ELECTROCHEMICAL STUDIES AND IN SITU ELECTROCHEMICAL NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS ON PLATINUM-BASED BIMETALLIC ELECTROCATALYSTS FOR DIRECT METHANOL FUEL CELLS

A Dissertation submitted to the Faculty of the Graduate School of Arts and Sciences of Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy In Chemistry

By

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Two parallel objectives of this thesis research are 1) to investigate the electrocatalytic activities of Pt-based bimetallic nanoparticles (NPs) towards methanol (MeOH) electro-oxidation reaction (MOR), carbon monoxide (CO) tolerance and oxygen reduction reaction (ORR); and 2) to use electrochemical nuclear magnetic resonance (EC-NMR) techniques to investigate the electronic properties of the Pt-based bimetallic electrocatalysts.

For the first objective, instead of utilizing the traditional bimetallic alloy model, a surface modification strategy was adopted in this thesis work to prepare Pt-modified M (M = Ru, Au) bimetallic electrocatalysts. By experimentally controlling the Pt coverage on the metal substrates via a spontaneous deposition method, the resulting Pt-modified Ru or Au substrates indicated Pt coverage-dependent electrochemistry. Most importantly, it was observed that the inactivity of Pt towards MeOH oxidation with very low coverage and, the emerging and increasing activity with increasing coverage coincided with the phenomena predicted by the ensemble effect, a hypothesis that had not earlier been supported directly by experimental evidence. Later a one-pot wet chemistry method was
developed to prepare Pt-decorated Ru nanoparticles with a submonolayer of Pt. The electrochemical characterization of the whole series of samples provided experimental evidence that strongly supported a bifunctional mechanism, rather than an electronic effect as the dominant factor contributing to the enhanced CO tolerance. Using a core(Au)/shell(Pt) model, a detailed investigation of electrocatalytic properties of Au@Pt nanoparticles was performed as a function of the Pt shell packing density and Au core size. It was observed that the electrochemical behavior of Pt deviated significantly from its bulk counterpart especially at low coverage. The data obtained so far indicated that the future of PtAu as an anode electrocatalyst for MOR is questionable.

In the second part of the thesis, a unique $^{195}$Pt NMR based in situ technique was developed to determine the local Pt concentration and electronic properties in Pt-based bimetallic systems with reasonable spatial resolution. Before this study, this was a challenging task in the area of Pt-based bimetallic systems, especially at the nanoscale. In combination with electrochemical characterization, this methodology opened a way to study, in much more specific terms and at higher resolution, the local elemental composition/electronic properties/catalytic activity relationship.
# TABLE OF CONTENTS

## Chapter 1. Introduction: Background and Literature Review

1. Concerns about Fossil Fuel Energy 1

2. Introduction to Fuel Cells 2

   2.1. History of Fuel Cells 2

   2.2. Introduction to DMFC(PEMFC) 4

      2.2.1. Working Mechanism of PEMFC 4

      2.2.2. Working Mechanism of DMFC 4

      2.2.3. Recent Progress in DMFC 6

      2.2.4. Problems in R&D of DMFC 7

   2.3. Electrocatalysis in DMFC 9

      2.3.1. Reaction Mechanism of Methanol Electro-oxidation 9

      2.3.2. Review of Pt-based Electrocatalysts 11

      2.3.3. Surface Modification Methodology for PtRu Electrocatalysts 18

      2.3.4. Application of EC-NMR in Electrocatalyst Research 21

3. References 23

## Chapter 2. Synthesis and Characterization Methods

2. Electrochemistry 29

2.1. Electrochemistry 29

2.2. Nanoparticle Synthesis 30

   2.2.1. 17.5nm Au Nanoparticles Synthesis 30

iv
Chapter 3. A Coverage-dependent Study of Platinum Spontaneously-Deposited on Gold and Ruthenium Substrates: Direct Experimental Evidence of the Ensemble Effect for Methanol Electro-oxidation on Platinum

<table>
<thead>
<tr>
<th>Section</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1. Abstract</td>
<td>37</td>
</tr>
<tr>
<td>3.2. Introduction</td>
<td>37</td>
</tr>
<tr>
<td>3.3. Experimental</td>
<td>39</td>
</tr>
<tr>
<td>3.4. Results and Discussions</td>
<td>41</td>
</tr>
<tr>
<td>3.4.1. Pt on Au Substrate</td>
<td>41</td>
</tr>
<tr>
<td>3.4.2. Pt on Ru Substrates</td>
<td>47</td>
</tr>
<tr>
<td>3.5. Conclusions</td>
<td>50</td>
</tr>
<tr>
<td>3.6. References</td>
<td>61</td>
</tr>
</tbody>
</table>
Chapter 4. Optimizing Methanol Electro-oxidation on Platinum-decorated Ruthenium Nanoparticles

4.1. Abstract 62
4.2. Introduction 63
4.3. Experimental 66
   4.3.1. Preparation of the Pt-decorated Ru NPs 66
   4.3.2. Electrochemistry 68
   4.3.3. XRD, TEM, XPS, and ICP-OES 68
4.4. Results and Discussions 69
   4.4.1. Pt Packing Density (PD): the formation of segregated atomic adlayers 69
   4.4.2. MeOH Electro-oxidation 76
4.5. Conclusions 80
4.6. References 95

Chapter 5. Electrocatalytic Properties of Gold-core Platinum-shell Nanoparticles:

Effect of Platinum Shell Packing Density and Gold Core Size 97

5.1. Abstract 97
5.2. Introduction 98
5.3. Experimental 100
   5.3.1. Au@Pt NPs Synthesis 100
   5.3.2. TEM and EDS 101
   5.3.3. Electrochemistry 102
5.4. Results and Discussions 102
   5.4.1. Pt Packing Density Calculation 102
   5.4.2. UV-vis Spectra 104
   5.4.3. Electrochemistry Results 104
      5.4.3.1. Cyclic Voltammograms 104
      5.4.3.2. CO Stripping Cyclic Voltammograms and Methanol Oxidation Reaction (MOR) 107
      5.4.3.3. Oxygen Reduction Reaction (ORR) 110
   5.5. Conclusions 111
   5.6. References 128

Chapter 6. Spatially-resolved $^{195}$Pt NMR of Carbon-supported Platinum-Ruthenium Electro catalysts: Local Electronic Properties, Elemental Compositions, and Catalytic Activities 130
   6.1. Abstract 130
   6.2. Introduction 131
   6.3. Physical Basis for Spatially-Resolved $^{195}$Pt NMR of Pt-Based NPs 132
      6.3.1. The spectral-geometric position correlation 133
      6.3.2. The RKKY J-Coupling Effect 135
   6.4. Experimental 136
      6.4.1. Electrochemistry 137
      6.4.2. $^{195}$Pt NMR Measurements 138
6.5. Results and Discussions 139

6.5.1. Analysis of Local Pt Distribution 139

6.5.2. Local Electronic Properties and Catalytic Activity 142

6.6. Conclusions 147

6.7. References 158

Concluding Remarks 160

Appendix: An Investigation of Sulfur Poisoning and Potential Remedies of Platinum-based Electrocatalysts 164

A.1. Introduction 164

A.2. Experimental 164

A.2.1. Preparation of the Sulfur-covered Pt NPs 164

A.2.2. Electrochemistry 165

A.3. Results and Discussions (Preliminary data) 165

A.4. Conclusions 168

A.5. References 173
LIST OF ILLUSTRATIONS

Figure 1.1 5
Schematic structure and working mechanism of a DMFC stack

Figure 1.2 7
Some DMFC-powered products: A) Toshiba cell phone; B) Fraunhofer camcorder; C) Toshiba notebook computer; D) DaimlerChrysler NECAR5 schematics

Figure 1.3 16
CO stripping curves of Pt black (solid) and PtRu alloy (dotted)

Figure 2.1 35
Three electrode electrochemical cell: reference electrode (RE); counter electrode (CE); working electrode (WE)

Figure 2.2 36
ORR experiment setup

Figure 3.1 52
Representative cyclic voltammograms of the Pt decorated Au electrode as a function of accumulative Pt deposition cycles (the black CV is that of the bare Au surface). The vertical lines indicate the reduction peaks for Pt (left) and Au (right) oxides. The region at which the Pt oxide starts forming is indicated by the black arrow and the oxidation current increases as the number of the deposition cycles. The inset shows the
corresponding Pt coverages estimated from the CO stripping CVs (solid dots, see Figure 3.2) and the Pt oxide reduction peaks (open triangles, see text for details).

**Figure 3.2**

The CO stripping CVs of the Pt-decorated Au electrode as a function of the number of the accumulative Pt deposition. The numerical values in the parentheses are the nominal Pt coverage calculated by using the CO stripping peaks. The CV of the Pt overlayer (blue, see the text for details on how it was generated) is presented as a reference. The inset shows the opposing trends of the low (circles) and high (squares) peak potential as a function of the Pt coverage. The straight line is a guide-of-the-eyes for the peak positions of the high-potential CO stripping waves.

**Figure 3.3**

CVs of the polycrystalline Au electrode with (solid curve) and without (dashed curve) CO bubbling. The almost identical CVs demonstrate that no discernible CO adsorption was observed on the Au surface.

**Figure 3.4**

The CVs with (solid curves) and without (dashed curves) the presence of 0.5 M MeOH. **A.** After the 1st Pt deposition cycle ($\theta_{Pt} = 0.22$) and **B.** after the 2nd Pt deposition cycle ($\theta_{Pt} = 0.31$)

**Figure 3.5**
The fractions of CO electro-oxidized at high (squares) and low (circles) potentials as a function of Pt coverage.

**Figure 3.6**

The MeOH electro-oxidation CVs as a function of the number of accumulative Pt deposition cycles. As can be seen, the MeOH activity increases as the accumulative number of Pt deposition cycles increases.

**Figure 3.7**

The CV of the Ru overlayer (red) and that after 1st Pt deposition cycle (blue). The substantial decrease of the pseudo-capacitive current is a clear indication of the presence of Pt on the Ru surface.

**Figure 3.8**

The CVs with (solid curves) and without (dashed curves) the presence of 0.5 MeOH of the Pt-decorated Ru overlayer after A. the 1st, B. the 3rd, and C. the 9th Pt deposition cycle. D. The CO stripping CVs for the Ru overlayer (black) and the Pt-decorated Ru overlayer after 1st (blue), 3rd (pink), and 9th (green) Pt deposition cycles. The current was normalized by the total accessible surface sites (including both Pt and Ru) determined by CO stripping (2e per site).

**Figure 3.9**
The CVs with (solid curves) and without (dashed curves) the presence of 0.5 M MeOH of the Pt-decorated Ru nanoparticles after A. 1\textsuperscript{st} Pt deposition cycle and B. 2\textsuperscript{nd} overnight Pt deposition cycle.

**Figure 4.1**

Comparison of the CVs of (A) the as-received Ru NPs and (B) the EG-cleaned Ru NPs.

**Figure 4.2**

The CO stripping CVs and those thereafter of the eight Pt-decorated Ru NP samples of the first batch. The dashed CVs in (a), (f), and (h) are those of pure J-M Ru, J-M PtRu (1:1) alloy, and J-M pure Pt NPs that are used as references for comparison. The percentage numbers are the values of Pt PD calculated by the method described in the text.

**Figure 4.3**

The CO stripping CVs of the three samples of the second batch.

**Figure 4.4**

Linear relationship between the measured and the nominal Pt packing density (PD). Squares are for the three second batch samples. The straight line goes through the origin.

**Figure 4.5**

The Ru (3d) and Pt(4d, 4f) XP spectra of Pt(40)-Ru of the second batch.

**Figure 4.6**

The TEM images of (a) the starting Ru NPs and (b) Pt(67)-Ru. The insets are the corresponding HRTEM snapshots where the distance between two adjacent atomic planes was measured to be 0.21 nm for both samples. (c) XRD patterns within the small
angle range for two representative Pt-decorated Ru samples of the 1\textsuperscript{st} batch and for the three samples of the 2\textsuperscript{nd} batch. Those for pure J-M Pt, J-M PtRu alloy, and pure Ru NPs are also shown for comparison. The vertical dashed lines indicate the respective standard angle positions of Pt(111) (left) and Ru(101) (right) as references.

**Figure 4.7**

The respective TEM images of Pt(12)-Ru(Left) and Pt(40)-Ru(Right) from 2\textsuperscript{nd} batch samples. The insets are the corresponding HRTEMs where the distance between two adjacent atomic layers is 0.21 nm.

**Figure 4.8**

The Pt coverage dependence of the CO stripping peak potentials. The CO stripping peak potentials of the pure J-M Ru, J-M PtRu(1:1) alloy, and J-M Pt NPs (as labeled) are also shown in the figure for comparison. (b) A linear relationship between the MeOH electro-oxidation peak current and the Pt PD. The straight line goes through the origin. The squares are of the three samples of the second batch.

**Figure 4.9**

The CVs of MeOH electro-oxidation on the 8 Pt-decorated Ru samples. The CVs (dashed curves) on the J-M Ru, J-M PtRu (1:1) alloy, and J-M Pt NPs are also shown in (a), (f), and (h) respectively for the purpose of comparison.

**Figure 4.10**

The MeOH electro-oxidation CVs of the 3 2\textsuperscript{nd}-Batch samples.
Figure 4.11

A. The CAs of the 8 Pt-decorated Ru NP samples. The CAs of the J-M Ru, J-M PtRu (1:1) alloy, and J-M Pt NPs are also shown for the purpose of comparison. B. The volcano-like curve of CA currents measured at 60 min as a function of the Pt coverage. The inset in (B) is a surface structure model (dark spheres for Pt atoms and light spheres for Ru atoms with each Pt 3-atom ensemble having 9 nearest Ru neighbors) that consists of ensembles of 3 Pt atoms on Ru(0001) and has simultaneously the maximum numbers of Pt ensembles and of Pt/Ru sites. The corresponding Pt PD = 3/7 = 0.43.

Figure 4.12

The CA of MeOH electro-oxidation of the 3 2nd-batch samples with the current values at 60 min.

Figure 4.13

The correlation between the long-term steady-state current density of the MeOH electro-oxidation and the potential of the CO stripping peak. The squares are for the three second batch samples. The Pt coverage is the implicit parameter in this plot with the arrows indicating the direction of the increasing coverage.

Figure 5.1

The TEM images of the 3.3 nm (A), 5.2nm (B) and the 17.5 nm (C) Au NPs. The insets are the corresponding UV-Vis spectra and size distributions.

Figure 5.2
The TEM images and corresponding size distributions of the Au@Pt NPs with the 3.3nm Au core: (A) Au(S)@Pt-0.24, (B) Au(S)@Pt-0.54, (C) Au(S)@Pt-0.83, (D) Au(S)@Pt-1.07, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60. The average particle sizes are 3.50nm, 3.49nm, 3.51nm, 3.52nm, 3.59nm and 3.64nm respectively. The scale bars equal to 20nm.

**Figure 5.3**

The TEM images and corresponding size distributions of the Au@Pt NPs with the 5.2nm Au core: (A) Au(M)@Pt-0.09, (B) Au(M)@Pt-0.34, (C) Au(M)@Pt-0.94, (D) Au(M)@Pt-1.22, (D) Au(M)@Pt-2.00, (D) Au(M)@Pt-2.22. The average particle sizes are 5.23nm, 5.46nm, 5.67nm, 5.97nm, 6.02nm and 6.13nm respectively. The scale bars equal to 20nm.

**Figure 5.4**

The TEM images and corresponding size distributions of the Au@Pt NPs with the 17.5 nm Au core: (A) Au(L)@Pt-0.74, (B) Au(L)@Pt-0.94, (C) Au(L)@Pt-1.3, (D) Au(L)@Pt-2.0, (E) Au(L)@Pt-3.0, and Au(L)@Pt-3.4. The average particle sizes are 17.9 nm, 18.0 nm, 18.6 nm, 18.7nm, 18.7 nm and 18.8 nm respectively. The scale bars equal to 50 nm.

**Figure 5.5**

UV-Vis spectra of the 3.3nm (A), 5.2nm (B) and 17.5 nm (C) Au core samples.

**Figure 5.6**
The CVs of (A) the Au(S)@Pt-0.24 and 3.3nm Au NPs (red curve as a reference), (B) the Au(S)@Pt-0.54 NPs, Au(S)@Pt-0.83 NPs, and (D) Au(S)@Pt-1.07 NPs, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60 and J-M Pt black (dashed curve). In (F), the arrow highlights the suppression of the formation of Pt oxides on Au(S)@Pt in general.

Figure 5.7

The CVs of (A) the Au(M)@Pt-0.09 and 5.2nm Au NPs (red curve as a reference), (B) the Au(M)@Pt-0.34 NPs, Au(M)@Pt-0.94 NPs, and (D) Au(M)@Pt-1.49 NPs, (E) Au(M)@Pt-2.00, (F) Au(M)@Pt-2.22 and J-M Pt black (dashed curve). In (F), the arrows (red for J-M Pt and black for Au@Pt) highlight the suppression of the formation of Pt oxides on Au(M)@Pt in general.

Figure 5.8

The CVs of (A) the Au(L)@Pt-0.74 and 17.5 nm Au NPs (red curve as a reference), (B) the Au(L)@Pt-0.91 NPs, the Au(L)@Pt-1.3 NPs, (D) the Au(L)@Pt-2.0 NPs, (E) the Au(L)@Pt-3.0 NPs, and (F) the Au(L)@Pt-3.4 NPs and J-M Pt black (dashed curve). In (F), the arrows (red for J-M Pt and black for Au(L)@Pt) highlight the suppression of the formation of Pt oxides on Au(L)@Pt in general.

Figure 5.9

Pt fraction on surface of the Au(S)@Pt NPs (triangle, black), Au(M)@Pt NPs (ball, red) and Au(L)@Pt NPs (square, blue) as a function of the Pt packing density.

Figure 5.10
The CO stripping CVs of the Au(S)@Pt (A), Au(M)@Pt (B) and Au(M)@Pt (C) samples. Only anodic scans are shown here for simplicity. The CO stripping CV of J-M Pt black (dashed curve) is also shown as a reference. The inset shows the opposing trends of the low (circles) and high (squares) peak potential as a function of the Pt coverage.

**Figure 5.11**

The MOR CVs of (A) the Au(S)@Pt-0.24, (B) the Au(S)@Pt-0.54 NPs, Au(S)@Pt-0.83 NPs, and (D) Au(S)@Pt-1.07 NPs, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60 and J-M Pt black (dashed curve).

**Figure 5.12**

The MOR CVs of (A) the Au(M)@Pt-0.09, (B) the Au(M)@Pt-0.34 NPs, Au(M)@Pt-0.94 NPs, and (D) Au(M)@Pt-1.49 NPs, (E) Au(M)@Pt-2.00, (F) Au(M)@Pt-2.22 and J-M Pt black (dashed curve).

**Figure 5.13**

The MOR CVs of (A) the Au(L)@Pt-0.74, (B) the Au(L)@Pt-0.91 NPs, the Au(L)@Pt-1.3 NPs, (D) the Au(L)@Pt-2.0 NPs, (E) the Au(L)@Pt-3.0 NPs, and (F) the Au(L)@Pt-3.4 NPs and J-M Pt black (dashed curve as a reference).
The RDE data of ORR on Au(S)@Pt (A), Au(M)@Pt (B), and Au(L)@Pt (C) samples obtained with a scan rate of 20 mV/s and a rotating speed 1600 rpm, the dashed lines indicated the currents of the half wave potential.

**Figure 5.15**  
127
The Pt packing density dependences of the transient peak current in MOR (A) and the half-wave potential in ORR (B). The horizontal dashed lines indicate the respective values of J-M Pt black for comparison and the straight line for eye-guiding purposes.

**Figure 6.1**  
149
The point-by-point \(^{195}\)Pt NMR spectrum (A) and its layer-model simulation (B) of a 2.5 nm commercial Pt/Vul XC-72 sample. The small dots in (A) represent the difference between the experimental data (circles) and the simulation (solid curve). Adapted from ref. 23.

**Figure 6.2**  
150
SEM image (A) of graphite nanofibers and TEM image (B) of carbon nanofibers.

**Figure 6.3**  
151
TEM images of PtRu/G (A) and PtRu/C (B). The insets show the corresponding XRD of carbon-supported PtRu nanoparticles.

**Figure 6.4**  
152
Diagram of EC-NMR sample preparation setup.
Figure 6.5

The point-by-point, area-normalized $^{195}$Pt NMR spectra of the PtRu/GNF and PtRu/CNF NPs at 80 K. The inset is a TEM image of the PtRu/G. B. The J coupling constants deduced by fitting the slow-beat curves to Eqn. (1). C. The Pt atomic fraction deduced by analyzing the $P_0$’s using Eqn. (2). The arrow indicates the resonance position of bulk Pt.

Figure 6.6

The slow beats measured at different spectral positions for (A) PtRu/GNF and (B) PtRu/CNF. The solid curves are the fits to Eqn. (1).

Figure 6.7

The across-the-spectrum $T_1$ data measured at 80 K for the PtRu/GNF (red circles) and the PtRu/CNF (black squares). The inset shows a representative spin-lattice relaxation curve with the three-parameter fit (solid curve). The error was directly given by the fitting program (Igor).

Figure 6.8

The s-like (C), d-like (B), and the total (A) $E_f$–LDOS values (red circles for PtRu/GNF and black squares for PtRu/CNF) deduced from the $T_1$ values and the Knight shifts of the spectral position at which the $T_1$ were measured. The open circles (PtRu/GNF) and squares (PtRu/CNF) are the respective s-like $E_f$–LDOS values calculated using RKKY J coupling constants determined by analyzing the slow beats.
Figure 6.9
A. CO stripping, B. CVs of MeOH oxidation, and CA of MeOH oxidation of the PtRu/GNF (red curves) and PtRu/CNF (black curves) respectively.

Figure A.1
The CO stripping curves of the Pt black after consecutive sulfur adsorptions. The red solid CV represents that of pure Pt black. The dashed line is the CV after the 6th deposition whose current scale is tripled.

Figure A.2
The sulfur stripping CVs of the sample after the 8th deposition. Multiple scans (up to 6) were needed to completely restore the Pt surface.

Figure A.3
The sulfur poisoning effect on H and CO adsorption and on Pt oxide formation.

Figure A.4
The sulfur poisoning effect on MeOH electro-oxidation. A. CVs without normalization (blank 8th = no methanol) and B. CVs normalized by the corresponding CO accessible areas.
LIST OF TABLES

Table 4.1 71
Comparison of the nominal and measured Pt packing densities (* indicates the 2\textsuperscript{nd} sample batch)

Table 5.1 104
Pt packing densities

Table 6.1 136
Physical properties of support materials

Table 6.2 140
PtRu/GNF data

Table 6.3 140
PtRu/CNF data
# Acronym Index

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPs</td>
<td>nanoparticles</td>
<td>ii</td>
</tr>
<tr>
<td>MeOH</td>
<td>methanol</td>
<td>ii</td>
</tr>
<tr>
<td>MOR</td>
<td>methanol oxidation reaction</td>
<td>ii</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide</td>
<td>ii</td>
</tr>
<tr>
<td>ORR</td>
<td>oxygen reduction reaction</td>
<td>ii</td>
</tr>
<tr>
<td>EC-NMR</td>
<td>electrochemical nuclear magnetic resonance</td>
<td>ii</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
<td>v</td>
</tr>
<tr>
<td>EDS</td>
<td>energy dispersive x-ray spectroscopy</td>
<td>v</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
<td>v</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
<td>v</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>inductively coupled plasma optical emission spectrometry</td>
<td>v</td>
</tr>
<tr>
<td>UV-vis</td>
<td>ultraviolet visible spectroscopy</td>
<td>v</td>
</tr>
<tr>
<td>PD</td>
<td>packing density</td>
<td>vi</td>
</tr>
<tr>
<td>RE</td>
<td>reference electrode</td>
<td>ix</td>
</tr>
<tr>
<td>CE</td>
<td>counter electrode</td>
<td>ix</td>
</tr>
<tr>
<td>WE</td>
<td>working electrode</td>
<td>ix</td>
</tr>
<tr>
<td>DOE</td>
<td>department of energy, US</td>
<td>1</td>
</tr>
<tr>
<td>PEMFC</td>
<td>proton exchange membrane fuel cell</td>
<td>3</td>
</tr>
<tr>
<td>DMFC</td>
<td>direct methanol fuel cell</td>
<td>3</td>
</tr>
</tbody>
</table>
RHE (reversible hydrogen electrode) 4
FTIR (Fourier transform infrared) 12
EXAFS (extended x-ray absorption fine structure) 16
ESR (electron spin resonance) 16
STM (scanning tunnel microscope) 19
ML (monolayer) 20
$E_f$-LDOS (Fermi level local density of states) 21
CV (cyclic voltammogram) 29
CA (chronoamperometry) 29
CNF (carbon nanofibers) 31
GNF (graphite nanofibers) 31
SPR (surface plasma resonance) 34
EC (electrochemical) 39
$\theta_{\text{Pt}}$ (Pt coverage) 43
EG (ethylene glycol) 62
J-M (Johnson-Matthey) 67
GC (glassy carbon) 68
HRTEM (high resolution TEM) 73
DFT (density functional theory) 99
RPM (rotation per minute) 101
Fcc (face-centered cubic) 103
RKKY (Ruderman-Kittel-Kasuya-Yosida) 133
CHAPTER 1
INTRODUCTION: BACKGROUND AND LITERATURE REVIEW

1.1. Concerns about Fossil Fuel Energy

It is well known that energy is the most important resource that enables the essential functions of the human society. In the past decades, accompanying a fast development of human society, the dilemma between a dramatically increasing consumption and a relatively unstable supply of energy emerged and became more and more obvious. Nowadays and in the foreseeable future, traditional energy sources, e.g. petroleum, natural gas and charcoal, that are also collectively named “fossil fuels”, are the most important energy sources. According to a Department of Energy (DOE)\(^1\), US report, fossil fuels are currently providing over 85% of the energy consumed in the United States, two-thirds of electricity power and all of the transportation fuels. The remaining share of energy sources is mainly provided by nuclear and hydroelectric power. Practically, fossil fuels are non-renewable resources since their formation took as long as millions of years, starting with the organic remains of prehistoric plants and animals. It has been estimated that the fossil energy sources so far on the earth can only provide 50–100 years’ supply to the human society. At the same time, the fuel burning process by which the chemical energy is released and finally transferred to electrical power generates a lot of gaseous byproducts, e.g. sulfur oxide, nitrogen oxide and carbon dioxide that are finally emitted into the atmosphere. Carbon dioxide is notorious for being a major contributor to the so-called “greenhouse effect” that has raised scientists’
concerns due to its negative impact on the climate change and the environment. The other two byproducts are also well known being the major chemicals leading to “acid rain” that has shown many adverse effects on natural environment and human health. According to the United Nations Framework Convention on Climate Change and the Kyoto protocol, the greenhouse gas emission should be controlled and reduced to as much as 80% in the coming 20 years to minimize the global climate change. The most important step proposed is controlling of the use of fossil fuels as well as developing new clean energy technology.

1.2. Introduction to Fuel Cells

1.2.1 History of Fuel Cells

Fuel cells therefore come up as promising candidates that meet the requirements for cleanness and sustainability. According to the fuel cell handbook released by the DOE, fuel cells are defined as electrochemical devices that could directly convert the chemical energy in the fuels into electrical energy. The history of fuel cells can be tracked back to over 150 years ago when Sir William Robert Grove built the first fuel cell in which sulfuric acid was used as the electrolyte, Pt as the electrocatalyst, and oxygen as the reductant to generate electricity. Ever since then, much effort has been made to push ahead this invention. In the late nineteen century, Mond et al. tried to use air and industrial coal gas to build a fuel cell. He also first coined the term of “fuel cell”. However it was not until the early 1960s that fuel cells first became the focus of worldwide research due to the application of alkaline fuel cells that were produced by
General Electric (GE) on Apollo space capsules for supplying the electricity and energy to produce drinking water. Ever since then, fuel cell science and technology has experienced a wave-like developing process. From the beginning of the space era in the 1960s and 1970s when the western countries suffered the energy crisis, fuel cells attracted a lot of attention and have been developed in a fast fashion. However, the abundant reserves of natural gas and petroleum resources evaluated by the energy economists then made the energy prices tend to decrease in the 1980s and 1990s, directly attenuating the passion for the R&D of fuel cell. Since late 1990s, fuel cells again became one of the hot focuses due to the increasing concerns about the environmental pollution all over the world.

The operational principles of fuel cells can be briefly and typically described as the following. On the anode side, fuels are oxidized in an electrochemical process and on the cathode side, oxidants are reduced at the same time. The ions, with the assistance of the carriers, are able to transport through the electrolyte that separates the anode and cathode and the electrons travel through the outside circuit converting chemical energy to electricity. Compared to the conventional internal-combustion engines that are used to generate energy using fossil fuels, fuel cells are very clean (emission of few pollutants) and of high efficiency (surpassing the maximum efficiency of an ideal Carnot engine). In terms of the different types of electrolyte employed, fuel cells can be primarily classified as follows:

1) polymer exchange membrane fuel cell (PEMFC)

2) direct methanol fuel cell (DMFC)
3) phosphoric acid fuel cell (PAFC)
4) alkaline fuel cell (AFC)
5) molten carbonate fuel cell (MCFC)
6) solid oxide fuel cell (SOFC)

1.2.2 Introduction to DMFC (PEMFC)

1.2.2.1 Working Mechanism of PEMFC

DMFC actually is a subset type of PEMFC in terms of the fuel cell structure and the working mechanism. The reactions in a hydrogen-fueled PEMFC can be summarized in equations (1) - (3), respectively.

\[
\begin{align*}
\text{H}_2 & \rightarrow 2\text{H}^+ + 2e^- & 0\text{V (vs. RHE)}
\end{align*}
\]

\[
\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} & \quad 1.229\text{V (vs. RHE)}
\]

\[
\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O} & \quad 1.229\text{V (vs. RHE)}
\]

1.2.2.2 Working Mechanism of DMFC

The term of DMFC was raised due to the pioneering work of DuBois\(^6\) and his collaborators when liquid hydrocarbons including methanol and ethanol were first used as the fuels. Since the purpose of the work in this dissertation is to investigate the Pt-based bimetallic electrocatalysts used in DMFC, a subset type of PEMFC, the
background introduction that follows will mainly focus on the review of recent progress made in the field of DMFC.

Compared to hydrogen-fueled PEMFC, the advantages of DMFC include 1) methanol is easy to be stored as a liquid while gaseous hydrogen stored in high pressure tank always brings some safety concerns during the use and transportation; 2) methanol has a higher energy density\(^7\) (17.6MJ/L, room temperature) than pressured hydrogen gas (1.9MJ/L, 20MPa).

A single DMFC (PEMFC) stack is schematically shown in Figure 1 below.

![Figure 1.1. Schematic structure and working mechanism of a DMFC stack](image)
According to the working mechanism, the reactions occurring in a DMFC are formulated by equations (4)-(6).

Methanol oxidation on the anode:

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad 0.016\text{V (vs. RHE)} \quad (4) \]

Oxygen reduction reaction on the cathode:

\[ \frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \quad 1.229\text{V (vs. RHE)} \quad (5) \]

The overall reaction:

\[ \text{CH}_3\text{OH} + \frac{3}{2}\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad 1.213\text{V (vs. RHE)} \quad (6) \]

1.2.2.3 Recent Progress of DMFC

DMFC is particularly suitable for transportation vehicles and other portable devices such as personal electronic products. In the past decades, much progress has been made in the application of DMFC into the real world. Many DMFC-powered substantial products have been reported, indicating a promising commercial future of the DMFC technology. For example, Toshiba\(^8\) and Samsung\(^9\) have released DMFC powered notebook computers. For even smaller DMFC, Hitachi\(^{10}\) has developed a DMFC-powered Personal Digital Assistant (PDA). The researchers from Germany’s Fraunhofer Institute have also developed a type of micro DMFC that could fit in a camcorder. It was reported that Toshiba has successfully put inside a cell phone a small DMFC with a capacity of ~3.3ml methanol\(^{11}\). In 2004, Yamaha named the first DMFC motor "FC06
Proto" and had a road test. Germany's Research Center Julich recently announced the development of a new DMFC-powered vehicle known as "JuMOVe".

![Some DMFC-powered products: A) Toshiba cell phone; B) Fraunhofer camcorder; C) Toshiba notebook computer; D) DaimlerChrysler NECAR5 schematics](image)

**Figure 1.2.** Some DMFC-powered products: A) Toshiba cell phone; B) Fraunhofer camcorder; C) Toshiba notebook computer; D) DaimlerChrysler NECAR5 schematics

### 1.2.2.4 Problems in the R&D of DMFC

The prototype products so far released have indicated a successful cooperation between scientists and engineers in the field of DMFC. However, although much progress has been made, there are still some challenging issues remaining unsolved in
terms of both fundamental research and engineering technology before the final commercialization of DMFC.

From Eqn. (6), it can be seen that the theoretical value of the cell potential should be around 1.213V. However, practically this value has never been obtained in a DMFC stack. There are several factors that account for this potential loss. The most important one is the sluggish kinetics of the methanol electro-oxidation reaction that makes the reaction efficiency far below its ideal thermodynamic value and leads to the so-called “kinetic loss” that is as high as 300mV. This is a major disadvantage of DMFC compared to hydrogen-fueled PEMFC since gaseous hydrogen itself has quite high reaction kinetics. To resolve this puzzling problem, electrocatalysts with better activities are needed to lower the activation energy for the reaction. On the cathode side, in addition to the slow reaction kinetics of oxygen reduction that also decreases the cell potential, a very small fraction of methanol molecules can always permeate through the solid electrolytes that separate the anode and cathode and form mixed potential on the cathode, accounting for a potential loss of ~100mV. Additionally, the transport of methanol molecules to the reaction sites (mass transport), which is principally related to the electrode structure, also makes a considerable potential loss of 50~100mV. From the above discussions, it can be easily concluded that kinetic loss is responsible for a major fraction of the overall potential loss and therefore research and development of the electrocatalysts is of great importance.

Besides the electrocatalysts, efforts also need to be made aiming at other technical issues. For example, Nafion® polymer film (DuPont) is currently the major solid
electrolyte adopted in DMFC (PEMFC). While having good proton conductivities, it is also permeable to methanol molecules that accounts for the potential loss from the mixed potential on the cathode\textsuperscript{15}. So developing new solid electrolyte that can block the permeation of methanol will be another possible remedy in addition to developing new cathode electrocatalysts.

1.2.3. Electrocatalysis in DMFC

1.2.3.1 Reaction Mechanism of Methanol Electro-oxidation

Numerous work has been done in the past years to develop Pt based anode electrocatalysts for methanol oxidation. In order to better guide the design for the electrocatalyst, it is of great importance to have a complete understanding of the reaction mechanisms of methanol oxidation on the Pt anode. Therefore, a good knowledge about the following issues is necessary\textsuperscript{5}: identification of the reaction intermediates and the final products; the dependence of the intermediate steps on the catalyst’s structure. Eqn. (6) only gives an overall reaction. What really matters are the step-by-step reactions occurring during the whole reaction process. Fortunately this topic has been well documented in the literature\textsuperscript{16}. Briefly, methanol oxidation occurring on the anode is comprised of 1) electrosorption of methanol molecules on Pt sites; 2) triple dehydrogenation of adsorbed methanol; 3) oxidation of the intermediate species with oxygenated species pre-adsorbed on Pt. The whole sequence of reaction steps are shown in the equations below\textsuperscript{16}.  

9
\[
\text{CH}_3\text{OH} + \text{Pt(s)} \rightarrow \text{Pt} - \text{CH}_2\text{OH} + \text{H}^+ + e^- \\
(7)
\]

\[
\text{Pt} - \text{CH}_2\text{OH} + \text{Pt(s)} \rightarrow \text{Pt}_2 - \text{CHOH} + \text{H}^+ + e^- \\
(8)
\]

\[
\text{Pt}_2\text{CHOH} + \text{Pt(s)} \rightarrow \text{Pt}_3 - \text{COH} + \text{H}^+ + e^- \\
(9)
\]

\[
\text{Pt}_3\text{COH} \rightarrow \text{Pt} - \text{CO} + 2\text{Pt(s)} + \text{H}^+ + e^- \\
(10)
\]

\[
\text{Pt(s)} + \text{H}_2\text{O} \rightarrow \text{Pt} - \text{OH} + \text{H}^+ + e^- \\
(11)
\]

\[
\text{Pt} - \text{OH} + \text{Pt} - \text{CO} \rightarrow \text{Pt} - \text{COOH} \\
(12a)
\]

or

\[
\text{Pt} - \text{CO} + \text{H}_2\text{O} \rightarrow \text{Pt} - \text{COOH} + \text{H}^+ + e^- \\
(12b)
\]

\[
\text{Pt} - \text{COOH} \rightarrow \text{Pt(s)} + \text{CO}_2 + \text{H}^+ + e^- \\
(13)
\]

According to this mechanism, the dehydrogenation of the adsorbed methanol occurs consecutively on Pt sites. Clearly at least three neighboring Pt sites (Pt ensemble) are required to complete this dehydrogenation process and after that, carbon dioxide was generated. Kuver et al.\textsuperscript{17} proposed another similar but slightly different reaction mechanism in which a methanol molecule is first adsorbed onto the Pt surface and then dehydrogenated triply on the Pt ensemble to form the linear or bridge-bonded or multi-bonded \text{CO}_{\text{ads}} which is consequently oxidized.

In summary, the above mechanisms illustrate the formation of CO as a reaction intermediate that is considered a poisoning species due to its strong bonding to Pt. Obviously, the rate-determining step should be either (12a) or (12b) by which adsorbed \text{CO}_{\text{ads}} reacts with \text{OH}_{\text{ads}} to generate \text{CO}_2 and water. As can be seen from the reaction
mechanism outlined above, the formation of Pt-OH in Equation (11) is critically important since it supplies oxygen species to react with Pt-CO and completes the oxidation process. However, the adsorption and dissociation of water molecules on Pt do not occur at potential lower than $0.5V^{18}$ (vs. RHE) while dissociative adsorption of methanol leads to strongly bound CO that poisons the surface. This renders quite a high overpotential of methanol oxidation in comparison to the theoretical value ($0.016V$ vs. RHE). On the other hand, at a potential above $0.75V$ (vs. RHE), Pt oxide is formed to block the surface and impede the further oxidation of methanol molecules$^{19}$. Therefore, generating oxygen-containing species at lower potential will be one effective strategy to accelerate the slow reaction kinetics of methanol oxidation.

In addition, a direct oxidation mechanism of methanol to carbon dioxide ($CO_2$) without the formation of intermediate CO has also long been discussed. This is the so-called “dual path mechanism”.$^{20}$ Much work has been done to investigate this dual path mechanism by using different Pt single crystalline surfaces$^{21-23}$. It has been concluded that this dual path mechanism is Pt surface structure specific and potential-dependent$^{24,25}$. Since this reaction pathway is not dominant in the interesting working potential of DMFC and doesn’t account for the low kinetics of methanol electro-oxidation, it will not be further discussed in this chapter.

1.2.3.2 Review of Pt-based Electrocatalysts

Due to its unique activity for the electro-oxidation of both hydrogen and methanol, Pt has always been a “hot pot” of electrocatalysts developed for hydrogen-fueled PEMFC
and DMFC. However, its high price and the fact that it is easily poisoned by the trace amount of CO that is present in the hydrogen gas during industrial production\textsuperscript{26} or by the intermediate CO generated during the dissociation of methanol limit the commercialization future of the PEMFC and DMFC to a noticeable extent. Accordingly, in the past decades, scientists have devoted themselves to R&D of new electrocatalysts with better CO tolerance and with lower cost.

It is well known that in heterogeneous catalysis, the reactivity and selectivity of the catalyst are always determined by its electronic and geometric structure\textsuperscript{26,27}. A complete understanding of the relationship between the structure and the reactivity is both a prerequisite and a great challenge in the design of the catalysts. Surface scientists in the past decades, with the assistance of the fast development of the modern instrumentation, have obtained many surface characterization methods to examine single crystalline surface \((hkl)\) of the metals\textsuperscript{28}. It will be feasible to extend their understandings obtained on single crystalline surface to more complex systems i.e. real world catalysts. Using Pt\((hkl)\) as the model, numerous amounts of research regarding the electrocatalysis of Pt have been accomplished. It was anticipated that some enlightenment for the catalyst design could be obtained by establishing a clear correlation between the reaction activity and surface orientation. For example, Xia et al.\textsuperscript{29} adopted the \textit{in situ} FTIR to examine the intermediate and final products of the methanol oxidation on Pt polycrystalline and Pt\((hkl)\). In combination with electrochemistry characterizations, they found that the main pathway of methanol oxidation includes the formation of CO\(_{\text{ads}}\) and the onset potential for the oxidation of CO\(_{\text{ads}}\) is in the order Pt(111) < Pt(110) < Pt(100). Stuve et al.\textsuperscript{30} also
found that once the potential is below 0.5V (vs. RHE), the Pt(100) surface exhibits a greater tendency to dehydrogenate the methanol oxidation, resulting in a higher CO$_{ads}$ coverage than Pt(111). When the potential is higher than 0.5V, Pt(111) indicated faster reaction kinetics towards CO$_{ads}$ oxidation. The highest CO tolerance of Pt (111) is thus verified. Similar observations have also been made by Lamy et al.$^{31}$.

Consequently, research interests turned to Pt and Pt-based binary or ternary electrocatalysts that were considered as the real world catalysts$^3$. It is well known that decreasing the size of the catalysts to the nanometer range increased the surface fraction of the atoms per unity mass of the catalysts and then the contact area between the catalysts and the reactants. Therefore, the utilization of the catalysts can be substantially improved. Nevertheless, small particle size will make the atoms on the surface of the nanoparticles undercoordinated and thus more active for catalytic reaction in term of the d-band center theory advanced by Norskov et al.$^{32}$ Thus, the size effect of Pt nanoparticles has been intensively investigated to optimize the particle size for methanol or CO oxidation. A common recognition here is that the particle size effect observed in methanol oxidation takes effect in terms of the formation of Pt-OH at lower potential and accordingly Pt-CO could be oxidatively removed with less overpotential. On the other hand, different opinions still exist on what is the optimal size. Rhee et al.$^{33}$ examined the methanol oxidation activities of carbon nanofibre supported Pt nanoparticles with a size range of 1.1nm to 5.6nm and compared the results to those from Pt(111), Pt(100) and Pt polycrystalline surface. They found that when particle size was larger than 1.8nm, Pt nanoparticles demonstrated higher catalytic activities. Once the particle size became
smaller, the aggregation of Pt nanoparticles counteracted the advantages brought with the size effect. Maillard et al. also found that by decreasing Pt particle size from 3.1nm to 1.7nm, the CO oxidation peak shifted positively by ~90mV, confirming a better CO tolerance of the former. Nart et al. studied the methanol oxidation on carbon black supported Pt nanoparticles and found that an optimal size range for efficient methanol oxidation was between 3 to 10nm. Otherwise too small or too large nanoparticles always led to the loss of reaction efficiency due to the formation of formaldehyde as a result of partial oxidation. Using polyalcohol reduction, Liu et al. found that the optimal size of Pt particles supported on Vulcan XC-72 carbon materials was about 3.5-4nm. Frelink et al. found that Pt/C showed a constant activity for methanol oxidation in a range of 4.5~10nm, but the activity decreased in a range of 1.2~4.5nm. They attributed this trend to the variation of the OH/methanolic species coverage ratio. That is, for too small Pt particles, OH coverage was too high, leaving less Pt sites available for the adsorption of methanol molecules. In addition, it has been noticed that the synthesis method also has an effect on determining the optimal size of Pt particles for methanol oxidation. For example, Tang et.al synthesized Pt nanoparticles by means of an organic sol method on the surface of a glassy carbon electrode and found that 3.8nm was best for methanol oxidation. However, Murakami et al. used a glass carbon electrode as the substrate and obtained Pt nanoparticles by electrochemical methods. They found that in the studied size range of 2nm to 7nm, the catalytic activities of Pt nanoparticles decreased with a decreasing particle size. A debatable study conducted by Arenz et al. indicated on one hand, a particle size-independent CO stripping peak and on the other hand, a particle
size-dependent CO oxidation rate with the carbon supported Pt nanoparticles having a size range of 1 to 5nm. Therefore, it’s practically impossible to make a definite conclusion on the optimal size of the Pt nanoparticles for methanol oxidation without regard to factors such as support materials, synthesis method, and experimental conditions. Further efforts need to be made to elucidate this confusing issue.

From a fundamental aspect, as mentioned above, the dissociation of water molecules and the consequent formation of OH$_{\text{ads}}$ at lower potential (< 0.5V vs. RHE) is a critical step toward lowering the overpotential caused by the strong bonding of Pt-CO$_{\text{ads}}$. Therefore, a simple idea is to incorporate into Pt catalysts certain components that can promote the formation of OH$_{\text{ads}}$ at low potentials. Following this strategy, a lot of Pt-based binary or ternary metal and metal oxide catalysts have been studied. An non-exhaustive search of the literature showed that the studied systems included PtRu$^{42}$, PtNi$^{43}$, PtCo$^{44}$, PtSn$^{45}$, PtWO$_3$$^{46}$, PtMoOx$^{47}$, PtRuM(M = W, Mo, V)Ox$^{48}$, PtRuOsIr$^{49}$, et al. To date, PtRu bimetallic nanoparticles have been considered the best electrocatalysts to promote the methanol oxidation via the so-called “bifunctional mechanism”$^{50,51}$ which can be expressed in the equations below.

\[ M + H_2O \rightarrow M - OH + H^+ + e^- \] (14)

\[ M = \text{promoting metals} \]

\[ M - OH + Pt - CO \rightarrow CO_2 + Pt + M + H^+ + 2e^- \] (15)

It has been observed that Ru-OH can be formed at a potential as low as 0.2V (vs. RHE)$^{52}$, ~0.3V lower than Pt (0.5V vs. RHE). Therefore, the presence of Ru in PtRu
makes the oxidative removal of Pt-CO much easier than pure Pt. Typical CO stripping curves of PtRu alloy and Pt black (from Johnson-Matthey) are shown in Figure 1.3 below.

![Figure 1.3. CO stripping curves of Pt black (solid) and PtRu alloy (dotted)](image)

In addition to “bifunctional mechanism”, the enhanced CO-tolerance of PtRu alloy has also been assigned to the electronic effect\textsuperscript{25}, in accordance with which, electronic alteration occurring between Pt and Ru atoms in close contact resulted in a weakened Pt-CO bonding. Lin et al.\textsuperscript{53}, with the assistance of thermal desorption, found that CO desorption from Pt occurred at a higher temperature in comparison to PtRu (50:50) alloy, confirming a weakened Pt-CO bonding on the latter. Goodenough et al.\textsuperscript{54} used XPS, EXAFS and ESR to examine the PtRu alloy nanoparticles and found an electron transfer from Ru to Pt, which was believed to account for the synergistic promotion of the CO
oxidation on PtRu. Babu et al.\textsuperscript{55} adopted a novel EC-NMR technique to obtain the electronic information of PtRu alloy nanoparticles and found that alloying Ru with Pt increased the d-orbital vacancies of Pt atoms, therefore reducing the back-donation of electrons from Pt to CO and consequently weakening the Pt-CO bonding.

For PtRu alloy nanoparticles, particle size effect has also been studied. Based on the research results respectively obtained by Ren et al.\textsuperscript{56} who studied unsupported PtRu black and by Takasu et al.\textsuperscript{57} who worked on Vulcan XC-72R supported PtRu nanoparticles, 3nm was considered as the optimal size for methanol oxidation. However it needs to be pointed out that all the samples studied had the same Pt:Ru ratio of 50:50. Therefore, the 3nm optimal size only applied to the PtRu (50:50) nanoparticles.

In addition to particle size, the atomic ratio of Pt:Ru is another important variable affecting the overall catalytic activities of PtRu. Since pure Ru is inactive towards methanol electro-oxidation at room temperature\textsuperscript{58} and pure Pt has an inferior CO tolerance compared to PtRu alloy, an optimal atomic ratio of Pt:Ru is expected between 0% (pure Ru) and 100% (pure Pt). Gasteiger et al.\textsuperscript{59} found that at room temperature, PtRu alloy with a surface composition of 10% Ru had the highest CO tolerance. However, when the temperature was elevated to 60ºC, this optimal composition became 33% Ru. Still, Dinh et al.\textsuperscript{59} concluded that a well-alloyed PtRu with a 50% Ru composition was the best catalyst. In conclusion, no definite conclusion on this issue has been reached yet. An effort has been made in this thesis to elucidate this remaining puzzle by means of a surface modification method. This part of work will be discussed in detail in the following chapters.
Additionally, the nature of the Ru present in PtRu alloy is also an interesting research topic due to its role as the promoter in PtRu alloy for methanol/CO oxidation. Babu et al.\textsuperscript{60} believed that in alloyed PtRu nanoparticles, the metallic Ru played a major role in the promoting effect. Their assertion does not conflict with the proposed reaction pathway shown in equation (14) through which water molecules dissociated on oxyphilic Ru surface to form Ru-OH that later participated in the methanol oxidation. On the other hand, Long et al.\textsuperscript{61} claimed that it’s hydrous ruthenium oxide (RuO\textsubscript{x}H\textsubscript{y}) that supplied the oxygen-containing species. This claim is also supported by the electrochemical behavior of Ru observed by Hadzi-Jordanov et al.\textsuperscript{62} whose results indicated that Ru is readily and reversibly oxidized in acidic media in a potential range of 0.2V ~ 0.4V (vs. RHE), coinciding with the potential range where the promoting effect worked\textsuperscript{59}.

1.2.3.3 Surface Modification Methodology for PtRu Electrocatalysts

As the best electrocatalyst so far for methanol oxidation, PtRu still has not met the requirements for commercial use in DMFC in terms of catalytic activity and long term durability as well as material cost. There is still much space to be filled in this research area. For example, it will be an interesting issue that whether or not other forms of PtRu could also provide comparable or even better electrocatalysts than PtRu alloy for methanol/CO oxidation. Recently Dubau et al.\textsuperscript{63} compared the simply mixed Pt and Ru colloid nanoparticles and the alloyed PtRu nanoparticles with same atomic ratio and same carbon support. They found that the mixture of Pt and Ru had a slightly better CO tolerance than the latter, indicating that alloy is probably not the only option as the form
of the electrocatalyst for DMFC. Previous research\textsuperscript{55,60} revealed that in a PtRu alloy nanoparticle, a Pt-enriched surface and Ru-enriched core always formed and the nominal atomic ratio thus does not hold across the whole nanoparticle. These previous works illustrated the possibility that Pt-modified Ru surfaces or Ru-modified Pt surfaces have the potential to be used as electrocatalysts. From the point of view of fundamental research, these types of bimetallic surfaces offer simple and effective models for further studies. This surface modification methodology can be tracked back to Watanabe et al.\textsuperscript{50} who electrochemically deposited Ru onto the Pt surface. After that, this electrodeposition method has been expanded to modify Pt(hkl)\textsuperscript{64,65} and Pt nanoparticles\textsuperscript{66}. According to the scanning tunnel microscope (STM) images, Ru nanoislands were formed on the Pt surface. By varying the deposition time, Ru coverage can be controlled\textsuperscript{65}. Later a spontaneous deposition method that was originally used to produce Bi\textsuperscript{67} and Sn\textsuperscript{68} adlayers onto Pt(hkl) without the assistance of the external potential was introduced by Wieckowski et al.\textsuperscript{69,70} to form Ru adlayers on Pt(hkl). The proposed reaction mechanism involved the reduction of Ru hydrate to RuO and oxidation of Pt.

\[
\text{[RuO(H}_2\text{O)}_4]^{2+} \rightarrow \text{RuO}_{\text{2ads}} + 3\text{H}_2\text{O} + 2\text{H}^+ \quad (16)
\]

\[
\text{RuO}_{\text{2ads}} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{RuO}_{\text{ads}} + \text{H}_2\text{O} \quad (17)
\]

\[
\text{Pt} + x\text{H}_2\text{O} \rightarrow \text{PtO}_x\text{H}_y + (2-y)\text{H}^+ + (2x-y)\text{e}^- \quad (18)
\]

It turned out that this type of well-defined Pt(hkl)/Ru bimetallic surface made it convenient to investigate the reaction mechanism of CO oxidation in term of electrochemistry\textsuperscript{71} and vibrational spectroscopic techniques\textsuperscript{72}. Afterwards Adzic et
al.\textsuperscript{73,74} successfully applied this spontaneous deposition method in an inverse way to form a Pt or Pd adlayer on a Ru(0001) surface by immersing a freshly cleaned Ru(0001) into \([\text{PtCl}_6]^{2-}\) or \([\text{PdCl}_6]^{2-}\) solution.

\[
\text{[PtCl}_6]^{2-} + 4\text{e}^- \rightarrow \text{Pt}^0 + 6\text{Cl}^- \quad (19)
\]

\[
\text{Ru}^0 + x(\text{H}_2\text{O}) \rightarrow \text{RuO}_x\text{H}_{y} + (2x-y)\text{H}^+ + (2x-y)\text{e}^- \quad (20)
\]

Taking into consideration materials cost, and the fact that Pt is fourteen times more expensive than Ru\textsuperscript{75}, a Pt-decorated Ru catalyst has a more promising future than a Ru-decorated catalyst if the former could indicate comparable catalytic activity to Pt. Not surprisingly further efforts have been made by the Adzic group\textsuperscript{76-78} to examine Pt-decorated Ru nanoparticles, which practically resemble real world catalysts. They found that even with only \(~0.11\) monolayer (ML) of Pt, the as-prepared Pt-decorated Ru/C (PtRu\textsubscript{20}, according to the atomic ratio) indicated almost identical activity in the hydrogen oxidation reaction in comparison to that of E-TEK PtRu(1:1)/C alloy nanoparticles\textsuperscript{76}. An even better CO tolerance was also observed in terms of the lower onset potential for CO oxidation on PtRu\textsubscript{20} compared to PtRu (1:1)/C and Pt/C\textsuperscript{78}! Nevertheless, in the same work, tested in an operating fuel cell for 1000 hours, the PtRu\textsubscript{20} also illustrated excellent long-term performance stability with the presence of a trace amount of CO. Obviously, in terms of both material savings and reaction activities, this Ru/Pt model offers a promising opportunity for the electrochemist to investigate its application in PEMFC/DMFC.
Meanwhile, a limitation to the application of the spontaneous deposition method is that a clean substrate surface is always a prerequisite for an effective deposition. For this purpose, the Pt(hkl) or Ru(hkl) that was used as the substrate has to be cleaned by annealing at ultrahigh temperature under ultrahigh vacuum (UHV) conditions. In case of nanoparticle substrates such as Ru, a 200~300ºC heating under a hydrogen atmosphere is required to maintain a metallic Ru surface. The special setup, use of hydrogen and high temperature demanded made this spontaneous deposition method practically difficult for industrial applications. Therefore, following this surface modification strategy, new experimental methods need to be developed to obtain such Ru/Pt catalysts in a large scale.

1.2.3.4 Application of EC-NMR in Electrocatalyst Research

EC-NMR spectroscopy was recently developed respectively by Wieckowski et al. and Reimer et al. as a novel technique to investigate nanosized electrocatalysts such as Pt and Pt/C nanoparticles. With the assistance of this technique, two types of research have been conducted. The first type is Pt NMR through which information about metal surface properties could be obtained by monitoring the change of the Fermi level local density of states (E_f-LDOS) on Pt sites. The other type of experiment is CO NMR in which CO was adsorbed onto the surface of Pt or Pt/C nanoparticles after the decomposition of labeled MeOH molecules. By means of examining the 2π*-like and 5σ-like E_f-LDOS on CO, the adsorbate-substrate bonding information was obtained. Notice that Pt-CO interaction is the main topic of the research in the area of...
electrocatalysis for DMFC and both of them could be directly examined by EC-NMR. Such a technique offered a lot of opportunities for the electrochemists to further investigate the Pt-based electrocatalysts. For example, with the assistance of EC-NMR, Babu et al.\textsuperscript{83} confirmed an electronic alteration caused by Ru in PtRu alloy nanoparticles in terms of the observation that $E_f$-LDOS of both metal surface and $2\pi^*$ orbital decreased. This is consistent with the electronic effect\textsuperscript{53} that was advanced in early research to account for the CO tolerance enhancement for PtRu systems. Using the same EC-NMR, Yano et al.\textsuperscript{84} found that for Pt/C with average diameters in a range of 1 to 5nm, the surface Pt atoms indicated a negligible change in electronic properties according to the surface peak position of $^{195}\text{Pt}$ and $T_1$ length, which cross validated the conclusion from the electrochemistry experiments by which the same Pt/C samples indicated size-independent reaction activities in oxygen reduction reaction (ORR) experiments. An earlier work accomplished by Tong et al.\textsuperscript{85} compared results of IR and $2\pi^*$-like $E_f$-LDOS from $^{13}\text{CO}$ adsorbed on Pt electrocatalysts and found them consistent with each other according to the variation of Pt-CO bonding strength. From the selective work above, it can be seen that EC-NMR either itself or in combination with the other techniques could provide a wealth of useful information about the surface electronic properties of Pt-based electrocatalysts.

As a relatively new technique, EC-NMR has a great potential to be applied for fuel cell electrocatalysis. For example, to date only very few types of Pt-based electrocatalysts have been studied with EC-NMR, e.g. Pt black, Pt/C, PtRu black. It will be of great significance to expand the studied objects to a wider scope. The most direct
research is to use the EC-NMR to study other Pt-based binary or ternary catalysts such as PtAu, PtSn and so on. Nevertheless, it was reported that forPt/C nanoparticles, the interaction between Pt nanoparticles and carbon support is more than physical in terms of the variation of the binding energy of Pt_{4f} electrons. EC-NMR is apparently a convenient tool to examine such an interaction and furthermore to screen the whole spectrum of carbon support materials used for Pt electrocatalysts, e.g. carbon black, carbon nanotubes, carbon nanocoils, carbon nanofibres and so on. It was expected that such a technique could eventually become a widely used characterization method in the near future in the field of interfacial electrochemistry.

1.3. References

(2) http://unfccc.int/kyoto_protocol/items/2830.php (Accessed Aug 29, 2009)


(75) Based on the data from Johnson Matthey website.


CHAPTER 2
SYNTHESIS AND CHARACTERIZATION METHODS

2.1. Electrochemistry

All the electrochemical characterization experiments, except ORR, were conducted in a traditional three-electrode electrochemical cell (shown in Figure 2.1) using an EG&G273A potentiostat (Princeton Applied Research) controlled by a PC with a CoreWare software package (Scribner) or a CHI 760C EC workstation (CHI Instrument) with CHI760 software. All cyclic voltammograms (CVs) were recorded with a scan rate of 50 mv/s. The commercial GC electrode, Pt gauze and Ag/AgCl (3M) (Bioanalytical) were used as the working, counter, and reference electrode, respectively. All electrode potentials in this paper were cited with respect to the Ag/AgCl (3M) reference electrode if not specified. A 0.1M HClO$_4$ solution prepared with Milli-Q water and 7M HClO$_4$ (double-distilled, GFS Chemicals) was used as the electrolyte. For CO stripping experiments, ultrahigh purity CO gas (MG Industries) was bubbled for 2 mins followed by Ar bubbling for another 5 mins. During the whole process, potential was held at 0V. At least two cycles of CVs were recorded to make sure that all of the CO molecules oxidized were from the electrode surface, not from the residual CO in the electrolyte solution. For MeOH electro-oxidation, a 0.1M HClO$_4$ solution with 0.5M MeOH was used. In the chronoamperometry (CA) experiments which were performed first, the electrode was pre-cleaned by holding potential at 0V until the current decayed to a
negligible level, and then the MeOH was injected under an active stirring condition. The CA curves were recorded while the potential was held at 0.2V for 1 hour. Under the same condition, the background current was measured without the presence of the MeOH and was subtracted from the CA curve. After the CA measurements, multiple cycles were run to obtain stable and repeatable MeOH electro-oxidation CVs. Other sample-specific procedures such as electrode preparation will be given in individual chapters.

ORR experiments were run on a modulated speed rotator (Pine Instrument Co.) synchronized with the CHI 760C electrochemistry workstation. Before running an ORR experiment, a 150mL 0.1 M HClO$_4$ solution was O$_2$-saturated by bubbling with ultrahigh pure O$_2$ (MG industries) for at least 30mins. During the measurements, the O$_2$ gas was flushed over the solution. The scan rate for all ORR measurements was set to 20mV/s. A photograph of the experimental setup was shown in Figure 2.2

2.2. Nanoparticle Synthesis

2.2.1. 17.5nm Au nanoparticles synthesis. The citrate reduction method first proposed by Frens$^1$ was used to synthesize the 17.5nm Au NPs. The detail procedure was described in a paper of Ji and Peng$^2$. A 100mL aqueous 0.25mM HAuCl$_4$ (Strem Chemicals) solution was boiled while being stirred, followed by the addition of 1.2mL 5% sodium citrate (Fisher Scientific) solution, in order to reach a molar ratio of sodium citrate to HAuCl$_4$ as 3.5. The reaction was run until the color of the solution became wine red, indicating the formation of the Au NPs. After the syntheses, the Au NP
solutions were stored in an aluminum-foil-wrapped vial and placed in the dark to prevent light induced damage to the NPs.

2.2.2. 5.2nm Au nanoparticle synthesis. Following the synthesis procedure described by Natan and his coworkers, 5.2nm Au nanoparticles were synthesized via a citrate reduction method at room temperature. 1 mL of 1% HAuCl₄ was added into 90mL water under vigorous stirring. While a homogeneous solution is formed, 2mL 38.8mM sodium citrate was added dropwise. After another minute, 1mL freshly prepared NaBH₄ solution (0.075% in 38.8mM sodium citrate) was added. The reaction continued 5mins and the resulting solution was stored in a bottle wrapped with aluminum foil in a 4ºC refrigerator.

2.2.3. PtRu Nanoparticles Synthesis (by Dr. In-Su Park, Seoul National University). Two PtRu bimetallic NPs supported on different carbon supports, graphite nanofibers (GNF) and carbon nanofibers (CNF) were synthesized by the conventional borohydride reduction method. The commercial GNF (Iljin Nanotech Co.) and CNF (Carbon Nano-Material Technology Co.) were used as support material. First, the carbon materials were dispersed in ultrapure water (18.2 MΩ·cm), and then a given amount (calculated to give a nominal total metal loading of 60% wt) of Pt salt (H₂PtCl₆·xH₂O) and Ru salt (RuCl₃·xH₂O) were added to the solution. After being mixed for ~ 1 h at room temperature, the metal salts were reduced by NaBH₄ while the solution was stirred vigorously. The resulting precipitates were washed with deionized water and freeze-dried without any heat treatment.
2.3. Transmission Electron Microscope (TEM)

TEM images were taken using a JEM-2100f TEM (JOEL Electronics) microscope located at Maryland nanocenter of University of Maryland, College Park. In grid preparation, the sample suspensions were diluted with 2-propanol. Normally one drop of the prepared solution was loaded onto a copper grid coated with carbon film (200mesh, Electron Microscopy Sciences). The grid was dried in a vacuum desicator and stored in a grid container for use. The detailed preparation procedures are sample-specific and will be described in detail in the following chapters respectively.

2.4. Energy Dispersive x-ray Spectroscopy (EDS)

EDS analysis was conducted through an EDS detector attached to the JEM-2100f TEM for quantitative analysis of the composition of PtAu nanoparticles. For each grid, at least 3 samplings from 3 different areas were taken and for almost all the samples, the 3 measurements gave the same ratios, indicating that the local compositions of the PtAu sample were invariable.

2.5. X-ray Diffraction (XRD)

XRD measurements were carried out using a Rigaku RAPID curved IP X-ray powder diffractometer with Cu Kα radiation (1.5406Å) and an image plate detector. For XRD sample preparation, the as-prepared samples were completely dried in a vacuum desicator and then transferred into a 0.5mm-diametered sampling tube (Mark-Rohrchen)
which was ready for measurement after a flame-sealing. This characterization technique was used to examine the crystalline structures of the Pt-decorated Ru nanoparticles.

2.6. X-ray Photoelectron Spectroscopy (XPS) (by Dr. Savelas A. Rabb, NIST*)

XPS data were acquired on a Kratos Axis Ultra DLD using an Al Ka (1486.7 eV) source. Samples were drop-cast from sonicated methanol suspensions onto cleaned Si substrates. Experiments were carried out on two different locations of the same substrate to ensure the consistency of the measurements. This characterization technique was adopted for the Pt-decorated Ru nanoparticles.

2.7. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) (by Dr. Christopher Zangmeister, NIST*)

ICP-OES measurements were conducted for Pt-decorated Ru nanoparticles, in the axial mode using a PerkinElmer Optima 5300 DC ICP-OES instrument. Operating conditions were as follows: power = 1.5kW; nebulizer gas flow = 0.6 L min⁻¹; auxiliary gas flow = 0.5 L min⁻¹; sample uptake = 1mL min⁻¹. A MiraMist nebulizer and cyclonic spray chamber were used to introduce the samples into the ICP. The calibration was performed by using the method of standard additions to compensate for any matrix effects. Pt 265.945 and Ru 240.272 were observed to determine the Pt and Ru sample concentrations with Sc 357.634 as an internal standard emission line. Three to four different aliquots were prepared for each sample and two measurements were performed.

* National Institute of Standards and Technology,
on each aliquot. The average values of these measurements were reported. As a control, the Johnson Matthey PtRu(1:1) alloy NPs sample was analyzed with the Pt-decorated samples in two independent runs. The averaged results of the Pt:Ru ratio from the alloy sample were 1.14±0.03 and 1.10±0.06, respectively.

2.8. Ultraviolet-Visible Spectroscopy (UV-vis)

UV-vis spectra were obtained using Agilent 8453 UV-vis spectrometer to investigate the Pt covering effect on the surface plasma resonance (SPR) of Au nanoparticles. In a typical measurement, the sample solution was introduced into 1-cm path length quartz cuvette. The scanned wavelength was usually in a range of 300-800nm and the expected SPR peak is usually between 500~520nm, depending on Au size and Pt packing density. For comparison, all the PtAu samples prepared for UV-vis have the same ppm of Au, in accordance with which a primitive quantitative analysis of the effect of the Pt packing density on Au core was acquirable.
Figure 2.1. Three electrode electrochemical cell: reference electrode (RE); counter electrode (CE); working electrode (WE)
2.9. References


CHAPTER 3

A COVERAGE DEPENDENT STUDY OF PLATINUM SPONTANEOUSLY-DEPOSITED ONTO GOLD AND RUTHENIUM SURFACES: DIRECT EXPERIMENTAL EVIDENCE OF THE ENSEMBLE EFFECT FOR METHANOL ELECTRO-OXIDATION ON PLATINUM*

3.1. Abstract

In this chapter, direct experimental evidence that can be unambiguously attributed to the need of an ensemble of a minimum number of neighboring Pt atoms for methanol electro-oxidation has been observed for the first time. This was realized by a Pt coverage-dependent investigation of methanol and CO electro-oxidation on Pt sites generated via spontaneous deposition onto both Au and Ru surfaces. CO stripping voltammograms also show clear evidence of a substantially strengthened CO-Pt bonding for submonolayer Pt deposited on the Au substrate over a range of ca. 0.22 to 0.77, which is in qualitative agreement with the theoretical prediction based on the Hammer-Nørskov d-band center model. However, the degree of the bond strengthening depends on the Pt coverage, being stronger for lower coverage.

3.2. Introduction

It has long been believed and also widely evoked in the mechanistic discussions of the MeOH electro-oxidation that a number of simultaneously accessible neighboring Pt sites are needed in order to extract three protons from the MeOH\textsuperscript{1}. Historically, such a

hypothesis of an ensemble of the neighboring Pt sites required for the dissociative MeOH adsorption was first critically discussed by Parsons and van der Noot in comparison with possible reaction routes for the electro-oxidation of formaldehyde and formic acid. The strongest (indirect) support of the ensemble hypothesis so far has probably been the work published by Gasteiger et. al. in which it was found that, for a series of well-characterized PtRu alloys in terms of their surface composition, the most active alloy surface for the MeOH electro-oxidation at room temperature was the one consisting of only 10 atomic% of Ru. This observation was rationalized by a statistical model that assumes that an ensemble of three Pt atoms pairing with a neighboring Ru is the best morphological configuration for the initial dissociative MeOH adsorption and the subsequent CO oxidation. Additional support to this binomial statistical model comes from the observation that a surface consisting of 50 atomic % of Ru is instead the most active surface for CO and HCOOH electro-oxidations which are believed to not require multiple neighboring Pt atoms. Still, as important and essential as it is to a detailed mechanistic understanding of the MeOH electro-oxidation on the Pt surfaces, it is to our best knowledge that no direct experimental proof of the ensemble hypothesis has ever been offered thus far. Research work in this chapter reports a coverage dependent investigation of Pt spontaneously deposited onto Au and Ru surfaces that provides the first direct experimental evidence of the ensemble effect postulated for methanol (MeOH) electro-oxidation on a Pt surface. That is, the Pt-decorated surfaces are inactive for the MeOH electro-oxidation at low Pt coverage but become active at high Pt coverage. Interestingly enough, however, it was also observed that, for the Pt deposited
on Au, the lower the Pt coverage is, the stronger the Pt-CO bond is compared to that on a pure Pt surface\(^5\).

On the other hand, it has also been predicted by the Hammer-Norskov d-band center model\(^6\) that both impurity (i.e., the isolated Pt atoms) and monolayer of Pt deposited on a Au substrate will have a much stronger CO-Pt bond than a pure Pt surface, being 0.46 eV stronger for the former and 0.43 eV for the latter\(^5\). A temperature-programmed-desorption investigation\(^8\) of chemisorbed CO on vapor-deposited Pt on a Au(111) surface indeed showed a strengthened Pt-CO bond on a deposited Pt monolayer. It, however, suggested an instead much weakened Pt-CO bond on isolated Pt atoms. While the latter weakening of the Pt-CO bond which is apparently in contradiction with the theoretical prediction was rationalized by a combination of unfavorable segregation, coordination, and entropic energies, more investigations are clearly needed to further disentangle this (apparent) controversy. Thus, it is within these contexts that the new experimental observations to be reported in the following are of current interest and therefore timely importance. They are offering additional insightful information that will better our understanding of both subjects.

3.3. Experimental

All electrochemical experiments were carried out in an Ar-blanketed conventional three-electrode electrochemical (EC) cell using an \(EG&G\ 273A\) potentiostat (Princeton Applied Research) controlled by a PC with a CoreWare software package (Scribner). For a given experiment, the Au electrode was always first carefully polished with alumina
powders in an order of decreasing diameter. The electrode was then electrochemically cleaned by cycling it between –0.25 to 1.2 V until repeatable cyclic voltammograms (CVs) with characteristics of a clean polycrystalline Au surface were obtained. For spontaneously depositing Pt directly on Au, the electrochemically cleaned Au electrode was first reduced by holding the potential at –0.25 V for about 10 mins. It was then quickly immersed in a 0.5 mM deaerated H₂PtCl₆ solution for about 5 seconds and was rinsed immediately with copious milli-Q water. This reduction-immersion-rinse cycle was repeated for the subsequent (accumulative) Pt deposition with increasing immersion time (approximately 1 min, 5 mins, 30 mins, 2 hrs, 4 hrs, and 6 hrs respectively). Before any further electrochemical characterizations, the Pt-decorated Au surface was always first reduced by holding potential at –0.25 V.

The method of spontaneous deposition of Pt on Ru was first pioneered by Adzic and co-workers⁹⁻¹¹. Instead of using their high temperature, gas-phase cleaning procedure for Ru surface, we employed an electrochemical procedure which is similar to that of spontaneously depositing Ru on Pt¹² and technically less demanding. Two types of Ru substrates were used here. The first type was a Ru overlayer that was electro-deposited onto the Au electrode by holding the potential of the clean Au electrode at –0.25 V in a 2 mM RuCl₃ solution for about 10 mins. A full coverage was achieved as evidenced by the lack of the characteristic reduction peak of the Au surface. The second type was Ru black (courtesy of Johnson-Matthey). No MeOH oxidation activity at room temperature was observed on both Ru surfaces, in agreement with previous observations³. The procedure for spontaneous Pt deposition was the same as for the Au surface except that
the reduction potential of the reduction-immersion-rinse cycle was –0.3 V and the immersion time followed the similar pattern. In order to prevent Ru leaching, the highest voltage limit for CVs was set to 0.8 V. And all CVs were normalized by total CO active sites (2e per site) estimated by charges under the CO stripping peak.

3.4. Results and Discussions

3.4.1. Pt on Au Substrate. Figure 3.1 shows the representative CVs of the Pt-decorated Au surface with different accumulative number of deposition. As the number of deposition increases, the amplitude of the reduction peak for Au oxide decreases while that for Pt oxide increases, indicating an increasingly covered Au surface by Pt. The actual surface area of the Au electrode was determined by using the method devised by Conway et. al.\textsuperscript{13} (~ 0.10 cm\textsuperscript{2}) and that of the Pt by conventional CO stripping (\textit{vide infra}). On the other hand, the total amount of Pt deposited was estimated by using the Pt oxide reduction peak as devised by Heyd and Harrington\textsuperscript{14} (a value of 390 μC/cm\textsuperscript{2} that was adjusted to the current experimental conditions was used) because it is reasonable to assume that all deposited Pt atoms should be oxidized during the anodic potential scan. The (nominal) Pt coverages so obtained are shown in the inset (solid dots for CO stripping and open triangles for Pt oxide reduction). Although the systematically higher values obtained by the Pt oxide reduction at high Pt loadings are consistent with the formation of Pt islands of more than mono-atomic layers, the ratios between these two sets of data, however, still suggest that most of the Pt islands (≥60%) are of mono-atomic layer, in particular at low Pt loadings. Additionally, while the reduction peak
potential of the Au oxide is almost independent of the Pt coverage, that of the Pt oxide is: the lower the Pt coverage is, the more negative the reduction peak potential is, which indicates a stronger bonding between Pt and oxygen containing species.

The corresponding CO stripping voltammograms are presented in Figure 3.2 (only anodic sweeps were shown for simplicity). As a reference, the CO stripping CV for a Pt overlayer generated on the Au electrode by electrodeposition (holding the potential at –0.25 V in a 2 mM H₂PtCl₆ solution for 3 mins) is also presented, and it behaves very much like a pure Pt surface as expected. The CO was adsorbed by bubbling the EC cell with CO for 10 mins while holding the electrode potential at -50 mV. The cell was then purged with Ar for 30 mins before the CO stripping CV was taken. The accessible Pt surface sites estimated by the total CO stripping charge (using 2 x 220 μC/cm²) as a function of the accumulative number of deposition is shown in the inset (solid dots), Figure 3.1, assuming that any remaining exposed Au surface does not adsorb CO at all. The latter assumption was checked by controlling experiments in which the Au substrate was subjected to the same CO bubbling and no CO oxidation waves were observed over the potential region of interest, as shown in Figure 3.3. Additionally, theoretical calculations⁷ have shown that the adsorption energy of CO on Au(111) is close to zero while that on Pt(111) is about –1.5 eV and that alloying Au surface with Pt would further reduce the CO adsorption energy on Au sites. Therefore, all CO oxidation waves observed here can be convincingly assigned to the Pt deposited on the Au substrate. The most striking observation in Figure 3.2 is that the CO stripping peak at the Pt coverage of 0.22 appears at 0.76 V, a positive shift as large as 0.33 V with respect to that of the Pt
overlay. It is also much broader. Most surprisingly, however, the surface is inactive for the MeOH electro-oxidation despite the clear presence of Pt. As shown in Figure 3.4A, the pair of CVs with and without the presence of 0.5 MeOH are identical and no MeOH electro-oxidation waves were observed.

At the next Pt coverage ($\theta_{Pt} = 0.31$), a small narrow CO stripping peak appears at a less positive potential (0.62 V) at the expense of the broad peak which is shifted oppositely to a more positive potential (0.78 V), Figure 3.2. Interestingly, coinciding with the appearance of this narrow CO stripping peak, the surface now becomes active for MeOH electro-oxidation, as demonstrated clearly in Figure 3.4B. A dominant MeOH electro-oxidation wave peaks at 0.64 V with a small shoulder at 0.80 V. The fact that the peak potential of the dominant MeOH electro-oxidation wave coincides with that of the small narrow CO stripping peak strongly suggests that the Pt sites associated with the narrow CO stripping peak are responsible for the observed MeOH electro-oxidation. The origin of the shoulder at 0.80 V is unclear. It might be a reflection of the complex pattern of the MeOH oxidation at this transition coverage. Or it could be due to the CO generated by now activated MeOH dissociative adsorption diffusing (via Au surface) to the dispersed Pt sites and then being oxidized there, as the potential value suggests. More interesting, however, as can be clearly seen in Figure 3.2, is the observation that only a slight further increase in the Pt coverage (from $\theta_{Pt} = 0.31$ to 0.33) makes the narrow CO stripping peak become the dominant one just as Figure 3.5 shows. The CO peak continues to shift to a lower potential (0.57 V), and the wave of the MeOH electro-oxidation also increases accordingly. Simultaneously, the broad peak becomes much
weaker and shifts oppositely to 0.80 V. These opposing trends continue as more Pt was deposited as evidenced by the corresponding higher MeOH electro-oxidation waves indicated in Figure 3.6.

The above opposing trends, as graphically illustrated in the inset, Figure 3.2, strongly suggest that there exist two qualitatively different types of Pt sites on the Au substrate: one is associated with the narrow CO stripping peak and active for the MeOH electro-oxidation, and the other is associated with the broad CO stripping peaks and inactive for the MeOH electro-oxidation. Since the electrochemical behavior of the former gets closer and closer to that of the Pt overlayer as the coverage of the spontaneously deposited Pt increases, it is reasonable to assign it to Pt islands whose number and/or size grow bigger accordingly. On the other hand, the latter type of Pt sites can be assigned to dispersed Pt adatoms, Pt dimmers, or groups of Pt atoms that do not possess the number of neighboring Pt sites required for an effective dissociative adsorption of MeOH, but otherwise are still active for CO adsorption and electrochemical stripping. Consequently, the appearance of the narrow CO stripping peak should indicate the formation of Pt ensembles that are large enough to become active for the MeOH electro-oxidation. Thus, the qualitative change from an inactive surface to an active one for the MeOH electro-oxidation as the Pt coverage increases, as shown in Figure 3.4, represents the first direct experimental proof of the ensemble hypothesis stating that a minimum number of neighboring Pt atoms are required for being active for the MeOH electro-oxidation. Notice that it is at this coverage that the total amount of Pt determined by the Pt oxide reduction peak starts deviating from the amount of the surface accessible Pt
determining by the CO stripping. In other words, second Pt layer starts forming. Although indirect, it is a good indication of the formation of larger islands which is consistent with the observation of the MeOH electro-oxidation activity.

Also worth noting is the substantial increase in the narrow, low potential CO stripping peak observed (whose fraction increases from ca. 0.2 to ca. 0.6) when the Pt coverage increases from $\theta_{\text{Pt}} = 0.31$ to 0.33 (vide supra). It is clear that the difference in the Pt coverage is too small to account for such a large fraction increase. It is also clear that the increase in the narrow, low potential CO stripping peak, i.e., the size and/or number of the Pt islands, is accompanied by a process that sacrifices the Pt sites associated with the broad, high potential CO stripping peak (see Figure 3.5). This observation points to an Ostwald ripening type process\textsuperscript{15} for the growth of the Pt islands. As a result, the dispersed Pt sites should become even more dispersed. A simple extrapolation based on the trend for the dispersed Pt sites shown in the inset, Figure 3.2 would suggest an even more positive CO stripping potential for a single Pt adatom.

Two main factors, i.e., hindered adsorption of oxygen-containing species and strengthened Pt-CO bonding, can contribute to the overall positive shift of the CO stripping peak. However, as can be seen from the CVs presented in Figure 3.1, the beginning of the rising oxidation current is at potentials no higher than 0.5 V, no matter what the Pt coverage is. In other words, the inhibition of the adsorption of oxygen-containing species at the low Pt coverage, if any, is not strong enough to account fully for the large positive shift of the CO stripping peak observed. Additionally, since all the electro-oxidation of adsorbed CO starts with a saturated CO coverage, it is highly
unlikely that the possible hindrance on the adsorption of oxygen-containing species caused by the pre-adsorbed CO can account for the large observed variations in the CO stripping peak potential. Thus, a more plausible cause for the positive shift in the CO stripping peak is the enhanced Pt-CO bonding by the Au substrate, and the data shown in Figure 3.2 indicate that such an enhancement exists for all sub-monolayer Pt coverages studied here, although the lower the coverage is, the larger the enhancement is. This is indeed in good qualitative agreement with the theoretical prediction based on the Hammer-Norskov d-band-center model\textsuperscript{7,*} which attributes the bond strengthening to an up-shift of Pt’s d band center. Furthermore, the expected up-shift of the Pt d-band center can also in general explain the strengthened bonding between Pt and oxygen-containing species\textsuperscript{16}, in particular at the low Pt coverage as indicated by the negative shift of the Pt oxide reduction peak. Notice that a similar positive shift of the CO stripping peak and a corresponding red-shift in the C–O stretching frequency were also observed previously on pre-formed small Pt nanoparticles deposited on Au substrates\textsuperscript{17,18}.

The width of the CO stripping peak may also contain revealing information related to the reaction kinetics. Qualitatively, the narrower the peak is, the faster the reaction kinetics are\textsuperscript{4,19}. It is likely that the broadness of the CO stripping peak associated with the dispersed Pt sites is a reflection of the inevitable chemical diversity of these Au based Pt sites and, indeed, this is in harmony with the observation that it is rather invariant. However, the width of the low-potential CO stripping peak narrows first as the Pt coverage increases, reaches its minimum at the Pt coverage of 0.51, and then broadens
again. This implies that the reaction kinetics of the CO oxidation on the surface of about 50% of Pt is fastest, even faster than on the Pt overlayer.

### 3.4.2. Pt on Ru Substrates.

Two types of Ru substrates were used: a Ru overlayer on the Au electrode and Ru nanoparticles from Johnson-Matthey. As shown in Figure 3.7, the formation of the complete Ru overlayer was demonstrated by the characteristically large pseudo-capacitive current in the corresponding CV which was subsequently reduced substantially by the deposited Pt, in agreement with the previous results\(^3\). The CVs recorded with (dashed curves) and without (solid curves) the presence of 0.5 M MeOH are shown in Figure 3.8 for the electrode after the 1\(^{st}\) (A), 3\(^{rd}\) (B), and 9\(^{th}\) (C) deposition cycles. The corresponding CO stripping CVs and that of the pure Ru overlayer (CO was adsorbed at –0.2 V) are shown in Figure 3.8D. A clear negative peak shift of about 0.11 V further indicates the presence of Pt. However, the Pt-decorated Ru surface after the 1\(^{st}\) deposition cycle is again surprisingly inactive for the MeOH electro-oxidation, as proved by the pair of CVs presented in Figure 3.8A. Such inactivity was also confirmed by potentiostatic measurements. As can be seen from Figure 3.8B and 2.8C, the Pt-decorated Ru surface becomes only slightly active after the 3\(^{rd}\) deposition cycle but clearly much more active after the 9\(^{th}\) deposition cycle for MeOH electro-oxidation. Although we were unable to determine electrochemically the exact Pt coverage because of lacking separable waves, it is expected that it should increase as the number of deposition cycles increases\(^{12}\). Thus, this qualitative, Pt coverage dependent transition from a surface that is inactive to a surface that is active for MeOH electro-oxidation is again a direct experimental proof of the ensemble hypothesis.
It is now interesting to look at the corresponding CO stripping peaks as shown in Figure 3.8D. First, after the initial large negative potential shift, the CO stripping peak potential surprisingly becomes independent of the Pt coverage, in great contrast to those on the Pt deposited on Au (Figure 3.2). Second, even though the surface shows a large negative potential shift after the 1\textsuperscript{st} deposition cycle, the CO stripping peak is featureless and broad. However, coinciding with the appearance of the MeOH oxidation activity (after the 3\textsuperscript{rd} deposition cycle), a shoulder appears at a higher potential that overlaps with that of the CO stripping on pure Ru surface. As the Pt coverage increases, the shoulder moves towards the coverage-independent main peak and the overall stripping peak becomes narrower. These variations can be rationalized as follows. After the 1\textsuperscript{st} deposition cycle, Pt atoms are rather dispersed on the Ru surface, in harmony with the observed inactivity for the MeOH electro-oxidation. The large negative potential shift is mainly due to a synergistic bifunctional mechanism that combines Ru’s higher oxygen affinity and Pt’s weaker CO binding. Because of the random nature of these dispersed Pt atoms, the CO stripping peak appears featureless and broad. As the Pt coverage increases, Pt islands starts forming, as indicated by the appearance of the MeOH oxidation activity. The formation of the Pt islands generates two dominant types of surface sites: the Pt sites within islands surrounded by peripheral Ru atoms and the uncovered Ru sites coordinated by other Ru atoms. The morphology of surface islands can cause distinguishable CO stripping features\textsuperscript{19-21}. This is indeed observed in Figure 3.4D. Presumably, the CO adsorbed on the Pt islands is oxidized via the bifunctional mechanism that is responsible for the main CO stripping peak while the oxidation of the
CO on the Ru sites produces the shoulder which moves closer to the main peak as the Pt coverage increases.

Very similar behavior was also observed for Pt spontaneously deposited onto Ru nanoparticles, as demonstrated in Figure 3.9A and B. Figure 3.9A shows the CVs with and without the presence of 0.5 M MeOH after the 1<sup>st</sup> deposition cycle (immersion time was about 1 hrs) and Figure 3.9B those after the an overnight (~15 to 16 hrs immersion time) deposition cycle. Insets are the corresponding CO stripping CVs that show clearly a negative peak shift as compared with that of bare Ru nanoparticles. This indicates the presence of Pt on Ru surfaces. Again, as can be clearly seen, the Pt-decorated Ru nanoparticles are inactive for the MeOH electro-oxidation after the 1<sup>st</sup> deposition cycle but become active after the overnight deposition cycle. However, it is worth noting that we have observed that it was much more difficult to deposit Pt on Ru nanoparticles than on Ru overlayer, although the exact reason is still currently unclear. Consequently, lower Pt loading is expected on the Ru nanoparticles which accounts for a lower MeOH electro-oxidation activity shown in Figure 3.9B.

3.5. Conclusions

In conclusions, we have reported remarkably general (i.e., on both Au and Ru substrates) experimental evidence that offers for the first time the direct experimental proof of the ensemble hypothesis that has been widely used in the mechanistic discussions of the MeOH electro-oxidation on Pt surfaces. The fact that the MeOH electro-oxidation can be switched on or off by simply controlling the Pt coverage is
clearly of both fundamental and practical importance for optimizing the performance of Pt-based electrocatalysts for direct MeOH fuel cells (DMFC) at both anode and cathode. For instance, the universally observed inactivity of the surfaces for the MeOH oxidation when the Pt coverage is low indicates strongly that the parallel reaction pathways\textsuperscript{22} for MeOH electro-oxidation may also require the presence of the ensembles of neighboring Pt atoms. Also, since oxygen reduction does not need an ensemble of neighboring Pt atoms\textsuperscript{23}, those MeOH oxidation inactive Pt-decorated surfaces could well be good candidates for developing active cathodes with high tolerance to MeOH cross-over. Additionally, in contrast to previously published results, our data have shown that over at least the sub-monolayer range of Pt coverage studied here, the Pt-CO bonding is always strengthened by the Au substrate and, most importantly, the degree of the bond strengthening increases as the Pt coverage decreases, confirming the theoretical prediction\textsuperscript{7}.

\* Outline of d-band center model: The d-band center is considered as an important parameter that determines the bonding strength of surface-adsorbate. The up-shift of d-band center always leads to a strengthened surface-adsorbate bonding and the down-shift of d-band center will weaken such bonding. In this model, when a “small” metal atom is deposited on the lattice of a “large” one, the d-band center will upshift in order to maintain the same d band filling that was originally decreased due to the reduced electron density of the deposited “small” metal atom that occupies more space. On the
other hand, it can be deduced that when a “large” metal atom is deposited on the lattice of a “small” one, the d-band center will downshift.
**Figure 3.1.** Representative cyclic voltammograms of the Pt decorated Au electrode as a function of accumulative Pt deposition cycles (the black CV is that of the bare Au surface). The vertical lines indicate the reduction peaks for Pt (left) and Au (right) oxides. The region at which the Pt oxide starts forming is indicated by the black arrow and the oxidation current increases as the number of the deposition cycles. The inset shows the corresponding Pt coverages estimated from the CO stripping CVs (solid dots, see Figure 3.2) and the Pt oxide reduction peaks (open triangles, see text for details).
Figure 3.2. The CO stripping CVs of the Pt-decorated Au electrode as a function of the number of the accumulative Pt deposition. The numerical values in the parentheses are the nominal Pt coverage calculated by using the CO stripping peaks. The CV of the Pt overlayer (blue, see the text for details on how it was generated) is presented as a reference. The inset shows the opposing trends of the low (circles) and high (squares) peak potential as a function of the Pt coverage. The straight line is a guide-of-the-eye for the peak positions of the high-potential CO stripping waves.
Figure 3.3. CVs of the polycrystalline Au electrode with (solid curve) and without (dashed curve) CO bubbling. The almost identical CVs demonstrate that no discernible CO adsorption was observed on the Au surface.
Figure 3.4. The CVs with (solid curves) and without (dashed curves) the presence of 0.5 M MeOH. A. After the 1st Pt deposition cycle ($\theta_{Pt} = 0.22$) and B. after the 2nd Pt deposition cycle ($\theta_{Pt} = 0.31$)
Figure 3.5. The fractions of CO electro-oxidized at high (squares) and low (circles) potentials as a function of Pt coverage.
Figure 3.6. The MeOH electro-oxidation CVs as a function of the number of accumulative Pt deposition cycles. As can be seen, the MeOH activity increases as the accumulative number of Pt deposition cycles increases.
Figure 3.7. The CV of the Ru overlayer (red) and that after 1st Pt deposition cycle (blue).

The substantial decrease of the pseudo-capacitive current is a clear indication of the presence of Pt on the Ru surface.
Figure 3.8. The CVs with (solid curves) and without (dashed curved) the presence of 0.5 MeOH of the Ptdecorated Ru overlayer after A. the 1st, B. the 3rd, and C. the 9th Pt deposition cycle. D. The CO stripping CVs for the Ru overlayer (black) and the Ptdecorated Ru overlayer after 1st (blue), 3rd (pink), and 9th (green) Pt deposition cycles. The current was normalized by the total accessible surface sites (including both Pt and Ru) determined by CO stripping (2e per site).
Figure 3.9. The CVs with (solid curves) and without (dashed curves) the presence of 0.5 M MeOH of the Pt-decorated Ru nanoparticles after A. 1st Pt deposition cycle and B. 2nd overnight Pt deposition cycle.
3.6. References

CHAPTER 4

OPTIMIZING METHANOL ELECTRO-OXIDATION ON PLATINUM-DECORATED RUTHENIUM NANOPARTICLES

4.1. Abstract

Controlled Pt adlayers were deposited on commercial Ru NPs using an industrially scalable one-pot ethylene glycol (EG) reduction based method and were characterized by XRD, electrochemical CO stripping voltammetry, ICP-OES, XPS, and TEM. Compared with the previously used “spontaneous deposition”, the wet chemistry based EG method is less technical demanding, i.e., no need to handle high-temperature hydrogen reduction, and offers a better control of the Pt packing density (PD), enables the formation of stable segregated Pt surface adlayers for optimal tuning and use of Pt, and prevents effectively NPs sintering. Two batches of a total of 11 (8 vs 3) samples with different values of Pt PD ranging from 0.05 to 0.93 were prepared with a time interval of more than 18 months between the syntheses of the two batches of samples and an excellent reproducibility of results was observed. All samples were investigated in terms of methanol (MeOH) electro-oxidation by cyclic voltammetry (CV) and chronoamperometry (CA). Although the peak current of CV increased as the Pt content increased, the long-term steady-state MeOH electro-oxidation current density of the Pt-decorated Ru NPs measured by CA

showed a volcano curve as a function of the Pt PD, with the maximum appearing at the PD of 0.31. The optimal peak activity was ~150% higher than that of the industrial benchmark PtRu (1:1) alloy NPs and could deliver the same performance at a half electrode material cost. Fundamentally, such a volcano curve in the reaction current is the result of the two competing processes of the electro-oxidation of MeOH: the triple dehydrogenation of MeOH that prefers more Pt ensemble sites and the elimination of poisonous CO that is enhanced by more adjacent Ru/Pt sites via the so-called bifunctional mechanism and also by possible electronic effect at the low Pt coverages.

4.2. Introduction

Pt has long been used as the major component of anode electrocatalyst for electro-oxidation of methanol (MeOH) in direct MeOH fuel cell (DMFC). However, two major long outstanding obstacles still exist that prevent large scale practical application of the DMFC. One is the CO poisoning during the electro-oxidation of MeOH, which quickly lowers the catalytic activity of Pt. And the other is the high loading of Pt needed in the anode to sustain the performance, which noticeably increases the cost of the whole fuel cell system. Numerous efforts have been made both to improve the CO tolerance and to reduce Pt loading. For both purposes, binary or ternary Pt-based metallic/metal oxide catalysts, such as PtRu, PtNi, PtSn, and PtRuTiO have been studied, and among which, PtRu alloy has been shown to have the best practical performance. Consequently, most of the recent research in this field has focused on manipulating PtRu from different perspectives, such as varying the molar ratio between Pt and Ru.
improving synthesis methods\textsuperscript{11,12}, and adopting different carbon supporting materials\textsuperscript{13-15}. Recently, Brankovic \textit{et al.}\textsuperscript{16} adopted a spontaneous deposition method (that was first used in depositing reversely Ru on single crystal Pt surfaces\textsuperscript{17}) to decorate the surface of carbon-supported Ru NPs with Pt. The method involved a necessary step of reducing Ru NPs with hydrogen gas at relatively high temperature (300 °C). The resulting NPs, according to that work, offered the advantage of maintaining the activity towards CO tolerance with a much reduced Pt loading of \(\sim\)10 wt\% compared to commercially available E-TEK PtRu (1:1) which has a Pt loading of \(\sim\)66 wt\%. Later on, Wieckowski and coworkers\textsuperscript{18} also applied a similar method to cover Ru and carbon-supported Ru NPs with different Pt loading using repetitive hydrogen reduction and spontaneous depositions. While the Pt packing densities (PDs) were determined using ICP-MS, the analysis of the true surface coverage and the associated activity was complicated by the possible Pt penetrating into Ru NPs and the observed sintering effect due to high temperature reduction. Although this spontaneous deposition method opens up a promising way of fabricating anode materials of low Pt loading, handling high temperature hydrogen reduction is technically less appealing and repetitive hydrogen reduction and spontaneous depositions are often tedious and hard to achieve quantitative control of the Pt coverage. Furthermore, the procedure would be difficult to implement in large industrial scale.

In an attempt to address the technically important controllability of the Pt PD and scalability of the operation, we have developed a superior, industrially scalable EG reduction based wet chemistry method that allowed us to achieve a quantitative
control of the Pt PD on Ru NPs and optimize the activity of the electro-oxidation of MeOH. It started with commercially available Ru NPs (~ 3 nm). Pt salt was then reduced using mild reduction power of EG to cover the Ru NPs. Careful electrochemical measurements showed that by varying the Pt:Ru molar ratio of the starting materials, the EG method enabled a relatively easy control of the Pt PD that followed linearly the nominal Pt:Ru molar ratio. ICP-OES and XPS measurements were carried out on three of the second batch samples and gave consistent Pt PDs as determined by the electrochemical method. Detailed TEM measurements on these three samples showed very similar particle size distributions and no evidence of pure Pt NP formation. Powder XRD measurements were carried out on two representative samples of the first batch and three samples of the second batch. These results indicated that the samples were neither pure Ru, Pt, nor PtRu alloy, in consistence with the formation of Pt adlayers on Ru NPs. Furthermore, the as-prepared Pt-decorated Ru NPs displayed Pt-PD dependent electrochemical characteristics in CO stripping and MeOH electro-oxidation. Particularly, a volcano curve peaked at the Pt PD of 0.31 in long-term steady-state MeOH activity as gauged by chronoamperometric (CA) current measured at 60 min and 0.2 V (with respect to the Ag/AgCl (3M) reference electrode) was observed. The peak activity was ~150% higher than that of the industrial benchmark PtRu (1:1) alloy NPs. Technologically, with the achieved higher activity and lower Pt loading, one could expect at least a 50% decrease in catalytic material cost. Fundamentally, the observation of the volcano curve as a function of the Pt coverage can be largely rationalized by the so-
called “bifunctional mechanism” in which the electro-oxidation of the poisonous CO intermediate preferentially adsorbed at Pt sites occurs at lower potential due to the supply of oxygen-containing species formed at the adjacent Ru sites.

4.3. Experimental

4.3.1. Preparation of the Pt-decorated Ru NPs

(All commercial high-surface area Ru, PtRu (1:1) alloy, and Pt NPs used either as the starting material or references in this study were courtesy of Johnson-Matthey). It has been experimentally confirmed that when in contact with air, Ru NPs are readily oxidized to form RuO$_x$.\textsuperscript{21,22} Previously published data from us\textsuperscript{23} (as shown in chapter 3) and others\textsuperscript{24} have reported that the presence of RuO$_x$ makes it difficult to deposit Pt onto the surface of Ru NPs. Thus, the first step is to completely reduce the Ru surface. Previous studies\textsuperscript{16,18} employed hydrogen gas reduction, usually at relatively high temperature (200 °C to 300 °C), to reduce the Ru surface. In order to vary the Pt coverage, tedious repetitive hydrogen reduction and spontaneous deposition cycles were employed, which could easily cause unwanted Pt penetrating the Ru NPs and electrocatalyst sintering\textsuperscript{18}, consequently make the control and tuning of the Pt PD very challenging. That is, the Pt PD is not known a priori. It would also be quite difficult to scale up this procedure for potential industrial applications.

Here we describe a wet chemistry based, homogeneous reaction like procedure using EG as both reaction media and reductant for the reduction of Ru NPs as well as the subsequent deposition of Pt. This new approach is advantageous in two respects.
One is that the homogeneous-reaction-like media is better in preventing sintering \textit{(vide infra)} and is in principle industrially scalable. The other is that the mild reduction power of EG offers a better control of depositing Pt on Ru NPs. Specifically, the samples studied in this paper were prepared as follows: 5 mg of the 3 nm Johnson-Matthey (J-M) Ru NPs was dispersed ultrasonically into ethylene glycol to form a homogeneous ink, which was heated at 140 °C for 2 hours with vigorous stirring to reduce oxide species on the Ru surface. The efficiency of this reduction step is clearly demonstrated by comparing the corresponding CVs of the Ru NPs as shown in Figure 4.1. According to Brankovic et. al.\textsuperscript{25}, the large anodic peak at around -0.2V in the CV of the cleaned Ru NPs (Figure 4.1B) was due to the adsorption of oxygen-containing species, e.g. OH group, and could be considered a hallmark of well reduced Ru NPs. Notice that this anodic peak was largely absent for the as-received Ru NPs because the surface had already been covered by RuO\textsubscript{x}. Green et.al.\textsuperscript{26}, however, attributed this peak to a co-adsorption of hydrogen and oxygen-containing species. In any case, the contributions from the adsorption of oxygen-containing species distinguish Ru from Pt and Pd in that the latter adsorb only hydrogen in this potential region.

The cleaned J-M Ru NPs were then collected and rinsed with ethanol and re-dispersed ultrasonically into a fresh EG solution with the calculated volume of H\textsubscript{2}PtCl\textsubscript{6} solution that gave the desired nominal Pt:Ru molar ratio. After a 30 min long ultrasonication, the mixture was heated at 120 °C for 4 hours to reduce Pt (IV) to Pt (0) on the surface of the J-M Ru NPs. The final product was collected and rinsed
several times with ethanol. The first batch of preparation consisted of eight samples with nominal Pt:Ru molar ratios of 1:20, 1:10, 1:6, 1:5, 1:4, 1:3, 1:2, and 1:1.5 respectively and the second batch of three samples with nominal Pt:Ru molar ratios of 1:13.3, 1:4, and 1:2.7, respectively. It was found that the degrees of the dispersiveness of the starting Ru NPs and of their reductive cleanness were critically important to obtaining good reproducibility.

4.3.2. Electrochemistry

All electrochemical experiments were run on an EG&G273A potentiostat. All current densities were calculated using the total surface area as determined by the CO stripping peak. The working electrode was prepared as follows. The as-prepared Pt-decorated Ru NPs were transferred into a mixed solution of 2-propanol and 5 wt.% Nafion® (Du Pont, Inc) solution. It was found that the following ratio among the above ingredients gave the optimum electrochemical results: 1mg PtRu sample: 0.2ml 2-propanol: 1μl Nafion solution. The mixture was then ultrasonicated for at least 10 min to form a uniform suspension which was drop-cast onto the surface of a commercial (Bioanalytical) 3 mm-diametered glassy carbon (GC) electrode. The electrode surface was air dried under a gentle Ar flow and rinsed with a copious amount of Milli-Q water (18.2MΩ.cm) to eliminate loosely attached NPs.

4.3.3. XRD, TEM, XPS, and ICP-OES

The details about XRD, XPS and ICP-OES have been described in experiment
chapter. Special care was taken while preparing TEM grids in order for a good
dispersion of the NPs. At least 15mins long sonication of the sample suspension was
always necessary before depositing it onto carbon-coated copper grids.

4.4. Results and Discussions

4.4.1. Pt Packing Density (PD): the formation of segregated atomic adlayers

The state of the Pt deposited on the Ru NP surface needs to be addressed first.
Technically, it is still a challenge to determine the fraction of Pt surface area in Pt-based bimetallic, particularly Pt-Ru, NPs. For pure Pt, the electrochemically active
surface area of Pt has been routinely determined by using the charge associated with
hydrogen desorption\textsuperscript{27}, CO stripping\textsuperscript{28}, or Pt oxide reduction\textsuperscript{23,29}. The former two
methods, however, may produce large uncertainty if used for Pt-Ru bimetallic surface
due respectively to the interference of the adsorption/desorption of oxygen-containing species (see Figure 4.1B) and the indiscriminating nature of CO adsorption with respect to the Pt and Ru sites. We therefore adopted a method that
combines the CO stripping and Pt oxide reduction. Because of the indiscriminating
nature of CO adsorption, the CO stripping with a well-known reaction stoichiometry
(2e per CO oxidation and the charge density of 420 \( \mu \)C/cm\(^2\) was used for calculating
the surface area) provides a good and straightforward estimate of the total surface
area accessible to CO adsorption. On the other hand, using Pt oxide reduction charge
to determine the Pt surface area is more complicated because the reaction
stoichiometry is not as well defined as the CO oxidation\textsuperscript{28}. But it can still offer a
reasonable estimate of the Pt surface area\textsuperscript{23}, particularly when the corresponding charge density is reasonably well calibrated by a known quantity. Here, we used the J-M Pt NPs as the reference in which the Pt oxide reduction charge was calibrated by the CO stripping charge (see the dashed CV in Figure 4.2h). This gave a charge density of 400 $\mu$C/cm$^2$ that we used to calculate the Pt surface area (notice that this charge density value is very close to the one obtained by Kozlowska et. al.\textsuperscript{30}). The Pt PD was then calculated by the ratio between the surface area determined by the Pt oxide reduction which was Pt specific and that determined by the CO stripping.

Figure 4.2 shows the CO stripping CVs and those thereafter of the eight samples of the first prepared sample batch. The dashed CVs in Figure 4.2a, f, and h are those of the J-M Ru (the starting material), J-M PtRu (1:1) alloy, and pure J-M Pt NPs respectively, used as references for the purpose of comparison. Reproducible results were obtained on the three samples of the second batch as shown in Figure 4.3. Using these data, the Pt PDs were calculated by the approach described above and the obtained values were listed in Table 4.1. For the purpose of comparison, the values of the nominal PD calculated using the nominal Pt:Ru molar ratios were also listed. Here, we assumed that all the Pt(IV) were reduced to Pt(0) on the metallic Ru surface sites that acted as nucleation centers for the Pt deposition\textsuperscript{24} and then formed adlayers of mono-atomic height. Taking an average size of 3 nm (see the TEM results below), the dispersion of the J-M Ru NPs was estimated to be $\sim$40\% according to the Benfield’s calculation\textsuperscript{31}. Thus, the values of the nominal Pt PD were then calculated by equation: $PD = \frac{Pt:Ru \text{ molar ratio}}{0.40}$. Notice that the values of the Pt PD as
determined by the charges of Pt oxide reduction and CO stripping, although being constantly lower than the respective nominal ones due likely either to that the value of 400 \( \mu \text{C/cm}^2 \) may overestimate the charge density for Pt oxide reduction on Ru surface (a value of 250 \( \mu \text{C/cm}^2 \) would give a slope of 1) or/and to 3D packing, followed linearly \((y=ax\) with \( R^2 = 0.99 \)) the trend of the nominal PD (Figure 4.4), therefore enabling a quantitative control of the Pt PD in one-pot synthesis. The red squares in Figure 4.4 are from the three samples of the second batch, demonstrating excellent reproducibility.

Table 4.1. Comparison of the nominal and measured Pt packing densities (* indicates the 2\(^{nd}\) sample batch)

<table>
<thead>
<tr>
<th>Pt:Ru ratio</th>
<th>1:20</th>
<th>1:13.3*</th>
<th>1:10</th>
<th>1:6</th>
<th>1:5</th>
<th>1:4</th>
<th>1:3</th>
<th>1:2.7*</th>
<th>1:2</th>
<th>1:1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal PD(%)</td>
<td>12</td>
<td>19</td>
<td>25</td>
<td>42</td>
<td>50</td>
<td>62</td>
<td>83</td>
<td>92</td>
<td>125</td>
<td>165</td>
</tr>
<tr>
<td>Measured PD(%)</td>
<td>5</td>
<td>12</td>
<td>16</td>
<td>31</td>
<td>36</td>
<td>39(40*)</td>
<td>54</td>
<td>67</td>
<td>79</td>
<td>93</td>
</tr>
</tbody>
</table>

The Pt PDs determined by ICP-OES for the three samples of the second batch are respectively 0.36, 0.66, and 0.86, which are in a good agreement with the nominal Pt PDs shown in Table 4.1. For the XPS measurements on the same samples, the Ru NP diameter (ca. 3 nm) is > 2 times the inelastic mean free path (IMFP, see below), thus modeling these systems as a 2-dimensional Ru surface was used. The attenuation of photoemission from the Ru core by the Pt overlayer was accounted for using the NIST Standard Reference Database 82 (NIST Electron Effective-Attenuation-Length Database, Ver. 1.1) using an IMFP of 1.329 nm at 462 eV (Ru 3d binding energy, 1025 eV kinetic energy). The Ru 3d intensity was compared to the Pt 4d and 4f.
Representative XP spectra are shown in Figure 4.5. Assuming a 0.7 nm Pt overlayer thickness (0.27 attenuation factor) and neglecting any other surface adsorbed species, the model analysis gave the Pt PD values as 0.55, 0.72, and 1.35, respectively. If an additional 0.5 nm carbon overlayer was used to model the ubiquitous surface adsorption, the corresponding PD values became 0.31, 0.40, and 0.79 respectively, in reasonable agreement with the values shown in Table 1. The fact that unphysically high Pt contents were obtained from the XPS data without using the Ru core–Pt shell structure suggested that what we had synthesized were indeed Ru@Pt NPs. Finally, for facilitating the following discussions, the as-prepared Pt-decorated Ru samples are named as Pt(electrochemically-measured PD)-Ru, e.g. Pt(16)-Ru = 16% Pt-decorated Ru.

Another important question that needs to be addressed convincingly is whether the Pt ended up on Ru NP surface or formed pure Pt NPs. For this purpose, we carried out detailed TEM and XRD measurements on the three samples of the second batch and on the starting Ru NPs. We also did XRD measurements on two representative samples of the first batch (Pt(31)-Ru and Pt(93)-Ru). The average particle sizes measured (with ~ 150 counts for each sample) by TEM are 3.1±0.4 nm, 3.1± 0.3 nm, 3.2±0.3 nm, and 3.0±0.4 nm for pure Ru NPs, Pt(12)-Ru, Pt(40)-Ru, and Pt(67)-Ru respectively. From these TEM data, it is clear that no sintering of the NPs happened and that the Pt shell was dominantly of mono-atomic height. Figure 4.6a and b compare the representative TEM images of the pure Ru and Pt(67)-Ru (see Figure 4.7 in the SI for the TEM images of Pt(12)-Ru and Pt(40)-Ru). The insets are the
corresponding high resolution TEM (HRTEM) images. By measuring almost exhaustively the distances between adjacent atomic planes as revealed by the HRTEM images, no evidence of Pt NP formation was found: all measured distances were about 0.21 nm (Figure 4.6b), the same as that measured on pure Ru NPs (Figure 4.6a).

The results of XRD are shown in Figure 4.6c together with those of the pure J-M Pt, J-M PtRu (1:1) alloy, and the pure starting J-M Ru NPs for comparisons. The XRD of the J-M Pt and Ru NPs reproduced all standard peak positions of which the main peaks within the angle range are located at 38.38º(100), 42.15º(002), 44.00º(101) for Ru (PDF#06-0663) and at 39.76º(111), 46.24º(200) for Pt (PDF#04-0802) respectively. The vertical dashed lines in Figure 4.6c indicate the respective standard positions of Pt (111) (left) and Ru (101) (right) as references.

As can be seen in Figure 4.6c, the Ru(101) peak amplitude decreases gradually but the peak position remains the same as the Pt PD increases. These are strong indications showing that the Ru NPs were gradually covered by Pt and no PtRu alloy was formed. At the same time, a growing peak corresponding to Pt appears with a peak position slightly larger than but not exactly at that of Pt(111). Using the Bragg’s law \( \lambda = 2d \sin \theta \), the \( d \) corresponding to the Pt(93)-Ru peak (\( \theta = 39.91^\circ \)) is 0.2256 nm. This value is very close to the height (0.2248 nm) of a Pt atom sitting in a close-packed fashion at a three-fold site of a Ru(0001) surface. Because of the mismatch of the close-packed atomic distances between Pt (0.2772 nm) and Ru (0.2701 nm), the height of a pseudo-morphic growth of a Pt (111) monolayer on a Ru(0001) surface is
expected to be larger than 0.2248 nm. On the other hand, the d of a close-packed Pt(111) planes is 0.2265 nm. Therefore, the d value of 0.2256 nm strongly suggests that the formed Pt adlayers were dominantly of mono-atomic height. The growth of the peak intensity indicated that Ru surface was covered more and more by Pt adlayers. Similar intensity was also reported recently for the synthesized Ru@Pt NPs with 1 to 2 Pt atomic layers\textsuperscript{32}. Such Ru@Pt structure was further corroborated by the strong dissimilarity between the XRD pattern of Pt(93)-Ru and that of J-M PtRu alloy NPs\textsuperscript{33,34} that largely eliminates any major formation of alloy in Pt(93)-Ru.

The formation and growth of the Pt adlayer on the Ru NP surface are further corroborated by the electrochemical data shown in Figure 4.2. For all the coverage values, no separated peak expected for pure Pt NPs was observed\textsuperscript{35}, indicating that few if any pure Pt NPs were formed during the Pt deposition. For Pt(5)-Ru (Fig. 2a), two features in the CO stripping CV are worth highlighting: One is the appearance of a narrower and small peak that was negatively shifted by as much as 0.17 V with respect to the broader CO stripping peak observed on the pure J-M Ru NPs (dashed CV in Figure 4.2a). This may be a direct manifestation of the bifunctional mechanism well-articulated for a Pt-Ru surface\textsuperscript{36,37} as well as a possible additional electronic (ligand and strain) effect\textsuperscript{38-40}, thus indicating a direct deposition of Pt on Ru. The other is the broad shoulder at the high potential that is different from that of the pure J-M Ru NPs but can be reasonably assigned to the CO oxidation at the Ru sites distant from the deposited Pt sites. As the Pt PD increased, the low-potential Pt/Ru peak grew larger at the expense of the broader high-potential Ru peak. These gradual
and monotonic changes strongly suggest that the Pt went onto the Ru surface forming nanosize Pt islands instead of forming pure Pt NPs, which is very similar to cases of Ru-decorated Pt NPs\textsuperscript{41}.

An intriguing observation is that, in great contrast to the PtRu alloy NPs in which no well defined Pt oxide reduction peak was observed (see dashed CV in Figure 4.2f), the 11 Pt-decorated Ru NP samples studied here all showed well defined Pt oxide reduction peaks that enabled the Pt surface area to be determined. This observation attests that no PtRu alloy but rather segregated Pt adlayer was formed on the Ru surface. Additionally, the monotonic decrease in the double-layer current as the Pt coverage increased also indicates that the Ru surface was gradually covered up by the Pt. Similar observations but on Ru-decorated Pt NPs were made previously\textsuperscript{19,42,43} in that for Ru-decorated Pt NPs, the deposition of Ru was accompanied by an increase in the double-layer capacitance, a decrease in the hydrogen adsorption area and a change in the oxide stripping peak\textsuperscript{41}. Notice that large double-layer capacitance of the characteristics of pure Ru NPs would show up if physically separated Pt and Ru NPs did exist\textsuperscript{35,44}. But it is clearly not the case here. In summary, the above observations made from several independent perspectives all together provide a convincing convergence that is consistent with the formation of Pt adlayers on Ru NPs surface.

The variations in the shape and potential of the CO stripping peak as a function of Pt PD are highly revealing (the latter is shown in Figure 4.8a). As the Pt PD increased, it started with a large (~0.17V) negative shift that peaked at the Pt PD of
0.31. (However, the shift is less negative than that observed on the Ru-decorated Pt NPs\textsuperscript{19,39}.) At the same time, it shows a fast rising front and a slow decreasing back, indicating a dominant electro-oxidation of CO at the peripheral Ru/Pt sites\textsuperscript{41}. The peak then moved positively in the opposite direction until the potential value of the pure Pt NPs was recovered at the Pt PD of 0.93, accompanied by a change to a slow rising front and a fast decreasing back which indicates a dominant electro-oxidation of CO on Pt terrace sites, in agreement with a fully Pt covered Ru surface. Indeed, the latter sample showed the characteristics almost identical to those of the pure Pt NPs (Figure 4.2h and vide infra). It is also interesting to point out that, although the Pt(54)-Ru and the J-M PtRu(1:1) alloy NPs showed very similar CO stripping peaks, their overall CVs were arguably dissimilar (Figure 4.2f), implying different surface structure, electronic properties, and catalytic behaviors. Most importantly, the pattern shown in Figure 4.8a strongly suggests that for the Pt adlayer–Ru substrate systems studied here, the bifunctional mechanism was the dominant force in the work for the enhanced CO-eliminating ability and the active sites were highly likely along the peripheries of the Pt adlayers, similar to the cases of Ru-decorated Pt surfaces\textsuperscript{45,46}. On the other hand, although the electronic effect of the Ru substrate on the Pt adlayers might play a stronger synergistic role at the lower Pt PDs\textsuperscript{38,39}, it would become smaller and smaller as evidenced by the recovering of the characteristics of the pure Pt surface towards the high Pt coverage.

\subsection*{4.4.2. \textit{MeOH Electro-oxidation}}
Figure 4.9 presents the MeOH electro-oxidation CVs of the 8 1st-batch and the reference samples. Those of the 3 2nd-batch samples are shown in Figure 10. The trend of variation is identical to that in Figure 9. For the J-M Ru, no MeOH electro-oxidation activity was observed (dashed CV in Figure 4.9a) which was in agreement with previous observations23, although a recent surface enhanced Raman scattering study by Zou et. al.47 suggested that Ru NPs may have observable MeOH activity at room temperature. However, a deposition of a merely 5% of Pt already initiated small but observable MeOH activity (Figure 4.9a). This is in clear contrast to the Pt deposited on a polycrystalline Au substrate on which no MeOH activity was observed at a coverage as high as 22%23. This may be rationalized by the difference in Pt-Au and Pt-Ru interactions: Pt solute has a very strong tendency of segregation in Ru host but a strong tendency of anti-segregation in Au host38. This difference led the Pt to form segregated Pt adlayer phase (islands) on Ru during the EG reduction period that satisfied the ensemble requirement for the MeOH electro-oxidation23.

With the increase of the Pt PD, the transient peak current density of MeOH electro-oxidation increased and there was a remarkably linear relationship between them as shown in Figure 4.8b ($y=ax$ with $R^2=0.98$). This linear relationship is a strong indication that all deposited Pt atoms were grouped in the form of surface islands since isolated Pt atoms would not be active for MeOH electro-oxidation. As the Pt PD increased, the pattern of the CV became more and more similar to that of the pure J-M Pt NPs: they almost overlapped at the Pt PD of 0.93 (Figure 4.9h). This resemblance indicates again that the electronic effect of the Ru substrate became
weaker at the higher Pt coverages, i.e., the atoms in the Pt adlayer supported by Ru NPs acted more like pure Pt atoms rather than those alloyed to the Ru, as already pointed out in the above discussions of the XRD results. This observation is further substantiated by the striking difference observed between the CV of the Pt(54)-Ru and that of the J-M PtRu(1:1) alloy NPs (Figure 4.9f). The latter resembled more to that of the Pt(5)-Ru (Figure 4.9a). Considering that a nominally 45 at.% Pt is expected on the surface of the PtRu alloy NPs, these observations are somewhat unexpected. Two reasons may account for the observations: One is a high segregation of the Ru on the surface of the alloy NPs as recently observed by $^{195}$Pt NMR of PtRu alloy NPs$^{48,49}$. The other is a solid solution of alloying that rendered a large part of Pt sites not having enough Pt neighbors to form an ensemble needed for MeOH electro-oxidation$^{23}$, i.e. the so-called ensemble effect$^9$.

In the real-world DMFC applications, the long-term CO tolerance of electrocatalysts is practically more important than the intrinsic MeOH electrochemical activity as measured by the transient peak current in Figure 4.9. In this regard, CA measurements were carried at 0.2 V on the 11 Pt-decorated Ru NP samples to gauge their respective CO tolerance in a 0.5M MeOH-containing electrolyte solution. The resulting CA curves of the 8 1$^{st}$-batch and the 3 2$^{nd}$-batch samples are shown in Figure 4.11A and Figure 4.12, respectively. As can be seen, and in agreement with the results presented in Figure 4.9 and the extrapolation of the straight line in Figure 4.8 to zero, the J-M Ru NPs did not show any observable MeOH reactivity. On the otherhand, the Pt(93)-Ru sample acted almost the same as
the pure J-M Pt NPs. However, the J-M PtRu showed a much higher activity (i.e. CO tolerance) than both Pt(5)-Ru, Pt(12)-Ru, and Pt(54)-Ru, which seems to be contradictory to the observation gleaned from Fig. 5a where higher CO stripping peak potential was observed for J-M PtRu. The exact reason is still unclear at present and warrants further carefully designed experimental and theoretical investigations.

On the other hand, the CA currents for the 11 Pt-decorated Ru samples follow closely the trend of the CO stripping peak potential as a function of the Pt PD, as shown in Figure 4.13. When the CA currents measured at 60 min. of the MeOH reaction is plotted as a function of the Pt PD, an expected volcano-like curve as shown in Figure 4.11B is observed with the maximum current at the PD of 0.31 that coincides with the lowest CO stripping peak potential (Figure 4.13). This volcano curve can be understood as the result of two competing processes in MeOH electro-oxidation on Pt-decorated Ru NP surface: the triple dehydrogenation reaction steps being facilitated by the more Pt ensemble sites that would lead to the generation of more poisonous CO and the enhanced CO eliminating ability through the bifunctional mechanism offered by the presence of more adjacent Ru/Pt sites as well as the possible synergistic electronic (ligand and strain) effect at the lower Pt PDs that weakens the Pt-CO bonding$^{38-40}$. As the Pt PD increased but before the volcano peak, the two processes could work in unison because both the dehydrogenating ensemble sites and the CO-eliminating ability increased (the latter is indicated by the continuous negative shift of the CO stripping peak potential) so did the reaction current. Beyond the volcano peak, although a further increase in Pt coverage would
increase the dehydrogenating ensemble sites, the accompanying decrease in the CO-eliminating ability, as indicated by the positive shift of the CO stripping peak potential (Figure 4.8 and 4.13), led to the decrease of the overall current. The difference in slope before and after the volcano peak as shown in Figure 4.13 may be indicative of the difference in electronic effect\(^5\) of the Ru substrate which appeared to be stronger at lower Pt PDs. Overall, one can conclude that the Pt(31)-Ru sample had the optimal compromising surface structure/electronic effect that maximized the overall reaction current. This should be compared to the Ru-decorated Pt NPs where the maximum activity appeared at 40% to 50% of Ru packing density\(^1\). Most remarkably, the Pt(31)-Ru sample showed an impressively high reactivity that was about 150% higher than that of the industrial benchmark J-M PtRu (1:1) alloy sample but with at least 3.5 times less Pt loading. It is also worth noting that the Pt(16), Pt(36), and Pt(39)/(40)-Ru samples all showed either higher or comparable MeOH long-term activity as compared to that of the J-M PtRu(1:1) alloy sample but with lower Pt loadings.

### 4.5. Conclusions

In conclusion, we have reported the development of a superior, industrially scalable one-pot EG based wet chemistry method to prepare Pt-decorated Ru NPs that offers an exquisite control of the Pt PD of the Pt adlayers with most likely mono-atomic height and prevents effectively the NPs sintering during the deposition. Using the 3 nm J-M Ru NPs as the starting material, 11 samples with different Pt PD ranging from 0.05 to 0.93
were prepared, characterized, and studied in detail for the MeOH electro-oxidation. A volcano curve in terms of long-term activity as a function of the Pt coverage was observed and peaked at the Pt PD of 0.31, attesting to the competition of the two processes that are both essential for the MeOH electro-oxidation: the triple dehydrogenation and the poisonous CO elimination. An increase of the Pt ensemble sites will facilitate the former via the ensemble effect while an increase of the adjacent Ru/Pt sites will enhance the latter via the bifunctional mechanism. Assuming an ensemble of minimum three Pt atoms is needed for electro-oxidation of MeOH, the surface structure shown in the inset of Figure 4.11b gives simultaneously the maximum numbers of ensembles and of Pt/Ru sites on a Ru(0001) surface. The corresponding Pt PD is $3/7 = 0.43$, reasonably close to the Pt PD (0.31) of the most active sample. Notice that Gasteiger et al. did a statistical analysis of a Pt/Ru alloy surface using a model of a 3 Pt atoms ensemble that had only one Ru atom as the nearest neighbor and found out the optimal Pt content was about 88%$^{10}$. Thus, this simple analysis suggests that on Ru@Pt, more than one Pt/Ru sites per Pt ensemble are needed for achieving the highest activity.

Additionally, the CO eliminating ability might also be enhanced at the lower Pt PDs by the electronic effect$^{38-40,50}$. The direct correlation between the long-term steady-state MeOH electro-oxidation current density and the CO stripping peak potential highlights again the technological importance of optimizing this CO-eliminating ability. However, evidence suggested that for the higher Pt PD adlayer formed on the Ru NP surface, electronic effect exerted by the Ru substrate was very weak if not at all. This is in contrast to the theoretical calculations$^{38,40,50}$ and warrants further scrutiny.
Most significantly, nonetheless, the reactivity of the Pt(31)-Ru sample was about 150% higher than that of the industrial benchmark J-M PtRu (1:1) alloy sample but with 3.5 times less Pt loading. The specific activity we obtained is generally higher than or at least comparable to those\textsuperscript{18} of the systems made by spontaneous depositions via repetitive hydrogen reductions. Considering that Ru is currently about much less expensive than Pt, using the Pt(31)-Ru NPs would lower the electrode material cost by more than 50% compared to using the industrial benchmark J-M PtRu(1:1) alloy NPs for DMFC applications. Furthermore, the wet chemistry based EG method for the controlled deposition of submonolayer Pt is advantageous in terms of processing and maximizing the use of Pt and can in principle be scaled up straightforwardly to an industrial level.
Figure 4.1. Comparison of the CVs of (A) the as-received Ru NPs and (B) the EG-cleaned Ru NPs.
Figure 4.2. The CO stripping CVs and those thereafter of the eight Pt-decorated Ru NP samples of the first batch. The dashed CVs in (a), (f), and (h) are those of pure J-M Ru, J-M PtRu (1:1) alloy, and J-M pure Pt NPs that are used as references for comparison. The percentage numbers are the values of Pt PD calculated by the method described in the text.
Figure 4.3. The CO stripping CVs of the three samples of the second batch.
Figure 4.4. Linear relationship between the measured and the nominal Pt packing density (PD). Squares are for the three second batch samples. The straight line goes through the origin.

Figure 4.5. The Ru (3d) and Pt(4d, 4f) XP spectra of Pt(40)-Ru of the second batch.
Figure 4.6. The TEM images of (a) the starting Ru NPs and (b) Pt(67)-Ru. The insets are the corresponding HRTEM snapshots where the distance between two adjacent atomic planes was measured to be 0.21 nm for both samples. (c) XRD patterns within the small angle range for two representative Pt-decorated Ru samples of the 1\textsuperscript{st} batch and for the three samples of the 2\textsuperscript{nd} batch. Those for pure J-M Pt, J-M PtRu alloy, and pure Ru NPs are also shown for comparison. The vertical dashed lines indicate the respective standard angle positions of Pt(111) (left) and Ru(101) (right) as references.
Figure 4.7. The respective TEM images of Pt(12)-Ru (Left) and Pt(40)-Ru (Right) from 2\textsuperscript{nd} batch samples. The insets are the corresponding HRTEMs where the distance between two adjacent atomic layers is 0.21 nm.
Figure 4.8. (a) The Pt coverage dependence of the CO stripping peak potentials. The CO stripping peak potentials of the pure J-M Ru, J-M PtRu(1:1) alloy, and J-M Pt NPs (as labeled) are also shown in the figure for comparison. (b) A linear relationship between the MeOH electro-oxidation peak current and the Pt PD. The straight line goes through the origin. The squares are of the three samples of the second batch.
Figure 4.9. The CVs of MeOH electro-oxidation on the 8 Pt-decorated Ru samples. The CVs (dashed curves) on the J-M Ru, J-M PtRu (1:1) alloy, and J-M Pt NPs are also shown in (a), (f), and (h) respectively for the purpose of comparison.
Figure 4.10. The MeOH electro-oxidation CVs of the 32nd-Batch samples
Figure 4.11. A. The CAs of the 8 Pt-decorated Ru NP samples. The CAs of the J-M Ru, J-M PtRu (1:1) alloy, and J-M Pt NPs are also shown for the purpose of comparison. B. The volcano-like curve of CA currents measured at 60 min as a function of the Pt coverage. The inset in (B) is a surface structure model (dark spheres for Pt atoms and light spheres for Ru atoms with each Pt 3-atom ensemble having 9 nearest Ru neighbors) that consists of ensembles of 3 Pt atoms on Ru(0001) and has simultaneously the maximum numbers of Pt ensembles and of Pt/Ru sites. The corresponding Pt PD = 3/7 = 0.43.
Figure 4.12. The CA of MeOH electro-oxidation of the 3 2nd-batch samples with the current values at 60 min.
Figure 4.13. The correlation between the long-term steady-state current density of the MeOH electro-oxidation and the potential of the CO stripping peak. The squares are for the three second batch samples. The Pt coverage is the implicit parameter in this plot with the arrows indicating the direction of the increasing coverage.
4.6. References

CHAPTER 5

ELECTROCATALYTIC PROPERTIES OF GOLD-CORE PLATINUM-SHELL NANOPARTICLES: EFFECT OF PLATINUM SHELL PACKING DENSITY AND GOLD CORE SIZE

5.1. Abstract

This chapter presents a detailed investigation of electrocatalytic properties of Au@Pt nanoparticles (NPs) as functions of Pt shell packing density and Au core size in terms of CO stripping, MeOH oxidation reaction (MOR) and oxygen reduction reaction (ORR). It addresses several important issues of current interest: Does the Au substrate always effect positively the Pt’s electrocatalytic performance? Does the influence of the Au core depend on its size? Does increasing surface site availability always improve ORR activity (V. R. Stamenkovic et. al., Science, 2007, 315, 493-497)? More specifically, Au@Pt NPs of three Au core size (3.3nm, 5.2 nm and 17.5 nm respectively) and a total of 18 different Pt shell packing densities ranging from 0.09 to 3.4 have been synthesized and whose sizes and elemental atomic ratios were characterized respectively by transmission electron microscope and energy dispersive X-ray spectroscopy. A gradual attenuation of the surface plasma resonance (SPR) of the Au core in UV-Vis spectrum was observed for both core sizes as the Pt packing density increased, but it was much stronger for the smaller core size. CO stripping cyclic voltammetric measurements indicated the existence of two types of Pt atoms formed on the Au NP surface as previously observed on bulk Au surface (chapter 2 in this thesis): (1) isolated Pt atoms that had dominantly Au coordination (as adatoms or/and incorporated in the Au surface
layer), had a large positive shift of the CO stripping peak (> 400 mV from that of Pt black), and showed no MOR activity, and (2) Pt atoms that had dominantly Pt coordination, formed Pt islands/adlayers, and showed MOR activity (ensemble effect). This similarity strongly suggests that the Au substrate effects the Pt’s electrocatalytic performance in a qualitatively same way at both nano and macroscopic scale. All the Au@Pt NPs studied here showed a much-suppressed formation of Pt oxides that would imply an increased availability of surface sites for initial oxygen adsorption. However, inferior ORR activities as compared to those of commercial Pt black were observed instead, suggesting that \( \text{O}_2 + 2* \rightarrow 2\text{O}^* \) (where * represents a surface site) was not the rate-limiting step on the Au@Pt NPs. All electrochemical properties measured on the Au@Pt samples, i.e., Pt oxides reduction, CO stripping, MOR and ORR, were much different from those of the commercial Johnson-Matthey Pt black but moved closer to them in a qualitatively similar fashion as the Pt packing density increased. Yet the recovering rate was substantially faster for the smaller two than for the large Au core samples, of which the underlying mechanism still eludes us.

5.2. Introduction

Bulk Au has long been used as a value-preserving noble material because of its proven chemical inertness. Consequently, it is a symbol of value and rich and was the very target of the historical California Gold Rush happened one and a half century ago in America. Coincidentally, Au has recently become again the target of a modern “gold rush”, triggered by the discovery of the exceptional catalytic activity of Au nanoparticles.
(NPs) of size smaller than 5 nm by Haruta and coworkers in 1987\textsuperscript{1}. But this time it is at the nanoscale and for exploring the newly-found unexpected chemical activities of the “nano” Au. Within this context, it is not surprising that nanoscale PtAu bimetallic systems have recently been receiving increasing attentions for potential uses as better electrocatalysts for methanol oxidation reaction (MOR)\textsuperscript{2}, oxygen reduction reaction (ORR)\textsuperscript{3,4}, or formic acid oxidation reaction\textsuperscript{5,6}. Several systems, e.g., PtAu alloy NPs\textsuperscript{7}, Pt-covered Au NPs\textsuperscript{8}, and Au-covered Pt NPs\textsuperscript{9}, have been studied from different perspectives and to different extent of detail. Yet as to how the nanoscale Au entities effect these systems for electrocatalysis, no clear consensus has emerged.

Recent density functional theory (DFT) calculations\textsuperscript{10} have predicted stronger surface bonding in general for both Pt impurity in and adlayer on Au surface than for pure Pt due to the up shift of Pt’s d-band center. An inferior ORR activity observed on Pt/Au(111) to that on the Pt(111)\textsuperscript{11} has been rationalized by the O-metal bonding being too strong for the Pt/Au(111) to be at the peak of the Sabatier volcano curve\textsuperscript{12}. In agreement with the DFT calculations, stronger CO-metal bonding has also been observed on Pt deposited on bulk polycrystalline Au electrode\textsuperscript{13} and on Au NPs\textsuperscript{14}, which led to an inferior MOR activity for largely isolated Au@Pt NPs with up to 10 Pt adalayers\textsuperscript{14}. On the other hand, enhanced MOR and ORR activities in PtAu NPs have been reported in other studies\textsuperscript{2,8,15-18}, notwithstanding the origin of these enhancements was largely either unknown or speculatively proposed.

With these in mind, research work presented in this chapter was aimed at having a detailed and systematic investigation of Au@Pt NPs in terms of CO stripping, MOR, and
ORR, all as functions of well controlled Pt packing density (a total of 18 values between 0.09 to 3.4) and Au core size (three core sizes of 3.3 nm, 5.2nm and 17.5 nm respectively). As compared to PtAu alloy NPs, Au@Pt core-shell structure offers in general a better control of surface composition by avoiding possible complications and uncertainties that may be caused by the immiscibility of bulk PtAu alloys over a large composition range, although it has been observed that Au and Pt can form miscible alloys at nanoscale\textsuperscript{19}. It has been observed that for all three core sizes, the Au cores exerted strong but size dependent influence on the electrochemical behavior of the Pt shells that showed a higher CO stripping potential (i.e., worsened CO poisoning), lower reduction potential for Pt oxides (i.e., strengthened Pt-O interaction), and lower MOR and ORR activities, which recovered monotonically towards those of pure Pt (i.e., commercial Johnson-Matthey Pt black that was used as a reference for comparison) as the Pt packing density increased.

5.3. Experimental

5.3.1. Au@Pt NPs Synthesis. Au@Pt NPs with different Pt packing densities were synthesized by using the pre-synthesized Au NPs as Au core seeds. The synthetic procedure was very similar to that used by Hu et.al\textsuperscript{20}. More specifically, a mixed solution of the pre-synthesized Au NPs and K\textsubscript{2}PtCl\textsubscript{4} (Pressure Chemical Co.) was first prepared by adding to 3mL Au NP solution (~0.25mM) a given volume of a 2mM K\textsubscript{2}PtCl\textsubscript{4} solution prepared with Milli-Q water (18.2M\textOmega.cm). The volume of the 2mM K\textsubscript{2}PtCl\textsubscript{4} solution was determined by the targeted nominal Pt:Au ratio. Under vigorous
stirring, a given volume (calculated according to the nominal Pt:Au ratio) of 10mM ascorbic acid solution was added drop wise at temperature 273K. After one hour long reaction under stirring, the resulting Pt-Au NPs were collected after an instant centrifugation of the mixture solution at 13,000 rotations per minute (RPM). The purpose of using ascorbic acid as reductant at 273K was to minimize the possible formation of Pt NPs. The ensuing electrochemistry characterizations (vide infra) confirmed the absence of individual Pt NPs, proving the success of such a coating strategy. The control of Pt packing density was achieved by varying the nominal Pt:Au ratio, although control experiments showed that not all Pt(II) ions in the solution were reduced at the end of the syntheses.

5.3.2. TEM and EDS. For 17.5nm Au core samples, usually a 0.5ml of the as-synthesized PtAu colloid solution was centrifuged at 13,000RPM for 10mins and the precipitate was collected and re-dispersed into 1ml 2-propanol for use. For 3.3nm and 5.25nm Au core samples, the as-synthesized PtAu colloid solution was directly mixed with 2-propanol as a volume ratio of 1 to 1 for use. One drop of the prepared solution was loaded onto the TEM grid which subsequently was dried in the vacuum. Since the JEM-2100f TEM is equipped with an energy-dispersive X-ray spectrometer (EDS), the actual molar ratios of Pt to Au were determined by the corresponding EDS data. All size distributions were based on ~250 counts to ensure that the results were statistically meaningful.

5.3.3. Electrochemistry. Two different glassy carbon (GC) electrodes were used as supporting electrodes for Au@Pt NPs for all electrochemical (EC) measurements that
were carried out in conventional three-electrode set-ups as shown in Figure 2.1. For ORR experiments, a 6-mm Teflon shrouded GC rotating disk electrode (RDE, Pine Instrument Co.) was used. For all the other experiments, a 3-mm GC electrode was used. The working electrodes were prepared as follows: the as-synthesized Au@Pt NPs or the commercial Pt black (courtesy of Johnson-Matthey) were transferred into a mixed solution composed of 1mL 2-propanol and 5μL 5 wt.% Nafion® (Du Pont, Inc) solution. The mixed solution was then sonicated for at least 10 min to form a uniform suspension which was drop-cast onto the surface of the supporting GC electrodes. The electrode surface was air dried under a gentle Ar flow and rinsed with a copious amount of Milli-Q water to eliminate loosely attached NPs. A 0.1M HClO₄ solution was used as the supporting electrolyte and all electrode potentials cited in the paper are with respect to the Ag/AgCl (3M) reference electrode.

5.4. Results and Discussions

5.4.1. Pt Packing Density Calculation Figure 5.1 presents the TEM images, size distributions, and UV-Vis spectra of the 3.3nm (A), 5.2nm (B) and 17.5nm (C) Au core NPs. They were rather homogenously distributed and the surface plasma peak positions and order (i.e., smaller NPs have shorter-wavelength peak) are in agreement with available literature values²¹. Figure 5.2 to Figure 5.4 presents the TEM images and corresponding size distributions of the 3.3nm, 5.2nm and 17.5nm Au core samples, respectively. Their average particle sizes were collected in Table 5.1. For the entire Au core samples, EDS data enabled the Pt packing densities be determined accordingly (see
Table 5.1 for the values). (The reason for using Pt packing density instead of Pt coverage is to account for the observed formation of PtAu surface alloy during the initial stage of adlayer growth\(^2\)).

For an ideal \(n\)-layer cubo-octahedral NP of fcc (face-centered cubic) crystal structure, the numbers of total (\(N_{\text{total}}\)) and surface (\(N_{\text{surf.}}\)) atoms can be express as\(^2\):

\[
N_{\text{total}} = \left(\frac{10}{3}\right)n^3 - 5n^2 - \left(\frac{11}{3}\right)n - 1 \quad (n \geq 1) \tag{1}
\]

\[
N_{\text{surf.}} = 10n^2 - 20n + 12 \quad (n \geq 2) \tag{2}
\]

On the other hand, for a TEM measured Au NP of diameter \(d\), the layer number \(n\) was determined with the known lattice constant of Au atom. Once the \(n\) was known, the corresponding \(N_{\text{surf.}}\) was calculated using Eqn. (1) and (2). The dispersion of the NPs, \(N_{\text{surf.}}/N_{\text{total}}\), was 37%, 21% and 7.9% respectively for the three Au cores. For given Au@Pt NPs, EDS data measured the overall atomic ratio of Pt and Au. Since all the Pt atoms were supposed to be deposited on the surface of the Au NPs, the Pt packing density was obtained in terms of the atomic ratio between Pt and the Au dispersed on the surface. For facilitating the following discussions, the samples will be named as Au(S, M or L)@Pt-packing density where S, M and L stand respectively for the small (3.3nm), middle (5.2nm) and (17.5nm) large Au cores.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Pt Packing Densities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(S)@Pt</td>
<td>0.24 0.54 0.83 1.07 1.50 2.54</td>
</tr>
<tr>
<td>Au(M)@Pt</td>
<td>0.09 0.34 0.94 1.49 2.0 2.22</td>
</tr>
<tr>
<td>Au(L)@Pt</td>
<td>0.74 0.91 1.3 2.0 3.0 3.4</td>
</tr>
</tbody>
</table>
5.4.2. UV-vis Spectra In Figure 5.5 we present the UV-Vis spectra of the Au(S)@Pt (A), Au(M)@Pt (B), and Au(L)@Pt (C) samples. All three Au cores had very well defined surface plasmon resonance (SPR) peaks. For all the three series of Au@Pt samples, the SPR amplitudes attenuated as the Pt packing density increased, indicating a Pt covering effect. However, the degree of attenuation of the SPR peak position differed in details. The Au(S)@Pt and the Au(M)@Pt samples showed a much stronger attenuation of the SPR amplitude than the Au(L)@Pt samples did, suggesting that the free electrons of the large Au core had a longer radial reach than those of the two smaller Au cores. In other words, the Pt adlayers on the large Au core would have a slower recovering to the properties of pure Pt, which was indeed observed (*vide infra*).

5.4.3. Electrochemistry Results

5.4.3.1. Cyclic Voltammograms Figure 5.6, 5.7 and 5.8 showed the CVs of the Au(S)@Pt samples (Figure 5.6), the Au(M)@Pt samples (Figure 5.7) and the Au(L)@Pt samples (Figure 5.8). All CVs, which were normalized by the Pt sites as determined by the CO stripping (*vide infra*), indicated the increasing presence of Pt on the Au NP surface by the increasing current signatures of hydrogen adsorption/desorption between -0.25~0V and Pt oxides reduction centered around 0.4V and by the gradual suppression and final disappearance of the Au oxides reduction peak at 0.88 V as the Pt packing density increased. The CVs also showed a much suppressed formation of Pt oxides (*vide infra*) for all the Au@Pt samples and more negative potential for their reduction, as
illustrated by the comparisons with the CV of the Johnson-Matthey (J-M) Pt black (dashed lines). The latter indicated a more stable Pt oxides, therefore a stronger Pt-O interaction, in agreement with the DFT prediction of a stronger surface bonding for Au supported Pt adlayers due to the up shift of Pt’s $d$-band center\textsuperscript{24}. No clear current features from pure Pt NPs were observed, which proved the success of the synthetic approach used for depositing Pt onto Au NPs and controlling the corresponding packing density. On the other hand, the reduction peak of Au oxides persisted up to a Pt packing density as high as 2 and only disappeared completely when the Pt packing density reached 3, suggesting a persistent appearance of surface Au atoms during the initial growth of the Pt shell. This observation is consistent with the proposed growth mechanism of Pt adlayers on Au(111) surface where a substantial exchange of the deposited Pt atoms with the underlying Au atoms for the first Pt adlayer was observed\textsuperscript{22}.

The actually fraction of the surface Pt atoms can be estimated as follows. It is reasonable to assume that the ratio of the reduction charge per atom between the surface Au and Pt atoms, $c$, is a constant for all the CV experiments. Once $c$ is known, the fraction of the Pt surface atoms, $\theta_{\text{Pt}}$, can be estimated by $\theta_{\text{Pt}} = cQ_{\text{Pt}}/(Q_{\text{Au}}+cQ_{\text{Pt}})$ where $Q_{\text{Au}}$ and $Q_{\text{Pt}}$ are the respective total reduction charges for the surface Au and Pt atoms that can be obtained from the CVs (Figures 5.6, 5.7 and 5.8). We chose to use the data obtained on the Au(L)@Pt-0.09 to determine the $c$ value because the corresponding Pt packing density was determined experimentally by the EDS and much less than 1 so it is a good approximation to write $\theta_{\text{Pt}}=0.09$. Additionally, the $Q_{\text{Au}}$ and $Q_{\text{Pt}}$ values for this sample can be measured from Figure 5.7B. With these quantities known, we found that
Using this \( c \) value, the \( \theta_{\text{Au}} \) for all the other samples were calculated and plotted as a function of the Pt packing density as shown in Figure 5.9. As can be seen clearly, the variation of the Pt fractions on surface for all the three sets of \( \text{Au@Pt} \) samples has the same pattern, indicating the Pt growth on the surface of the Au NPs follows a quite same model.

The ubiquitous suppression of the Pt oxides formation observed on the \( \text{Au@Pt} \) NPs (a similar suppression has been observed previously for Pt deposited on bulk Au polycrystalline surface\(^{13}\)) is quite interesting. On pure Pt surface, oxygen-containing species, i.e., OH, are first adsorbed onto Pt surface at a potential as low as 0.2 V via a dissociation of water molecules, which are then dehydrogenated to form \( \text{PtO}_x \)\(^{25}\) when the potential reaches 1.0 V and above. The DFT calculations\(^{12}\) showed that the binding energies of O and OH to Pt/Au, Pt, and Pt/Pd surfaces are respectively -4.20, -3.88, -3.81 and -2.17, -2.09, -1.99 eV. The order of these binding energetics indicates that the Pt/Au surface is the most and the Pt/Pd the least oxophilic among the three. One would thus expect an earlier and enhanced formation of the Pt oxides on Pt/Au rather than a suppressed one. On the other hand, a suppressed Pt oxides formation on Pt\(_{\text{ML}}\)/Pd(111) has indeed been observed previously, in agreement with the calculated order of the binding energetics, although an enhanced repulsive interaction of OH groups on Pt\(_{\text{ML}}\)/Pd(111) has been evoked to account for the suppression in the original paper\(^{26}\). Apparently, the suppression of the Pt oxides formation on Pt/Au in general and \( \text{Au@Pt} \) NPs in particular is somewhat counter intuitive and the reasons for that are not clear. If the enhanced repulsive interaction of the adsorbed OH groups was the reason, then the
repulsive interaction would have to be very strong for the Au@Pt samples. Another possible reason might be that the energy barrier for water activation is higher on Pt/Au surface in general. Clearly, this issue warrants further investigations.

5.4.3.2. CO Stripping Cyclic Voltammograms and Methanol Oxidation Reaction (MOR) Figure 5.10 present the CO stripping CVs of the A) Au(S)@Pt, B) Au(M)Pt, and C) Au(L)@Pt samples respectively. Only anodic scans are shown for simplicity. The CV of the J-M Pt black (dashed curve) is also shown as a reference for comparison. As can be seen clearly, the CO stripping as a function of Pt packing density showed very similar trends for all three types of samples. At low Pt packing densities (i.e., Au(S)@Pt-0.24 Au(M)@Pt-0.09 and Au(L)@Pt-0.74), the CO oxidation showed broad peaks at 0.78 V, 0.89 V, and 0.9V respectively, a positive shift of more than 400 mV from that of J-M Pt black. No MOR activity was observed on these three samples (see Figures 5.11A, Figure 5.12A and 5.13A). As the Pt packing density increased, a small and ill-defined shoulder first appeared at lower potentials but grew gradually into a well-defined narrow peak with increasing amplitude and peak potential approaching that of the J-M Pt black, as indicated by the left arrows in the Figures. The growth and negative shift of the low-potential peak took place at the expense of the broad high-potential peak whose position was shift further positively, as highlighted by the right arrows in the Figures and was ascribed to an Ostwald ripening-type process. The opposing directions of variations in the low- and high-peak potentials as the Pt packing density increased, as shown in the insets of Figure 5.10, are qualitatively the same as observed on bulk polycrystalline Au
surface\textsuperscript{13}. This observed similarity strongly suggests that the growth of Pt on Au surface follows the same process on Au nano-facets as on bulk Au surface.

Concurrent with the appearance of the low potential shoulder, observable, although small, MOR activities started showing up on all three Au@Pt samples (see Figures A in 5.11-5.13) and became more prominent as the Pt packing density increased. However, even at a Pt packing density as high as 3, the dominant narrow low potential peak of CO stripping was still more than 100 mV positive to that of the J-M Pt black, implying a more severe CO poisoning problem. Indeed, the MOR activities on the Au@Pt NPs having the highest Pt packing densities studied here were still about 4 times lower than that of the J-M Pt black (see Figure F in 5.11-5.13).

The observed overall positive shift of the CO stripping potential with respect to that on pure Pt can be ascribed to the Au induced strengthening of Pt surface bonding due to the up shift of Pt’s \textit{d}-band center as predicted by the DFT calculations\textsuperscript{24} and perhaps also to the suppressed formation of Pt-OH as observed. The strengthened Pt-CO binding and suppressed formation of Pt-OH aggravated the problem of CO poisoning and led to the reduced MOR activity. In Figure 15A, the peak current of the anodic sweep for the MOR is plotted against the Pt packing density. Although as expected that the peak currents were much lower than that of Pt black, they followed a recovering trend that interestingly was linear and had a Au core size dependent recovering slope that was much steeper for the Au@Pt samples of smaller Au core size. The latter indicated that the degree of influence depended on the Au core size.
Notice that the same pattern of behavior in terms of CO stripping and MOR has been observed previously on Pt adlayer deposited on bulk polycrystalline Au surface\textsuperscript{13}. This similarity strongly suggests that the observed phenomena are very general for Pt/Au systems, be it nanoscale Au@Pt core-shell structures or bulk Au supported Pt adlayers. From the pattern of CO stripping, it is clear that there existed two types of Pt atoms formed during the growth of the Pt shells/adlayers: those associated respectively with the high- and low-potential CO stripping peaks. The former was attributed to the isolated Pt impurities/adatoms that coordinated mainly with Au atoms so they were not MOR active because of lacking enough number of nearest Pt neighbors to form minimum sized ensembles needed for MOR. Because of the concurrent appearing of MOR activity, the latter was attributed to Pt islands/adlayers where Pt atoms had sufficient number of nearest Pt neighbors to form MOR active Pt ensembles.

5.4.3.3. Oxygen Reduction Reaction (ORR) The ORR data are presented in Figure 5.14 where the linear anodic sweeps in an O\textsubscript{2}-saturated 0.1 M HClO\textsubscript{4} supporting electrolyte are shown for the respective Au(S)@Pt (A), Au(M)@Pt (B) and Au(L)@Pt (C) samples supported on a GC rotating disk electrode (RDE). The scan rate was 20mV/s and rotating speed 1600 RPM. Half-wave potential ($E_{1/2}$) was used as the reactivity descriptor for comparison, which was determined by the potential at which the reaction current was half of the diffusion limited current. The $E_{1/2}$ so determined is plotted as a function of the Pt packing density in Figure 5.15B. Notice that all the values measured were less positive than 0.52 V, the value of the J-M Pt black. This indicates that all the Au@Pt NPs studied here had an ORR reactivity that was inferior to that of
the J-M Pt black. But as in the case of the MOR (Figure 5.15A), the Pt packing density dependence of the $E_{1/2}$ shows an interesting linear trend for all three Au@Pt samples, with the former also having a much steeper slope of approaching the value of pure Pt, which is another evidence that the degree of influence depended on the Au core size.

According to the dissociative mechanism, a four-electron ORR comprises of the following sequential elemental steps\textsuperscript{27}:

$$\begin{align*}
O_2 + * &\rightarrow 2O* \quad (4) \\
2O* + 2H^+ + 2e &\rightarrow 2OH* \quad (5) \\
2OH* + 2H^+ + 2e &\rightarrow 2H_2O \quad (6)
\end{align*}$$

Here * denotes a surface site. Since all the three sets of Au@Pt samples have shown a much suppressed formation of Pt oxides as compared to pure Pt, one would therefore expect higher ORR activities as proposed previously\textsuperscript{28-30} because the suppressed Pt oxides formation would make more surface sites available for the reaction step (4). Instead, lower ORR activities have been observed. This suggests that the surface sites availability for $O_2$ adsorption, i.e., reaction step (4), was not the rate-limiting step for the ORR on the Au@Pt NPs. On the other hand, these samples all showed stronger Pt-O interaction than pure Pt, which could slow down the reaction step (5) and make the Au@Pt NPs less ORR active. Thus, it is likely that the reaction step (5) was actually the rate-limiting step for ORR on the Au@Pt NPs, which is in agreement with the DFT calculations\textsuperscript{12}.

5.5. Conclusions
As to addressing the questions raised in Abstract, i.e., does the Au substrate always effect positively the Pt’s electrocatalytic performance? does the influence of the Au core depend on its size? does increasing surface site availability always improve ORR activity? the detailed investigation of the Au@Pt NPs as functions of Pt adlayer packing density and Au core size in terms of CV, CO stripping, MOR, and ORR, as presented above, enables us to offer the following answers.

1. Pt shells supported on the Au NPs of different sizes did not show improved activities for both MOR and ORR as compared to the commercial J-M Pt black because the strengthened Pt-CO and Pt-O/OH binding aggravated the problem of CO poisoning in MOR and slowed down the rate-limiting step in ORR. The DFT calculations ascribe the strengthened surface bonding to the up shift of Pt’s $d$ band center upon depositing onto Au surface. It seems that further increasing the Pt shell thickness would only bring the MOR and ORR activities closer to but not surpassing those of Pt black.

2. The strength of influence of the Au core as the Pt packing density increased was core size dependent. This is well illustrated by the variations in SPR amplitude (Figure 5.5), in transient MOR peak current (Figure 5.15A), and in ORR half-wave potential (Figure 5.15B). Interestingly, most of the variations seem to be linear and have a steeper slope for the Au@Pt samples with smaller Au cores. In other words, the Au@Pt samples with smaller Au cores showed a faster recovery towards the properties of the Pt black.

3. The fact that no MOR activity was observed on the Au@Pt samples with low Pt packing densities, together with a similar observation made previously on Pt deposited on polycrystalline bulk Au surface$^{13}$ (see chapter 3), highlights the generality of the
phenomenon. That is, for MOR to happen on Pt, a minimum number of nearest Pt neighbors are needed, i.e., the ensemble effect. The observations also confirm what has been previously proposed that two types of Pt atoms exist as the Pt adlayer grows, i.e., the Pt atoms have dominant Au coordination and those have dominant Pt coordination, and they behave very differently in terms of CO stripping and MOR.

In summary, the above conclusions are believed to be fundamentally important because they clarify in a timely fashion several issues that are fundamentally critical to any attempts of developing/designing Pt/Au systems for MOR/ORR applications.
Figure 5.1. The TEM images of the 3.3 nm (A), 5.2nm (B) and the 17.5 nm (C) Au NPs. The insets are the corresponding UV-Vis spectra and size distributions.
Figure 5.2. The TEM images and corresponding size distributions of the Au@Pt NPs with the 3.3nm Au core: (A) Au(S)@Pt-0.24, (B) Au(S)@Pt-0.54, (C) Au(S)@Pt-0.83, (D) Au(S)@Pt-1.07, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60. The average particle sizes are 3.50nm, 3.49nm, 3.51nm, 3.52nm, 3.59nm and 3.64nm respectively. The scale bars equal to 20nm.
Figure 5.3. The TEM images and corresponding size distributions of the Au@Pt NPs with the 5.2nm Au core: (A) Au(M)@Pt-0.09, (B) Au(M)@Pt-0.34, (C) Au(M)@Pt-0.94, (D) Au(M)@Pt-1.22, (D) Au(M)@Pt-2.00, (D) Au(M)@Pt-2.22. The average particle sizes are 5.23nm, 5.46nm, 5.67nm, 5.97nm, 6.02nm and 6.13nm respectively. The scale bars equal to 20nm.
Figure 5.4. The TEM images and corresponding size distributions of the Au@Pt NPs with the 17.5 nm Au core: (A) Au(L)@Pt-0.74, (B) Au(L)@Pt-0.94, (C) Au(L)@Pt-1.3, (D) Au(L)@Pt-2.0, (E) Au(L)@Pt-3.0, and Au(L)@Pt-3.4. The average particle sizes are 17.9 nm, 18.0 nm, 18.6 nm, 18.7nm, 18.7 nm and 18.8 nm respectively. The scale bars equal to 50 nm.
Figure 5.5. UV-Vis spectra of the 3.3nm (A), 5.2nm (B) and 17.5 nm (C) Au core samples.
Figure 5.6. The CVs of (A) the Au(S)@Pt-0.24 and 3.3nm Au NPs (red curve as a reference), (B) the Au(S)@Pt-0.54 NPs, Au(S)@Pt-0.83 NPs, and (D) Au(S)@Pt-1.07 NPs, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60 and J-M Pt black(dashed curve). In (F), the arrow highlight the suppression of the formation of Pt oxides on Au(S)@Pt in general.
Figure 5.7. The CVs of (A) the Au(M)@Pt-0.09 and 5.2nm Au NPs (red curve as a reference), (B) the Au(M)@Pt-0.34 NPs, Au(M)@Pt-0.94 NPs, and (D) Au(M)@Pt-1.49 NPs, (E) Au(M)@Pt-2.00, (F) Au(M)@Pt-2.22 and J-M Pt black(dashed curve). In (F), the arrows (red for J-M Pt and black for Au@Pt) highlight the suppression of the formation of Pt oxides on Au(M)@Pt in general.
Figure 5.8. The CVs of (A) the Au(L)@Pt-0.74 and 17.5 nm Au NPs (red curve as a reference), (B) the Au(L)@Pt-0.91 NPs, the Au(L)@Pt-1.3 NPs, (D) the Au(L)@Pt-2.0 NPs, (E) the Au(L)@Pt-3.0 NPs, and (F) the Au(L)@Pt-3.4 NPs and J-M Pt black (dashed curve). In (F), the arrows (red for J-M Pt and black for Au(L)@Pt) highlight the suppression of the formation of Pt oxides on Au(L)@Pt in general.
Figure 5.9. Pt fraction on surface of the Au(S)@Pt NPs (triangle, black), Au(M)@Pt NPs (ball, red) and Au(L)@Pt NPs (square, blue) as a function of the Pt packing density.
Figure 5.10. The CO stripping CVs of the Au(S)@Pt (A), Au(M)@Pt (B) and Au(M)@Pt (C) samples. Only anodic scans are shown here for simplicity. The CO stripping CV of J-M Pt black (dashed curve) is also shown as a reference. The inset shows the opposing trends of the low (circles) and high (squares) peak potential as a function of the Pt coverage.
Figure 5.11. The MOR CVs of (A) the Au(S)@Pt-0.24, (B) the Au(S)@Pt-0.54 NPs, Au(S)@Pt-0.83 NPs, and (D) Au(S)@Pt-1.07 NPs, (E) Au(S)@Pt-1.50, (F) Au(S)@Pt-2.60 and J-M Pt black(dashed curve).
Figure 5.12. The MOR CVs of (A) the Au(M)@Pt-0.09, (B) the Au(M)@Pt-0.34 NPs, Au(M)@Pt-0.94 NPs, and (D) Au(M)@Pt-1.49 NPs, (E) Au(M)@Pt-2.00, (F) Au(M)@Pt-2.22 and J-M Pt black (dashed curve).
Figure 5.13. The MOR CVs of (A) the Au(L)@Pt-0.74, (B) the Au(L)@Pt-0.91 NPs, the Au(L)@Pt-1.3 NPs, (D) the Au(L)@Pt-2.0 NPs, (E) the Au(L)@Pt-3.0 NPs, and (F) the Au(L)@Pt-3.4 NPs and J-M Pt black (dashed curve as a reference).
Figure 5.14. The RDE data of ORR on Au(S)@Pt (A), Au(M)@Pt (B), and Au(L)@Pt (C) samples obtained with a scan rate of 20 mV/s and a rotating speed 1600 rpm, the dashed lines indicated the currents of the half wave potential.
Figure 5.15. The Pt packing density dependences of the transient peak current in MOR (A) and the half-wave potential in ORR (B). The horizontal dashed lines indicate the respective values of J-M Pt black for comparison and the straight line for eye-guiding purposes.
5.6. References

6.1. Abstract

While bimetallic nanoparticles (NPs) offer greater tunability of their catalytic performance than their monometallic counterparts, their detailed mechanistic characterizations are still of a great challenging prospect, particularly at nanoscale. In this chapter, we describe a unique $^{195}$Pt nuclear magnetic resonance (NMR) based in situ technique that in principle enables us to access local elemental composition and electronic information across the dimension of the Pt-based NPs with decent spatial resolution. When combined with electrochemical analysis, it opens a way to correlate the local elemental composition and electronic properties with the catalytic activity of the bimetallic NPs. Specifically, from the $^{195}$Pt NMR analysis, we concluded that (1) the local Pt distribution within PtRu NPs can be determined in a layer-by-layer fashion, (2) alloying Ru substantially reduces the $E_f$-LDOS at the Pt atoms and (3) the larger variation in s-like $E_f$-LDOS at the surface region of the PtRu/graphite nanofibers (GNF)
may imply a higher diversity of catalytic sites available for reactions therefore explains the observed higher reactivity in methanol electro-oxidation.

6.2. Introduction

Bimetallic nanoparticles (NPs) well-dispersed on non-catalytic supports are among the most widely used heterogeneous (electro)catalysts that lie at the heart of numerous important industrial applications\textsuperscript{1,2}. For example, Pt-Ir and Pt-Re catalysts are the major workhorses in the petroleum industry for the production of lead-free gasoline with high octane numbers\textsuperscript{1}; Pt-Rh and Pd-Rh are indispensable ingredients in three-way catalysts used in combustion cars for substantially cutting down the environmentally-detrimental emission of NO\textsubscript{x} and CO\textsuperscript{3,4}; and more recently, Pt-Ru\textsuperscript{5}, Pt-Ni\textsuperscript{6}, Pt-Au\textsuperscript{7}, and many other bimetallic systems\textsuperscript{8,9} are poised to become major CO-tolerant hydrogen or/and methanol electro-oxidation and more efficient oxygen reduction electrocatalysts for future low- or zero-emission fuel cell applications. In general, bimetallic systems offer many more possibilities than their single-metallic counterparts in terms of tailoring their physical and chemical properties\textsuperscript{10-13} in searching for more efficient and less expensive catalytic materials. However, their greater tunability brought about by having the second element in the system inevitably comes with greater challenges in terms of their physical characterization, particularly at the nanoscale that matters the work of real-world catalysts\textsuperscript{14}. One of such challenges for bimetallic NPs is that it is generally difficult to access local elemental composition and electronic information across the dimension of
the NP with sufficient spatial resolution. Although catalytic actions take place on the NP surface, it is still highly desirable to access not only the surface but also the spatially-resolved compositional and associated physical properties across an entire NP. Since the latter define the electronic properties of the NP, they may also play an important role in shaping the surface catalytic performance. Geometrically, a spherical metal NP can be mentally considered as being made of onion-like atomic layers starting from a central atom. But no available three-dimensional imaging techniques can deliver a spatial resolution at the atomic layer scale, not even at the nanometer scale. The current methods of choice for gaining such information are probably the x-ray based spectroscopic techniques such as XPS and EXAFS. Still, at least in their current versions, they usually can only provide particle-averaged information such as average elemental specific coordination numbers and radial electron density distributions. In this chapter, we describe a unique $^{195}$Pt nuclear magnetic resonance (NMR) based in situ technique that in principle will enable us to determine the local Pt concentration and electronic properties in Pt-based bimetallic systems with decent spatial resolution, thus open a way to study, in much more specific and finer terms, the local elemental composition/electronic properties–catalytic activity relationships. Such an established relationship is critical in order for achieving a full mechanistic understanding of the catalytic actions of the bimetallic NPs, which in turn can assist in the rational design of new catalysts.

6.3. Physical Basis for Spatially-Resolved $^{195}$Pt NMR of Pt-Based NPs
The spatially-resolved $^{195}$Pt NMR approach utilizes two unique and well-known features of the $^{195}$Pt NMR of Pt NPs$^{17,18}$: 1) the spectral-geometric position correlation$^{19,20}$ and, 2) the Ruderman-Kittel-Kasuya-Yosid (RKKY) J-coupling caused oscillatory modulation (slow beat) of spin-spin relaxation$^{21,22}$, which will be briefly described in the following.

**6.3.1. The spectral-geometric position correlation.** As an illustrative example, Figure 6.1 shows a typical point-by-point $^{195}$Pt NMR spectrum of clean surface Pt NPs (Figure 6.1A) and the results of a layer-model simulation (Figure 6.1B). The sample was a commercial carbon black (Vul XC-72) supported Pt NPs (20 wt% Pt loading and an average particle size of 2.5 nm)$^{23}$. The physical basis of the layer-model simulation is the ubiquitous satellites observed in many diluted binary alloys of Pt that were interpreted as resulting from the (nearest, next nearest, and so on) coordinating Pt atoms around the impurity (solute) element$^{24,25}$. It has been empirically observed that these satellite positions approached that of bulk Pt (at 1.138 G/kHz as indicated by the arrow in Figure 6.1A) exponentially as the distance between the Pt atoms and the impurity center increased. In the layer-model simulation for the Pt NPs$^{26}$, the surface takes the analogous role of the impurity so as the Pt atoms move deeper inside of the particle from the surface, it is assumed that the corresponding Knight shift also approaches the bulk value exponentially in accordance to the rule $K_n = K_\infty - (K_\infty - K_0)\exp(-n/m)$ where $K_\infty$ and $K_0$ are respectively the Knight shifts of bulk and surface Pt atoms, $n$ is the number of the layer starting from zero for the surface layer and increasing as the atomic position...
moves inwards, and \( m \) is the so-called “healing length” characterizing the rate of recovery towards the Knight shift of bulk Pt atoms. Furthermore, the NPs are represented by ideal fcc cuboctahedra so that Pt atoms in the NPs can be dissected mathematically into atoms from surface layer, sub-surface layer, sub-sub (sub\(^2\))-surface layer, sub\(^3\)-surface layer, and etc. By resorting to the size distribution obtainable from TEM measurements, one can acquire a layer statistics that details the statistic fraction of atoms in a given layer. The superposition of all Pt atoms in the given layer results in a Gaussian that is fully determined by its peak position (which is subject to the exponential rule) and width and whose integral is constrained to be proportional to the atomic fraction of the layer. The success of the layer-model simulation, as shown in Figure 6.1, justifies an important premise that we utilize here, that is, \textit{the Pt atoms in different atomic layer resonate at different spectral position that monotonically varies between the value of the surface atoms and that of the bulk}. In more qualitative terms, the information for geometric position is encoded in the resonance frequency: the lower the field (or the higher the frequency) of the resonating Pt spins, the closer these spins are to the surface. It is this unique spectral-geometric position correlation that is enabling us to access spatially-resolved local information within the Pt NPs under scrutiny\(^{19,20}\). Although no quantitative layer-model analysis has been done yet for Pt-based bimetallic NPs, available data on PtPd\(^{27}\) and PtRh\(^{28}\) bimetallic NPs, however, indicate strongly that at least the qualitative statement of the spectral-geometric position correlation outlined
above still holds. Experimental data (vide infra) also strongly suggested that it would be the case for the PtRu NPs studied here.

6.3.2. The RKKY J-Coupling Effect. The J-coupling effect in metals refers to the oscillatory modulation of an otherwise normal nuclear spin-spin relaxation curve caused by the nuclear spin-spin interaction mediated by the conduction electrons\textsuperscript{21,22,29}. The criterion\textsuperscript{30} for observing the oscillatory J-coupling effect is that the difference in resonant frequency between two neighboring spins should be much larger than the J coupling constant $J$, a condition that is largely satisfied for Pt-based bimetallic alloys in general and NPs in particular as evidenced by the very broad lineshape (the spectral width of Pt NPs is about 3 MHz in a 400 MHz magnet). Theoretically, the J-coupling modulated relaxation curve can be expressed as\textsuperscript{22,30}

$$
S(\tau)/S_0 = \exp(-2\tau/T_2) \{ P_0 + \exp[-(\tau/T_{2J})^2] \sum_{n=1}^{12} P_n \cos^n(J\tau) \}
$$

where $\tau$ is the time interval between the two pulses in the conventional Hahn spin-echo sequence, $T_2$ is the nuclear spin-spin relaxation time, $T_{2J}$ accounts for a Gaussian-type spread in $J$ due to the inevitable environmental heterogeneity, and $P_n$ is the probability of having $n$ nearest neighboring nuclear spins and therefore a function of their concentration. For all the practical purpose, the effect caused by the spins beyond the nearest neighbors can be neglected. Thus only $P_0$, $P_1$ and $P_2$ are retained for the $T_2$ relaxation curve fittings, but the constraint $P_2 = 1 - P_0 - P_1$ applies. By determining the $P_n$, one can in principle access concentration of the unclear spin under observation.
Additionally, by measuring the nuclear-spin relaxation rate and using the phenomenological two-band model\textsuperscript{31}, we can deduce the s- and d-like Fermi level local density of states ($E_{f}$-LDOS). These are important electronic attributes that may be used to gauge the catalytic activity. In summary, therefore, by varying the observing frequency and using the spectral-geometric position correlation, spatially resolved information can be so obtained.

### 6.4. Experimental

The synthesis and physical characterizations for PtRu/GNF and PtRu/CNF were done by Dr. In-Su Park, Seoul National University. Figure 6.2 below shows the SEM and TEM images of GNF and CNF respectively. Some physical properties of GNF and CNF are listed in Table 6.1. The TEM images and corresponding XRD of as-synthesized PtRu/GNF and PtRu(CNF) patterns are included in Figure 6.3. The average particle sizes of PtRu/GNF and PtRu/CNF were determined in terms of TEM as 4.1 nm and 3.9 nm, respectively.

<table>
<thead>
<tr>
<th></th>
<th>GNF</th>
<th>CNF</th>
</tr>
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<tbody>
<tr>
<td><strong>Shape</strong></td>
<td>graphite fiber</td>
<td>Segmented carbon fiber</td>
</tr>
<tr>
<td><strong>Diameter</strong></td>
<td>~ 80 nm</td>
<td>~ 200 nm</td>
</tr>
<tr>
<td><strong>Length</strong></td>
<td>10 ~ 25 μm</td>
<td>~ 30 μm</td>
</tr>
<tr>
<td><strong>Purity</strong></td>
<td>&gt; 90 vol%</td>
<td>&gt; 90 wt%</td>
</tr>
<tr>
<td><strong>Specific Surface area</strong></td>
<td>~ 51.36 m²/g</td>
<td>&gt; 300 m²/g</td>
</tr>
</tbody>
</table>

Table 6.1. Physical properties of support materials.
6.4.1. Electrochemistry. For electrochemical characterizations of the PtRu NPs, the working electrode was prepared as follows. An aqueous suspension of the PtRu NPs was first prepared by dispensing ~5mg PtRu sample into 1ml 2-propanol containing ~5μl 5% Nafion® solution (Aldrich), followed by ~10 min sonication. A tiny amount of suspension was then drop-cast using a micropipette onto a 3-mm glass carbon (GC) electrode (Bioanalytical) which had been pre-cleaned by successively polishing it using alumina oxide powders of decreasing size of 1μm, 0.3μm, and 0.05μm respectively. After air-drying, copious amount of deionized water jet was used to rinse away the loosely attached particles from the GC electrode surface.

All electrochemical measurements were carried out using a CHI 760C potentiostat (CHI Instrument Inc.) in a conventional three-electrode setup (Figure 2.1). The experimental procedures of CO stripping and MeOH electro-oxidation were same as those described in chapter 4 except that 1) in order to avoid any possible Ru dissolution, electrode potential was always kept below 0.7 V, 2) before running CO stripping experiments, multiple cyclic voltammetries (CVs) (~20) were first run (50 mV/s and between -0.25 V and 0.7 V) under CO bubbling until stable and reproducible CO stripping peak was obtained (CO annealing). For chronoamperometry (CA) experiments, the electrode was first cleaned by holding potential at 0 V in a cell without MeOH until the current died down to minimum (~10 min) then transferred immediately into another cell containing MeOH for the measurement of a 60-minute CA at 0.2 V. Background
current was recorded in the same fashion but without the presence of MeOH and subtracted from the CA current.

**6.4.2. $^{195}$Pt NMR measurements.** All $^{195}$Pt NMR measurements reported here were carried out at 80 K on a “home-assembled” spectrometer equipped with an active-shielded 9.395T widebore superconducting magnet, an Oxford SpectrostatCF cryostat (Oxford Instruments, UK), an AMT (Lancaster, PA) 1 kw power amplifier, a Tecmag (Houston, TX) Appollo data acquisition system, and a home-built single channel solenoid probe. For NMR sample preparation, about 80 mg of the PtRu NPs was loaded into a 5 mm ($d$) x 25 mm ($l$) NMR glass sample cell which was then attached to a three-electrode electrochemical setup as a working electrode compartment (see the diagram shown in Figure 6.4). Electrical contact was achieved by burying a gold wire into the sedimented PtRu NPs in the sample cell. The supporting electrolyte was 0.5 M HClO$_4$ and the reference electrode and counter electrode were a commercial Ag/AgCl (3M) electrode and a Pt gauze respectively. The sample was first electrochemically cleaned by holding potential at 0.2 V until current decayed down to and stabilized at about 60 $\mu$A (which usually took 48 to 72 hrs). During the cleaning process, the cell was periodically blanked by ultra-pure Ar. After the electrochemical cleaning, the NMR sample cell filled with the supporting electrolyte was detached from the EC setup under the blanking of Ar, sealed immediately with a one-to-one grounded glass stop, inserted into the NMR probe, and then loaded down to the cryostat which was pre-cooled at 80 K. After the NMR measurements, the sample cell was re-attached to the electrochemical setup and
open circuit potential was checked. In all cases, the open potential was within 10 mV difference before and after the NMR measurements, indicating that the surface EC environment was intact. The conventional “$\pi/2$–τ–$\pi$–τ–echo” Hahn spin-echo sequence was used to acquire data at a specific spectral position. The values of $\pi/2$ pulse length and $\tau$ were 3μs (corresponding to a $B_1$ of 90G) and 25μs respectively. For nuclear spin-lattice relaxation measurements, a saturation comb composed of four $\pi/2$ pulses of varying intervals were used to saturate the NMR signal preceding the Hahn echo acquisition sequence. 14 data points were acquired for each relaxation curve and the relaxation time $T_1$ was obtained via the standard three-parameter exponential saturation-recovery fit.

6.5. Results and Discussions

6.5.1. Analysis of local Pt distribution. Figure 6.5A presents the point-by-point area-normalized $^{195}$Pt NMR spectra of the two samples (red circles for PtRu/GNF and blue squares for PtRu/CNF respectively). The effectiveness of the electrochemical surface cleaning was ensured by the lack of Pt oxide signal at 1.089 G/kHz$^{32}$. The overall lineshape of the spectra is similar to each other and to that of a PtRu black sample published previously$^{33}$. As a comparison, the simulated spectrum of the pure Pt sample in Figure 6.1 is also represented here (dashed blue curve).

Figure 6.6 presents the across-the-spectrum oscillatory spin-spin relaxation $T_2$ curves (or slow beats) data. The solid curves are the fits to Eqn. (1) with $T_2$, $T_{2J}$, $J$, $P_0$, $P_1$ as fitting parameters and $P_2 = 1 - P_0 - P_1$; all other $P_n$ could be neglected. The following
Tables present the fitting parameters to Eqn. (1) that gave the solid curves in Figure 6.6. Also included are the Pt atomic fractions $C_{Pt}$ calculated from $P_0$’s using Eqn. (2) (*vide infra*).

Table 6.2. PtRu/GNF data

<table>
<thead>
<tr>
<th>Field/Freq</th>
<th>$P_0$</th>
<th>$C_{Pt}$</th>
<th>$P_0^{calc}$</th>
<th>$P_1$</th>
<th>$P_1^{calc}$</th>
<th>$J$ (kHz)</th>
<th>$T_2$ ($\mu$s)</th>
<th>$T_{2J}$ ($\mu$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.09786</td>
<td>0.82</td>
<td>0.42</td>
<td>0.82</td>
<td>0.18</td>
<td>0.16</td>
<td>2.08</td>
<td>518</td>
<td>400</td>
</tr>
<tr>
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<td>0.34</td>
<td>0.85</td>
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<td>0.13</td>
<td>3.53</td>
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<td>0.80</td>
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<td>0.84</td>
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<td>0.14</td>
<td>3.37</td>
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Table 6.3. PtRu/CNF data

<table>
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<tr>
<th>Field/Freq</th>
<th>$P_0$</th>
<th>$C_{Pt}$</th>
<th>$P_0^{calc}$</th>
<th>$P_1$</th>
<th>$P_1^{calc}$</th>
<th>$J$ (kHz)</th>
<th>$T_2$ ($\mu$s)</th>
<th>$T_{2J}$ ($\mu$s)</th>
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</thead>
<tbody>
<tr>
<td>1.09915</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
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<td>0.83</td>
<td>0.17</td>
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The $J$ constants so obtained are shown in Figure 6.5B, which to a large degree are invariant across the spectrum for both samples and very close to those obtained on pure Pt NPs. On the other hand, the $P_0$ ($P_1$) values for the PtRu/C show a strong variation.
across the spectrum. This is qualitatively evident by simply inspecting the slow beat curves in Figure 6.6B of which the most obvious is the lack of slow beat at 1.09915 G/kHz. In order to extract quantitatively the Pt concentration from the $P_0$ values, a model developed by Slichter and companies$^{28}$ was adapted. Accordingly $P_n$ can be expressed as

$$P_n = \sum_{i=1}^{12} A_{ni} Q_n$$  \hspace{1cm} (2)

In Eqn (2), $Q_n$ is the probability of having $n$ nearest neighbors, whose spins can be flipped by the radiating radio-frequency field $B_1$, $A_{ni}$ is the probability of $i$ out of the $n$ nearest neighbors being the $^{195}$Pt isotope (nature abundance is 0.337). While $A_{ni}$ is a function of the Pt atomic fraction $C_{Pt}$ (=1 for bulk Pt), $Q_n$ is a function of the $\delta$, a parameter related to the Knight shift gradient: $\delta = \omega_1 / (a \omega_0 |\nabla K|)$ where $a$ is the distance between nearest neighbors, $\omega_1$ and $\omega_0$ are the Larmor frequencies under $B_1$ and the external static field $B_0$. Eqn (2) applies to the condition $\delta << 1$, which holds for the Pt-based NPs where the Knight shift gradient $\nabla K$ is large enough. The maximum value of $n$ for the model used here is 6$^{30}$. For simplicity, we also assume that $\delta$ is a constant across the spectrum and take an ad-hoc value of 0.1 (estimated from the values obtained on pure Pt NPs at 1.1145 G/kHz$^{19}$ and 1.117 G/kHz$^{30}$ respectively where similar values of $\delta$ are expected). The $C_{Pt}$ was then deduced from $P_0$ by solving Eqn. (2) under the constraint of $\sum P_n=1$. The results so obtained are also presented in Figure 6.5C (also in Tables 2 and 3). Using the $C_{Pt}$’s so obtained and $\delta = 0.1$, the corresponding $P_1$’s were calculated using Eqn. (2). Overall, these calculated values were in excellent agreement
with those determined by the slow-beat fits, substantiating further the internal consistency of the analysis. Most remarkably, the results show that PtRu/GNF had a rather homogeneous distribution of Pt but not so for PtRu/CNF whose data indicate that there was Pt segregation at the core (high-field end) and depletion at the surface (low-field end) of the NPs and a rather homogeneous distribution in-between. Notice that the Pt segregation at the core is consistent with the observation that the spectral amplitude above 1.115 G/kHz for PtRu/CNF was higher than that for PtRu/GNF (Figure 6.5A). Also, the NMR-amplitude-weighed average $C_{Pt}$’s are 0.42 and 0.47 for PtRu/G and PtRu/C respectively, very close to the nominal value of 0.5. In summary, the local Pt distribution within PtRu NPs could be defined in term of such a (semi-) spatially-resolved analysis utilizing the unique $f$ - $r$ correlation offered by $^{195}$Pt NMR of Pt-based NPs. This approach is applicable to other Pt-based alloy NPs and a broader availability of such spatially-resolved elemental composition in NPs will have profound ramifications for achieving a fundamental understanding of the catalytic actions of a given Pt-based alloy NP catalyst.

6.5.2. Local electronic properties and catalytic activity. Compared to the spectrum of the pure Pt NPs, the spectra of the PtRu NPs (Figure 6.5) were compressed from both the low- and high-field ends (much more from the high-field end if the difference in particle size, 4 nm for PtRu vs. 2.5 nm for pure Pt NPs, is taken into consideration). However, the spectra still have comparable linewidth. While no NMR shifts of PtRu bulk alloy are currently available, it is reasonable, however, to expect that these shifts
would appear at lower field end as compared to that of Pt bulk, as strongly suggested by the known shift values of all other Pt alloys\textsuperscript{34}. It seems that the low-field shift of the $^{195}$Pt NMR resonant position ubiquitously observed in diverse bulk Pt alloys has much to do with the breaking of the Pt translational symmetry by the alloying element that alters the s and d hybridization\textsuperscript{35}, though the degree of the shift is alloying element and concentration dependent\textsuperscript{34}. This would rationalize the high-field spectral compression observed here.

One noticeable difference as compared to the pure Pt NPs is that no clearly discernible surface peak was observed for the PtRu NPs. The one-directional broadening toward the low-field end of the $^{195}$Pt NMR spectrum of the Pt NPs from the rather narrow resonance peak (~ tens kHz as compared to several MHz for the NPs) of the bulk Pt as indicated by the arrow in the figure is rather unique. It is due to the presence of the surface that reduces the d-like $E_{f}$-LDOS monotonically as the Pt atoms get closer to the surface\textsuperscript{36}. For bulk Pt alloys, the presence of the alloying elements not only shifts the $^{195}$Pt resonance frequency to the low-field end but also significantly broadens the resonance peak\textsuperscript{34}. It is unclear \textit{a priori} if the presence of the surface as happened in NPs would cause a further low-field shift of the $^{195}$Pt resonance frequency but can be checked by either double resonance technique or detailed spin-lattice relaxation measurements across the spectrum as has been done on PtRh\textsuperscript{28} and PtPd\textsuperscript{35} NPs (the latter is technically easier). In Figure 6.7, we present the $T_1$ data measured at different spectral positions and at 80 K for both
PtRu samples. The inset shows a representative $T_1$ curve which could be well represented by a three-parameter single exponential function.

The general trend of the $T_1$ data as a function of the spectral position is very similar to those observed on the PtPd and on the pure Pt NPs\textsuperscript{35}. That is, the lower the field (or the higher the resonance frequency), the longer the $T_1$. This suggests that the spectral-geometrical position correlation still qualitatively holds, although we still don’t know where the exact resonance position of the surface atoms is. This nonetheless was further corroborated by the corresponding values of the $E_f$–LDOS that were deduced from the $T_1$ values and the Knight shifts of the spectral positions at which the $T_1$ were measured by using the two-band model\textsuperscript{31} and are presented in Figure 6.8.

Several interesting observations can be made. Firstly, the values of the d-like $E_f$–LDOS were almost identical for both samples and followed the same pattern of variation, i.e., increasing monotonically towards the high-field end. This may be a reflection of the localized characteristics of the d-like orbitals as well as a manifestation of the Friedel-Heine invariance theorem\textsuperscript{37} of which the latter states that the integral electronic properties at an atom in a solid, such as the $E_f$–LDOS, are determined primarily by the nearest and the next-nearest coordinating medium and then finely-tuned by the presence of the impurities including surface/interface if they are within a few electronic wavelengths. Particularly important is the monotonic pattern of variation in the d-like $E_f$–LDOS as a function of the spectral position. It is exactly the same as that observed in the pure Pt NPs which forms the basis for the layer-model analysis of the $^{195}$Pt NMR
spectra and therefore also the foundation of the spectral-geometric position correlation. On the other hand, the values of the s-like $E_r$–LDOS were rather flat across the spectrum (except for the lowest-field point for the PtRu/GNF). This pattern of variations is also very much alike to that of the pure Pt NPs$^{31}$.

Secondly, the overall s-like $E_r$–LDOS of the PtRu/GNF is slightly larger than that of the PtRu/CNF (3.62 vs. 3.30 atom$^{-1}$$\cdot$Ry$^{-1}$, 1 Ry = 13.6 eV), which is a direct reflection of the overall shorter $T_1$ for the former. But the most interesting observation is probably the much larger variation in the s-like $E_r$–LDOS observed at the low-field end for the PtRu/GNF sample ($\sim$ 1 atom$^{-1}$$\cdot$Ry$^{-1}$ vs $\sim$ 0 atom$^{-1}$$\cdot$Ry$^{-1}$ for the PtRu/CNF, estimated from the two left most points). If this is the surface resonance region (most likely it is, *vide supra*), then a larger variation in s-like $E_r$–LDOS may imply the availability of a larger variety of sites at the surface that would render the surface more active$^{38}$, particularly for multi-step reactions such as MeOH electro-oxidation. As will be seen in the following, electrochemical activity measurements indeed corroborate with this line of reasoning.

Thirdly, while similar trends have been firmly established between the PtRu and pure Pt NPs that were used to support the existence of the spectral-geometric position correlation for the PtRu NPs, alloying Ru also alters strongly the electronic properties of the Pt atoms. This is most evident if the values of the $E_r$–LDOS are examined at the surface region. For the pure Pt NPs that produced the spectrum in Figure 6.1, the s-like $E_r$–LDOS was 5.1 (atom$\cdot$Ry)$^{-1}$ and the d-like $E_r$–LDOS 13.5 (atom$\cdot$Ry)$^{-1}$ at 1.10000 G/kHz$^{23}$. This should be compared with 3.4 and 11.1 (atom$\cdot$Ry)$^{-1}$ for the PtRu/GNF and
3.6 and 11.5 (atom•Ry)$^{-1}$ for PtRu/CNF respectively, both at 1.10172 G/kHz. Thus, alloying Ru generally reduces the $E_f$–LDOS at Pt atoms. Previously, such a reduction was inferred from the indirect $^{13}$C NMR of CO adsorbed on PtRu surface$^{39}$ and may have the implication that at Pt atoms, the electron density available for bond formation with adsorbed CO was also reduced, leading to a weakening Pt-CO bonding.

In establishing the spectral-geometric position correlation for the PtRu NPs, i.e., the Pt atoms deep inside the NPs resonate at high field end but those at surfaces resonate at low-field end, it is now interesting to look at the spectra in Figure 6.5 in a more quantitative manner. While the overall shape of the spectra are alike with each other and with a previously published spectrum of the PtRu black$^{33}$, they however differ in amplitude at some spectral regions: the PtRu/CNF had higher amplitude above 1.116 G/kHz but lower amplitude between 1.1095 and 1.105 G/kHz. These observations imply that there were less Pt atoms in the surface region but more inside the NPs for the Pt/CNF than for the PtRu/GNF. Using the RKKY J-coupling constants so determined in table 2 and table 3, we calculated the values of the s-like $E_f$–LDOS$^{19}$. These values are plotted in Figure 6.8C for comparing with those determined by the independent $T_1$ measurements via the two-band analysis. Except for the lowest-field point, very good agreement has been found between the results obtained from these two independent measurements, therefore providing an excellent self-consistent check of the soundness of the analyses.
Now it is interesting to correlate the results of the above spatially-resolved $^{195}$Pt NMR analysis with those of EC analysis. We present in Figure 6.9 the data of electrochemical characterizations of the two samples (red curves for PtRu/GNF and black curves for PtRu/CNF respectively): A. the CO stripping, B., the CVs of the MeOH electro-oxidation, and C. the CAs, also of the MeOH electro-oxidation. From the CO stripping data, it can be seen that the PtRu/GNF had a narrower CO stripping peak with a slightly negative peak position and higher hydrogen desorption current. These observations imply that more Ru was present at the surface for the PtRu/CNF than for the PtRu/GNF and are consistent with the conclusion obtained from the NMR analysis that stated that there was a segregation of Ru on the surface for the former sample$^{40}$.

From the NMR analysis, we suggested that the PtRu/GNF would have a higher reactivity than the PtRu/CNF because of the availability of more diverse sites at the surface, as inferred by the large variations in s-like $E_F$-LDOS. This was indeed observed here. While for the PtRu/GNF sample the long term activity for MeOH electro-oxidation, as determined by CAs in Figure 6.9C, was only slightly higher (and sometimes less certain because the surface composition may slowly change as the reaction continues), the short term (intrinsic) activity is definitively and reproducibly much higher, as shown by the CVs in Figure 6.9B and CA currents in Figure 6.9C for times less than 500s.

**6.6. Conclusions**
In this chapter, we have presented a rather detailed $^{195}$Pt NMR analysis of two PtRu NPs of almost the same average particle size but supported on two different carbon supports: graphite and carbon nanofibers and argued that $^{195}$Pt NMR is capable of providing spatially-resolved compositional and electronic information of Pt-based bimetallic NPs in general and PtRu NPs in particular. More specifically, we found that (1) the local Pt distribution within PtRu NPs can be determined in a layer-by-layer fashion (2) alloying Ru substantially reduces the $E_f$-LDOS at the Pt atoms, and (3) the larger variation in s-like $E_f$-LDOS at the surface region observed on PtRu/GNF may imply the availability of more diverse sites for catalytic action and therefore may be the reason for the observation of higher MeOH oxidation activity. We believe that the spatially-resolved in situ $^{195}$Pt NMR analysis, as discussed in this paper, offers a unique and powerful technique to the mechanistic investigations of Pt-based alloy electrocatalysts.
Figure 6.1. The point-by-point $^{195}$Pt NMR spectrum (A) and its layer-model simulation (B) of a 2.5 nm commercial Pt/Vul XC-72 sample. The small dots in (A) represent the difference between the experimental data (circles) and the simulation (solid curve). Adapted from ref. 23.
Figure 6.2. SEM image (A) of graphite nanofibers and TEM image (B) of carbon nanofibers.
Figure 6.3. TEM images of PtRu/G (A) and PtRu/C (B). The insets show the corresponding XRD of carbon-supported PtRu nanoparticles.
Figure 6.4. Diagram of EC-NMR sample preparation setup.
Figure 6.5. A. The point-by-point, area-normalized $^{195}$Pt NMR spectra of the PtRu/GNF and PtRu/CNF NPs at 80 K. The inset is a TEM image of the PtRu/G. B. The J coupling constants deduced by fitting the slow-beat curves to Eqn. (1). C. The Pt atomic fraction deduced by analyzing the $P_0$’s using Eqn. (2). The arrow indicates the resonance position of bulk Pt.
Figure 6.6. The slow beats measured at different spectral positions for (A) PtRu/GNF and (B) PtRu/CNF. The solid curves are the fits to Eqn. (1).
Figure 6.7. The across-the-spectrum $T_1$ data measured at 80 K for the PtRu/GNF (red circles) and the PtRu/CNF (black squares). The inset shows a representative spin-lattice relaxation curve with the three-parameter fit (solid curve). The error was directly given by the fitting program (Igor).
Figure 6.8. The s-like (C), d-like (B), and the total (A) $E_f$–LDOS values (red circles for PtRu/GNF and black squares for PtRu/CNF) deduced from the $T_1$ values and the Knight shifts of the spectral position at which the $T_1$ were measured. The open circles (PtRu/GNF) and squares (PtRu/CNF) are the respective s-like $E_f$–LDOS values calculated using RKKY $J$ coupling constants determined by analyzing the slow beats.
Figure 6.9. A. CO stripping, B. CVs of MeOH oxidation, and CA of MeOH oxidation of the PtRu/GNF (red curves) and PtRu/CNF (black curves) respectively.
6.7. References

(18) van der Klink, J. J.; Brom, H. B. *Prog. NMR Spectrosc.* **2000**, 36, 89.
CONCLUDING REMARKS

Pt-based bimetallic systems have been intensively studied in the past decades due to their potential as electrocatalysts for both oxygen reduction reaction and methanol electro-oxidation that occur at the anode and cathode respectively in a DMFC. While great progress has been made, there are still noticeable gaps left between current research achievements and the requirements for commercial applications in terms of catalytic activity, material savings and so on. Therefore, more effort still needs to be made in this research area for further accomplishments.

This research concentrated on 1) the investigation of the electrochemical performance of Pt-Ru and Pt-Au bimetallic systems obtained in terms of the surface modification strategy; 2) the application of EC-NMR technique in the field of Pt-based electrocatalysts. The contributions of this research to the electrocatalysis can be summarized as follows:

*Experimental evidence for the ensemble effect.* According to the so-called “ensemble effect”, a minimum number of simultaneously accessible neighboring Pt sites are needed in order to extract three protons from MeOH to complete the oxidation reaction. By adopting a method of spontaneous deposition and delicately manipulating the experimental conditions, a series of Pt coverage, from very low to high ones, on different substrates of Ru and Au was obtained. The inactivity of Pt towards MeOH oxidation with very low coverage as well as the emerging and increasing activity with increasing
coverage coincided with the phenomena predicted by the hypothesis, evidencing the presence of the ensemble effect.

*Experimental evidence for the bifunctional mechanism.* Bifunctional mechanism and electronic effect have been proposed to explain the origin of CO-tolerance enhancement of PtRu compared to pure Pt. According to the former, the oxidative removal of CO adsorbed on Pt becomes easier due to the supply of oxygen-containing species generated on oxophilic Ru sites at low potentials. The latter, however, attributed the enhancement to the weakened Pt-CO bonding resulting from the electronic interaction between Pt and Ru atoms in close contact. By using Pt-decorated Ru NPs as a model, the electrochemical behavior towards MeOH electro-oxidation and CO stripping experiments were carefully investigated. As a function of the Pt packing density, both the long-term activity (in terms of current density) of the Pt-decorated Ru NPs towards MeOH electro-oxidation measured by chronoamperometry and the CO tolerance (in terms of peak shift) showed an interesting volcanic curve. This observation together with the monotonic increasing transient MeOH oxidation activity (in terms of current density) as a function of Pt packing density, was precisely rationalized in terms of the synergetic effect of the ensemble effect and the bifunctional mechanism. The electronic effect, if any, should not be the dominating factor contributing to the enhancement.

*Wet chemistry method for preparation of Pt-decorated Ru nanoparticles.* A one-pot ethylene glycol reduction based method was developed to prepare Pt-decorated Ru nanoparticles and through which Pt coverage was quantitatively controlled. Compared with the “spontaneous deposition” applied in the previous research for the same purpose
of surface modification, the wet chemistry based ethylene glycol method is technically less demanding (i.e., no need to handle high-temperature hydrogen reduction) and industrially scalable in operation. Most importantly, it can control the Pt coverage in an efficient and straightforward way. This method therefore, has the potential to be widely used to prepare other Pt-based bimetallic nanoparticles.

*Investigation of Au(core)@Pt(shell) nanoparticles.* Au has been intensively studied as a possible promoter to Pt for both MeOH electro-oxidation and oxygen reduction reaction (ORR) occurring on the cathode. Using a Au@Pt model, a detailed investigation was performed on electrocatalytic properties of Au@Pt NPs as functions of Pt shell packing density and Au core size in terms of CO stripping, MeOH electro-oxidation and ORR. It was observed that the electrochemical behavior of Pt quite much deviated from its bulk counterpart especially at low coverage. The strengthened Pt-CO bonding indicated a mechanism different from that in case of Pt-Ru. In conclusion, although this Au@Pt structure demonstrated an even inferior CO tolerance than pure Pt black in the whole range of the as-synthesized samples, two samples with small Au cores (3.3nm and 5.2nm respectively) and high Pt packing densities (2.2 and 2.4 respectively) does indicate comparable activities towards ORR than Pt black. In terms of materials savings, such Au@Pt maybe has the potential to be used as cathode electrocatalyst for ORR.

*Spatially-resolved Pt distribution in PtRu nanoparticles.* It has been recognized that while bimetallic NPs offer greater tenability of their catalytic performance than their monometallic counterparts, their detailed mechanistic characterization are still of a great challenging prospect, particularly at nanoscale. That is, before our work, there were still
no efficient methods available to access local elemental composition and electronic
information across the dimension of the NP with sufficient spatial resolution. In this part
of work, we adopted a unique $^{195}$Pt NMR based \textit{in situ} technique that in principle enables
us to determine the local Pt concentration and electronic properties in Pt-based bimetallic
systems with decent spatial resolution. When combined with electrochemical analysis, it
opens a way to correlate the local elemental composition and electronic properties with
the catalytic activity of the bimetallic NPs.
APPENDIX: AN INVESTIGATION OF SULFUR POISONING AND POSSIBLE REMEDIES OF PLATINUM-BASED ELECTROCATALYSTS

A.1. Introduction

In “hydrogen economy”, proton exchange membrane fuel cells (PEMFC) have long been considered as one of the most suitable candidates to provide electrical energy for portable devices. The hydrogen fuel so far obtained through reforming the hydrocarbons inevitably contains some trace amount of impurities, e.g. carbon monoxide (CO) and hydrogen sulfide (H$_2$S)$^1$, that poison the Pt electrocatalysts and greatly decrease the available catalyst sites for H$_2$ oxidation on anode$^2$ and oxygen reduction reaction (ORR)$^3$ on the cathode. Between these two well-known poisonous molecules, the H$_2$S generated sulfur poisoning is more potent and widely spread (i.e., it also happens in high-temperature solid-oxide fuel cells). In this work, the results of the following efforts will be described and discussed: 1) clarify the sulfur poisoning mechanism and 2) find effective remedies to the sulfur poisoning.

A.2. Experimental

A.2.1. Preparation of the Sulfur-covered Pt NPs. 5mg commercial Pt NPs (~3nm, courtesy of Johnson-Matthey) was dispersed into 1ml 2-propanol containing 5μl 5 wt.% Nafion® (Du Pont, Inc) solution. The mixture was then sonicated for at least 10 min to form a uniform suspension which was drop-cast onto the surface of a commercial (Bioanalytical) 3 mm-diametered glassy carbon (GC) electrode. The electrode surface
was air dried and rinsed with a copious amount of Milli-Q water (18.2MΩ.cm) to eliminate loosely attached NPs. Eight consecutive depositions have been carried in 1mM (1to5 depositions) and 10mM (6to8 depositions) Na\textsubscript{2}S solutions with different immersing time: 1min, 3min, 5min, 10min, 10min, 15s, 3min, and 10min for the 1 to 8 depositions respectively.

**A.2.2. Electrochemistry.** All electrochemical experiments were carried out in an Ar-blanketed conventional three-electrode electrochemical cell using an EG&G273A potentiostat (Princeton Applied Research) controlled by a PC with a CoreWare software package (Scribner). All cyclic voltammograms (CVs) were recorded with a scan rate of 50mv/s. The commercial GC electrode, Pt gauze and Ag/AgCl (3M) (Bioanalytical) were used as working, counter, and reference electrode, respectively. All electrode potentials in this paper were cited with respect to the Ag/AgCl (3M) reference electrode. A 0.1M HClO\textsubscript{4} solution prepared with Milli-Q water was used as the electrolyte. For CO stripping experiments, ultrahigh pure CO gas (MG Industries) was bubbled for 2 mins followed by Ar bubbling for another 5 mins. During the whole process, potential was held at 0V. At least two cycles of CVs were recorded to make sure that all of the CO molecules oxidized were from the electrode surface, not from the residual CO in the electrolyte solution. For MeOH electro-oxidation, a 0.1M HClO\textsubscript{4} solution with 0.5M MeOH was used.

**A.3. Results and Discussions (Preliminary data)**
As the figure below shows, multiple depositions reduce sequentially the amounts of chemisorbed hydrogen and CO and the formation of Pt oxide as indicated by the arrows. The corresponding shift of the peak is indicative of changes in the chemical/physical properties of the Pt surfaces after sulfur adsorption. While CO electro-oxidation becomes more difficult, featured by positive shift of oxidation peak, the reduction of Pt oxide becomes easier, featured by negatively shifted reduction peak.

The total sulfur uptake after the 8 consecutive depositions was 1.4ML, as calculated from the sulfur stripping data shown in Figure A.2 assuming that reaction was run via the following equation:\(^4\):

\[
Pt - S + 4H_2O \rightarrow Pt + SO_4^{2-} + 8H^+ + 6e^-
\]

The gradual deactivation of the Pt surface for the adsorption of H and CO and the formation of Pt oxide normalized by the respective values of the clean Pt surface as a function of the number of deposition is shown in Figure A.3. The importance of these sets of data is that they have clearly shown that the amount of sulfur adsorption can be controlled quantitatively by varying the deposition time and/or concentration of the Na\(_2\)S solution. Additionally, the data in Figure A.3 show that CO site blocking was always the lowest, followed by that of hydrogen and then by Pt oxide formation. This may explain the observed anodic shift of the CO stripping peak as the sulfur coverage increased. After the 6\(^{th}\) deposition cycle, H adsorption and Pt oxide formation were completely blocked. However, CO stripping still showed a small peak but this time had a negative shift as shown in Figure A.1.
In addition to the peak shift (CO oxidation and Pt oxide reduction) observed in Figure A.1, the sulfur stripping also shows the sulfur coverage-dependent characteristics in term of the negative shift of the onset potential in the 6 consecutive oxidation cycles. It can be expected that after each stripping cycle, a certain fraction of adsorbed sulfur will be oxidatively removed, implying a coverage decrease. Meanwhile, the onset potential of sulfur oxidation was decreased, indicating that the adsorbed sulfur becomes easier to be oxidized. Although the exact mechanism is not clear, if using CO oxidation as a reference, the negative shift of the onset potential for the oxidation of the adsorbed sulfur should be related to either the change of the Pt-S bonding or oxygen containing species supply (H\textsubscript{2}O) or both. Actually both of the two factors depend on the amounts of Pt sites available, which in turn is dependent on the sulfur coverage on the Pt surface. Thus the control of the sulfur coverage as demonstrated above will make it possible to investigate the Pt-S interaction in the whole strength range.

The possible sulfur poisoning effect on methanol electro-oxidation is presented in Figure A.4 above. The most intriguing observation is that the total methanol electro-oxidation current did not decrease until the 6\textsuperscript{th} deposition. Even more surprisingly, there was still methanol activity after the 7\textsuperscript{th} and 8\textsuperscript{th} deposition after which the Pt surface should have been completely covered by sulfur as indicated by the fact that no definable CO stripping peak could be observed. Actually, all of the sulfur covered Pt surfaces show higher specific activity (normalized by CO accessible areas) than pure Pt surfaces do, as shown in Figure A.4B (because no definable CO adsorption peaks were observed, the activities after the 7\textsuperscript{th} and 8\textsuperscript{th} depositions could not be normalized). The most reactive
was the one after the 6th deposition. Clearly more research on these highly interesting observations is very much warranted.

A.4. Conclusions

In this work, the sulfur-coverage dependent study of the commercial Johnson-Matthey Pt black will be discussed in term of electrochemical CO stripping and MeOH electro-oxidation. Incremental sulfur coverage up to 1.4 ML on Pt NPs was achieved by using open potential deposition in Na$_2$S solution. The sulfur coverage-dependent electrochemical characteristics and unexpected high activities towards MeOH electro-oxidation observed indicate that there is much more to learn of the sulfur poisoning mechanism. Additionally, potential remedies such as using bimetallic Au@Pt and Ag@Pt will be investigated in the follow-up work.
Figure A.1. The CO stripping curves of the Pt black after consecutive sulfur adsorptions. The red solid CV represents that of pure Pt black. The dashed line is the CV after the 6th deposition whose current scale is tripled.
Figure A.2. The sulfur stripping CVs of the sample after the 8th deposition. Multiple scans (up to 6) were needed to completely restore the Pt surface.
Figure A.3. The sulfur poisoning effect on H and CO adsorption and on Pt oxide formation.
Figure A.4. The sulfur poisoning effect on MeOH electro-oxidation. A. CVs without normalization (blank 8th = no methanol) and B. CVs normalized by the corresponding CO accessible areas.
A.5. References