Ru incorporation into the fcc lattice, possibly from an amorphous region, which results in decreased catalytic activity due to a considerable reduction of Pt surface sites, together with generation of the Ru-associated CV features, Figure 4C. A schematic representation of Pt-black and Pt-Ru nanoparticles, based on the present results, is shown in Figure 7. Our model for the as-received sample is that of a Ru-rich core with a Pt alloy overlayer (Figure 7B). Heat treatment at 220 °C in H<sub>2</sub> results in a slightly enhanced Ru content in the alloy overlayer (Figure 7C), together with reduction of surface Ru oxides, but heating to 600 °C results in a large incorporation of Ru into the Pt-Ru alloy overlayer, Figure 7D, and decreased catalytic activity due to loss of surface Pt (which moves to the core region, Figure 7D).

# Conclusions

The effect of heat treatment on commercial Pt–Ru alloy nanoparticles was investigated via TEM, electrochemical, and <sup>195</sup>Pt NMR experiments. In general, heat treatment led to an increase in the average particle size and surface Ru content, as indicated by TEM and electrochemical measurements. A sample heat-treated to 600 °C showed a considerable decrease in catalytic activity, which is ascribed to a reduction in the number of surface Pt atoms. The shift in the center of gravity of the NMR spectrum indicates that Pt atoms move to the interior layers of the nanoparticles on high-temperature treatment. CO tolerance and methanol oxidation reactivity showed a consider-

able increase for the sample heat-treated at 220 °C in H<sub>2</sub>. The slight increase in the Korringa product for the samples heattreated at 220 °C (in both Ar and H<sub>2</sub>) suggests that there is a small decrease in the E<sub>F</sub>-LDOS of Pt atoms due to this heat treatment. However, the resulting electronic alteration cannot completely account for the observed enhancement toward methanol oxidation,<sup>7,8</sup> suggesting that the increased amount of surface metallic Ru (produced by the reduction of surface ruthenium oxides by  $H_2$ ) is the dominant factor that leads to enhanced catalytic activity. Therefore, the bifunctional mechanism involving the Ru metallic sites is likely to be more important in determining the catalytic properties of Pt-Ru bimetallic systems than the ligand effect. Combining the electrochemical and NMR data together with lattice parameter estimations, we arrive at a model of the Pt-Ru alloy nanoparticles consisting of a Ru-rich core and a Pt-Ru alloy overlayer, and the core Ru gets incorporated into the fcc lattice structure as a result of the heat treatment. We also showed that it is possible to optimize the reactivity of a bimetallic catalyst by tuning the surface composition.

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