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A COMBINED ELECTROCHEMICAL AND X-RAY PHOTOELECTRON SPECTROSCOPIC APPROACH TO ELECTROCATALYSIS

BY

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DISSERTATION

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ABSTRACT

Photoelectron spectroscopy and electrochemical techniques have been used to study commercial and model electrocatalysts for fuel cell applications. The overlying goal of this work is to gain a better understanding of the effects that electronic structure changes have on electrocatalytic systems.

As a starting point, commercial Pt/Ru alloy nanoparticles of different compositions were investigated as catalysts for the electrooxidation of methanol and formic acid. In the course of the study of electrooxidation of methanol, it was found to be very difficult, if not impossible, to separate the effects of the bifunctional mechanism and the electronic structure effects that might play a role in the activity. However, due to the difference in reaction pathways, data for electrooxidation of formic acid, in conjunction with photoelectron spectroscopy, confirm a definitive contribution from electronic structure on the reactivity, demonstrating a direct connection with theory in heterogeneous catalysis.

Another commercially available catalyst, nanoparticle Pt$_3$Co alloy, was studied as an electrocatalyst for the oxygen reduction reaction in both acidic and alkaline media. X-ray photoelectron spectroscopy and electrochemical methods indicated that the as-received catalyst consisted of both metallic cobalt and cobalt oxides, and that a dissolution of the cobalt oxides occurred during electrochemical treatments in acidic media to form a Pt-skin structure, whereas the catalyst was stable in alkaline media. The Pt$_3$Co catalyst was found to have better activity than Pt black catalysts in acidic media, but worse activity in alkaline media. Photoelectron spectroscopic results showed that the core-level binding energy of the platinum shifts to higher values in the alloy. This result
indicates that an electronic effect is the probable reason for the improved activity of the Pt-skin catalyst.

Attention was then turned to model catalysts, which provide a simplified method of studying fundamental electrocatalyst properties. To this end, platinum was deposited on a Rh(111) surface in order to obtain a range of coverage. The resulting Pt-decorated electrodes were probed by photoelectron spectroscopy in order to determine the shift in the core-level binding energy of platinum as a function of coverage. The platinum core-levels were found to shift to higher binding energy, in a manner consistent with electronic effects induced by lattice strain, charge transfer, and orbital rehybridization.

In order to provide more information on the nature of electronic effects in metal-metal bonds, the core-level binding energies of underpotentially-deposited copper and silver on a Rh(111) electrode surface were examined by X-ray photoelectron spectroscopy. Through XPS, the examined surfaces were found to contain carbon, oxygen, and sulfur or chlorine species, which confirmed the presence of anions at the Rh(111) surface, in addition to the deposited metals. The core-level binding energies for underpotentially-deposited copper and silver displayed negative shifts with respect to both the bulk deposits and clean metal references. These negative shifts were explained in terms of contributions from charge transfer, orbital rehybridization, and lattice strain.
To all those who have shown me love and support over the years.
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CHAPTER 1
INTRODUCTION

1.1 Fuel Cells and Electrocatalysis

Since the first fuel cell design in the mid-nineteenth century by Sir William Grove\textsuperscript{1}, there has been much interest and activity in the research and development of fuel cells as power sources. Many key advances have been made since the first work by Grove two hundred years ago.\textsuperscript{2} Francis Thomas Bacon, in the mid-twentieth century, developed the first practical fuel cell, which electrochemically produced electricity through the conversion of hydrogen and air, and did extensive work on alkaline fuel cells.\textsuperscript{3} In the 1950’s, Grubb and Niedrach designed a polymer membrane which could be used as an electrolyte and turned it into a catalyst assembly by depositing platinum on it.\textsuperscript{4,5} In the following decades, interest turned to acid electrolytes, and to improving the performance and lowering the cost of fuel cells.

A fuel cell is an ensemble of cathode, anode, and electrolyte. At the anode, a chemical species (i.e. - a fuel) is oxidized. The freed electrons travel through an external circuit to the cathode, where another chemical species is reduced. The purpose of the electrolyte is to complete the circuit. The interest in fuel cells lies in their high efficiency and potential benefits for the environment, as well as in reducing the dependence on the limited oil supply.\textsuperscript{2,6} There exist several fuel cell platforms, and they can be classified according to the temperature of operation, the type of electrolyte, and the type of fuel, some of which will be briefly described below.
High-temperature fuel cells, including molten carbonate, solid oxide, and protonic ceramic fuel cells, are useful in stationary applications, such as for providing electricity to a home or hospital.\textsuperscript{2,7} The waste heat may be used for heating or for further generation of power by other means. Because of the high operating temperature, chemical reactions are faster, spontaneous internal fuel reforming is possible, and efficiency is relatively high. There is also no need for noble metal catalysts, which reduces the cost of production.

Low-temperature fuel cells are attractive for use in applications that involve intermittent use, such as automotive applications, since they have a shorter start time. However, because of the low temperature, these types of fuel cells require a higher loading of catalyst material and are more vulnerable to poisoning species. The most common low-temperature fuel cells include alkaline fuel cells, polymer electrolyte membrane fuel cells, and direct methanol, ethanol, or formic acid fuel cells.

The proton-exchange membrane fuel cell (PEMFC or, simply PEM) is one of the simplest and most popular fuel cell platforms. It uses a polymer membrane as the electrolyte and separator between the anode and cathode.\textsuperscript{8} Its advantages include a low operating temperature, a tolerance to CO\textsubscript{2}, which allows atmospheric air to be used as the oxidant, and high power densities. The membrane, however, needs to be humidified. The PEMFC is still a fairly immature technology, and is improving rapidly. Currently, solid polymer fuel cells can reach a power density of 20 kW m\textsuperscript{-2} of active surface area and a power-to-mass ratio of 0.7 kW kg\textsuperscript{-1}.\textsuperscript{9} Typically, pure hydrogen is fed into the cell as the fuel. However, hydrogen poses some problems with transport and storage because of its low density.\textsuperscript{2} To get around this, hydrogen is sometimes generated by reforming
other fuels, such as methanol, ethanol, or formic acid.\textsuperscript{10,11} While one problem with this process is that it results in the formation of impurities, such as carbon monoxide, that could affect the overall cell performance, it does somewhat simplify fuel storage and transport, although a separate set of equipment for processing the fuel would be required.\textsuperscript{9} The anode is typically Pt or a Pt/Ru alloy, where the Ru improves the tolerance to CO impurities, and the cathode is typically Pt. Remaining issues for PEMFCs include reducing production costs through the use of cheaper catalyst and membrane materials and improving the durability of the cell.\textsuperscript{9,12}

One way to improve the portability and convenience of handling of PEMFCs is to directly use a liquid fuel, such as methanol, ethanol, or formic acid, so that there is no need for reforming.\textsuperscript{6} Another benefit of using a liquid fuel is that it prevents the membrane from becoming dried out.\textsuperscript{9} The most common of this type of fuel cell is the direct methanol fuel cell (DMFC). DMFCs use a fairly high loading of catalyst, which is usually Pt/Ru alloy. Carbon monoxide is one of the major intermediates in the electooxidation of methanol. The purpose of the ruthenium, then, is to increase the reaction kinetics by improving the tolerance to CO through the bifunctional mechanism, which is described in more detail in Section 2.1. The basic function of the ruthenium is to provide oxygen-containing species that assist in the oxidative removal of CO. Another issue for DMFCs is that of fuel crossover. Methanol passes through the membrane from the anode to the cathode, where it can be oxidized by the same reaction that occurs at the anode. This process reduces the efficiency of the cell, and work is being done to find membranes that resist crossover of methanol.\textsuperscript{9}
Direct formic acid fuel cells (DFAFC) offer another alternative.\textsuperscript{13-15} This type of fuel cell works very well with a Pd-based anode, avoiding costly Pt. Although fewer electrons are produced per fuel molecule, as compared with methanol, DFAFCs have a high efficiency. This is due to the fact that fuel crossover is not a problem when formic acid is used as the fuel. Additionally, formic acid is not as toxic as methanol and it occurs in nature, most notably in ants.\textsuperscript{9} Because of its advantages over the DMFC, the DFAFC is already being commercialized for use in portable electronic devices, such as cell phones and laptop computers.\textsuperscript{9,13-17}

Yet another direct liquid fuel cell alternative is the direct ethanol fuel cell (DEFC). Ethanol is of interest for a couple of reasons. First, the electrooxidation of ethanol involves the transfer of twelve electrons, giving a theoretical electrical energy that is much higher than that of methanol.\textsuperscript{18} Power densities of DEFCs are currently not as good as those of DMFCs, but much work is being done to improve this. At this time, the best anode materials are either Pt/Ru or Pt/Sn bimetallic catalysts or Pt/Ru-based or Pt/Sn-based ternary catalysts.\textsuperscript{18,19} The second reason is that ethanol is available in large quantities from agricultural products and biomass.\textsuperscript{18,19} DEFCs do suffer from fuel crossover, however, similar to DMFCs.

Alkaline fuel cells, which are prominently used in the space program,\textsuperscript{2} typically use liquid potassium hydroxide as electrolyte. The use of an alkaline electrolyte eliminates corrosion issues that are a problem for fuel cells that use acidic electrolytes. However, this type of fuel cell has a low tolerance to CO\textsubscript{2}, which limits the types of fuels and oxidants that can be used, has a relatively short lifetime, and the liquid electrolyte could pose some handling problems. Fuel cells utilizing an alkaline electrolyte have
recently been designed with a laminar flow setup, where the reactants are continuously fed into the cell and products are carried out of the cell.\textsuperscript{20-23} The laminar flow setup eliminates the need for a membrane, and has been shown to improve the reaction kinetics of both methanol and ethanol electrooxidation.\textsuperscript{23}

This dissertation focuses on fundamental electrocatalytic studies of catalyst materials for low-temperature fuel cells. In order to make possible the widespread use of these types of fuel cells for practical applications, improved catalyst materials must be developed. The performance of catalyst materials (i.e. – electrocatalysts) is dependent on the nature and the structure of the electrode.\textsuperscript{24} Therefore, one of the main thrusts in electrocatalysis, which is the field encompassing the study of heterogeneous catalysis of electrochemical reactions by an electrode material\textsuperscript{24}, is to gain a better understanding of electrocatalyst properties that affect performance, and to then use this knowledge in the directed design of new, improved electrocatalysts. This is done through a combination of electrochemical, surface analytical, and theoretical experiments in the study of both commercial nanoparticle electrocatalysts and model single crystal and alloy single crystal electrocatalysts.

A common method to try to improve electrocatalytic performance is to combine different metals to form an alloy. In this case, the metals work synergistically to improve performance. There are multiple reasons for this behavior. The addition of a transition metal to form a bulk alloy will provide oxygen-containing species at a relatively low potential, which will aid in the removal of adsorbed carbon monoxide – a common surface poison. This is called the bifunctional mechanism, and is well-studied in the case of Pt/Ru alloys.\textsuperscript{25-29} Another benefit of mixing metals is the electronic effect, where the
In order to try to take advantage of this, one recent development has been in the design of core-shell electrocatalyst materials, where one metal is completely surrounded by a layer of another metal. Electronic effects in electrocatalysis are not well-understood, and the study of these effects is the main focus of this dissertation.

1.2 Electronic Effects in Electrocatalysis

The reason for the high electrocatalytic activity of platinum lies in its ability to chemisorb and dissociate reactant molecules. These chemisorption and dissociation properties are directly linked with the valence electronic structure of the metal, specifically, the density of states near the Fermi level. In a heteronuclear system, the interaction of bonding atoms results in the mixing of the atomic orbitals to form molecular orbitals. Due to the Pauli exclusion principle, the molecular orbitals must shift in energy relative to the atomic orbitals. This results in a bonding orbital at slightly lower energy and an antibonding orbital at slightly higher energy. In the case of a metal, there are many atoms interacting with and bonding to one another. The number of molecular orbitals is equal to the number of atoms. So, when the number of atoms is large, as is the case for a metal electrode, the number of discreet energy levels becomes very large. It can then be considered as a continuum band, since the difference in energy between the resulting orbitals is so small. Metal sp bands are broad, since the electrons are highly delocalized. The d states are much more localized, resulting in less overlap, and, thus, a narrower band. In a metal, it is the variation in the degree of filling of the narrow d band
that affects adsorption bond strengths and the activation energies for dissociation of bound molecules.

In the case of an atomic adsorbate, interaction with the broad sp band of a transition metal will cause a broadening and downward shift of the adsorbate levels. There is also a strong interaction of the adsorbate levels with the narrow d band. This interaction causes the adsorbate levels to split into a pair of bonding and antibonding chemisorption orbitals. The strength of the adsorption then depends on the filling of the antibonding component of the chemisorption orbitals as it shifts down toward, and possibly below, the Fermi level. The bonding of a molecule is similar (Figure 1.1). In this case, both the bonding and antibonding molecular orbitals will be broadened and shifted by interaction with the metal sp band and split by interaction with the metal d band. Both the bonding and antibonding orbitals of the molecule split into pairs of bonding and antibonding orbitals, so that the initial pair of bonding and antibonding orbitals becomes two pairs of bonding and antibonding orbitals. The strength of chemisorption depends on the degree of filling of both the bonding and antibonding orbitals of the molecule. Filling of the bonding orbital that was originally an antibonding orbital in the molecule has two effects: it both strengthens the interaction of the molecule with the metal surface and weakens the intramolecular bond of the chemisorbed molecule. The filling of the originally antibonding orbital of the molecule is referred to as “back donation”. In terms of electrocatalysis, this dual effect means that there must be a balance between adsorption strength and the ability to dissociate chemical bonds, as described by the Sabatier principle. Weak adsorption will not allow dissociation of the
molecular bonds of the adsorbate, while strong adsorption will dissociate the bonds, but not allow the dissociated adsorbates to desorb from the surface.

Theoretical studies by Nørskov et al.\textsuperscript{40-47} indicate that changes in adsorption energies and reaction activation barriers have a direct correlation with changes in the center of gravity of the d band (a shift in energy toward or away from the Fermi level). A shift in the d band centroid will affect the degree of interaction with the adsorbate levels, changing the bonding and activation properties through the mechanisms described above. Contributions from charge transfer, orbital rehybridization, and geometric effects all play a role in shifting of the center of the d band.\textsuperscript{32,45,48} In a metal-metal bond, for instance, charge transfer is dependent on relative electronegativities and the degree of filling of the valence levels.\textsuperscript{32} The flow of electron density from one metal to another will result in respective shifts in the center of the d band for each metal. When a metal gains electron density, the d band shifts up (to lower energy) due to a negative change in the effective nuclear charge and increased electron-electron repulsion. The opposite is true for the metal that loses electron density in the transfer. Chemical bonding between two dissimilar metals also causes orbital rehybridization. In this type of rehybridization, deeper valence levels are promoted to higher levels, forming new orbitals. When this happens, the electron-electron repulsion in the core-levels is reduced and the effective nuclear charge becomes more positive, which leads to higher binding energies.\textsuperscript{48,49} Geometric effects include lattice strain/stress and changes in coordination (surface effects and size effects).\textsuperscript{30,31} Both of these mechanisms involve changes in the degree of overlap of electron levels, and, therefore, the environmental charge density in between atoms. The energy width of the d band is dependent on the amount of overlap of the bonding
atoms, since the Pauli exclusion principle dictates the shifting of electron levels. In the case of either reduced coordination, as is the case for surface atoms, or lattice expansion, the atomic electron levels will have less overlap, resulting in a less negative environmental charge density between atoms, and a narrowing of the d band. Since the degree of filling of the d band must remain constant, and in order to conserve energy, the d band must then shift up to lower energy. The converse occurs during lattice compression.

For a given metal-metal interaction, the shift of the d band center will depend on the summation of all of the mechanisms described above. Separating the contributions of the different mechanisms is then extremely difficult, if not impossible. Still, work is being done toward this goal, through a coupling of theory and experimentation. Quite conveniently, shifts in the center of the d band are linked to shifts in core-level binding energies, which make it possible to use X-ray photoelectron spectroscopy (XPS) to observe changes in the surface electronic structure. However, the use of XPS brings in another possible contribution to the shifts. Whereas the contributions listed above can all be considered as initial-state effects due to the metal-metal interaction, the generation of a core hole by ejection of a photoelectron creates a final-state effect, where changes in the screening of the core hole can lead to shifts in the core-level binding energies. In the past several years, studies on both bimetallic model catalysts and fuel cell electrocatalysts have been done by XPS, sometimes in combination with electrochemistry.
1.3 Dissertation Goals

The main goals of this dissertation are to contribute to a better understanding of electronic effects in metal-metal interactions and of the role of electronic effects in electrocatalysis, particularly as pertaining to fuel cells. A fundamental understanding of this phenomenon is critical to the ability to design effective electrocatalysts from first principles. The studies reported herein make use of X-ray photoelectron spectroscopy in conjunction with electrochemistry. The main instrument used for this work consists of two chambers: one where the electrochemical experiments are performed under argon atmosphere and an ultrahigh vacuum (UHV) chamber where the XPS experiments are done. The instrument design (Figure 1.2) is such that ex situ spectroscopic characterization can be done on line with electrochemical measurements; that is, the electrodes are protected from the atmosphere during both electrochemical treatments and transfer between the electrochemical and spectroscopic chambers, which preserves the electrode integrity by preventing contamination. Chapter 2 will explore the role of the electronic effect in the electrooxidation of methanol and formic acid at commercial Pt/Ru alloy nanoparticle electrodes. By creatively changing experimental parameters, the aim is to demonstrate the role of an electronic effect, in addition to the bifunctional mechanism. In Chapter 3, a study of another commercial electrocatalyst, Pt₃Co alloy nanoparticles, with respect to the oxygen reduction reaction is summarized. The author was not the lead researcher on this project, but substantial time and effort was committed to this project, and it fits well with the theme of the dissertation, so it is included here. For details of this project, the reader is referred to Hung Tuan Duong’s Ph.D. dissertation and Duong et al.⁵⁶,⁵⁷ Chapter 4 makes a transition to model electrocatalysts, where core-
level binding energy shifts of platinum deposits on a Rh(111) surface are evaluated. Another set of model systems, underpotentially-deposited (UPD) copper and silver on Rh(111), is examined in Chapter 5. While these UPD systems are not typically used as electrocatalysts, some groups have begun to use substitution of UPD layers in the synthesis of working electrocatalysts. More importantly, these systems involve metal-metal bonds, and, as such, could provide valuable information about electronic effects through core-level binding energy measurements.
1.4 Figures

Figure 1.1: The interaction of a transition metal with a molecule having bonding (σ) and antibonding (σ*) orbitals. Interaction with the s-p band lowers and broadens the bands, while interaction with the d band splits them into bonding and antibonding orbitals. This figure is based on Figure 6.25 in Chorkendorff and Niemantsverdriet.\textsuperscript{38}
Figure 1.2: Schematic of the EC-XPS system at UIUC.
1.5 References

(2) Andujar, J. M.; Segura, F. Renewable & Sustainable Energy Reviews **2009**, *13*, 2309.
(36) Stamenkovic, V. R.; Mun, B. S.; Mayrhofer, K. J. J.; Ross, P. N.; Markovic, N. M. Journal of the American Chemical Society 2006, 128, 8813.
(56) Duong, H. T. Enhancement of platinum cathode catalysis by addition of transition metals, University of Illinois at Urbana-Champaign, 2009.
CHAPTER 2
THE EXPERIMENT AND THEORY OF FUEL CELL CATALYSIS:
METHANOL AND FORMIC ACID DECOMPOSITION ON NANOPARTICLE 
Pt/Ru*

2.1 Introduction

As a result of motivating factors such as cost, increasing energy demand, and environmental concerns, there is much interest in developing fuel cell technology, which has the potential to provide a cleaner and cheaper source of power. Direct liquid fuel cells, using methanol, ethanol, or formic acid, could be used as replacements for power sources in cell phones or laptop computers. However, the high cost of platinum catalysts, slow reaction kinetics, poor selectivity, and catalyst poisoning have so far precluded the widespread use of fuel cells. Various bimetallic anode catalysts have been studied over the years in an effort to eliminate or reduce the negative effects of these issues. While not providing much benefit in terms of cost, Pt/Ru has been shown to be effective in regards to the other factors, and is therefore one of the most commonly studied anode catalysts.

It is generally accepted that in bimetallic catalysts, enhancement of catalytic activity, as compared to monometallic catalysts, can be attributed to a bifunctional mechanism and/or an electronic effect. Via enhanced oxidation, the bifunctional mechanism of bimetallic catalysts assists in the removal of surface poisoning species, such as carbon.

monoxide, with each metal in the alloy playing a separate role. The effects of the electronic structure, on the other hand, are still not completely understood. A fundamental insight, including theoretical understanding of these mechanisms is necessary in order to design novel catalysts that can be used in new fuel cells. The density functional theory approaches developed by Nørskov et al.\textsuperscript{13-20} have, for instance, indicated that changes in adsorption energies and activation barriers for reaction are directly linked to changes in position of the center of the metal/alloy d-band with respect to the Fermi level. The strength of binding of an atom or molecule to a surface depends on the degree of filling of the antibonding states between the two interacting species, and this, in turn, is dependent on the density of metal d states near the Fermi level. Consequently, one would expect to be able to tune the activity of a catalyst by inducing changes in its surface electronic structure. In an alloy, the surface electronic structure is affected by lattice strain\textsuperscript{12,21-23} and charge transfer\textsuperscript{24}. According to Nørskov’s d-band center theory, these effects lead to narrowing or widening of the d-band and a subsequent shift in its center of gravity toward or away from the Fermi level to conserve energy and maintain a constant filling of the d-band. Conveniently, these shifts in the position of the center of the d-band are linked to shifts in core-level binding energies, making it possible to use core-level photoelectron spectroscopy to observe changes in surface electronic structure.\textsuperscript{15,25-27}

There has been much effort to verify the d-band center theory through experimental techniques. While the theory has been found to not hold for some systems\textsuperscript{28-32}, there have been major successes in connecting changes in adsorption to changes in position of the center of the d-band. One such example is the oxidation
(desorption) of surface CO, which could be a useful measure of catalytic activity. In the study of Pt/Ru nanoparticles containing CO, Tong et al. found that the addition of ruthenium to platinum led to a decrease in the local density of states of platinum. This change in electronic structure, due to the addition of ruthenium, reduces the $2\pi^*$ back-donation, and thereby weakens the metal-CO bond. Since CO is an important poisoning reaction intermediate in the oxidation of small organic molecules, this has major implications for catalytic oxidation of fuels like methanol and formic acid. In fact, Lu et al. have demonstrated that the electronic (or ligand) effect has a definite contribution to the total enhancement of CO oxidation on Pt/Ru as compared to pure Pt, although the contribution is only about one-fourth that of the bifunctional mechanism. Recently, Alayoglu et al. synthesized a ruthenium core-platinum shell nanoparticle catalyst based on first principles. This catalyst had low light-off temperatures for both CO and H$_2$, demonstrating a direct correlation between the electronic structure and activity in the gas-phase, as predicted by theory. However, despite the large amount of work, the relationship between surface electronic structure and catalytic activity towards the electrooxidation of small organic fuels is not completely understood.

In this study, a series of Pt/Ru nanoparticles (produced by Johnson & Matthey), ranging in nominal composition from 0 to 100 atomic % Ru, were analyzed by synchrotron radiation photoelectron spectroscopy (SRPS) and chronoamperometry in an effort to determine whether a correlation between the d-band center theory and reactivity towards methanol and formic acid electrooxidation exists, and if it can be observed experimentally. It is generally accepted that, for sufficiently positive potentials, methanol electrooxidation on Pt/Ru alloys proceeds through a dual-pathway mechanism involving
a strongly adsorbing CO intermediate (Figure 2.1).\textsuperscript{9,10,44} Thus, although the electronic effect is believed to have some effect on the reactivity, the bifunctional mechanism, where Ru sites provide adsorbed oxygen-containing species for enhanced oxidative removal of adsorbed CO, is expected to play a larger role in the electrooxidation of methanol. On the other hand, formic acid is oxidized through a triple-pathway mechanism, consisting of a direct pathway, an adsorbed CO intermediate pathway, and an adsorbed formate intermediate pathway (Figure 2.2).\textsuperscript{45,46} At short reaction times and potentials below \(~0.6\) V vs. RHE, the direct pathway to CO\textsubscript{2} formation dominates.\textsuperscript{37,45,47} Under these conditions, where strongly adsorbed CO should play a negligible role, it may be possible to examine the effects of the bifunctional mechanism and the surface electronic structure separately, and thus to gain a better understanding of the processes involved.

2.2 Experimental Methods

The unsupported nanoparticle samples used in this study were obtained from Johnson & Matthey, and included the following: Pt black, Pt90Ru10, Pt80Ru20, Pt67Ru33, Pt50Ru50, Pt40Ru60, Pt34Ru66, and Ru black (where numbers indicate atomic % of the elements in the sample). For reactivity measurements, the nanoparticles were dispersed in Milli-Q water (18.2 M\textOmega), sonicated for 30 minutes, and deposited (~20 \(\mu\)L of an \(~100\) \(\mu\)g/mL solution) onto a gold disk (10 mm in diameter).\textsuperscript{42} A thin film of nanoparticles over the entire disk was obtained after drying. The measurements were done in a conventional three-electrode cell with a platinum gauze counter electrode, Ag/AgCl (3 M NaCl, Bioanalytical Systems) reference electrode, and 0.5 M H\textsubscript{2}SO\textsubscript{4}
(GFS, doubly-distilled from Vycor) electrolyte solution. Reactivity measurements were done in either 0.5 M CH$_3$OH/0.5 M H$_2$SO$_4$ or 0.2 M HCOOH/0.5 M H$_2$SO$_4$. For formic acid experiments, the current density was sampled at reaction times of 3 seconds and 1 hour (then, under apparent steady-state), while for methanol experiments, only the steady-state current (at 1 hour) was recorded. Methanol was purchased from Sigma-Aldrich and double distilled formic acid was purchased from GFS. Ultra-high-purity (UHP) argon and carbon monoxide gases were provided by S. J. Smith Welding Supply. The catalyst surface area was calculated from CO stripping experiments, assuming a stripping charge of 420 µC cm$^{-2}$.

All samples were fully reduced by holding the electrode potential at -100 mV vs. RHE for 2 hours.

The composition of the nanoparticles was verified and the core-level binding energies were measured using photoelectron spectroscopy at a synchrotron source (SRPS). These SRPS measurements were obtained at Bessy-II in Berlin, using the undulator beamline U49/2-PGM 2 at the SoLiAS end station at photon energies of 160, 370, and 650 eV. The standard error for core-level binding energies at the synchrotron was 0.03 eV. The Au 4f signal from the Au substrate electrodes (10 mm in diameter) was kept at a negligible level (below 5 atomic %, as compared to the sum of Ru and Pt, see Figure 2.3). The instrumental and experimental details for the synchrotron measurements were reported previously.

Structural and size properties were determined from powder X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM, JEOL 2010F). XRD showed characteristic peaks for bulk Pt/Ru alloy, while no peaks for Ru oxides were observed. XRD and HRTEM gave similar particle size results (Table 2.1).
2.3 Results and Discussion

2.3.1 Synchrotron radiation photoelectron spectroscopy of Pt/Ru nanoparticles.

Prior to recording core-level binding energies for the nanoparticle catalysts, the samples were all electrochemically pretreated as described in the Experimental Methods section. This pretreatment ensured an oxide-free surface, as confirmed by the synchrotron measurements. The typical wide-range survey spectra of the Ru/Pt samples are shown in Figure 2.3. Core-level binding energies of these samples (shown in Figure 2.3 inset) were reported previously\textsuperscript{49} and are used here for further treatment. From Figure 2.3, there is a definite shift in the platinum core-level binding energy with changing composition. To demonstrate this more quantitatively, Figure 2.4 shows the relationship between Pt 4$f_{7/2}$ binding energy and Ru content of the catalysts measured at photon energies of 160, 370, and 650 eV, where the Pt 4$f_{7/2}$ binding energy increases linearly with increasing Ru content, with a slope of about 0.07 eV per 10% Ru. We have observed that the positive shift in the Pt 4$f$ binding energy corresponds to a shift of the center of the d-band\textsuperscript{15,25-27,40,50} towards higher binding energy, away from the Fermi level. As previously discussed, such a shift in the d-band center can be brought about by lattice strain and charge transfer. Our theoretical studies, which were previously reported\textsuperscript{49}, indicate that the primary source of the shifts in core-level binding energies for the nanoparticles is lattice strain. This is in contrast to the results of a study of Pt single crystals, where the core-level shifts were clearly due to both lattice strain and charge transfer.\textsuperscript{51} A change in the Pt-Pt bond distance with increasing alloyed Ru was confirmed by powder XRD, and the results are given in Table 2.1. As Ru is added to the alloy, the Pt lattice undergoes compressive strain, shortening the Pt-Pt bonds. This shortening of
bond distances causes the d orbitals to overlap to a larger degree. Since the d-band of Pt is more than half-filled, broadening the d-band would be expected to lead to a subsequent downshift in the center of gravity of the d-band with respect to the Fermi level in order to maintain constant filling and to conserve energy. This is, in fact, what is observed through the core-level binding energy measurements.

The SRPS data was also used to determine the approximate surface composition of the nanoparticle catalysts based on the ratio of peak intensities of Pt 4f\(_{7/2}\) and Ru 3d\(_{5/2}\). Since the apparent surface composition calculated from SRPS depends on the photon energy used\(^{52}\), it was important to try to minimize the photon energy while matching the inelastic mean free paths for the two metals.\(^{40}\) Both Pt 4f and Ru 3d core electrons have a kinetic energy of about 90 eV when Pt is measured with photon energy of 160 eV and Ru at 370 eV. The inelastic mean free path under this condition is ca. 4.2 Å,\(^{52,53}\) which means that the SRPS signal is characteristic of predominantly the surface atoms. The surface composition of each catalyst was calculated using these photon energies, and the results are listed in Table 2.1. These data indicate an enrichment of Pt at the surface of the nanoparticles, which is in agreement with previous results by Babu et al.\(^{54}\) using EC-NMR. It is likely that the Pt enrichment is a consequence of the strongly reducing environment that the samples are subjected to just prior to all experiments.\(^{55,56}\)

**2.3.2 Methanol electrooxidation on Pt/Ru nanoparticles.** Decomposition of methanol on Pt results in a strong poisoning of surface Pt sites by carbon monoxide (Figure 2.1), and the oxidative removal of this CO requires the presence of a surface oxygen-containing species, as discussed above (the bifunctional mechanism). The enhancement
provided by Ru is due to the ease with which water is activated over Ru, as compared to Pt, to form adsorbed oxygen-containing species.\textsuperscript{8,9,44} In this work, the activity of the Pt/Ru nanoparticle catalysts towards electrooxidation of methanol was investigated by chronoamperometry. Figure 2.5 shows the current-time curves for methanol electrooxidation at 450 mV vs. RHE for the different nanoparticle samples. There are two important features of these curves that should be noted. First, it is clear that the reactivity depends on the catalyst composition, as the current density is different for each sample at a given time. Second, the reactivity decreases over time until an apparent steady-state current is reached (at ca. 1 hour). This decrease in reactivity is evidence of the poisoning effect, presumably of adsorbed CO formed as an intermediate in methanol electrooxidation.\textsuperscript{44,57} In Figure 2.6, the steady-state current density is plotted as a function of Ru content. The obtained graph is a typical volcano plot\textsuperscript{58,59}, where the current density is found to peak at a nominal composition of about 20-30\% Ru. This behavior cannot be explained by the electronic effect alone. Rather, it proves that the bifunctional mechanism is dominant. For these catalysts, an increase in the Pt 4f\textsubscript{7/2} binding energy (a downshift in the d band center to higher energy) would lead to weaker adsorption of the poisoning CO species, and, therefore, reduced poisoning effects. Thus, if the electronic effect was the dominant enhancement mechanism, the reactivity at high CO coverage might be expected to increase with increasing Ru content, in contrast to what is observed (Figure 2.6). At the same time, however, shifting the d band center down would lead to weaker interaction between the methanol and the metal surface, which leads to a Sabatier effect, where a maximum in activity might be expected. Although other groups, including Lu \textit{et al.}\textsuperscript{35}, have found that the bifunctional mechanism
contributed more significantly than the electronic effect, it is not possible to distinguish between the electronic effect and the bifunctional mechanism using the data presented here.

The bifunctional mechanism leads to a volcano behavior because of an ensemble effect. It is assumed that an active site consists of the “ensemble” of three Pt atoms and one Ru atom. Gasteiger et al.\textsuperscript{9,60} calculated the probability of finding such an ensemble of atoms on the surface of a Pt/Ru catalyst at room temperature, and found that the probability distribution curve peaks at a composition of about 10 atomic % Ru. In Figure 2.6, the current density peaks at a nominal composition of about 20-30 atomic % Ru. However, for the nanoparticles used in this study, it can be seen in Table 2.1 that a nominal composition of 20-30 atomic % Ru corresponds to a surface composition of about 17-18 atomic % Ru. The discrepancy between the most active Ru concentration and the peak probability suggests that the bifunctional mechanism is not the only active mechanism. While our data does not allow for the separation of the different mechanisms, our results are in agreement with previous results\textsuperscript{9,10,34,35,44} that suggest that the bifunctional mechanism is the primary, but not the only, source of enhancement in the electrooxidation of methanol.

\textbf{2.3.3 Formic acid electrooxidation on Pt/Ru nanoparticles.} Since the results from electrooxidation of methanol were inconclusive in terms of determining a contribution from an electronic effect (showing predominance of the bifunctional mechanism), electrooxidation of formic acid was next investigated. Formic acid is a promising fuel for study because of its ease of electrooxidation.\textsuperscript{6,7,61-66} Decomposition of formic acid has
been shown to occur via a triple-pathway mechanism (Figure 2.2), involving a direct pathway to CO\(_2\), an indirect pathway through an adsorbed CO intermediate, and an adsorbed formate intermediate pathway (at higher potentials).\textsuperscript{45-47} However, studies have shown that at low potentials (below ~0.6 V vs. RHE) and at short reaction times, the direct pathway is dominant on Pt electrodes, and the amount of adsorbed intermediates should be negligible.\textsuperscript{37,45} This should provide an opportunity to investigate any possible effects from electronic structure changes separate from the effects of the bifunctional mechanism.

Figure 2.7 shows the current density for formic acid electrooxidation on the Pt/Ru alloys at 500 mV vs. RHE over a period of 1 hr. Similar curves were obtained at 450 mV vs. RHE. The inset in the figure shows the current density over a period of 100 s. As was the case for methanol electrooxidation, it can be seen that the current density is dependent on the catalyst composition, and that the catalyst is poisoned over time. Based on the known reaction pathways\textsuperscript{37,45-47,67}, the primary poisoning species is presumed to be CO. The interesting observation, however, arises when the current density is plotted as a function of the catalyst composition (Figures 2.8 and 2.9). At steady-state (1 hr, Figure 2.9), a volcano behavior is observed, similar to the behavior for methanol electrooxidation. However, at short reaction times (3 s, Figure 2.8), a linear correlation is found, where the instantaneous current density decreases as a function of increasing Ru content.

From the data in Table 2.1, there appears to be a trend in particle size. It is known that particle size has an effect on the reactivity of a catalyst, largely due to increasing surface area with decreasing size. Both the methanol and formic acid electrooxidation
currents were normalized to the surface area of the catalyst, so this effect of particle size should not influence the trends seen in the data. Particle size could still play a part, however, since lattice parameter changes, which are directly connected to binding energy shifts, go along with changes in particle size. As pointed out above, and shown in Table 2.1, as the particles get smaller, the lattice parameter gets smaller, and the Pt 4f binding energy increases. However, the three samples with the most Ru are all the same size, while the lattice parameters and binding energies continue with the same trends, not connected with particle size. So, while the particle size certainly plays a role in changing the electronic structure of the Pt/Ru catalyst, it doesn’t appear to be the reason for the trends that were observed.

In order to verify the correlation between the current density and the amount of Ru in the catalyst, the turnover frequency (TOF) of Pt active surface sites was calculated, where the TOF is the number of formic acid molecules decomposed to CO$_2$ per unit time per Pt active site. This calculated value provides a relative measure of the activity specific to Pt surface atoms by normalizing the current to the number of available active sites. Formic acid is known to decompose on Pt via a dehydration reaction that produces surface CO, which is oxidatively removed at potentials above ~0.4 V vs. RHE. Formic acid also decomposes on Ru surfaces. However, by comparing the current at 0% and 100% Ru in Figure 2.7, it is clear that the current on Pt is much greater than that on Ru, which is just above 0 mA cm$^{-2}$ at steady state. While there is some contribution from electrooxidation on Ru, it is very small and should not have a significant effect on the calculation of the TOF of Pt active sites. The surface concentration of Pt active sites for each catalyst, determined with SRPS, see above, is
listed in Table 2.1. In Figures 2.10 and 2.11, the TOF is plotted as a function of Ru content with the core-level binding energy plotted on the upper x-axis. In Figure 2.10, the TOF at short reaction times (3 s), where the amount of adsorbed species poisoning the surface is assumed to be negligible, is found to decrease linearly as a function of both increasing Ru content and increasing Pt 4f7/2 binding energy. As shown in Figure 2.11, the TOF at steady-state (1 hr) shows a volcano dependence on the Ru amount and Pt 4f7/2 binding energy.

For these results to be meaningful in terms of the electronic effect, any source of rate-control other than reaction kinetics, namely, mass transport, needs to be excluded as a possible cause of the observed behavior. The contribution of mass transport effects to the reaction rate has been explored previously. In a study of the oxidation of formic acid at platinum and palladized platinum electrodes, Lu et al.47 demonstrated, using a combination of chronoamperometry and fast cyclic voltammetry, that mass transport is not the rate-limiting step at potentials of interest to HCOOH reactivity. Therefore, we believe that kinetics, rather than mass transport, control the behavior of our catalysts under the conditions used in this work.

In order to be oxidized, formic acid molecules must first be activated at the surface by adsorption. Stronger adsorption of HCOOH results in easier activation, and thus higher reactivity, whereas the opposite is expected for weaker adsorption (of the HCOOH molecule). As already mentioned, Nørskov and coworkers13 have shown that adsorption energies and activation barriers are correlated to the position of the d-band center with respect to the Fermi level. For the catalysts examined here, the addition of Ru to the catalyst causes the Pt lattice to be compressed, leading to a downshift in the center of
gravity of the d-band of Pt with respect to the Fermi level. Since this downshift in the d-band center of Pt results in weaker bonds between the metal surface and the adsorbate, the activation barrier for reaction increases (surface activation of formic acid molecules becomes more difficult). This explains the linear decrease in TOF with increasing Pt 4f\textsubscript{7/2} binding energy, a relationship which confirms the role of the electronic structure in fuel cell electrocatalysis, as predicted by the d-band center theory.

The data for electrooxidation of formic acid at steady-state (after 1 hour of reaction) do not give conclusive evidence of the d-band center theory that was provided by the data at short reaction times. At steady-state, the indirect reaction pathways (through the CO intermediates in the studied potential range\textsuperscript{45,67}) are active, complicating the interpretation. The observed behavior, however, is likely due to a combination of the electronic effect and the bifunctional mechanism, as in the case of the methanol study (see above). In addition to the effect of electronic structure on the activation of formic acid molecules, which was demonstrated by the data at short reaction times, there should be an effect on the adsorption strength of CO. As the Ru content and Pt 4f\textsubscript{7/2} binding energy increase, the surface coverage by poisoning intermediates should be reduced, freeing up active surface sites for further electrooxidation of formic acid molecules. This effect would be expected to result in an increase in the TOF with increasing Ru content. Thus, the two effects induced by changes in electronic structure are cancelling, not additive. On top of these electronic effects, however, is the bifunctional mechanism. It is well-known that the bifunctional mechanism enhances the oxidative removal of adsorbed CO molecules, and that the enhancement is maximized at a certain composition of Ru due to the ensemble effect\textsuperscript{73} (as observed, Figure 7).
2.4 Conclusions

This work presents a new approach, involving the use of SRPS, to studying electrocatalysis at bimetallic surfaces that may lead to more detailed insights into the mechanisms of bimetallic systems in fuel cell applications. This study has explored the connection between surface electronic structure and reactivity of small organic molecules as it relates to the d-band center theory proposed by Nørskov and coworkers. As the Ru content in Pt/Ru nanoparticles was increased, the binding energy of Pt 4f\textsubscript{7/2} was found to increase linearly, as predicted from the theory. Previous theoretical calculations have indicated that the main reason for the shifts in binding energy in Pt/Ru alloy nanoparticles is lattice strain. Our XRD data give some support to this conclusion, as the Pt lattice was found to compress with the addition of Ru. According to the d-band center theory, compression of the Pt lattice broadens the d-band, and results in a subsequent downshift in energy of the center of the d-band with respect to the Fermi level. In the case of methanol electrooxidation, the production of the strongly-adsorbing CO intermediate means that the bifunctional mechanism plays a large role and it is difficult to determine any possible effects of electronic structure changes. Thus, for this system, no conclusive results were obtained regarding a connection between electronic structure and reactivity. On the other hand, this study has demonstrated that it is possible to separate the effects of the electronic structure and the bifunctional mechanism for the case of formic acid electrooxidation by examining the reactivity at different points in time. At steady-state, the turnover frequency of Pt active sites as a function of both the amount of Ru in the catalyst and the Pt 4f\textsubscript{7/2} binding energy was shown to have a volcano behavior, which is likely due to competition between formic acid activation, adsorption strength of reaction
intermediates, and the bifunctional mechanism. The data at short reaction times, however, clearly demonstrate the dependence of the reactivity on the electronic structure of the Pt active sites. The turnover frequency was found to decrease linearly with increasing Ru content and increasing Pt 4f/2 binding energy. As predicted by the d-band center theory, the downshift in the center of the d-band increases the activation energy of formic acid electrooxidation, and thereby reduces the reactivity.
### 2.5 Tables

Table 2.1: Physical Characterization of Pt/Ru Nanoparticles

<table>
<thead>
<tr>
<th>Nominal Ru Atomic%</th>
<th>Crystalline Size (nm)</th>
<th>Lattice Parameter (Å)</th>
<th>Surface Ru Atomic% from SRPS</th>
<th>Pt 4f&lt;sub&gt;7/2&lt;/sub&gt; BE (±0.03 eV) (hν=160 eV)</th>
<th>Catalyst Surface Area from CO Stripping (cm&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.0 ± 0.5</td>
<td>3.921</td>
<td>0</td>
<td>71.06</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>10</td>
<td>8.8 ± 1.0</td>
<td>3.917</td>
<td>12</td>
<td>71.08</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>20</td>
<td>5.5 ± 1.2</td>
<td>3.909</td>
<td>17</td>
<td>71.17</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>33</td>
<td>4.4 ± 1.0</td>
<td>3.904</td>
<td>18</td>
<td>71.27</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>50</td>
<td>3.1 ± 0.6</td>
<td>3.885</td>
<td>28</td>
<td>71.41</td>
<td>1.0 ± 0.2</td>
</tr>
<tr>
<td>60</td>
<td>3.0 ± 0.4</td>
<td>3.878</td>
<td>38</td>
<td>71.45</td>
<td>0.86 ± 0.07</td>
</tr>
<tr>
<td>66</td>
<td>3.0 ± 0.6</td>
<td>-</td>
<td>37</td>
<td>71.46</td>
<td>1.0 ± 0.2</td>
</tr>
</tbody>
</table>
2.6 Figures

Figure 2.1: A schematic representation of the pathways for electrochemical oxidation of methanol on platinum electrodes. The broken line 2 signifies the assumption that CO$_{ad}$ is not oxidized between 0.2-0.45 V vs. RHE. This figure is reproduced from Cao et al.$^{57}$
Figure 2.2: Schematic representation of the triple pathway mechanism of formic acid electrochemical oxidation. This figure is reproduced from Chen et al.\textsuperscript{46}
Figure 2.3: Typical wide-range survey spectra for three of the Pt/Ru nanoparticle samples recorded at Bessy-II (hν=370 eV). The inset shows the Pt 4f region of the spectra for all samples (increasing Ru from top to bottom). The vertical line marks the binding energy of pure Pt(111) as a reference.
Figure 2.4: Pt $4f_{7/2}$ binding energy determined from synchrotron radiation experiments at Bessy-II ($\nu=160, 370, \text{ and } 650 \text{ eV}$) as a function of Ru content in Pt/Ru nanoparticles. The linear fit is for the average binding energy for the three photon energies. The standard error was 0.03 eV for each measurement.
Figure 2.5: Current density for methanol electrooxidation on Pt/Ru alloy catalysts in 0.5 M methanol + 0.5 M H$_2$SO$_4$ at room temperature, up to 1 hr. The surface area was normalized from CO stripping experiments.
Figure 2.6: Volcano plot of methanol electrooxidation on Pt/Ru nanoparticles. Uncertainties were calculated from at least 3 independent measurements.
Figure 2.7: Current-time plots for oxidation of 0.2M HCOOH in 0.5M H$_2$SO$_4$ recorded at 500mV vs. RHE. The inset shows the current-time data at short reaction time.
Figure 2.8: Current density for formic acid electrooxidation at 3 s as a function of the Ru amount for Pt/Ru alloy in 0.2 M HCOOH + 0.5 M H₂SO₄ recorded at 450 and 500mV vs. RHE.
Figure 2.9: Current density for formic acid electrooxidation at 1 hr as a function of the Ru amount for Pt/Ru alloy in 0.2 M HCOOH + 0.5 M H₂SO₄ recorded at 450 and 500mV vs. RHE.
Figure 2.10: The calculated turnover frequency of Pt active sites as a function of the Ru amount and the Pt 4\textit{f}_{7/2} binding energy at 3 s. Measurements were done in 0.2 M HCOOH + 0.5 M H_2SO_4 and recorded at 450 and 500mV vs. RHE.
Figure 2.11: The calculated turnover frequency of Pt active sites as a function of the Ru amount and the Pt $4f_{7/2}$ binding energy at 1 hr. Measurements were done in 0.2 M HCOOH + 0.5 M H$_2$SO$_4$ and recorded at 450 and 500mV vs. RHE.
2.7 References

(3) Song, S. Q.; Tsiakaras, P. Applied Catalysis B-Environmental 2006, 63, 187.
(9) Gasteiger, H. A.; Markovic, N.; Ross, P. N.; Cairns, E. J. Journal of Physical Chemistry 1993, 97, 12020.


(38) Markovic, N. M.; Ross, P. N. *Surface Science Reports* 2002, 45, 121.


(52) Seah, M. P. *Surface and Interface Analysis* 1980, 2, 222.


(56) Han, B. C.; Van der Ven, A.; Ceder, G.; Hwang, B. J. *Physical Review B* 2005, 72.


(58) Balandin, A. A. *Advances in Catalysis* 1958, 10, 96.

(59) Ichikawa, S. *Chemical Engineering Science* 1990, 45, 529.


CHAPTER 3

ELECTROCHEMICAL AND X-RAY PHOTOELECTRON SPECTROSCOPIC
STUDY OF THE Pt₃Co ALLOY TOWARD OXYGEN REDUCTION IN ACIDIC
AND ALKALINE MEDIA*

3.1 Introduction

Just as for the anode, much work has been done, and continues to be done, to move away from platinum cathodes for fuel cells. The two routes of cathode development are the design of non-platinum materials¹⁻⁸ and reducing the amount of platinum through alloying with a transition metal⁹⁻²¹ or through formation of a monolayer of platinum on another metal²²⁻²⁷. Focusing on the alloys, it has been found that the addition of a transition metal to platinum sometimes results in higher oxygen reduction activity than pure platinum in acidic media, either through modification of the platinum electronic structure¹⁹,²⁰, changes in the surface morphology⁹,¹¹, or decreased coverage by surface oxides¹⁷,²⁸. In alkaline media, there are conflicting results, where the alloys sometimes show higher activity and other times show lower activity than pure platinum.¹²⁻¹⁶,²¹ The higher activity has been attributed to electronic structure modifications¹³, while the lower activity has been attributed to the blocking of platinum active sites by OH adsorbed on cobalt sites¹⁶.

* This chapter is a summary of the work presented in:
Duong, H. T. Enhancement of platinum cathode catalysis by addition of transition metals, University of Illinois at Urbana-Champaign, 2009.
The goal of this work, carried out jointly with Hung Tuan Duong, was to investigate the electrocatalytic activity and stability of a Pt/Co alloy with respect to the oxygen reduction reaction (ORR) in both acidic and alkaline media. Commercial Pt$_3$Co alloy nanoparticles (E-TEK) and commercial Pt black (Johnson Matthey) were compared through electrochemical methods and X-ray photoelectron spectroscopy (XPS). The activity of the alloy was found to be better than that of Pt black in acidic media, and worse in alkaline media, while the alloy was stable only in alkaline media. A summary of the results is presented here. For complete details of the experiments and results, including figures and tables, the reader is referred to Duong et al.$^{29}$ and Duong$^{30}$.

### 3.2 Summary of Results

XP spectra of the Pt$_3$Co revealed that the cobalt is present in both metallic and oxide form. Upon electrochemical treatment of the catalyst, either by cycling or holding the potential, in acidic media, the cobalt oxides were found to dissolve from the catalyst. No such dissolution was observed when the catalyst was electrochemically treated in alkaline media. It was concluded that the dissolution of cobalt oxides resulted in the removal of cobalt species from the surface of the nanoparticles and in the formation of a so-called platinum skin structure, where the platinum atoms in the skin are electronically modified by the underlying layer.$^{18\text{-}20,31,32}$ From the XPS results, for both the as-received catalyst and the electrochemically treated catalyst, the Pt 4f$_{7/2}$ binding energy was found to be shifted positively by 0.2 eV, confirming that alloying with cobalt alters the electronic structure of platinum. The positive shift in core-level binding energy corresponds to a downshift in the d band center with respect to the Fermi level.
Electrochemical measurements support the conclusion from XPS, that is, that cobalt oxides dissolve from the catalyst during electrochemical treatments in acidic media. Cyclic voltammograms recorded before and after ORR activity measurements show no change when the measurements are done in alkaline media, but the voltammogram shows more platinum character after the measurements done in acidic media. After 25 potential cycles in acid, the Pt$_3$Co catalyst showed the characteristics of pure platinum, again suggesting the formation of a platinum skin.

ORR activity measurements were performed in O$_2$-saturated solutions using a rotating-disk electrode. Differing results were obtained depending on the solution pH. In alkaline media, the half-wave potential for oxygen reduction was shifted negatively by 30±4 mV with respect to the Pt black sample, while in acidic media, the half-wave potential was shifted positively by 10±2 mV. A negative shift with respect to pure platinum indicates reduced activity toward the ORR, and a positive shift indicates enhanced activity. The difference in activity in the two media can be explained in terms of OH adsorption. In alkaline media, OH adsorbed to cobalt sites blocks the platinum active sites, reducing the overall activity.$^{16}$ Supporting this conclusion is the fact that, after electrochemical treatment in acid, the alloy catalyst, with a platinum skin, showed the same activity as pure platinum in alkaline media. In acidic media, the downshift in the d band center of platinum in the skin configuration, as demonstrated by the positive core-level binding energy shift, leads to a positive shift in the potential for formation of OH$_{ads}$, resulting in an increase in the number of active platinum sites available for O$_2$ adsorption and reduction.$^{9,11,17,20,28,32}$
3.3 Conclusions

In this study, a commercial Pt₃Co alloy nanoparticle catalyst was compared to a commercial Pt black catalyst in terms of ORR activity and stability as a function of solution pH. XPS results indicated that the as-received alloy catalyst consisted of both metallic cobalt and cobalt oxide. Cyclic voltammetry and XPS both confirm the dissolution of cobalt oxides during electrochemical treatment in acid. It was concluded that this dissolution produces a platinum skin structure. The core-level binding energy of platinum in the alloy was found to be shifted to larger values as compared to that of the platinum black catalyst, demonstrating an electronic effect due to alloying of the platinum with cobalt. ORR measurements showed different results depending on the solution pH. The reduced activity of the alloy with respect to the pure platinum in alkaline media was attributed to a blocking of platinum active sites by OH adsorbed on cobalt surface species. The enhanced activity in acidic media was attributed to a positive shift in the potential for formation of OH_ads, freeing up platinum surface sites for adsorption and reduction of O₂. These results demonstrate the role of electronic effects, as well as surface structure, for the ORR.
3.4 References


(30) Duong, H. T. Enhancement of platinum cathode catalysis by addition of transition metals, University of Illinois at Urbana-Champaign, 2009.


CHAPTER 4

BINDING ENERGY STUDIES OF Pt/Rh(111) SURFACES

4.1 Introduction

In order to study the fundamental principles behind catalysis, it is often beneficial to look at model catalysts, rather than experimenting with the types of materials that would be used in a commercial application.\textsuperscript{1-5} Model catalysts provide a simpler alternative, where individual effects can be more easily analyzed and understood. Once the fundamentals are understood, the knowledge can be put to use in the design and development of catalyst materials for commercial application. In fuel cell catalysis, the anode and cathode materials are typically some type of nanomaterials. The enhanced mass transport and large surface area of nanomaterials gives them a superior ability to catalyze reactions at a high rate.\textsuperscript{6,7} However, these types of materials have characteristics that make any fundamental studies more difficult. For example, it is impossible to synthesize nanoparticles in such a way as to obtain a completely uniform collection of particles in terms of size, structure, and composition. A nanoparticle will have many crystalline facets, which is an important feature because different facets have different electrochemical properties.\textsuperscript{4,8} Any analysis merely gives an average of the sizes, structures, and compositions that are present. Therefore, using single crystal surfaces as model catalysts, which have a known geometry and composition, is of interest to the fuel cell catalysis community. The single crystal surfaces can be modified by the addition of either noble or non-noble metal adsorbates to generate bimetallic single crystal surfaces.\textsuperscript{9,10} Another type of model catalyst that is sometimes used is the intermetallic
crystal, where two or more metals are mixed in proper proportion to create an ordered chemical compound. Since the chemical bonding of these compounds can be known, intermetallics avoid some of the problems of bimetallic single crystal model catalysts, as well as nanoparticle electrocatalysts, and may provide further insight into the processes involved in electrocatalysis. Model catalysts simplify the electrocatalytic system, providing several potential benefits in the study of the fundamentals of electrocatalysis.

Decoration of single crystal surfaces to create bimetallic noble metal electrodes can be accomplished by several methods, which can be divided into wet and vacuum techniques. The wet techniques include electrodeposition, spontaneous deposition, underpotential deposition, and forced deposition. Vacuum techniques include evaporation, sputtering, and chemical vapor deposition. Of interest to this study are electrodeposition, spontaneous deposition, and evaporation.

Electrodeposition usually uses an applied potential to thermodynamically deposit a noble metal from an ionic solution onto the surface of a noble metal electrode. While it is difficult to deposit the adsorbate metal in small amounts using bulk electrodeposition techniques, the application of a pulsed potential or current can afford much improved control over the characteristics of the deposit. This technique is called pulsed electrodeposition. The pulses initiate grain nucleation with a much higher grain density (grains per unit surface area) than conventional electrodeposition techniques, giving a more uniform deposit. The composition, morphology, and thickness of the films can be controlled by adjusting the pulsing parameters, but this technique requires careful calibration of these parameters. The other wet chemistry option is spontaneous deposition. With this technique, the electrode is immersed at open circuit potential in a
solution containing ions of the metal to be deposited. The deposition mechanism has been attributed either to cementation, where reductive adsorption of the metal ion results in oxidative dissolution of the substrate, to chemical reaction with adsorbed hydrogen, to interaction of the metal ions with oxides on the substrate surface, or to the formation of platinum oxides. Spontaneous deposition typically results in a low coverage by noble-metal adsorbates, making it a useful technique to generate bimetallic, decorated surfaces. Physical vapor deposition is the most common vacuum technique, and is useful when UHV analysis is desired. Due to the condensation process, the deposits are typically not permanent unless there is some sort of interaction between the deposit and the substrate or the deposit is highly clustered.

As discussed in Chapter 2, besides platinum, the Pt/Ru alloy is the most widely studied catalyst for fuel cells. This makes it an attractive candidate for model catalyst studies, as well. Several groups have recently done work with Pt-decorated Ru single crystals or nanoparticles in order to get a better understanding of the fundamental aspects of this electrocatalyst. Spontaneous deposition of platinum on ruthenium nanoparticles was found to produce a catalyst with very low platinum loading and improved catalytic activity toward carbon monoxide and methanol oxidation. In a study of Pt-decorated Ru(0001), electrodeposition of platinum was found to proceed via the Volmer-Weber growth mode. As a motivating factor, theoretical calculations predicted that the bond strength between platinum and CO would be weakened on a platinum monolayer on a ruthenium substrate. Experimental results confirm this, as CO oxidation was found to occur at potentials more negative than on pure Pt surfaces. As a further investigation of this effect, Zhou et al. examined shifts in the core-level
binding energy of platinum deposits on a Ru(0001) surface as a function of coverage. A clear positive shift in the core-level binding energy with decreasing platinum coverage was demonstrated. Through theoretical modeling, it was concluded that the shifts were due to both lattice strain and charge transfer, but that the lattice strain had a larger contribution.\textsuperscript{28}

Based on the results from the studies of ruthenium single crystals decorated with platinum, it would be of interest to compare experimental and theoretical results from other Pt/M(hkl) or Pt/M(ijkl) systems, in order to build a more complete picture of the electronic effects that are of importance in electrocatalysis. Along this line, several groups have experimented with rhodium deposits on platinum single crystal surfaces.\textsuperscript{29-34} Platinum—rhodium binary alloy catalysts have also received attention.\textsuperscript{35-39} Platinum-decorated rhodium surfaces, on the other hand, have been the subject of few studies.\textsuperscript{34,40,41} Tanaka \textit{et al.}\textsuperscript{34} investigated the structure and catalysis (toward NO + H\textsubscript{2}) of platinum and rhodium single crystal electrodes electrochemically decorated by rhodium and platinum, respectively. In another study, Oliver \textit{et al.}\textsuperscript{40} used low energy Li-ion scattering to determine the structure and thermal stability of thin platinum films on a Rh(100) surface. Finally, Housmans \textit{et al.}\textsuperscript{41} electrochemically deposited platinum on a Rh(111) electrode surface and studied both the electrochemistry and the CO adlayer oxidation activity. It was shown by STM that, due to the relative free surface energies, it was difficult to obtain monolayer-height islands of platinum by electrodeposition, but that it could be achieved by depositing very small amounts of platinum. The CO adlayer oxidation was found to be enhanced with respect to the pure metals, confirming the presence of electronic effects that had been predicted by density functional theory.\textsuperscript{25,42}
To the author’s knowledge, there have been, to date, no investigations of the core-level shifts associated with deposition of platinum submonolayers on a rhodium surface. This poses an interesting possibility for a model electrocatalyst, as it would provide an opportunity to study the electronic effects that arise as a result of the metal-metal interaction. The results could be combined with the previous work on Pt/Ru(0001) in order to develop better theoretical models. For this work, a decorated, bimetallic noble metal electrode was generated by depositing platinum on a Rh(111) surface and the resulting electrode was characterized by cyclic voltammetry and photoelectron spectroscopy. Spontaneous deposition and electrodeposition from a Pt(II)-containing solution were used to obtain a range of coverage extending to less than 0.1 ML. In order to obtain high precision binding energy data, particularly at the low coverage end, experiments were also done, using physical vapor deposition, at the Synchrotron Radiation Center at the University of Wisconsin-Madison. The high intensity beam and high-resolution analyzer available at the synchrotron helped to reduce the experimental scatter. In keeping with the main goal of the dissertation, gaining understanding of the electronic effects involved in metal-metal interactions and electrocatalysis, the aims of this study were to collect high-quality binding energy data for a wide range of platinum coverage on the rhodium substrate and to evaluate the binding energy shifts of the platinum deposits in terms of a fundamental study of electronic effects in electrocatalysis. The binding energy data can later be used in the development of improved theoretical calculations.
4.2 Experimental Methods

4.2.1 Methods Used at UIUC

The Rh(111) crystal (6 mm diameter x 2 mm thick, polished to <0.1°) that was used in this study was purchased from MaTeck GMbH. For mounting to the sample holder, a platinum wire was spot welded to the back side of the crystal. Prior to performing any electrochemical measurements, the crystal was prepared in ultrahigh vacuum (UHV) first by sputtering with argon ions to clean the surface and then by a series of resistive heating (Sorensen DLM 8-75 current source) and hot sputtering steps. Following the final hot sputtering, the crystal was annealed by cycles of heating without and with oxygen at a pressure of approximately 7.5 x 10^{-9} torr of O_2. Ultrahigh purity (UHP) argon and oxygen cylinders were obtained from S. J. Smith Welding Supply. The cleanliness of the crystal surface was checked by X-ray photoelectron spectroscopy (XPS).

The design of the XPS instrumentation was described in Chapter 1.3 (Figure 1.2), and consisted of an ESCA M-Probe high resolution, multi-channel hemispherical electron analyzer (Surface Science Instruments) and a monochromatic Al Kα source (hν = 1486.6 eV) operated at 110 W with a constant pass energy of 25 eV. The XPS spectral peaks were fitted according to mixed Gaussian-Lorentzian line shapes and Shirley baselines using the ESCA 2005 software (Service Physics, Inc.). Following major maintenance on the XPS system, the binding energy scale was calibrated using the gold and copper standards: Au 4f_{7/2} (at 84.00 eV) and Cu 2p_{3/2} (at 932.75 eV). The standard error in binding energy was then determined by repeatedly measuring the Rh 3d_{5/2} binding energy on a clean Rh(111) surface. The standard deviation obtained from this method was ±0.05
eV. Based on this standard error, binding energies are reported to the nearest 0.1 eV. The errors in the binding energies, listed in Table 4.1, are estimated based on the equation given by Vasil’ev:  

\[ \sigma_1^2 = \sigma_e^2 + \frac{w^2}{1 - \omega_{21}(t)} \left\{ \frac{1 + \omega_{21}(t)\xi_{21}(t)}{n_1 - n_f} + \frac{(\omega_{21}(t) + \xi_{21}(t))(n_2 - n_f)}{(n_1 - n_f)^2} \right. \]

\[ + \frac{8(1 + \omega_{21}(t))n_f}{3(n_1 - n_f)^2} + \frac{4\gamma_f^2(1 + \omega_{21}(t))n_f^2}{3(n_1 - n_f)^2} \]

\[ + \frac{8\gamma_d^2(n_1^2 + \omega_{21}(t)n_f^2)}{3(n_1 - n_f)^2} + \frac{4\gamma_n^2}{3} \left( 1 + \omega_{21}(t) \frac{(n_2 - n_f)^2}{(n_1 - n_f)^2} \right) \]  

\[ \text{Eq. 4.1} \]

Equation 4.1 takes into account the instrument standard deviation (\(\sigma_e\)), the full width at half-maximum (\(w\)), the spacing between spectral lines (\(R\)) (\(R = 2R/w\)), a spectral line overlap function (\(\omega_{21}(t)\)), the relative errors for the spectrometer, fitting error, and background calculation (\(\gamma_d\), \(\gamma_n\), and \(\gamma_f\), respectively), and the number of counts for spectral lines 1 and 2 (\(n_f\) and \(n_2\)) and the background noise (\(n_f\)). This equation was then simplified by assuming that \(\gamma_d\), \(\gamma_n\), and \(\gamma_f\) were zero. In addition, because of the Pt 4f\(_{7/2}\) and 4f\(_{5/2}\) peaks separation, the overlap function could be taken as zero. The simplified form (Eq. 4.2) was used for error analysis.

\[ \sigma_1^2 = \sigma_e^2 + w^2 \left( \frac{1}{n_1 - n_f} + \frac{8n_f}{3(n_1 - n_f)^2} \right) \]  

\[ \text{Eq. 4.2} \]
Electrochemical measurements were done in a conventional three-electrode cell with a platinum gauze counter electrode, Ag/AgCl (3 M NaCl, Bioanalytical Systems) reference electrode, and either 0.5 M H$_2$SO$_4$ (GFS, doubly-distilled from Vycor, 95-98.0% purity) or 0.1 M HClO$_4$ (GFS, 69-72% purity) electrolyte solution using a PAR 263A potentiostat at room temperature. Solutions were prepared using Milli-Q water (18.2 MΩ). All potentials are reported vs. the reversible hydrogen electrode (RHE). The cell is designed in such a way that it fits into a Teflon tube which is then inserted into the chamber from the bottom. Following the UHV crystal preparation, the ordering of the electrode surface was checked by cyclic voltammetry. Platinum was spontaneously deposited onto the electrode surface from 0.01, 0.05, 0.5, or 5 mM K$_2$PtCl$_4$ (Sigma Aldrich, 99.99% metals basis) in either 0.5 M H$_2$SO$_4$ or 0.1 M HClO$_4$ by holding at open circuit potential for times ranging from 5 seconds to 16 minutes. To get higher coverage, platinum was deposited from the same solutions by cycling between 0 and 0.8 V. After spontaneous deposition, the cell was rinsed multiple times with acid and water. The electrode was then cycled again in the clean electrolyte solution in order to reduce/stabilize the platinum deposits. Upon completion of the electrochemistry, the chamber was pumped down to high vacuum by using, in series, liquid nitrogen sorption pumps, a turbomolecular pump (Varian Task V301), and a cryopump (Marathon 8LP), and then the electrode was transferred to the UHV chamber for XPS analysis. The glassware was cleaned by soaking in a concentrated sulfuric acid bath containing Nochromix, followed by several rinses with hot Milli-Q water.
4.2.2 Methods Used at the University of Wisconsin’s Synchrotron Radiation Center

Experiments at the Synchrotron Radiation Center (SRC) at the University of Wisconsin were done at the 071 PGM Undulator Branch B beamline, which has a photon energy range of 8-180 eV. A Scienta SES 2002 analyzer was used with a resolution of 80 meV. The Rh(111) crystal and a Pt(111) crystal (used as a reference), were mounted in the cold finger sample holder, consisting of tantalum sandwich plates screwed to a copper block, diagrams for which are located on the SRC website. Each crystal was cleaned by sputtering and annealed by an e-beam that was directed to the back surface. Platinum was deposited by vapor deposition from a wire that was wound around a tungsten filament. The evaporator was constructed in-house, and was operated by an external current source. After depositing for a certain amount of time, the spectroscopic data was collected, and the process was repeated without cleaning the surface in between depositions. Since the available photon energy range for the beamline that was used was too low to access the Rh 3d peaks, Rh 4p was used as a reference instead. The error in the binding energy was determined in the same manner as for the data collected at UIUC. The standard error for measurements at the synchrotron was 0.03 eV.

4.3 Results and Discussion

4.3.1 Results from UIUC

4.3.1.1 Electrochemical characterization and deposition of Pt

Following the UHV crystal preparation procedure that was outlined above, the order of the crystal surface was checked by cyclic voltammetry in either 0.5 M H₂SO₄ or 0.1 M HClO₄. The Rh(111) surface displays characteristic voltammetric features in each
The peaks on the negative end of the voltammogram are due to the adsorption and desorption of hydrogen and anions from the electrolyte. The Rh(111) surface oxidizes above ~0.8 V vs. RHE. Oxidation of the surface results in disordering, so it is necessary to choose an appropriate potential bias so as to preserve the electrode surface. For a well-ordered surface in sulfuric acid, the hydrogen adsorption/desorption peaks will be sharp and have a current ratio of approximately 2:1 (adsorption:desorption) and a peak separation of approximately 60 mV. In addition, the double-layer region should be narrow (on the current axis). A thick double-layer region could indicate a contaminated or disordered surface or contaminated solution, where insufficient purging of the electrolyte solution by bubbling of argon is often the cause. In perchloric acid, the hydrogen adsorption/desorption peaks should have a peak height ratio of at least 3:1 (adsorption:desorption). The peaks near 0.2 V are due to the reduction of perchlorate from the electrolyte. There is also a reversible redox process near 0.6 V, which appears as a sharp peak in both the anodic and cathodic directions. The appearance of these so-called butterfly peaks is a characteristic feature of cyclic voltammograms recorded in perchloric acid. During potential cycling in the perchloric acid at 50 mV/s, the voltammetric peaks gradually changed over time, shifting along the potential axis and becoming less sharp. When the scan rate was changed to 100 mV/s, the peaks became sharper again and shifted back toward the original positions, indicating an electrode process with slow kinetics, likely involving adsorption and reduction of anions. For this work, a clean, well-ordered surface was all that was required, so this process was not investigated further, and the electrode was scanned.
primarily at a scan rate of 100 mV/s. Some difficulty was encountered in obtaining consistent results from the UHV crystal preparation, and deposition was only done on electrodes that showed the characteristics of a well-ordered surface.

For the purposes of fundamental study, it was important to look at a wide range of coverage for the platinum deposits on Rh(111). In the analogous study of Pt-decorated Ru(0001), it was concluded that spontaneous deposition resulted in monolayer height deposits at low coverage. Based on the assumption that platinum will deposit on Rh(111) in a similar fashion, the low coverage end is particularly important because the reduced interaction between platinum atoms on the surface means that the interaction between platinum and rhodium, which is the interaction of interest in this study, will be stronger. To accomplish the low coverage, spontaneous deposition was utilized. As described in the previous section, the deposition was done by immersing the electrode in a solution of K$_2$PtCl$_4$ in electrolyte at open circuit potential (~0.8 V). Different concentrations were used in order to optimize the deposition conditions. At 5 mM K$_2$PtCl$_4$, it was difficult to get less than ~0.1-0.2 monolayer (ML) of Pt (calculated from XPS data; refer to next section). Decreasing the concentration to 0.05 mM or 0.01 mM consistently gave less than 0.1 ML of Pt, but it was difficult to deposit larger amounts. In addition, the spontaneous deposition seemed to be very inconsistent with respect to the amount of platinum deposited. Data was collected during two periods of time separated by a few months. During the first set of experiments, the amount of Pt deposited was found to linearly correlate with the amount of time that the electrode was immersed in the Pt solution. However, when the experiments were done again some time later, the amount of Pt deposited had no correlation with the deposition time, where repeating a
certain deposition time gave very different coverage. The reason for the inconsistency in the coverage as a function of deposition time is unknown, but could be related to one or more of the following factors: a change in the electrode surface over time due to repeated experiments, a slight difference in the deposition/cycling/cleaning procedure that could have gone unnoticed, or a change in the platinum salt as it sat in the glass bottle for several months. While the inconsistency in the coverage results made it impossible to repeat experiments at a specified coverage, a significant range of coverage was nonetheless obtained.

After spontaneous deposition, the cell was thoroughly rinsed with acid and water. It was determined from the XP spectrum of the Pt 4f region of the Pt/Rh(111) electrode that Pt spontaneously deposited in an oxidized state, as the observed binding energy of Pt$^{4f\gamma/2}$ was found to be within the typical range for Pt(II). For this reason, the electrode was cycled between $\sim$0-0.8 V vs. RHE in pure electrolyte after deposition in order to reduce the deposit. Figure 4.3 shows the stabilized cyclic voltammogram of Pt/Rh(111) in comparison to that of the clean surface, while Figure 4.4 illustrates the change in the voltammetric features in sulfuric acid as the platinum coverage is increased. With just a small amount of Pt added, the hydrogen adsorption/desorption peaks become very sharp and the peak current ratio changes to approximately 1:1. As the amount of Pt is increased, the two peaks become smaller, while another set of broad peaks begins to show up to the positive side of the sharp peaks. At high coverage, the cyclic voltammogram resembles that of polycrystalline platinum. Even at high coverage, the sharp peaks are still present, though with a much reduced charge. The observed voltammetric behavior is consistent with that seen by Housmans et al.$^{41}$ These sharp
peaks have been attributed to hydrogen adsorption/desorption at rhodium sites, where platinum atoms are in the vicinity. As the platinum coverage increases, the active surface area of rhodium decreases, so the peaks become smaller, while the broad peaks for adsorption/desorption on platinum sites become larger as the platinum surface area increases. In perchloric acid, the addition of a very small amount of platinum causes a significant change (Figure 4.5). The redox couple centered at 0.35 V for the clean surface disappears, while a shoulder peak appears on the positive side of both the hydrogen adsorption and desorption peaks. There is no noticeable change in the cyclic voltammogram up to a coverage near one monolayer, where the shoulders disappear, the hydrogen adsorption/desorption peaks shorten and broaden somewhat, and the butterfly peak is greatly suppressed.

The cyclic voltammograms of clean and platinum-decorated rhodium were used to estimate the coverage of platinum based on the cathodic hydrogen charge. Under the assumption that platinum is site-blocking for hydrogen adsorption/desorption on the rhodium surface, the coverage can be calculated by subtracting the hydrogen charge for the platinum-decorated surface \((Q_{\text{final}})\) from the hydrogen charge for the clean surface \((Q_{\text{initial}})\) according to Equation 4.3, according to the method used by Zhou et al.2

\[
\theta_{\text{Pt,charge}} = \frac{Q_{\text{initial}} - Q_{\text{final}}}{Q_{\text{initial}}} \tag{Eq. 4.3}
\]

The coverage calculated using this equation is listed in Table 4.1 for each experiment. Since the CVs in perchloric acid do not show a similar behavior, the coverage could not be calculated from the charge in the same manner for these data.
4.3.1.2 X-ray photoelectron spectroscopy of Pt/Rh(111)

Figure 4.6 shows the survey spectrum of the clean Rh(111) surface. The survey spectrum has characteristic peaks for rhodium and served as a diagnostic for the cleanliness of the surface. The lack of peaks for oxygen, carbon, sulfur, and other possible contaminants confirms that the surface is clean. The clean electrode could then be transferred to the EC chamber for the electrochemical measurements. Following a cyclic voltammogram to check that the surface was properly ordered, platinum was spontaneously deposited according to the procedure described above and reduced by cyclic voltammetry. The Pt/Rh(111) electrode was then transferred back to the UHV chamber for analysis by XPS. A survey spectrum was first recorded to do a quick evaluation of the electrode. Even at very low coverage, the Pt 4f peaks are visible (Figure 4.7). There is also evidence, in some cases, of oxygen, carbon, sulfur, and chlorine species from the electrolyte solution.

The Pt 4f, Rh 3d, O 1s, C 1s, and S 2p or Cl 2p peaks, depending on the electrolyte used, were recorded for each sample. Pt 4f and Rh 3d were chosen as the peaks for analysis because they are the most intense peaks in the spectrum for the respective metals. The peaks were fit using an asymmetric mixed Gaussian-Lorentzian lineshape and a Shirley baseline with the ESCA 2005 software (Service Physics, Inc.). For the fitting of the Rh 3d peaks, the peak separation was held near 4.74 eV and the peak ratio for 5/2:3/2 was about 3:2, while for the Pt 4f peaks, the peak separation was held close to 3.33 eV and the 7/2 to 5/2 ratio was about 4:3. Figure 4.8 shows the Rh 3d region for a Pt/Rh(111) sample. The binding energy for the Rh 3d$_{5/2}$ was found to remain nearly constant over the set of experiments (307.4 ± 0.05 eV). This is not surprising,
since such a small amount of platinum would not be expected to affect the long-range electronic structure of the rhodium substrate. At low coverage, the platinum deposits, on the other hand, would be expected to exhibit significant changes in electronic structure due to the interaction with the rhodium substrate. Figure 4.9 displays the Pt 4f region for three separate samples after (a) 15 seconds, (b) 106 seconds, and (c) 15 minutes of spontaneous deposition. The platinum coverage was calculated according to Eq. 4.4:

\[
\Theta = \frac{A_{Rh(111)}}{\left(\frac{I_{Rh}S_{Pt}}{I_{Pt}S_{Rh}} + 1\right)\left(1 - \exp\left(-\frac{\alpha_{Pt}}{\lambda_{Pt}(E_{Pt})\cos\beta}\right)\right)\alpha_{Pt}^2}
\]

Eq. 4.4

where \(A_{Rh(111)}\) is the surface unit cell area for the Rh(111) substrate (0.0564 \(\text{nm}^2\)), \(I_{Rh}\) and \(I_{Pt}\) are the relative intensities (peak area divided by number of scans) of the rhodium and platinum, respectively, \(S_{Rh}\) and \(S_{Pt}\) are the atomic sensitivity factors for the two elements (4.179 for Rh 3d and 4.674 for Pt 4f), \(\alpha_{Pt}\) is the atom size for the Pt adsorbate (0.249 \(\text{nm}\)), \(\lambda_{Pt}(E_{Pt})\) is the inelastic mean free path of photoelectrons of kinetic energy \(E_{Pt}\) (\(\lambda_{Pt} = 1.72\) nm at \(E_{Pt} = 1415\) eV), and \(\beta\) is the escape angle of the photoelectrons (45°). Using this equation, the samples in Figure 4.9 were found to have an estimated platinum coverage of (a) 0.03 ML, (b) 0.2 ML, and (c) 2.2 ML.

Figure 4.10 plots the coverage calculated from the electrochemical charge versus the coverage calculated from XPS. This technique was used to analyze the platinum island growth. The straight line indicates \(\theta_{Pt,\text{charge}} = \theta_{Pt,\text{XPS}}\). Points that represent Pt monolayer islands will fall on the line, while points that represent Pt multilayer islands will fall below the line. This follows from the assumption that platinum is site-blocking.
for hydrogen adsorption sites on rhodium. If a platinum atom stacks on top of another platinum atom rather than a rhodium atom, the charge from the cyclic voltammetry will not account for it. So, a difference between the two coverage calculations indicates columnar (Volmer-Weber), rather than layer-by-layer (Frank-van der Merwe) growth.\textsuperscript{24}

As can be seen in the figure, the data at low coverage is very near the line, while, at coverage above about 0.3 ML, the points lie well below the line. While the XPS measurements indicated the deposition of multiple layers of platinum, the CVs continued to show evidence of bare rhodium surface atoms up until the highest coverage point. It was concluded that spontaneous deposition of platinum on rhodium is very similar to that on ruthenium, in that it occurs through the Volmer-Weber growth mechanism.\textsuperscript{2,24}

The binding energy of the 4f\textsubscript{7/2} peak (Figure 4.9) was found to be 71.4 eV for the electrode with 0.03 ML of platinum, while the binding energy was 71.6 eV for the electrode with 0.2 ML and 71.5 eV for 2.2 ML of Pt. Comparing to a pure Pt(111) substrate, for which a binding energy of 71.1 eV was found\textsuperscript{57}, the Pt 4f of the Pt/Rh(111) is shifted toward higher binding energy. Table 4.1 lists the binding energy and coverage results for all of the XPS measurements in both sulfuric and perchloric electrolytes. The binding energy data have also been plotted as a function of the coverage in order to get a better visualization of the relationship (Figures 4.11 and 4.12). The lowest coverage data points have been omitted from Figure 4.11 because the large error bars for these data made the plot much more difficult to read. Because of the magnitude of the error, it is impossible to define a trend in the binding energy as a function of coverage, especially for the data obtained from perchloric acid.
As a result of the inconsistency in the spontaneous deposition process, it was impossible to repeat experiments with a desired coverage. Because of this, many depositions were done in an effort to provide as many data points as possible for the purpose of looking for a trend. However, the large error associated with these measurements, as well as the lack of repeatability, makes any attempt to accurately interpret these data futile. In order to sufficiently improve the precision of the binding energy measurements, one would need to use high-intensity synchrotron radiation, where the large photon flux and high resolution would greatly decrease the error in the binding energies. This was the goal of the experiments described below.

4.3.2 Results from SRC

As demonstrated in the previous section, the data that was collected by the conventional XPS instrument does not provide conclusive results because of the magnitude of the error associated with the binding energies. For this reason, additional experiments were done at the Synchrotron Radiation Center at the University of Wisconsin-Madison with the aim of reducing the standard error in measuring the core-level binding energies, particularly at the low coverage end. Another benefit of the synchrotron radiation is that it greatly reduces the amount of time required to collect a spectrum. All binding energies from the synchrotron data are reported with respect to the measured Fermi level.
4.3.2.1 Surface core-level shifts on Pt(111)

The first set of experiments that were carried out at the synchrotron were for Pt(111). The Pt(111) provided a reference for the Pt 4f binding energy, and also served as a means of training on the use of the synchrotron and the equipment. Following a heat-treatment cleaning cycle of the crystal inside the UHV chamber, the region of the spectrum containing Pt 4f was recorded. Figure 4.13 illustrates the spectrum of Pt 4f recorded at a photon energy of 160 eV. The electron internal mean free path is near the minimum at this energy, so it should provide maximum surface sensitivity. In the spectrum, there is clearly a shoulder on the high binding energy side of each peak, indicating a contribution from at least two different types of atoms. In Figure 4.14, the 4f$_{7/2}$ region is shown more clearly. Here, there is a main peak at 70.95 eV and a smaller peak at 71.42 eV. Platinum oxides typically have a 4f$_{7/2}$ binding energy near 74 eV, suggesting that oxides are not the source of the extra peak. The difference between the two peaks of 0.47 eV is very similar to previous data for surface-bulk shifts on platinum, although the absolute binding energies are a little higher, likely due to a slight difference in the binding energy scale.$^{58,59}$ For these two reasons, the conclusion is drawn that the two peaks are attributable to bulk and surface atoms of the Pt(111) crystal. Surface core-level shifts are a direct result of reduced coordination of atoms at the surface compared with those in the bulk.$^{60}$ The result is a decrease in the atomic orbital overlap, which has two effects. First, the reduced overlap causes a narrowing of the d band. For elements, such as platinum, that have a d band that is more than half-filled, the narrowed band will shift toward the Fermi level. Second, the reduced overlap will weaken the hybridization between the d band and the conducting s-p band, increasing the density of d electrons,
and, therefore, lowering the effective nuclear charge, in the surface atoms. Both of these mechanisms lead to a lower core-level binding energy for surface atoms than for atoms in the bulk.\textsuperscript{59} This successful observation of a surface-bulk shift on the Pt(111) surface demonstrates the power of synchrotron radiation in the collection of data that is not accessible by conventional XPS.

4.3.2.2 Photoelectron spectroscopy of clean and Pt-decorated Rh(111)

The Rh(111) crystal was placed inside the chamber, then sputtered and annealed. An initial survey spectrum revealed the presence of aluminum and tantalum contaminants, which could not be removed by the typical sputtering/annealing process. As mentioned in the Experimental section, the samples were mounted to the holder by sandwiching them between two tantalum plates, which was the only source of tantalum. The aluminum came from the shroud around the samples. The aluminum and tantalum contaminants likely resulted from either an improper alignment of the sputter gun or evaporation due to the intense heat generated during the annealing process. The aluminum peak was observed at a binding energy of 72.93 eV (literature value is 72.9 eV)\textsuperscript{57}, which is in the region where Pt 4f would be observed. The presence of aluminum complicated the fitting of the platinum peaks slightly, but did not prevent the experiments from being done.

Using the home-built evaporator, platinum was deposited onto the rhodium surface in successive steps, and spectra were recorded after each step. After 14 minutes of deposition, there is a small amount of platinum at a binding energy of 71.43 eV (Figure 4.15). Note that the Al 2p peak overlaps the two platinum peaks, which makes
the peak fitting slightly more complicated. The platinum peaks become more intense with each deposition step, confirming the successive addition of platinum (Figures 4.16-4.19). The Pt 4f\textsubscript{7/2} binding energies are listed in Table 4.2 for each deposition. Figure 4.20 plots the Pt 4f\textsubscript{7/2} binding energy vs. the deposition time. Note that the binding energy of Pt 4f\textsubscript{7/2} jumps up to 72.03 eV after the second deposition step. With subsequent depositions, the 4f\textsubscript{7/2} binding energy shifts to smaller values nearly linearly as a function of deposition time. A rough estimate of the relative coverage for each deposition cycle was obtained by normalizing the background signals and comparing peak signal intensities to the surface peak of the Pt(111). For the purpose of the calculations, the Pt(111) surface peak intensity was considered to be a monolayer, so the calculated coverage values are relative to this standard. The coverage estimated by this method was used in Figure 4.21 to demonstrate the change in core-level binding energy as a function of platinum coverage. Translating from deposition time to relative coverage does not change the overall shape of the curve. It does, though, show that the final deposition cycle did not result in the addition of more platinum. Due to time limitations, only five data points were obtained, and nothing was repeated. However, the preliminary synchrotron results are promising, since the standard error in the binding energy is much less and there is an apparent trend. While the only conclusion that could be drawn from the laboratory XPS results was that there was a positive core-level binding energy shift, the synchrotron results suggest that the binding energy reaches a maximum. The following discussion of the mechanisms that lead to core-level binding energy shifts is based on the apparent trend observed in the preliminary synchrotron results. Clearly, though, further data is needed for a more rigorous and less speculative interpretation.
As explained in Chapter 1, changes in the core-level binding energy are related to changes in the center of the metal d-band, which affects bonding and reactivity at the metal surfaces. For fundamental studies of model catalysts, as in this case, the purpose is to look for changes in the electronic structure and to try to identify the source of the effect. It was stated in Chapter 1 that the possible reasons for a shift in the d-band center, and therefore core-level binding energies, are geometric effects, charge transfer, and orbital rehybridization. These factors are intimately connected with one another, and the final core-level binding energy shift will depend on the summation of the various effects. In the following discussion, each of these contributing factors will be addressed individually.

Orbital rehybridization is related to several factors, including size effects, surface effects, electronegativity, and bond formation. In this case, platinum and rhodium have the same Pauling electronegativity (2.28, unitless). However, this value for electronegativity is for the bulk metal. Consider that the electronegativity of a given atom depends on the orbitals that are involved in bonding. As explained by Rodriguez and Goodman, changes in the orbital overlap, through changes in coordination number or geometrical arrangement, will affect the hybridization of the orbital, which will result in an electronegativity that is different from the bulk value. This can also be considered as a size effect or a surface effect, since the coordination is reduced on surfaces and in small clusters. Thus, when dealing with adatoms or overlayers on a surface, the surface electronegativity, rather than the bulk electronegativity, must be taken into consideration. The reduced coordination of atoms on surfaces and in small clusters decreases the orbital overlap and weakens the hybridization, resulting in a negative shift.
in the platinum core-levels, as demonstrated in the previous section. The hybridization of a bulk metal is what gives it its metallic properties. Thus, when the hybridization is weakened, a metal gains more nonmetallic qualities as the electronic properties begin to resemble that of the free atom.\textsuperscript{78}

The formation of a chemical bond between platinum and rhodium will also lead to orbital rehybridization through the promotion of d electrons to the s-p band.\textsuperscript{68,79} The promotion of electrons from the localized inner orbital to a more diffuse outer orbital makes the effective nuclear charge more positive and decreases electron-electron repulsion, causing the core-level binding energies to increase. The degree of hybridization, as well as the magnitude of charge transfer, which is a closely related effect that is involved in bond formation, is dependent on the number of electrons in the valence band of the substrate metal. Since platinum is [Xe]4f\textsuperscript{14}5d\textsuperscript{9}6s\textsuperscript{1} and rhodium is [Kr]4d\textsuperscript{8}5s\textsuperscript{1}, a small electronic charge would be expected to transfer from platinum to rhodium. The small difference in the degree of filling of the valence bands of these two metals suggests that the overall magnitude of the orbital rehybridization and charge transfer effects will be small. The effects of charge transfer and orbital rehybridization due to bond formation both lead to a more positive net nuclear charge. The coulombic effect would be lead to larger core-level binding energies for platinum.

Lattice strain is closely related to the orbital rehybridization that is due to surface and size effects. Since lattice strain changes the overlap of atomic orbitals, the effect is similar to that on a surface or in a small cluster, where the coordination of the individual atoms is altered. In addition to inducing a change in the orbital hybridization, the change in lattice size causes the d band to narrow or broaden. A corresponding shift in the center...
of the d band and the core levels will follow in order to conserve energy. In the case of platinum and rhodium, there is a difference of about 2-3% in lattice size. Since the rhodium atoms are smaller, the platinum lattice undergoes contraction. The resulting increase in overlap of the d orbitals of platinum leads to broadening of the d band and, thus, a positive shift in the core-level binding energy.

With these mechanisms in mind, consider the Pt/Rh(111) surface. At very low coverage, the platinum atoms are well-dispersed and have little direct interaction with one another. In this regime, the size effects will be stronger (negative BE shift), as the platinum more closely resembles a free atom than a metallic atom. Lattice strain (positive BE shift) does not affect isolated atoms, so the effects of geometric arrangement are minimal at the lowest coverage, and increase once the deposits begin to grow into islands. Charge transfer from platinum to rhodium (positive BE shift) will occur any time that a bond between the two is formed, though the magnitude could be influenced slightly by the size effects hybridization. As the coverage is increased, direct interaction between platinum atoms increases, and the lattice strain effect becomes stronger. Through a comparison of the coverage calculated from electrochemical charge and from XPS (Figure 4.10), it was concluded that platinum follows the Volmer-Weber growth mode, where multilayer islands become prominent at about 0.3 ML. This type of growth has also been previously observed for Pt electrodeposited on Rh(111) surfaces. Thus, the sharp rise in core-level binding energy could be interpreted as a combination of increased lattice strain and decreased size effects. The charge transfer effect would not reach further than about the first layer, since it is a direct result of bond formation. Lattice strain, on the other hand, may influence the electronic structure of the platinum
through a few monolayers. So, as the islands continue to grow in size, the platinum environment in the islands begins to more closely resemble bulk platinum, and the core-level binding energies will shift closer to the bulk platinum value. Since the direction and magnitude of the binding energy shift is determined by the combination of all effects and most of the effects discussed would lead to a positive shift in the core-levels, it is easy to see why a positive shift is observed. It is much more difficult, however, to attempt to separate the effects without the help of theoretical calculations. If the trend observed in the synchrotron measurements is correct, it can also be rationalized by the various effects. In order to draw any firm conclusions about the binding energy shifts, more data are needed.

One factor that could improve the consistency of the data is the deposition technique. The spontaneous deposition method requires sputtering and UHV preparation of the surface prior to each experiment. As stated previously, it was very difficult to obtain a consistently well-ordered surface every time. Small differences in the surface could affect the adsorption of platinum atoms and the rate at which islands begin to grow three-dimensionally, which would influence the core-level binding energies of the platinum deposits at low coverage. For that reason, the physical vapor deposition method might have an advantage. The high intensity of the synchrotron radiation allows for spectra to be recorded in much less time than they could be with a conventional X-ray source. Since the vapor deposition is done in UHV, the electrode can remain under UHV conditions during the entire deposition and spectroscopic process. Then, several data points could be acquired consecutively within a single day, without the need to clean and prepare the surface again each time. With this technique, the crystal surface could be
taken as virtually the same over the course of all of the experiments in a given day, making it easier to compare and look for a trend in a set of binding energy values.

4.3.3 Comparison of Pt/Ru(0001) and Pt/Rh(111) systems

The motivation for this work was to generate analogous data to compare with the Pt/Ru(0001) system that was reported by Zhou et al.2 In the Pt/Ru(0001) work, platinum was spontaneously deposited on the ruthenium surface in order to obtain low coverage data. Higher coverage data was obtained by electrodeposition. For this system, STM and RHEED studies had already been done for the characterization of Pt deposits on the metal surface, so it was known that Pt forms pseudomorphic islands on ruthenium via the Volmer-Weber growth mode.23,80 Other studies demonstrated through electrochemical-nuclear magnetic resonance81, XPS44, and X-ray absorption spectroscopy82 that the interaction between ruthenium and platinum modifies the electronic structure of the platinum. This information made the Pt/Ru(0001) system ideal for a binding energy study of Pt deposits of different amounts. In the case of Pt/Rh(111), the only report of this type of work, by Housmans et al.41, investigated the structure of electrodeposited platinum on rhodium, as well as the CO electrooxidation activity of this surface. As mentioned in Section 4.1, it was found that platinum tends to grow via the Volmer-Weber mechanism during electrodeposition on rhodium. Through the CO adlayer activity measurements, the group demonstrated that an electronic effect is active for this system.

For Pt/Ru(0001), Zhou et al.2 reported that the lowest coverage resulted in the highest Pt 4f7/2 binding energy. The core-level binding energy was observed to drop by a small amount up to about 0.5 ML, which was the maximum coverage achieved by
spontaneous deposition. For the higher coverage, achieved by electrodeposition, the binding energy dropped off by about 0.2 eV at 0.5 ML, and remained relatively constant with further addition of platinum. The observed behavior was ascribed to a combination of charge transfer and lattice strain. At low coverage, the deposits were monolayer islands (as concluded from a comparison of the coverage calculated from the charge and from XPS, as well as from the previous STM and RHEED studies), so the Pt-Ru direct interaction was large, and charge transfer from platinum to ruthenium played a significant role. The slight decrease in the positive shift of the core-level binding energy with increasing coverage, up to 0.5 ML, was attributed to changes in the charge transfer. Once multilayer islands began to form, the Pt-Ru interaction was reduced, leaving lattice strain as the main contributor at higher coverage.

Overall, the results obtained in the study of Pt/Rh(111) are similar to those reported for the Pt/Ru(0001) system, in that the core-level binding energy shifted positively for platinum deposits on the foreign metal surface. From the laboratory XPS data, this is the extent of the comparison that can be done due to the large standard error in binding energy. Using the preliminary synchrotron results, however, the trend observed for each system appears to be different. As discussed in the previous section, the core-level binding energy appeared to reach a maximum for the Pt/Rh(111) system (Figures 4.20 and 4.21), whereas no such peak was observed for Pt/Ru(0001). This result for the decorated rhodium surface needs to be verified by further synchrotron investigations. However, if the general trend observed is real, this difference would indicate a significant, distinct difference in the modification of platinum deposits depending on the substrate.
As previously discussed, at the low coverage, where the difference is observed, charge transfer will play a larger role. For this reason, a variation in the magnitude of charge transfer from platinum to the different substrates is likely the reason for the distinctive behaviors. Since charge will flow in the direction of the metal with the lowest degree of filling in its valence band, platinum will transfer charge to the ruthenium or the rhodium substrate. However, ruthenium (4d⁷) has a lesser degree of filling of its valence band than does rhodium (4d⁸), so the magnitude of the charge transfer effect will likely be somewhat larger for the Pt/Ru(0001) system. This could account for the difference at very low coverage, where the lattice strain effect is weaker. Differences in the charge transfer at a certain coverage depending on specific surface properties could also be used to explain some of the scatter seen in the binding energy data for both systems.²

There is also a difference in size between ruthenium and rhodium, so the lattice strain effects will be different for these two systems. Both are smaller than platinum, though, so the trend should be the same for the core-level binding energies of platinum deposits on either substrate, just with differing degrees of modification. Therefore, the main difference observed, namely, the apparent peak in core-level binding energy for Pt on Rh(111), is likely due to differences in charge transfer from platinum to the different substrates. This is clear evidence for the value in this type of core-level binding energy information. Multiple factors contribute to the shifting of core-level binding energies, and the relative contribution of each mechanism will vary depending on the properties of both the admetal and the substrate. Here, it is concluded that charge transfer effects are probably weaker for Pt/Rh(111) than for Pt/Ru(0001).
4.4 Conclusions

Model catalysts provide a route to studying the fundamental mechanisms of catalysis. This can be quite beneficial in the development of new catalysts, as information that is learned from the fundamental studies can be used to effectively design catalysts that will have superior activity toward the reaction of interest. In this study, the electronic structure of platinum in the Pt/Rh(111) system was investigated. One of the reasons for the interest in this system is for comparison with the analogous Pt/Ru(0001) system, which has been more thoroughly characterized. Based on the results from the Pt/Ru(0001) study, platinum was expected to display a positive core-level binding energy shift due to both charge transfer and lattice strain. The difference in the number of valence band electrons for platinum and rhodium is only one, so orbital rehybridization and charge transfer effects were expected to be weaker than in the Pt/Ru(0001) system. Because of the difference in size of the admetal and substrate atoms, it was expected that lattice strain would be a driving force for change in the core-level binding energies. Through both conventional XPS and synchrotron photoelectron spectroscopy, platinum core-levels were found to shift to higher binding energy, as expected. The large standard error in the conventional XPS results due to low signal-to-noise ratios and broad peaks made it impossible to assign any trend to the binding energy data, other than to say that it shifted positively. The power of the synchrotron method was demonstrated first by observing a surface core-level shift in the binding energy of Pt(111). The preliminary synchrotron data had much lower standard error for Pt/Rh(111) experiments, and displayed first a sharp increase in binding energy for Pt 4f\(_{7/2}\), followed by a linear decrease in binding energy with increasing coverage. If this observed trend is indeed
accurate, it demonstrates a distinct difference between the electronic modifications of the platinum deposits due to ruthenium and rhodium. From analysis of the results, it is concluded that charge transfer effects are weaker for Pt/Rh(111) than for Pt/Ru(0001). By finding a way around the issues that were encountered at the SRC, high quality binding energy data would likely be obtained. Also, the use of scanning tunneling microscopy could give additional information on the structure of the deposits (i.e. – two-dimensional vs. three-dimensional islands), which would aid in the interpretation. The aim of this work was compare the ruthenium and rhodium systems, and to generate data that could be used for the development of improved theoretical models that would make it possible to separate the relative contributions of the various mechanisms and predict the core-level shifts. The extension of this work to other metal surfaces in the future would provide a larger set of data to work with in the model development. This type of knowledge could assist in predicting catalytic properties, and the required experiments should be pursued.
### 4.5 Tables

Table 4.1: Results for spontaneous and electrochemical deposition of Pt on Rh(111).

<table>
<thead>
<tr>
<th>Spontaneous deposition time (min)</th>
<th>Concentration of PtCl$_4$ (mM)</th>
<th>Pt coverage from XPS (ML)</th>
<th>Pt coverage from EC charge (ML)</th>
<th>Pt $4f_{7/2}$ BE (eV)</th>
<th>Estimated error in BE (± eV)</th>
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<tr>
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Table 4.2: Photoelectron spectroscopy results from the Synchrotron Radiation Center.

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<th>Evaporation Time (min)</th>
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4.6 Figures

Figure 4.1: Cyclic voltammogram of Rh(111) in 0.5 M H$_2$SO$_4$. Scan rate = 50 mV/s
Figure 4.2: Cyclic voltammogram of Rh(111) in 0.1 M HClO₄. Scan rate = 100 mV/s
Figure 4.3: Comparison of cyclic voltammogram of clean electrode and Pt-decorated electrode in 0.5 M H$_2$SO$_4$. $\Theta_{Pt} = 0.08$ ML. Scan rate = 50 mV/s
Figure 4.4: Cyclic voltammograms of Pt-decorated Rh(111) in 0.5 M H₂SO₄. The arrows indicate the direction of change of the peaks as the amount of platinum increases. Scan rate = 50 mV/s
Figure 4.5: Cyclic voltammograms of Rh(111) surface after depositing platinum in 0.1 M HClO₄. Scan rate = 100 mV/s
Figure 4.6: XP survey spectrum of clean Rh(111).
Figure 4.7: XP survey spectrum of Pt/Rh(111), showing the presence of Pt, S, C, and O on the surface. $\theta_{\text{Pt}} = 0.08$ ML
Figure 4.8: Rh 3d XP spectral region on Pt/Rh(111) surface. \( \theta_{\text{Pt}} = 0.08 \) ML.

The average Rh 3d\( _{5/2} \) BE = 307.41 ± 0.05 eV for the entire set of experiments.
Figure 4.9: Pt 4f\textsubscript{7/2} and Rh 4s XP spectral region of representative Pt/Rh(111) surfaces. The dotted lines mark the reference binding energy of 71.1 eV for the Pt 4f\textsubscript{7/2} peak of a Pt(111) surface.\textsuperscript{57} The solid lines mark the Pt 4f\textsubscript{7/2} binding energies for the fitted data.
Figure 4.10: The coverage calculated from the electrochemical charge using Equation 4.3 ($\theta_{\text{Pt,charge}}$) is plotted as a function of the coverage calculated from XPS using equation 4.4 ($\theta_{\text{Pt,XPS}}$). The straight line indicates $\theta_{\text{Pt,XPS}} = \theta_{\text{Pt,charge}}$. Points that lie on the line correspond to monolayer islands, while points that lie below the line correspond to multilayer islands.
Figure 4.11: Pt 4f\textsubscript{7/2} BE as a function of Pt coverage for experiments done in 0.5 M H\textsubscript{2}SO\textsubscript{4}. Each point on the plot represents a single experiment. The error was estimated based on the instrument standard deviation and the peak fitting (Eq. 4.2).\textsuperscript{46}
Figure 4.12: Pt 4f<sub>7/2</sub> BE as a function of Pt coverage for experiments done in 0.1 M HClO₄. Each point on the plot represents a single experiment. The error was estimated based on the instrument standard deviation and the peak fitting.⁴⁶
Figure 4.13: Pt 4f spectral region on Pt(111) disc recorded at 160 eV photon energy. The resolution was set to 80 meV for all experiments at SRC.
Figure 4.14: Pt 4f$_{7/2}$ spectral region on Pt(111) recorded at 160 eV, showing a surface-bulk core-level shift.
Figure 4.15: Pt 4f and Al 2p on Rh(111) after 14 minutes deposition. $h\nu=160$ eV
Figure 4.16: Pt 4f and Al 2p on Rh(111) after 27 minutes deposition. $h\nu=160$ eV
Figure 4.17: Pt 4f and Al 2p on Rh(111) after 37 minutes deposition. $h\nu=160$ eV
Figure 4.18: Pt 4f and Al 2p on Rh(111) after 42 minutes deposition. \( h\nu = 160 \text{ eV} \)
Figure 4.19: Pt 4f and Al 2p on Rh(111) after 50 minutes deposition. $h\nu=160$ eV
Figure 4.20: Pt 4f$_{7/2}$ BE for Pt/Rh(111) as a function of deposition time. $h\nu=160$ eV.

The error bars were estimated from the standard error and Equation 4.2.\textsuperscript{46}
Figure 4.21: Pt 4f$_{7/2}$ BE for Pt/Rh(111) as a function of coverage ($h\nu=160$ eV) from SRC data. The coverage is a rough estimate based on a normalization of background intensities and comparison of peak heights to the surface peak on Pt(111).
4.7 References

(30) Bakos, I.; Szabo, S. *Journal of Electroanalytical Chemistry* 2003, 547, 103.
(34) Tanaka, K.; Okawa, Y.; Sasahara, A.; Matsumoto, Y. Structure and catalysis of Rh-Pt(100), Rh-Pt(110), Pt-Rh(100), and Pt-Rh(110) surfaces prepared by electrochemical metal deposition. In *Solid-Liquid Electrochemical Interfaces*, 1997; pp 245.
(50) Hourani, M.; Wieckowski, A. *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 1988, 244, 147.
(64) Hammer, B.; Nørskov, J. K. *Surface Science* 1995, 343, 211.
5.1 INTRODUCTION

Underpotential deposition (UPD) systems, which involve the formation of a metal-metal bond between an adatom and a foreign metal substrate at potentials positive of the Nernst potential, have found application in a number of areas, including electrocatalysis.\(^1,2\) Sn, Pb, Ni, and Sb UPD layers have all been added to Pt catalysts as a means of improving the catalytic activity of the Pt toward electrooxidation of small organic molecules, such as formic acid, through a combination of a bifunctional mechanism and an electronic interaction.\(^3-8\) Others have used a method of replacement of UPD adlayers by platinum to form a monolayer, or less, on a substrate particle, such as a Au nanoparticle, in order to obtain electrocatalysts that have a low platinum loading and that can be used in fuel cell applications.\(^9-13\) In addition to these application-based studies, UPD systems are also well-suited for use as model catalysts, both experimentally and theoretically.\(^14-19\) Studies have focused on the structure of the deposits, as well as on the role of anions and the electronic properties of the adlayer. In particular, UPD adlayers are expected to display perturbations in the electronic structure of the atoms. Information about the perturbations in electronic structure can be obtained through core-level photoemission spectroscopy, offering yet another model system for use in the study of metal-metal interactions. One benefit of using UPD adlayers is that the deposition

* This work was carried out jointly with Dr. Daniela Marques dos Anjos, who also created figures and tables that are presented here.
amount and morphology can be known and controlled to a greater extent than deposits prepared by other methods, which should aid in the interpretation of core-level binding energy shifts. In the present work, copper and silver were underpotentially-deposited on a Rh(111) surface. Following a scan past each cathodic peak, stepwise, the electrode was emersed and the surface was probed by on line X-ray photoelectron spectroscopy. The core-level binding energy shifts have been interpreted in terms of the most prominent sources of core-level shifts: lattice strain, charge transfer, and hybridization.

5.2 EXPERIMENTAL METHODS

In a three-electrode electrochemical cell used for this study, a platinized Pt electrode was a counter electrode and a commercial Ag/AgCl ($c_{Cl} = 3$ M) was a reference electrode. However, all results of this work are reported with respect to RHE. Ultra-high purity argon was used to purge the solutions and Millipore ultrapure water was used to prepare the solutions. All the glassware (cells and volumetric flasks) were cleaned overnight using NOCHROMIX bath, and they were thoroughly washed/rinsed using the ultrapure water. The rhodium single crystal electrode was purchased from MaTeck GmbH (6 mm x 2 mm). Solutions of metal cations to be deposited ($Cu^{2+}$ and $Ag^+$) were prepared in supporting electrolytes of 0.1 and/or 0.5 mol L$^{-1}$ of $H_2SO_4$ (95-98.0% purity) and $HClO_4$ (69-72% purity). For the deposition in sulfate medium, $Ag_2SO_4$ 99.999% and $CuSO_4$ 99.99% salts were used (from Alfa Aesar and Aldrich, respectively). For the deposition in perchlorate medium, the solutions were prepared with $AgClO_4.H_2O$ 99.9% and $Cu(ClO_4)_2.6H_2O$ 99.999% (both from Alfa Aesar). Cyclic voltammograms (CVs) in $H_2SO_4$ and/or in $HClO_4$ were recorded at 50 mV s$^{-1}$ between potential biases such that
disordering of the rhodium electrode surface did not occur. The UPD voltammograms were recorded at 2 mV s⁻¹.

Electrochemical and spectroscopic measurements were carried out in a combined electrochemistry-X-ray photoelectron spectroscopy (EC-XPS) instrument (Figure 1.2), which was described in Sections 1.3 and 4.2.1. The calibration and instrument standard error determination (±0.05 eV) is the same as reported in Section 4.2.1. Errors calculated from Equation 4.2 were typically smaller than ±0.1 eV. All binding energies are reported to ±0.1 eV.

The preparation of the single crystal surfaces in UHV followed the same procedure as described in Section 4.2.1 of Chapter 4, using cycles of sputtering, hot sputtering, and annealing with and without oxygen. The UPD voltammograms were recorded at 2 mV s⁻¹, starting from 0.8 V vs. RHE and stopping just after the peak to be analyzed by XPS, so that only the cathodic scan was recorded. The salt solution (of silver or copper) was drained from the electrochemical cell, which was cleaned by rinsing several times with acid solution and further with water. The electrode was rinsed with water, the resulting water droplet was removed by aspiration, and the electrode was dried under vacuum before being transferred to the XPS chamber.

5.3 RESULTS AND DISCUSSION

5.3.1 Characterization by on line X-ray photoelectron spectroscopy

The nature of underpotential deposits has been widely discussed in the literature, but it is still not well-understood. Electrochemical methods alone, as reported in dos Anjos et al., do not provide enough information to give much insight into the nature of
the UPD and bulk peaks of copper and silver on rhodium surfaces. As an extension of this work, these UPD and bulk peaks were investigated by XPS on line with electrochemical methods (EC-XPS) in order to clarify the state of the surface after each deposition. The XPS measurements provided information on the core-level binding energy shifts of adatoms (silver or copper) and substrate (Rh(111)), giving some information on the interaction of the deposit with the substrate. In addition, it is useful in identifying the adatoms at the Rh(111) surface and in determining, with reasonable approximation, the concentration and number of monolayers of all elements involved in each identified electrochemical peak.

5.3.2 The nature of underpotential deposition of copper on Rh(111)

The XPS measurements were performed after scanning, in the cathodic direction, in the range of potentials of the peak(s) to be evaluated. From a survey spectrum of the Rh(111) surface following an electrochemical scan past the first two copper UPD peaks in sulfuric acid media, core-level peaks are observed for the substrate and copper adatoms, as well as for anions from the electrolyte (Figure 5.1). The peaks of copper, rhodium, oxygen and sulfur are clearly identified, and these regions were scanned individually at higher resolution for the evaluation of binding energy shifts and adatoms coverage. The coverage of a metal adatom on the substrate (Rh(111)) was calculated from XPS data using Equation 4.1,\(^{34,35}\) where \(S_{Cu2p} = 4.798\), \(S_{Ag3d} = 5.198\), \(\lambda_{Cu} = 1.15\) nm, \(\lambda_{Ag} = 1.59\) nm, \(\alpha_{Cu} = 0.228\) nm, and \(\alpha_{Ag} = 0.258\) nm.

As shown in dos Anjos et al.\(^{19}\), the voltammetry of Rh(111) in the presence of copper ions, with either sulfuric or perchloric acid electrolyte, shows two peaks in the
region of potential before the bulk deposition (Figure 5.2). From Figure 5.2, it can be seen that the choice of electrolyte affects the position and charge of the UPD peaks. This suggests that the interaction of anions with the rhodium surface plays a role in the UPD process. Another important observation from Figure 5.2 is that peak II occurs at approximately the same position (~0.7 V vs. RHE) as oxide reduction on the clean rhodium surface.\(^\text{19}\) This raised some doubt as to the origin of this high-potential peak. However, the XPS results for this peak indicate the presence of a small amount of copper among a high coverage of anions from the electrolyte (Figures 5.3 and 5.4, Table 5.2), proving that this peak does involve underpotential deposition of copper. Calculated from the XPS data, this copper coverage is approximately 0.07 ML in sulfuric and 0.04 ML in perchloric electrolyte, respectively. The coverage calculated from the electrochemical charge is slightly higher than that estimated from XPS (Table 5.1), although the agreement is considered satisfactory, given all factors that could be involved in formation of the peak at 0.7 V (i.e. – charge from anions).

Two important aspects can be evaluated from the XPS spectra: (1) the coverage of copper and (2) the binding energy shifts associated with each peak. These data are presented in Table 5.1 for copper UPD, and are discussed below. Figures 5.3 and 5.4 show the Cu 2p\(\frac{3}{2}\) peaks that were observed after scanning past peak II, peak I, and the bulk deposition peak in the two electrolytes, as indicated in the insets. In the case of each electrolyte, just by comparing the relative signal intensities, an increase in the amount of copper is observed as the electrode is scanned past each peak in the cathodic direction. The addition of copper during each scan is confirmed by the coverage calculations (Table 5.1). The relative amounts of anions were also determined from spectral scans of the S
2p, Cl 2p, and O 1s regions. In the perchloric acid experiments, chlorine and oxygen species were found. For each successive deposition, the relative concentration of chlorine on the surface compared to copper decreases. A slightly different behavior was observed for experiments in sulfuric acid. For peak II (0.7 V), sulfur and oxygen species were found to be present at a higher concentration than copper, with a relative distribution of Cu:S:O 1:3:4. For peak I, the coverage of copper (0.6 ML) increases compared to that of sulfur and oxygen species (Cu:S:O 86:7:19), while for the bulk deposition (2.4 ML copper), the concentration of anions increases again (Cu:S:O 21:10:10). This suggests that the anions are initially adsorbed to the rhodium surface, blocking adsorption sites for copper. As the UPD takes place, the anions are displaced. Once the bulk deposition has occurred, they are then able to adsorb directly onto the copper.

In addition to the changes in relative concentrations, the chemical state of the anions could be monitored. The core-level binding energy for the chlorine species indicates chloride, a product of the reduction of perchlorate. Perchlorate was not observed on any surface. The core-level binding energies of chloride were observed to shift positively with each addition of copper: peak II (198.0 eV), peak I (198.5 eV), and the bulk (199.0 eV). From this shift, it would seem that the adsorption environment of the chloride changes as the potential is changed. Similarly, the type of sulfur species was also seen to change, depending on the stage of deposition. For the UPD peaks, the binding energy of S 2p was near 162 eV, while for the bulk peak, there were two different species, one near 162 eV and one near 168 eV. The high binding energy peak is consistent with sulfate, while the low binding energy peak is consistent with sulfide.
However, since sulfate is such a stable anion, it is not likely that it would be reduced during the UPD process. Therefore, the low binding energy peak is probably due to either a different type of interaction with the surface or to some type of experimental artifact, where the sulfate breaks down after the electrochemical measurements have been completed. Preliminary experiments at low anion concentrations and where emersion and rinsing of the electrode were done at a controlled potential gave similar results. This suggests that this observation is not the product of an electrochemical artifact due to the loss of potential control. It could, however, be an artifact due to the \textit{ex situ} nature of the spectroscopic measurements. The fact that the observation of the different species is consistent for the various deposition potentials over multiple experiments, even if there is breakdown \textit{ex situ}, suggests that the nature of the anions on the surface during the various stages of deposition is different. It has been shown by, for instance, dos Anjos \textit{et al.}\textsuperscript{19}, that differences in types and concentrations of anions present in solution influence the UPD process. From the XPS results, it is clear that the anions are present on the surface and that there are slight differences depending on the deposition potential, though it is not clear from these experiments what is the nature and role of the anions, and further work is needed.

Information on the electronic structure of the copper deposits, which is the data of most interest in this study, can be obtained from the XPS results in Figures 5.3 and 5.4. The copper was found to be in metallic form in all cases, as the characteristic satellite peaks of Cu\textsuperscript{2+} are not present. Furthermore, the Cu 2p\textsubscript{3/2} peaks are found to be shifted negatively with respect to the measured bulk copper reference (932.8 eV, dashed line), and the measured Cu 2p\textsubscript{3/2} binding energies for all experiments are listed in Table 5.1.
The peak II deposit showed the largest negative shift in binding energy, being shifted by 0.7 eV in each electrolyte. As the coverage increased, so did the binding energy. At a coverage of about 0.6 ML (peak II), deposited in sulfuric acid, the binding energy was 932.6 eV. In perchloric electrolyte, the copper coverage for peak I was about 0.3 ML and the binding energy was 932.3 eV. Bulk deposition resulted in 2.4 and 2.9 ML of copper, with binding energies of 932.6 and 932.7 eV for experiments in sulfuric and perchloric electrolytes, respectively. The potential shift for peak I matches very well with the shift expected based on theory for UPD of copper on Rh(111).\(^\text{19}\) The peak at 0.7 V (peak II), however, is not expected based on the theory. While these results demonstrate that peak II involves deposition of copper, it is not clear why copper deposits at this potential. The influence of anions likely plays an important role in this process. It is possible that the adsorbed anions change the electronic properties of the rhodium surface to the extent that the interaction with copper results in underpotential deposition at a higher potential than expected. Or, there could be another factor that is not accounted for in the theory that is influencing the underpotential deposition.

Previous studies\(^\text{36-40}\) of vapor-deposited copper layers on Rh(100) reported that the core-level binding energy of copper was shifted negatively by ~ 0.6 eV with respect to a bulk copper reference, and the shift was constant up to one monolayer coverage.\(^\text{36}\) At higher coverage, the binding energy shift decreased sharply, so that, with just a few monolayers, the core-level binding energy was comparable to the bulk reference value. The negative shift of about 0.6 eV is comparable to the results reported here. The origin of these shifts involves the interplay of the different mechanisms that have been described in previous chapters.\(^\text{37,38,41-43}\) A discussion of the core-level binding energy
shift must take into account all contributing factors. Here, the shift will be discussed in terms of orbital rehybridization, lattice strain, and charge transfer.

As was described in Chapter 4, the loss of metallic character at low surface concentrations is a result of the size effect, where smaller clusters have reduced interaction and overlap of the d orbitals of the individual atoms. In this regime, orbital rehybridization will lead to a different d density of states depending on the cluster size. The ground state electronic configuration of atomic copper is \([\text{Ar}]3d^{10}4s^1\). Overlap of the orbitals between neighboring copper atoms in metallic copper leads to a promotion of d electrons to the valence s-p band, leaving the metal with an electronic configuration of \([\text{Ar}]3d^{10-x}4s^{1+x}\). As the copper clusters become smaller (reduced coordination), the hybridization involving d electrons and the conducting s-p band will be weakened, leading to a larger number of electrons in the d orbital. Since the effective nuclear charge depends on the number of electrons in the compact d shell, the binding energy of core-level electrons will shift according to this Coulombic effect. For copper, the result is that small clusters, or less-coordinated adatoms, that approach nonmetallic behavior should display a negative core-level binding energy shift due to the less positive effective nuclear charge. The effects of orbital rehybridization are typically small compared with other factors.

In addition to size effects, the d-d interactions will be affected by lattice strain. Copper has been shown to grow pseudomorphically on rhodium by the Frank-van der Merwe mechanism, where two-dimensional islands grow into a monolayer and subsequent layers nucleate as three-dimensional islands. However, this work involved thermal evaporation of copper onto the rhodium surface, rather than underpotential
deposition. The definition of UPD, though, would suggest that copper deposits directly onto rhodium, forming a monolayer. So, while in situ STM experiments would be needed to confirm this, it is assumed that copper will most likely grow pseudomorphically according to the Frank-van der Merwe mechanism during the UPD process. Since a copper atom is smaller than a rhodium atom, the pseudomorphic growth results in an increase in the copper-copper interatomic distance. This increase in spacing reduces the interaction between the d orbitals of neighboring atoms in the overlayer. The resulting narrowing of the bands leads to an upshift in the center energy of the d band and a negative shift in the core-level binding energies.

The charge transfer effect must also be considered. The charge transfer is a result of orbital mixing due to bonding, as well as surface electronegativities, and depends on the degree of filling of the valence bands of the adatom and substrate. The valence band of copper has a half-filled s shell, while the valence band of rhodium has a d shell that is 80% filled. Thus, when a copper overlayer has a bonding interaction with a rhodium surface, the electron density will flow in the direction of copper. The added electron density will cause a negative shift in the core-level binding energies due to the less positive effective nuclear charge and increased electron-electron repulsion. This can also be described as an increase in the shielding of the core levels. There is, however, orbital rehybridization that is intimately connected with the forming of bonds. For bond formation, electrons from the compact d orbitals are promoted to the s-p band, which increases the core-level binding energies. Thus, the electronic effects due to bond formation are a balance between charge transfer and orbital rehybridization.
Based on the above discussion, it is not surprising that the core-level binding energies were found to shift to more negative values. For the vapor-deposited copper overlayers on Rh(100), Rodriguez et al.\textsuperscript{36,37} attributed the negative binding energy shift to a combination charge transfer and lattice strain effects, but concluded that the lattice strain effects were secondary to the admetal—substrate interaction. The same explanation can be used for underpotentially deposited copper overlayers on Rh(111).

For peak II, the Cu 2p\textsubscript{3/2} binding energy was found to be 932.1 eV, which is \(\sim 0.7\) eV less than the bulk copper reference value. In the Rodriguez et al.\textsuperscript{36} work, the core-level binding energy was consistently 0.6 eV below the bulk value for any coverage less than about one monolayer. However, for peak I, the Cu 2p\textsubscript{3/2} binding energy was found to be slightly larger than that of peak II (Table 5.1). This could be due to a couple of different factors. There could be an influence on the electronic structure from anions in the vicinity, where the negatively charged adsorbates draw electrons away from the copper. The presence of localized multilayer islands, though not expected in the UPD regime, would also increase the core-level binding energies due to the increased local d—d interaction that comes with higher coordination. For bulk deposition, the core-level binding energy was found to be nearly the same for the two electrolytes (932.6 eV for sulfuric acid and 932.7 eV for perchloric acid), and is very near, but just below, the bulk copper reference value. This discrepancy can be explained by lattice strain or surface effects. The lattice of the copper overlayer will be affected by the substrate up to a few monolayers thickness, so a slight shift could be expected for deposits of 2-3 monolayers (the coverage was just over 2 ML in sulfuric acid and just under 3 ML in perchloric acid). The shift could also be partly due to the reduced coordination of the surface atoms. A
more appropriate comparison for the binding energy shift of the bulk deposition would be to that of the surface core-level shift. The surface core-level shift for copper is just below 0.2 eV, so the bulk deposition results are in good agreement with this shift.

Overall, the core-level binding energy shifts of copper underpotential deposits are due to a combination of various factors. Orbital rehybridization due to size and surface effects, lattice strain, and charge transfer all contribute to a negative core-level binding energy shift. Orbital rehybridization due to bond formation and interaction with anions on the surface contribute to a positive shift in the core-level binding energy of copper. The final core-level shift depends on the summation, and, therefore, the magnitude, of the various contributing factors. In this case, the majority of mechanisms lead to a negative shift. Since orbital rehybridization generally has a smaller effect, charge transfer and lattice strain are likely the dominant contributors. The observed core-level shifts also match well with theoretical calculations, which predict an upshift of the d band center in copper overlayers on rhodium.49

5.3.3 The nature of underpotential deposition of silver on Rh(111)

As discussed in dos Anjos et al.19, silver UPD on Rh(111) in the presence of perchloric or sulfuric acid has distinctly different characteristics from copper UPD on Rh(111). The cyclic voltammogram of silver UPD shows a multipeak feature (Figures 5.5 and 5.6), which is highly dependent on the electrolyte, the concentration of silver ions in solution, and the ordering of the substrate surface. Figure 5.7 displays the XP survey spectrum for UPD of silver in perchloric acid, showing evidence of chlorine, oxygen, and silver species. Table 5.4 shows that there is a significant amount of chloride on the
surface after the first deposition peak, and that the amount is dramatically decreased after the second peak. In equivalent experiments with sulfuric acid, sulfur species were observed. In contrast to what was observed for copper UPD, most of the sulfur species present had a binding energy consistent with sulfate at all points that were measured (Table 5.4), as expected for the stable sulfate anion. Since the same method was used for all copper and silver experiments, the difference in the decomposition of the surface sulfate anion suggests the influence of differing adsorption environments. Once again, the presence and changes in concentration of adsorbed anions suggest that affect the deposition process. Unfortunately, this role cannot be determined through \textit{ex situ} XPS measurements.

From the XPS results listed in Table 5.3, the first voltammetric peak in perchloric acid produced a low coverage of silver, while the second peak produced approximately one monolayer. On the other hand, approximately the same coverage of silver (~ 1 ML) was found regardless of whether the voltammetric scan was stopped after the first, second, or third peaks in sulfuric acid. This behavior could be an artifact from differing surface qualities for the set of experiments, or could be related to phase transitions of silver on the surface. Phase transitions in UPD layers have been identified previously for silver, as well as for other systems.\textsuperscript{31,50-52} They are due to the influence of anions and do not involve deposition of metal, showing up in the voltammetry as sharp peaks. The significant changes in anion coverage (Table 5.4) would fit with the idea of phase transitions. An \textit{in situ} technique, such as STM, would be needed in order to draw firm conclusions on the nature of the silver deposits.
In Figures 5.8 and 5.9, the Ag 3d$_{5/2}$ spectra are plotted together for UPD in sulfuric and perchloric acid electrolytes, respectively. Just as for copper UPD, the silver core-levels are found to shift to more negative binding energies, although the shift (0.3-0.4 eV) is smaller than for copper. The bulk silver 3d$_{5/2}$ reference binding energy is 368.3 eV.$^{53}$ For the first deposition, the core-level binding energy was measured at 368.0 eV in sulfuric (1.0 ML) and 367.9 eV in perchloric acid. For the sulfuric acid experiments, the binding energy shift changed by no more than about 0.1 eV for the second and third voltammetric peaks. The shift decreased by 0.2 eV in going from the first to the second voltammetric peak in perchloric acid experiments. Bulk deposition gave identical results in each electrolyte, with coverage of 1.7 ML and a core-level binding energy of 368.2 eV.

The core-level binding energy shifts in silver UPD layers can be explained in a process analogous to that used for the shifts in copper UPD layers. Orbital rehybridization due to size effects, surface effects, and bond formation will produce negative core-level shifts for the same reasons as outlined previously. Silver ([Kr]4d$^{10}$5s$^1$) has the same degree of filling of the valence band as copper, so it would be expected to behave similarly to copper in regards to charge transfer; a transfer of charge from the rhodium to the silver proceeds because of the half-filled s band of silver. The lattice strain, though, has the opposite effect on silver compared to copper. Silver is larger than rhodium, so pseudomorphic growth would lead to higher core-level binding energies as the silver lattice is compressed. Thus, in the case of silver adlayers on Rh(111), lattice strain and charge transfer effects, which are typically stronger than the other effects, influence the shifting of the d band center in opposite directions. The
observed negative core-level shifts are the result of the summation of all of the effects. At low coverage, the charge transfer effect is apparently dominant over the lattice strain effect. With increasing coverage, as seen in going from the first to the second voltammetric peak in perchloric acid, the core-level binding energy shifted to a slightly higher value. The bulk deposits are both less than two monolayers, as estimated from the XPS results, so the electronic effects are still active. This is also confirmed by comparison of the observed core-level binding energy shift (0.1 eV) to the surface core-level shift for silver, which is 0.08 eV. As was the case for copper, the observation of a negative shift in the core-level binding energy is consistent with theoretical calculations.

5.4 CONCLUSIONS

In order to acquire collective information on the electronic properties of (i) the substrate, (ii) submonolayer/monolayers and bulk layers of the UPD adatoms, and (iii) the anions present on the surface, systematic XPS experiments for copper and silver UPD on Rh(111) in different electrolytes were performed. The results from the XP spectra of anions suggest a key role of anions in the UPD process, as the type and concentration of the anions changes for each voltammetric region. For silver UPD in sulfuric acid, the changes in anion coverage, along with the almost unchanging silver coverage for the different voltammetric peaks, suggest a single UPD process involving multiple phase transitions. Both copper and silver UPD adlayers display a shift to lower core-level binding energies, which has been attributed to a summation of effects. The negative shift seen for silver adlayers indicates that lattice strain is not the primary factor affecting the
core-level binding energies for these UPD systems, contrary to what has been found for other systems, like Pt/Ru.$^{54}$ Overall, the copper and silver UPD systems display an interesting influence of electronic effects on the core-level binding energies of copper and silver. Above all, though, these results demonstrate the need for care and discretion when attempting to explain or predict shifts in core-level binding energies, as there is usually no easy answer.
Table 5.1: Binding Energy shifts and number of monolayers (ML) for copper UPD and bulk deposition calculated from electrochemical charge and XPS peaks areas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>Binding Energy (eV)</th>
<th>Cu coverage (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cu 2p$_{3/2}$</td>
<td>Rh 3d$_{5/2}$</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>--</td>
<td>--</td>
<td>307.3</td>
</tr>
<tr>
<td>Cu poly</td>
<td>--</td>
<td>932.8</td>
<td>--</td>
</tr>
<tr>
<td>1$^{st}$ peak</td>
<td>H$_2$SO$_4$</td>
<td>932.1</td>
<td>307.4</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>932.1</td>
<td>307.4</td>
</tr>
<tr>
<td>1$^{st}$ and 2$^{nd}$ peaks</td>
<td>H$_2$SO$_4$</td>
<td>932.6</td>
<td>307.3</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>932.3</td>
<td>307.5</td>
</tr>
<tr>
<td>Bulk deposition</td>
<td>H$_2$SO$_4$</td>
<td>932.6</td>
<td>307.3</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>932.7</td>
<td>307.4</td>
</tr>
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</table>
Table 5.2: Relative distribution of ions at the surface after copper deposition on Rh(111)

<table>
<thead>
<tr>
<th>Sample Cu/Rh(111)</th>
<th>Peaks</th>
<th>Cu</th>
<th>S (&lt; 164 eV)</th>
<th>S (&gt; 164 eV)</th>
<th>Cl⁻</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄ 1 mM +</td>
<td>II</td>
<td>1</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>H₂SO₄ 0.1 M</td>
<td>I</td>
<td>86</td>
<td>7</td>
<td>0</td>
<td>0</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>Bulk</td>
<td>21</td>
<td>7</td>
<td>3</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Cu(ClO₄)₂ 1 mM +</td>
<td>II</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>17</td>
</tr>
<tr>
<td>HClO₄ 0.1 M</td>
<td>I</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Bulk</td>
<td>32</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 5.3: Binding Energy shifts and number of monolayers (ML) for silver UPD and bulk deposition calculated from electrochemical charge and XPS peaks areas. The reference value for Ag 3d$_{5/2}$ was taken from Moulder et al.$^{53}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Electrolyte</th>
<th>Binding Energy (eV)</th>
<th>Ag coverage (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ag 3d$_{5/2}$</td>
<td>Rh 3d$_{5/2}$</td>
</tr>
<tr>
<td>Rh(111)</td>
<td>--</td>
<td>--</td>
<td>307.3</td>
</tr>
<tr>
<td>Ag poly</td>
<td>--</td>
<td>368.3</td>
<td>--</td>
</tr>
<tr>
<td>Ag UPD 1$^{st}$ peak</td>
<td>H$_2$SO$_4$</td>
<td>368.0</td>
<td>307.3</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>367.9</td>
<td>307.4</td>
</tr>
<tr>
<td>Ag UPD 1$^{st}$ and 2$^{nd}$ peaks</td>
<td>H$_2$SO$_4$</td>
<td>368.0</td>
<td>307.3</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>368.1</td>
<td>307.4</td>
</tr>
<tr>
<td>Ag UPD 3$^{rd}$ peak</td>
<td>H$_2$SO$_4$</td>
<td>368.1</td>
<td>307.3</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>np</td>
<td>np</td>
</tr>
<tr>
<td>Ag deposition</td>
<td>H$_2$SO$_4$</td>
<td>368.2</td>
<td>307.3</td>
</tr>
<tr>
<td></td>
<td>HClO$_4$</td>
<td>368.2</td>
<td>307.4</td>
</tr>
</tbody>
</table>

np: no peak
Table 5.4: Relative distribution of ions at the surface after silver deposition on Rh(111)

<table>
<thead>
<tr>
<th>Sample Ag/Rh(111)</th>
<th>Peaks</th>
<th>Ag</th>
<th>S (&lt; 164 eV)</th>
<th>S (&gt; 164 eV)</th>
<th>Cl</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag$_2$SO$_4$ 1mM +</td>
<td>III</td>
<td>12</td>
<td>3</td>
<td>4</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>H$_2$SO$_4$ 0.1M</td>
<td>II</td>
<td>6</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>9</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Bulk</td>
<td>16</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>AgClO$_4$ 1mM +</td>
<td>II</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>3</td>
<td>26</td>
</tr>
<tr>
<td>HClO$_4$ 0.1M</td>
<td>I</td>
<td>9</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
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<td></td>
<td>Bulk</td>
<td>6</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>
Figure 5.1: Representative XPS spectra (survey) after depositing copper on Rh(111) by scanning the Rh(111) electrode in the potential range between 0.9 and 0.25 V at 2mV s\(^{-1}\) in 0.1 M H\(_2\)SO\(_4\) + 1mM CuSO\(_4\).
Figure 5.2: Copper UPD on Rh(111). Electrolyte: 0.1 M H₂SO₄ + 1mM CuSO₄ (solid line) and 0.1 M HClO₄ + 1mM Cu(ClO₄)₂ (dashed line). Scan rate 2 mV s⁻¹. This figure is reproduced from ref. 18.
Figure 5.3: XPS spectra of the Cu 2p$_{3/2}$ after depositing copper on Rh(111) by scanning the Rh(111) electrode in the range of potentials shown in the insert for the peaks I, II and bulk. Electrolyte: 0.1 M H$_2$SO$_4$ + 1mM CuSO$_4$. The electron core-level binding energy for the Cu 2p$_{3/2}$ peak of the bulk copper standard is marked by the vertical dashed line.
Figure 5.4: XPS spectra of the Cu 2p\textsubscript{3/2} after depositing copper on Rh(111) by scanning the Rh(111) electrode in the range of potentials shown in the insert for the peaks I, II and bulk. Electrolyte: 0.1 M HClO\textsubscript{4} + 1mM Cu(ClO\textsubscript{4})\textsubscript{2}. The electron core-level binding energy for the Cu 2p\textsubscript{3/2} peak of the bulk copper standard is marked by the vertical dashed line.
Figure 5.5: Silver UPD on Rh(111). (a) 0.1 M H$_2$SO$_4$ + 1mM Ag$_2$SO$_4$; (b) 0.5 M H$_2$SO$_4$ + 1mM Ag$_2$SO$_4$; (c) 0.5 M H$_2$SO$_4$ + 10mM Ag$_2$SO$_4$. The scan rate was 2 mV s$^{-1}$. This figure is reproduced from ref. 18.
Figure 5.6: Silver UPD on Rh(111) in 0.1 M HClO$_4$ + (a) 1 mM AgClO$_4$; (b) 2.5 mM AgClO$_4$; (c) 5 mM AgClO$_4$ (d) 10 mM AgClO$_4$. The scan rate was 2 mV s$^{-1}$. This figure is reproduced from ref. 18.
Figure 5.7: Representative XPS spectra (survey) after depositing silver on Rh(111) by scanning the Rh(111) electrode in the potential range between 0.9 and 0.6 V at 2mV s\(^{-1}\) in 0.1 M HClO\(_4\) + 1mM AgClO\(_4\).
Figure 5.8: XPS spectra of the Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ after depositing silver on Rh(111) by scanning the Rh(111) electrode in the range of potentials shown in the insert for the peaks I, II, III and bulk. Electrolyte: 0.1 M H$_2$SO$_4$ + 1mM Ag$_2$SO$_4$. The electron core-level binding energies for the peaks of the silver standard are marked by the vertical dashed line.
Figure 5.9: XPS spectra of the Ag 3d$_{5/2}$ and Ag 3d$_{3/2}$ after depositing silver on Rh(111) by scanning the Rh(111) electrode in the range of potentials shown in the insert for the peaks I, II, III and bulk. Electrolyte: 0.1 M HClO$_4$ + 1mM AgClO$_4$. The electron core-level binding energies for the peaks of the silver standard are marked by the vertical dashed line.
5.7 References


CHAPTER 6

CONCLUSIONS AND FUTURE DIRECTIONS

6.1 Conclusions

An insufficient understanding of the factors that affect the electrocatalytic performance of fuel cells is one of the main issues that are holding back these devices as a major source of alternative energy. The results presented in the preceding chapters represent a major step forward in the understanding of electrocatalysis in the fundamental perspective. These studies included characterization of both commercial nanoparticle electrocatalysts and bimetallic single crystal model catalysts. Each type of material, nanoparticles vs. single crystal, offers some advantages. The characterization of commercial nanoparticle materials and their electrocatalytic properties gives a good idea of the actual activity of the material, in other words, its usefulness as an electrocatalyst. However, it is difficult to draw from these materials the reasons behind the observed activity. This is where the bimetallic single crystal model catalysts can be advantageous. The known composition and structure of these catalysts greatly simplify the study of fundamentals of electrocatalysis.

The key result in this collective work is the confirmation of Nørskov’s theory involving the center of the d band and reactivity. A correlation between heats of adsorption of certain species, such as CO and H₂, and the center of the d band of the substrate metal had already been demonstrated. Prior to the work presented here, a direct correlation between the center of the d band and the reactivity of a metal toward the electrooxidation of a small, organic fuel had not been demonstrated. It was found that the
electrooxidation of methanol at a Pt/Ru alloy electrode is too complicated for any fundamental study of electronic effects on reactivity, but that the electrooxidation of formic acid presents an ideal case for this type of investigation. For the first time, a direct correlation between reactivity and the center of the d band was demonstrated for the electrooxidation of formic acid at Pt/Ru alloy nanoparticles. As predicted by the theory, the activity, in the limit of zero CO coverage, decreased as a function of increasing platinum core-level binding energy, indicating a weakening of the interaction of formic acid with the electrocatalyst surface. The study of commercial nanoparticle catalyst materials was then extended to Pt₃Co alloy for the oxygen reduction reaction (ORR). The results of this work point toward the formation of a Pt skin layer on the nanoparticle surface, which, through electronic effects by the shifting of the d band center, increase the activity of the nanoparticles toward the ORR in acidic media. While the effects are not beneficial in alkaline media, the results in acidic media demonstrate a connection between the d band center and the activity toward the ORR.

Once the d band center theory had been confirmed to apply to electrooxidation of fuel molecules, it became even more important to learn more about the fundamental aspects of the d band shifts. The results of core-level binding energy measurements of Pt spontaneously-deposited on Rh(111) demonstrate a shift in the d band center for platinum adlayers. Due to the low signal intensities, the error associated with the conventional XPS measurements made it impossible to determine any specific trend in the binding energy. Preliminary results from the University of Wisconsin’s Synchrotron Radiation Center, however, had a much smaller standard error, and the limited data suggested a maximum in the binding energy near the lowest coverage. The various mechanisms,
which are all intimately connected, that affect core-level shifts were discussed in terms of the Pt/Rh(111) system. It was concluded that charge transfer effects are rather weak for this system, but that all of the mechanisms contribute to the total core-level shifts.

Underpotential deposition (UPD) of one metal onto another has found application in the design of electrocatalysts, and also provides a convenient method of forming a bimetallic model catalyst. Through X-ray photoelectron spectroscopy measurements, anions were found to play a crucial role in the underpotential deposition process, which is a likely factor in the mismatch between experiment and theory. The possibility of phase transitions in the silver UPD process was also identified. The principle result from the UPD study, however, comes from the metal core-level binding energy shifts. For the case of UPD of either copper or silver, a negative shift in the core-level binding energy of the adlayer was observed. The negative shifts are the result of the sum of the various effects that influence the position of the center of the d band. It was concluded that charge transfer effects are strong for the copper and silver adlayers on rhodium, and that they dominate over the other mechanisms for these UPD systems. One of the main conclusions drawn from this work is that the determination of the origin of binding energy shifts is not a straight-forward task. Without the help of theoretical modeling, one cannot always predict the direction of the core-level shifts based on simple expectations. The shifts will depend on the relative magnitudes of the various effects. This demonstrates the need for caution and conservative assignments when interpreting or predicting core-level shifts, and also demonstrates the need for highly accurate theoretical methods.
6.2 Future Directions

Despite the knowledge gained from the studies presented here, there is still a great need for better understanding of the electronic effects as they relate to electrocatalysis. While the d band center theory provides a good starting point, it does not work universally. This just points to the fact that better theoretical descriptions of electronic structures and bonding are needed. To this end, further study of simple model catalysts is recommended.

The results of the UPD study suggest that UPD systems have a great potential for use as model catalysts, since the amount of admetal present on the surface can be controlled very well. The use of UPD would eliminate the problems encountered with other deposition techniques, as was seen for spontaneous deposition of platinum. UPD has been used to synthesize nanoparticles with monolayer coverage of a desired metal by displacement of an underpotentially-deposited monolayer of copper. A similar technique might could be used in lieu of spontaneous deposition in order to get more consistent deposition of platinum, which could ease the interpretation of binding energy data for the Pt/Rh(111) system.

An extension of the UPD work would involve the investigation of the anion effects. The keys to this are to obtain information on the specific species that adsorb and the structure of the adsorbed anions on the surface, particularly in relation to the admetal structure. For this, in situ techniques are needed. in situ STM would provide information on the structures, while in situ FTIR could be used to determine the adsorbed species. This knowledge could lead to a better understanding of the UPD process.
In this work, preliminary results for core-level binding energy shifts in vapor-deposited platinum on Rh(111) were reported. The use of a synchrotron greatly improves this experimental setup. Because of the intense photon beam, measurements can be completed in a matter of minutes, as compared to the hours required with a standard X-ray source. The rate of data collection could greatly improve the scatter of the binding energy data, since the crystal surface would remain unchanged, aside from the addition of platinum, over the course of an entire set of experiments. This would reduce the negative effects of the inconsistent crystal surfaces obtained from UHV preparation. This type of experiment could be extended to other substrates, as well as other admetals, and would provide a significant amount of data that could be used for development of theoretical models. Further investigations of the structure of platinum deposits by a technique like STM would provide valuable information for the interpretation of core-level binding energy shifts, and this type of characterization of the decorated electrode surfaces is recommended.

An alternative to decorated single crystals, intermetallic crystals provide a consistent and known structure and composition, which is very important in theoretical modeling. The only problem with this type of model electrocatalyst is that the properties cannot be varied. So, unlike for platinum deposition on rhodium, a single data point is collected. However, if several of these intermetallic crystals are investigated, a set of precise binding energy and composition/structure data would be available. Pursuit of studies involving ordered intermetallics is recommended.

In the study of Pt/Ru alloy nanoparticles, the contributing factors in the electrooxidation of methanol could not be separated. One of the main reasons for this
was that the surface composition and structure of the nanoparticles was not known to a degree of accuracy high enough to allow for further treatment of the data. If the composition of an active site could be established, and if the surface structure and composition were well-controlled, the current density could be normalized according to the probability of finding an active site on the surface. If this could be accomplished, then the bifunctional mechanism could be separated from the electronic effects for the case of methanol as well. Techniques to synthesize nanoparticles are improving, and scientists are gaining more and more control over the structure and composition of synthesized nanoparticles, so it may be feasible to synthesize such a sample using platinum and ruthenium in the near future.

In summary, much work is left to be done in the pursuit of a fundamental understanding of electronic effects in electrocatalysis. Bimetallic model catalysts provide a more simple way of examining the various effects. The results of high quality experimental work would aid in the development of more accurate theoretical models that can better account for observed experimental behaviors. Therefore, it is recommended to continue the study of core-level binding energy shifts in model systems, and to extend the model systems to a variety of metals and types.
CURRICULUM VITA

Matthew Aaron Rigsby was born September 4, 1981 in Beech Grove, Indiana to Walter E. and Phyllis B. Rigsby. He grew up in the Indianapolis area with one brother, Grayson, and graduated as valedictorian from Decatur Central High School in 2000. He attended Indiana University – Purdue University at Indianapolis (IUPUI) on a full scholarship from the University Honors Program, as well as a valedictorian scholarship. He did undergraduate research on manganese(III)-poly(pyrazolyl)borate complexes under the guidance of Prof. Franklin Schultz. He graduated magna cum laude from IUPUI in 2005 with a B.S. in chemistry and a minor in mathematics. He then began his graduate studies in analytical chemistry at the University of Illinois at Urbana-Champaign in the fall of 2005, joining Prof. Andrzej Wieckowski’s research group the following semester to study fuel cell electrocatalysis. After graduation, he will join Prof. Héctor Abreuña’s research group at Cornell University as a post-doctoral research associate.

PUBLICATIONS

1. Corcoran, C. J.; Rigsby, M. A.; Duong, H. T.; Tavasol, H.; Bagus, P. S.; Wieckowski, A. Application of XPS to study electrocatalysts for fuel cells. To be submitted.


**CONFERENCE PRESENTATIONS**


**AWARDS AND HONORS**

Algernon Gorman Award for the outstanding analytical chemistry University of Illinois literature seminar, by vote of the graduate students (2007)

Loren T. Jones Award for the graduating senior with the highest academic achievement in a B.S. degree program (2005) IUPUI

School of Science Scholars List (Highest Honors) (2003-2004) IUPUI
PROFESSIONAL MEMBERSHIPS

American Chemical Society (2005-present)  Analytical Division
                                                 East Central Illinois Local Section

Electrochemical Society (2007-present)  Central Illinois Student Chapter
     Position held: Treasurer (Student Chapter, 2008-2010)

International Society of Electrochemistry (2009-present)