USE OF A COMBINATORIAL SEARCH FOR THE DISCOVERY OF NEW FUEL CELL ANODE ELECTROCATALYSTS

A Dissertation

Presented to the Faculty of the Graduate School

of Cornell University

In Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

by Mark David Prochaska August 2007 © 2007 Mark David Prochaska

USE OF A COMBINATORIAL SEARCH FOR THE DISCOVERY OF NEW FUEL CELL ANODE ELECTROCATALYSTS

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Cornell University 2007

Polymer electrolyte fuel cells are devices that convert chemical energy to electrical energy through oxidation of a fuel (typically hydrogen, methanol, or ethanol) at the anode and reduction of oxygen at the cathode. They have the potential to be more efficient and less environmentally harmful than combustion engines and other heat transfer processes for the extraction of energy. Pt is a typical anode electrocatalyst, but it suffers from slow kinetics for methanol and ethanol oxidation and is susceptible to poisoning from impurities, even for hydrogen oxidation. Although several notable materials discoveries have improved anode electrocatalysts, the materials are far from ideal. While previous research has shown that ordered intermetallic compounds may be better electrocatalysts than those presently used, an investigation through all possible binary and ternary component electrocatalysts using traditional synthesis methods would take an inordinate amount of time.

We use a combinatorial method to more quickly search through the majority of compositions in binary and ternary phase diagrams for better fuel cell anode electrocatalysts than Pt. We deposit thin film composition spreads of up to three elements that cover up to 75% of a phase diagram. We test the compositions for electrocatalytic activity for methanol and ethanol oxidation using a fluorescence screening method and characterize the composition, surface morphology, and crystal structure of active regions.

We synthesized and tested films of Pt-Ru-X (where X = Pb, Co, Ni, Ag, V, Mo, Fe, In, and Sb), Pt-Pb-X (where X = Bi, Sn, Mo, Co, Cr, Fe, Nb, Ni, Si, Ta, and In), and Pt-Nb-X (where X = Co, In, Ni, Sb, and Fe). Of all the films tested, a Pt-Pb-Ta film deposited at 405°C has an active region for methanol oxidation with the lowest onset potential of -50 ± 25 mV vs. Ag/AgCl, bulk composition of Pt_{0.65}Pb_{0.02}Ta_{0.24}O_{0.09} (measured by WDS), and an fcc Pt structure type. Pt-Ru-Pb films deposited at ambient temperature have regions with the lowest onset potentials for ethanol oxidation: the average onset potential is -235 ± 25 mV vs. Ag/AgCl, the average bulk composition is Pt_{0.42}Ru_{0.45}Pb_{0.04}O_{0.09} (measured by WDS), and the structure type is fcc Pt.

BIOGRAPHICAL SKETCH

Mark Prochaska was born on May 2, 1973 in Alexandria, Virginia and grew up in the Northern Virginia area. He first acquired a fondness for physical science in the 8th grade at Franklin Intermediate School where he enjoyed experiments on electricity, mechanics, and light. From 1987 to 1991, he attended the Thomas Jefferson High School for Science and Technology in Alexandria, Virginia, where he benefited from exceptional educational opportunities in math and physical science, including courses in AP Chemistry, AP Physics, and a senior research project in the Optics and Modern Physics Lab.

Mark attended The College of William and Mary in Williamsburg, Virginia from August 1991 to December 1994. He acquired a B.S. in Physics and completed a senior thesis entitled "Particle Energy Transfer to Magnetic Perturbations of Toroidal Plasma Configurations" under the direction of Professor Allen Boozer. At the time, his research interests were in plasma physics theory as it pertained to fusion reactors.

Following graduation, Mark continued research in theoretical plasma physics with an internship in the Fusion Energy Division of Oak Ridge National Laboratory in Oak Ridge, TN. He was planning on continuing such research in graduate school, but he couldn't stand being cooped up in small, windowless offices with a computer any longer. Instead, he decided to pursue a career in teaching, an idea that had been brewing in his mind ever since he took classes taught by the excellent teacher Mrs. Follansbee at Thomas Jefferson High School.

Mark returned to the College of William and Mary in August 1995 to pursue an M.A.Ed. in secondary science education and be near his girlfriend Marcy Coon, who also attended William and Mary. Mark's student teaching experience in graduate school confirmed his interest and talents in education, and he received the Galfo Science Teaching Award for excellence in science education. Mark finished graduate school and his bachelorhood in the summer of 1996; Mark and Marcy were engaged that same summer and were married on December 21, 1996.

Mark began teaching physics at James River High School in Midlothian, Virginia in August 1996. He taught courses in Conceptual Physics, Honors Physics, AP Physics C, and AP Calculus BC. He developed a reputation as a difficult teacher (which he enjoyed very much), but most students appreciated his challenging courses and dry sense of humor. Although Mark enjoyed the art of teaching high school students, the interference from politicians who know nothing of education soured the experience. Sadly, Mark left teaching in June 2000.

Mark took a job as a computer programmer at the corporate headquarters of Circuit City in Richmond, Virginia in July 2000. He realized within months that having a job unrelated to science was not fulfilling for him, and he remained unsure of what to do. A wise friend asked why he was not in graduate school pursuing a Ph. D. in science, to which he replied that it was too late since he was "too old". However, Professor Morton Eckhause of the College of William and Mary Physics Department advised that it was a great idea. Although Mark and Marcy at first objected to the idea, they eventually decided to take the risk. They moved to the Ithaca, New York area in July 2002 where Mark began his pursuit of a Ph. D. in Applied and Engineering Physics at Cornell University.

In June 2003, Mark began research under the direction of Professors Frank DiSalvo and R. Bruce van Dover, developing a combinatorial method for discovering new fuel cell anode electrocatalysts. During graduate school, Mark gained experience in experimental science and, toward the end of his schooling, experience in fatherhood when his and Marcy's first child, Amy, was born on November 19, 2006.

Mark found experimental research to be fulfilling and meaningful when the necessary equipment works. However, teaching has remained his passion. Mark will

graduate from Cornell in the summer of 2007 having gained needed experience in experimental research. He will return to teaching science at Culver Academies in Culver, Indiana. "Just ask this scientician..."

-Troy McClure

ACKNOWLEDGMENTS

Many people and organizations have made this dissertation possible. Special thanks go to my advisory committee, Professors Frank DiSalvo, R. Bruce van Dover, and Héctor Abruña. Their areas of expertise complemented each other very nicely for the development of this dissertation: Frank in solid state chemistry, Bruce in thin film materials and combinatorics, and Professor Abruña in electrochemistry. They are passionate about research and their many years of experience have helped me understand the nature of scientific research more fully.

Jing Jin deserves much credit, having performed all the fluorescence screenings and providing me with images, graphs of fluorescence intensities, and onset potential determinations. Professor Dominic Rochefort was instrumental in developing the fluorescence screening to use early in the project.

The Cornell Center for Materials Research provided many of the instruments I used for analysis, including GADDS, SEM, RBS, and electron microprobe. Maura Weathers was an excellent teacher for the use of GADDS and X-ray diffraction. John Hunt provided training on SEM and electron microprobe and provided expert advice on such analyses. Stephen Menasian performed RBS runs and assisted me with the subsequent analysis of data.

Several undergraduate students helped collect and analyze data. David "Friends Forever" Kim was an excellent researcher, synthesizing and analyzing several Pt-Bi-Pb and Pt-Ru-Pb films. Alex Tumminelli made several Pt-Ru-Pb composition spreads and provided helpful analysis. Xinning Ho was very helpful in perfecting the use of GADDS in my analysis of films.

The direction of research was guided by enlightening conversations with other researchers. Jing Jin, Maxim Kostylev, and John Gregoire, members of the

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combinatorics group in the Cornell Fuel Cell Institute, were all very helpful in providing insight into analyses and direction for new experiments. Paul Mutolo, who single-handedly keeps the entire Cornell Fuel Cell Institute organized, put together many symposia to promote discussions about fuel cell research and did an excellent job of translating German research articles. Michael McGuire offered helpful advice on XRD and revealed numerous secrets of presenting such spectra.

Several people helped maintain the beast that is our sputtering chamber, "Gilgamesh", and fixed it when I just couldn't take it anymore. Special thanks to Maxim Kostylev, David Kim, and Jon Petrie for their help in fixing vacuum leaks, broken hoists, broken cryopumps, etc., etc., etc.

The DiSalvo group and members of the Cornell Fuel Cell Institute provided feedback on many oral presentations during our beloved group meetings. The van Dover group answered many of the day-to-day questions about equipment and materials. Sara Barron, Steve Kirby, Jon Petrie, Karen Downey, Matt Drudge, and Maxim Kostylev provided enlightening conversations about research and other interesting topics.

The Department of Energy supplied funds for research through grant number DE-FG02-03ER46072. Other funding was supplied by the National Science Foundation.

Thanks also to Dr. Morton Eckhause of the College of William and Mary, who convinced me that I wasn't too old to go back to graduate school.

Finally, I thank my wife Marcy for providing moral support during the 5 years we spent at Cornell. She has sacrificed much to make this possible. Thank you also to my daughter Amy, who made sure I didn't spend too much time writing during the last months of graduate school.

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CHAPTER 1 AN INTRODUCTION TO FUEL CELLS AND ANODE ELECTROCATALYSTS

Approximately 85% of the United States' current energy needs are met through the combustion of fossil fuels¹. However, experts project that easily recoverable oil deposits, such as those in Saudi Arabia, will reach their maximum output in the next 10 to 50 years while the world's demand for energy will continue to increase. While there are considerable coal resources, especially in the United States, which could meet energy needs for two centuries or more, coal produces more CO₂ per unit of energy output than any other fossil fuel. Furthermore, coal contains many toxic metals that combustion releases into the atmosphere. The correlation between atmospheric CO₂ concentrations and global mean temperature suggest that carbon emissions from fossil fuel combustion may be responsible for increases in global mean temperature^{2, 3}. The sustainability of fossil fuels is therefore uncertain and has the potential to cause severe economic and environmental hardship. This situation makes it urgent to explore alternative fuels and more efficient methods of extracting energy.

Combustion engines and large-scale power plants rely on heat flow from a high-temperature to a low-temperature reservoir. The efficiency of energy conversion from heat to other forms of energy (mechanical or electrical) is limited by the Second Law of Thermodynamics. Only a fraction of the heat from the high-temperature reservoir can be converted to useful forms of energy, while the rest must be dispensed to the low-temperature reservoir. The maximum possible efficiency is determined by the temperature of the two reservoirs. A modern automobile engine has an efficiency of about 25%, while an electric generator plant typically has an efficiency of 35%.

Fuel cells convert chemical energy to electrical energy through an oxidationreduction reaction, much like a battery. However, unlike a battery, the reactants are supplied continuously from outside the cell instead of being depleted. This method of transforming energy does not rely on the transfer of heat from a high-temperature to a low-temperature reservoir and in principle can approach 100% efficiency. However, for fuel cells to be commercially feasible a number of technical and economic barriers must be overcome.

Overview of Fuel Cells

Incentives for Use

Fuel cells have the potential to solve the problems of energy efficiency and environmental harm associated with processes that use fossil fuels. As noted above, their efficiency is not limited by the Second Law of Thermodynamics. Currently, some of the most efficient fuel cells are capable of operating at over 60% efficiency^{4, 5}, much higher than the approximately 20% to 25% efficiency of an internal combustion engine. The main limitations in approaching 100% efficient fuel cells are found in the catalysts used in the electrodes. This is especially true for fuel cells that operate at or near room temperature. Fuel cells can operate with alternative fuels such as hydrogen or ethanol, thus reducing the demand for fossil fuels and reducing pollution⁵. Fuel cells are viewed as an integral part of a "hydrogen economy" in which hydrogen is an efficient and environmentally harmless energy carrier⁶.

Fuel cells have potential use in a wide range of devices. These include transportation vehicles, remote devices requiring their own power source, local power plants for buildings, and portable electronics. Fuel cells can potentially bring the benefits of energy efficiency to each of these devices with minimal environmental impact. However, several challenges remain to such realizations, as we discuss below.

Construction and Operation

Figure 1.1 shows a schematic diagram of a fuel cell that uses hydrogen. A proton exchange membrane (a polymer electrolyte that may be thought of as a thin sponge for water and acids) is sandwiched between two electrodes, the anode and the cathode. The proton exchange membrane is capable of conducting H⁺ ions (but not electrons) between the electrodes. Both electrodes typically contain Pt electrocatalysts. In fact, Sir William Grove used Pt at both electrodes when he invented the hydrogen fuel cell in 1839⁷. Catalysts are generally used to increase chemical reaction rates, often by many orders of magnitude. In fuel cells, Pt electrocatalysts are essential to produce useable power densities, which are directly proportional to the reaction rate. However, Pt has many problems when used as an electrocatalyst, as we discuss later. Various systems external to the fuel cell supply hydrogen to the anode and oxygen (or air) to the cathode.

The anode electrocatalyst oxidizes hydrogen and the cathode electrocatalyst reduces oxygen. H^+ ions from the anode migrate across the membrane to the cathode where they are consumed during the reduction of oxygen to produce water. Electrons from hydrogen oxidation at the anode flow through the external circuit to the cathode under the influence of the potential difference between the electrodes (determined by the difference in the reduction potentials between the anode and cathode half-reactions).

Other types of fuel cells exist with different electrolytes and electrocatalysts^{4, 6}. However, the operation of each is similar to that described above, with oxidation of a fuel at the anode, reduction of oxygen at the cathode, and transfer of ions between the electrodes across an ion-conducting (but electrically insulating) membrane. The fuel cell of Figure 1.1 is called a polymer electrolyte membrane fuel cell (PEMFC). The membrane consists of a polymer, typically Nafion®, that conducts H^+ ions when humidified. Typical electrocatalysts are Pt or other Pt-based alloys such as Pt_xRu_{1-x} . PEMFCs operate at temperatures from 0°C to 80°C on fuels such as hydrogen and methanol (called direct methanol fuel cells), and are potential power sources for portable electronics and transportation vehicles where engineers think that low temperature operation is necessary.



Figure 1.1 Schematic diagram of a hydrogen fuel cell.

Alkaline fuel cells (AFC) operate at temperatures close to those of PEMFCs. The electrolyte usually consists of KOH, NaOH, or other basic solutions⁸ that transport OH^- ions from the cathode to the anode. Typical electrocatalysts are Ni compounds, Ag, or other noble metals⁹. AFCs are also potential power sources for transportation vehicles¹⁰.

Other fuel cells operate at higher temperatures and are therefore more useful for stationary applications such as backup power supplies for buildings. Phosphoric acid fuel cells have an electrolyte solution of H_3PO_4 that conducts H^+ ions. The

electrocatalyst is Pt and the operating temperature is around 200°C. Molten carbonate fuel cells have Ni electrocatalysts, a Li_2CO_3/K_2CO_3 electrolyte that conducts $CO_3^{2^-}$ ions, and an operating temperature around 650°C. Solid oxide fuel cells, operating at temperatures between 700°C and 1000°C, use solid Zr-Y oxides as membranes that conduct O^{2^-} ions. The electrocatalysts are typically oxides of Co-Zr or Ni-Zr.

Historical Uses of Fuel Cells

The original fuel cell, developed by Sir William Grove in 1839, operated at room temperature and had Pt electrocatalysts, used hydrogen fuel, and contained a sulfuric acid solution as electrolyte⁷. A few scientists attempted to use the invention for stationary power plants later that century. In the late 1800's Mond and Langer¹¹ attempted to increase the output of fuel cells for industrial applications by using a porous matrix to hold the electrolyte and electrocatalysts in powdered form (Pt black). However, they faced problems with electrocatalyst poisoning from impurities in their hydrogen fuel source (a common problem in PEMFCs even today), derived from coal and coke. In 1896, W.W. Jacques constructed fuel cells that used carbon for fuel, Pt as an electrocatalyst, and molten KOH as an electrolyte⁸. His device operated at higher temperatures (400°C to 500°C) than Grove's and produced a maximum power output of 1.5 kW, but the electrolyte became contaminated with carbonate (a common problem with AFCs). In the early 1900's, E. Baur tested several direct coal fuel cells with molten salts (carbonates, silicates, and borates) and molten silver electrolytes, carbon anodes, and silver cathodes^{12, 13}. He also showed that oxide mixtures at cathodes, especially iron, enhanced activity. However, the temperature of operation enabled only partial oxidation of carbon to carbon monoxide instead of full oxidation to carbon dioxide.

In the mid-20th century, new fuel cell designs became the main power sources of spacecraft. W.T. Grubb invented a fuel cell with a polymer electrolyte in 1955^{14, 15} and General Electric further developed the technology for the U.S. Gemini space program. In 1933, Sir Francis Bacon began work on fuel cells that used an alkaline electrolyte, nickel-oxide electrodes, and hydrogen fuel.¹⁶ Pratt and Whitney obtained a license for the technology in 1959 and used it in the U.S. Apollo and Space Shuttle programs.

PEMFCs that use methanol fuel are currently used as prototype power supplies in several portable devices. These include laptop computers, portable digital assistants, and cell phones^{4, 17}. They have also been tested as power sources in military applications^{5, 17}. In each portable device, the fuel cell replaces rechargeable batteries and eliminates the need for recharging. Instead, a methanol fuel cartridge provides immediate power.

Fuel cells have been used when commercial electrical supplies are interrupted or not available in the immediate area. These include remote applications such as meteorological stations and TV transmitters¹⁰. They have been used as backup power supplies for buildings⁴ and even for large-scale commercial electric generation¹⁸⁻²⁰.

Fuel cells such as PEMFCs and AFCs are currently in exploratory development for use in transportation vehicles. Some prototypes have already been developed as power sources for commuter buses and automobiles^{10, 21-23}. Such fuel cells have the potential to increase vehicle efficiency and reduce harmful emissions, but many obstacles remain before commercialization can occur.

Fuels for PEMFCs

The research described in this thesis will pertain mainly to polymer electrolyte fuel cells (PEMFCs) operating at temperatures between 0°C and 80°C in portable and transportation applications. PEMFCs can operate on several types of fuels.

Hydrogen Fuel

Hydrogen is a lightweight fuel and has been used in the fuel cells of space vehicles. Although it is featured as a possible fuel for PEMFCs in transportation vehicles, issues concerning storage remain and offer research opportunities^{6, 24, 25}. To circumvent the storage problem, a reformer is sometimes suggested for use in conjunction with the fuel cell²⁶⁻²⁹. A reformer converts a liquid fuel that is easy to store (such as ethanol or gasoline) into hydrogen gas, but the conversion must take place without excessive production of impurities such as CO that can impede fuel cell performance.

In a fuel cell that operates with hydrogen fuel, the following reactions take place at the anode and cathode:

anode:
$$2 \text{ H}_2 \rightarrow 4 \text{ H}^+ + 4 \text{ e}^-$$

cathode: $O_2 + 4 \text{ H}^+ + 4 \text{ e}^- \rightarrow 2 \text{ H}_2 O$

Under standard conditions, the open circuit potential of a hydrogen fuel cell is 1.23 V. The by-product of the fuel cell is water, motivating its use in transportation vehicles since it is deemed environmentally "harmless" if a carbon-neutral method of generating it can be developed. The standard free energy of the reaction is -119 MJ/kg of H₂.

Methanol Fuel

As noted above, methanol is popular in fuel cells for portable devices because it is a liquid and therefore easy to distribute. However, methanol is toxic and therefore requires special packaging as a fuel cartridge. Some see methanol as a possible fuel in transportation and larger applications to ease a transition to a "hydrogen economy"⁶.

A direct methanol fuel cell operates with the following reactions at the anode and cathode:

anode:
$$2 H_2O + 2 CH_3OH \rightarrow 2 CO_2 + 12 H^+ + 12 e^-$$

cathode: $3 O_2 + 12 H^+ + 12 e^- \rightarrow 6 H_2O$

Unlike a fuel cell operating with hydrogen, the direct methanol fuel cell requires water to take part in the anode reaction in addition to fuel. Also, the fuel cell produces carbon dioxide as a by-product, a potential greenhouse gas. However, if high efficiency direct fuel cells can be developed, less CO_2 per unit of energy would be produced than by any other method of using carbon-based fuels. Under standard conditions, the open circuit potential of the direct methanol fuel cell is 1.18 V. The standard free energy of the reaction is -22 MJ/kg of methanol, less than one-fifth that of the hydrogen reaction.

Ethanol Fuel

Ethanol is considered a possible fuel for both portable and transportation applications. It can be made from $biomass^{30}$, and production of ethanol from trees and grasses may be especially efficient³¹. The output of CO₂ from applications using ethanol fuel is less than that of fossil fuel combustion³¹ since the CO₂ would be consumed in growing more biomass (carbon neutrality). Ethanol may therefore be less harmful to the environment than fossil fuels.

Currently, a direct ethanol fuel cell operating at room temperature is not possible because there is no anode electrocatalyst that will oxidize a C-C bond completely to CO_2 . Studies show that the final product of ethanol oxidation over Pt and Pt_xRu_{1-x} alloys is predominantly acetic acid and ethanal, with CO_2 as only a minor product³²⁻³⁴. If an electrocatalyst that could break C-C bonds efficiently at room temperature were invented, the following reactions would be exploited:

anode:
$$3 H_2O + C_2H_5OH \rightarrow 2 CO_2 + 12 H^+ + 12 e^-$$

cathode: $3 O_2 + 12 H^+ + 12 e^- \rightarrow 6 H_2O$

The open circuit potential of a direct ethanol fuel cell is 1.12 V, and the standard free energy of the reaction is -29 MJ/kg of ethanol, comparable to that of the methanol reaction. Like the direct methanol fuel cell, water is required for the anode reaction in addition to fuel.

Other possible fuels include formic acid, hydrazine, and ammonia^{4, 35, 36}. In this thesis we will focus on the use of methanol and ethanol.

PEMFC Issues

Despite the advantages of PEMFCs over combustion engines and other heat transfer processes, they have yet to enter large-scale commercial markets due to poor performance of the electrocatalysts and membrane (low output potentials and poor membrane durability). Much research is geared toward solving issues associated with the membrane. Nafion is susceptible to degradation³⁷⁻³⁹, limiting the lifetime of fuel cells. In direct methanol fuel cells, methanol tends to penetrate the membrane due to its solubility in water and reacts with oxygen directly at the cathode, reducing power^{40, 41}. There are issues related to water management in the membrane, which must expel excess water produced at the cathode and maintain water at the anode in direct

methanol fuel cells⁴²⁻⁴⁵. The cost of membrane materials also prevents large-scale use of PEMFCs.

In this thesis, we will focus on issues related to the electrocatalysts. The history of fuel cell use, described above, shows that Pt has been the most common electrocatalyst for fuel cells, especially for PEMFCs. This situation has not changed significantly since 1839. But Pt has numerous disadvantages, the most important of which are cost and poor kinetics. Figure 1.2 shows a theoretical graph of current density vs. potentials of the anode and cathode in a hydrogen fuel cell. At zero current and under standard conditions, the potential difference between the anode and cathode is 1.2 V, as stated above. If the anode and cathode electrocatalysts are ideal, the potential difference between them is 1.2 V regardless of the current density, as shown by the dashed lines in Figure 1.2. However, at high current densities real electrocatalysts such as Pt cannot oxidize hydrogen (unless it is of high purity) or reduce oxygen at sufficient rates to maintain a potential difference of 1.2 V. The potential of the anode shifts higher while the potential of the cathode shifts lower in order to drive the oxidation and reduction reactions at higher rates and supply the necessary current. The shift in potentials, called overpotential, is illustrated by the solid lines in Figure 1.2. The result of overpotentials is a lower potential difference across the electrodes and lower efficiency of the fuel cell.

Many oxidation and reduction reactions have severe overpotentials on Pt electrocatalysts. Perhaps most serious is the oxygen reduction overpotential of 300 to 400 mV ⁶, which diminishes the potential difference across the electrodes in a hydrogen fuel cell by almost one-third. Although Pt is a poor cathode electrocatalyst, it is the best available. The overpotential of methanol oxidation on Pt is approximately 350 mV at reasonable current densities⁴⁶; when combined with the oxygen reduction overpotential, direct methanol fuel cells become very inefficient. In addition, Pt

suffers from poisoning from various impurities. CO, an intermediate in methanol oxidation^{47, 48} and a common impurity in hydrogen gas prepared by steam reforming of methane, adheres to Pt and blocks electrocatalytic sites⁴⁹. CO concentrations as low as 10 parts-per-million (ppm) can degrade fuel cell performance. Sulfur at 1 part-perbillion (ppb) will likewise poison Pt catalysts, and Pt alloy electrocatalysts are also highly sensitive to sulfur poisoning. Poisoning results in the appearance of a significant overpotential at the electrode. However, several intermetallic compounds, described below, are much less sensitive to sulfur and apparently completely insensitive to CO poisoning⁵⁰⁻⁵².



Figure 1.2 Theoretical graphs of the current density vs. potential for a hydrogen fuel cell. The dashed lines show the equilibrium potentials of the anode (on the left) and cathode (on the right) for ideal electrocatalysts. The solid lines show the potentials of the anode and cathode for real (non-ideal) electrocatalysts. The difference between the ideal and real potential at a given current is called the overpotential. The potential difference between the electrodes at a given current is determined by the two overpotential curves.

Pt is also one of the more expensive electrocatalysts available. The cost is considered one of the major factors in preventing PEMFCs becoming economically feasible⁵.

It should be noted that most of the issues described above are related to materials; improved engineering will not solve the problems with fuel cells. In this thesis, we will focus on finding new materials to replace Pt anode electrocatalysts. We seek materials that oxidize methanol or ethanol with low overpotentials, resist poisoning, and cost less than pure Pt.

Attempted Solutions to the Anode Electrocatalyst Problem

Pt-Ru Alloys

Pt-Ru alloys have been investigated extensively as anode electrocatalysts for methanol oxidation⁵³⁻⁶³ and are frequently used as a standard of comparison for novel electrocatalysts. Gasteiger *et. al.* measured the electrocatalytic activity of alloys of Pt_xRu_{1-x}, annealed and sputter-cleaned in ultra-high vacuum, for methanol oxidation^{56, 64}. They found the highest electrocatalytic enhancement compared to pure Pt for alloys with x = 0.9. In an electrolyte containing 5.0 mM methanol at 25°C, the oxidation current was 12 times that of Pt at 0.5 V vs. RHE; in an electrolyte with 0.5 M methanol, the current was greater by a factor of 30. In an investigation of the oxidation current at different temperatures, Gasteiger *et. al.* found that the optimal atomic fraction of Ru in the Pt_xRu_{1-x} electrocatalyst shifted to x = 0.7 with increasing temperatures up to 60°C ⁵⁵. They also found evidence that the electrocatalyst works through a bifunctional mechanism in which methanol adsorbs to Pt sites while water adsorbs to Ru sites; the two species interact to fully oxidize methanol to CO₂. More information concerning Pt-Ru methanol oxidation electrocatalysts and the bifunctional mechanism can be found in Chapters 5 and 6.

Alloys of Pt_xRu_{1-x} may also serve as better hydrogen oxidation electrocatalysts than Pt because of their greater resistance to CO poisoning. Oetjen *et. al.* tested PEMFCs operating with hydrogen fuel and anode electrocatalysts of Pt, $Pt_{0.7}Ru_{0.3}$, and $Pt_{0.5}Ru_{0.5}^{49}$. They added CO impurities to the fuel stream at concentrations of 25 to 250 ppm. The fuel cells with alloy electrocatalysts showed increased CO tolerance relative to Pt; $Pt_{0.5}Ru_{0.5}$ showed the greatest tolerance, with four times the power density of Pt. In fact, the power density of the fuel cell with $Pt_{0.5}Ru_{0.5}$ remained unchanged, for current densities up to 0.4 A/cm², with CO added to the fuel stream at concentrations of 100 ppm.

Other Alloys

A few researchers have studied compositions of Pt and Sn as electrocatalysts for several fuels. Sobkowski *et. al.* studied oxidation of methanol over Sn ions adsorbed on Pt surfaces⁶⁵. They found enhanced oxidation currents at potentials between 0.4 and 0.8 V. Frelink *et. al.* also found small increases in methanol oxidation activity with the addition of Sn to the surface of Pt⁶⁶, with an optimum surface coverage of 10%. Colmati *et. al.* prepared Pt-Sn alloys as ethanol oxidation electrocatalysts by reducing Pt and Sn precursors with formic acid⁶⁷. Linear sweep voltammetry showed improved ethanol oxidation activity over Pt for alloys of Pt₃Sn and Pt₂Sn.

Ley *et. al.* tested methanol oxidation on several arc-melted Pt-Ru-Os alloy electrocatalysts⁴⁸. The ternary alloys had greater CO-adsorption tolerance relative to Pt under a flow of 1% CO/99% Ar. An electrocatalyst of composition $Pt_{0.65}Ru_{0.25}Os_{0.10}$ oxidized methanol at a higher current density of 340 mA/cm² at 0.4 V vs. RHE than $Pt_{0.5}Ru_{0.5}$ with a current density of 240 mA/cm².

Papageorgopoulos *et. al.* studied the CO tolerance of alloys of Pt-X and Pt-Ru-X, where X is either Mo, Nb, or Ta⁶⁸. Each of the binary electrocatalysts partially oxidized CO at potentials close to 0 V vs. RHE (lower than that of Pt), with Pt₄Mo doing so at the lowest potential. The Pt₄Mo electrocatalyst also showed more tolerance to CO than Pt in a fuel cell operating under a stream of hydrogen and up to 225 ppm CO. None of the ternary electrocatalysts showed changes in stripping voltammetry of CO compared to Pt. Furthermore, the CO tolerance of each electrocatalyst was worse than that of Pt_{0.5}Ru_{0.5} in a fuel cell operating under a fuel stream of hydrogen and up to 225 ppm CO. Of the alloys tested, only Pt₉Ru₉Mo₂ showed a higher current density than Pt_{0.5}Ru_{0.5} under a hydrogen/CO fuel stream with up to 250 ppm CO.

Liang *et. al.* tested CO oxidation of nanocomposites of Pt, Ru, and Ni⁶⁹. A ternary nanocomposite, with equal mole fractions of Pt, Ru, and Ni, had a peak CO-oxidation current at a potential 200 mV lower than that of a similarly prepared $Pt_{0.5}Ru_{0.5}$ nanocomposite. The ternary catalysts also had a higher cell voltage for current densities up to 1.5 A/cm² in a fuel cell operating under a fuel stream of hydrogen and 100 ppm CO.

Ordered Intermetallic Compounds

An ordered intermetallic compound differs from an alloy (solid solution) in that each atom has a specific site in the unit cell that is typically 100% occupied. In contrast, atoms in alloys can substitute for each other randomly at occupied sites without a substantial change in energy. In an ideal solid solution the probability of site occupation is determined only by the alloy composition. For example, in Pt_{1-x}Ru_x, the probability that a Ru atom is found at the occupied positions is 100x %. In recent years, the DiSalvo and Abruña research groups at Cornell University have made important discoveries concerning the electrocatalytic activity of several intermetallic compounds for the oxidation of formic acid, methanol, and ethanol. The studies grew out of investigations of formic acid oxidation on Pt surfaces modified by Bi atoms^{70,} ⁷¹

Their first tests of an intermetallic compound electrocatalyst, with PtBi for formic acid oxidation⁵⁰, showed a current density 40 times that of pure Pt and an onset potential approximately 300 mV lower than that of Pt according to cyclic voltammetry. Furthermore, PtBi showed no poisoning effects in a CO saturated solution after 0.5 hours.

A subsequent study investigated the oxidation of formic acid, methanol, and ethanol over several other intermetallic compounds, including PtBi, PtPb, PtBi₂, PtIn, PtIn₂, Pt₃In₇, PtSn₂, PtSn₄, PtSb, PdBi, and PdSb⁵¹. Of these compounds, PtPb showed the greatest activity toward methanol and ethanol oxidation. For methanol oxidation, the onset potential was 100 mV lower than that of Pt and the peak current density was nearly 40 times higher than that of Pt. For ethanol oxidation, the onset potential was 240 mV lower than that of Pt and the peak current density was over 20 times higher than that of Pt. Other notable electrocatalysts for methanol oxidation were PtIn and PtSn, both of which had lower onset potentials than Pt. PtIn had a peak current density for methanol oxidation that was over 5 times that of Pt. For ethanol oxidation, PtBi and PtIn also had higher peak current densities than Pt. The results of these studies and subsequent investigations are discussed further in Chapter 4.

The discovery of improved electrocatalytic activity for ordered intermetallic compounds opens a wide range of materials that may be electrocatalytically active in addition to alloys. If we investigate combinations of suitable elements (non-radioactive metals and solid non-metals), there are over 1000 possible binary phase diagrams and over 20,000 ternary phase diagrams to explore. Furthermore, each of these may include several different thermodynamically stable compounds (different

compositions and structures). Finally, synthesis conditions may allow access to metastable phases. Clearly, if we are to search for fuel cell anode electrocatalysts to replace Pt, it will take decades to synthesize and test such combinations using conventional one-at-a-time methods. Fortunately, recent advances in combinatorial chemistry can make such a search much more efficient. The exploitation of combinatorial methods to search for new electrocatalysts is the main focus of this dissertation.

Combinatorial Chemistry and the Search for New Anode Electrocatalysts Previous Synthesis Methods of Combinatorial Chemistry

Combinatorial chemistry uses methods that allow researchers to synthesize libraries of materials with incremental variations in some parameter (usually composition) and test them for desired properties. The methods are designed to be completed more quickly than traditional methods of synthesis so as to sample as many materials as possible in a reasonable amount of time.

A common combinatorial method to search for new pharmaceuticals and investigate biological materials uses a pool and split method^{72, 73}. A set of *n* different chemical components is combined into a common pool. This pool is then split into *n* samples containing all *n* chemical components. Each of the *n* samples are then mixed with one of another set of *n* chemical components, and part of each sample is pooled together to produce *n* samples containing n^2 chemical component combinations. The experimenters repeat the "rounds" of splitting and pooling for however many sets are needed. Each round of *n* samples is screened for the desired property to determine which combination of chemical components is optimal.

More recently, researchers have modified combinatorial methods to synthesize libraries of solid state materials. An example method is discrete combinatorial
synthesis in which arrays of isolated materials are synthesized on a substrate. This can be done by depositing different materials with physical vapor deposition on a substrate covered by a series of masks. Xiang *et. al.* have demonstrated this method on combinations of BaCO₃, Bi₂O₃, CaO, CuO, PbO, SrCO₃, and Y₂O₃ to find expected superconducting materials⁷⁴. Danielson *et. al.* and Wang *et. al.* also used this method to search through libraries of photoluminescent materials^{75, 76}.

Another method of discrete combinatorial synthesis is the deposition of isolated mixtures of inorganic salt solutions, with metals combined in pre-determined ratios, onto a substrate. The salts are reduced to metals and dried for testing. This method has been used to investigate oxygen reduction and water oxidation electrocatalysts⁷⁷ and methanol oxidation electrocatalysts⁷⁸. The method can be automated with the use of a computer-controlled inkjet printer that deposits the precursor salts. Inkjet printing of precursors has been used to investigate luminescent materials⁷⁹ and ceramics⁸⁰.

Jayaraman *et. al.* have created discrete libraries of materials through electrochemical deposition onto patterned substrates⁸¹⁻⁸³. They injected metal salts into a sol-gel and allowed the salts to diffuse for a time to create a gradient in composition. The salts were then electrochemically reduced onto the patterned substrate to create a library of isolated compositions. They tested libraries of binary and ternary materials for hydrogen oxidation fuel cell electrocatalysts.

Pool and split and discrete combinatorial syntheses leave gaps of untested materials from phase diagrams. A thin film composition spread technique is less likely to have such gaps in composition. A popular method for producing such films involves moving masks across a substrate during physical vapor deposition. Chang *et. al.* used this method to deposit thin film libraries of dielectric materials by pulsed laser deposition^{84, 85}. They moved a mask across a substrate during deposition to produce

layers of different materials with thickness gradients across the substrate. Subsequent annealing of the substrate mixed the layers and produced thin films whose compositions vary continuously across the substrate.

Composition spreads can also be produced without annealing. Takahashi *et. al.* used several specially designed masks to deposit a series of materials by pulsed laser deposition⁸⁶. They deposited each component material in sequence and repeatedly, nanometers at a time, to produce films with sufficient vertical mixing between materials. A computer determined the mask shape and time of deposition to ensure continuous variations in composition across the substrate. Takahashi *et. al.* tested the libraries for photoluminescent properties. This method has also been used to investigate bandgaps of materials⁸⁷ and gate dielectrics⁸⁸.

Van Dover *et. al.* used a more elegant method of creating thin film composition spreads⁸⁹, without the use of masks or computer-assisted designs, to investigate dielectric materials. The method is based on work by Hanak⁹⁰. They deposited films on substrates using off-axis sputtering from three magnetron sputter guns, each positioned at different edges of the substrate. Since each gun deposits material on the substrate at decreasing rates with distance from the gun, simultaneous deposition produces a thin film whose composition varies continuously with position on the substrate.

Applications of Combinatorial Chemistry to Anode Electrocatalyst Issues

As noted above, combinatorial methods can make the search for new fuel cell electrocatalysts more efficient. Researchers have only begun applying such methods to finding new PEMFC cathode electrocatalysts^{77, 91-96}, while anode combinatorial research began over a decade ago.

Many have demonstrated combinatorial methods for the production of libraries of Pt and Pt-Ru alloy electrocatalysts. Guerin *et. al.* investigated CO tolerance, oxygen reduction, and methanol oxidation on libraries of electrocatalysts with discrete variations in Pt loading⁹¹. As noted above, Jayaraman *et. al.* created arrays of Pt_xRu_{1-x} alloys with discrete variations in x and tested them for hydrogen oxidation and CO poisoning⁸². Cooper *et. al.* demonstrated the deposition of continuous composition spreads of Pt-Ru alloys using masks and physical vapor deposition⁹⁷.

Combinatorial methods have also been applied to searches for new anode electrocatalysts. Reddington *et. al.* used inkjet printing of precursor salts to produce discrete variations in ternary and quaternary compositions of Pt, Ru, Os, and Ir⁹⁸. They tested the libraries for methanol oxidation and found an optimal composition of $Pt_{0.44}Ru_{0.41}Os_{0.10}Ir_{0.05}$. Jayaraman *et. al.* expanded their combinatorial method, noted above, to studies of hydrogen oxidation on discrete variations in compositions of $Pt_xRu_yMo_{1-x-y}^{81}$. They found optimal electrocatalysts for y = 0.06 and 0.74 < x < 0.84. These experimental designs are discussed in more detail in Chapter 2.

Other combinatorial experiments were performed by Gruber *et. al.*, who used discrete variations in compositions of Pt_xSn_{1-x} to investigate methanol oxidation electrocatalysts⁷⁸. They found optimum compositions for 0.7 < x < 1. Strasser *et. al.* deposited ternary thin film composition spreads of Pt-Ru-Co, Pt-Ru-Ni, Pt-Ru-W, Pt-Co-Ni, Pt-Co-W, and Pt-Ni-W⁹⁹. They used a system of masks and repeated sequential deposition of elements to produce such films. They found the best activity for methanol oxidation on a composition of PtRuCo₃. Whitacre *et. al.* used a method similar to that of van Dover *et. al.* to co-deposit films of Ni, Zr, Pt, and Ru compositions onto an array of 64 isolated electrodes¹⁰⁰. They found that the composition Ni_{0.31}Zr_{0.13}Pt_{0.33}Ru_{0.23} had electrocatalytic activity for methanol oxidation

produces films by a composition spread technique, the fact that the testing was done with individual electrodes only allows testing of average compositions of each electrode.

For the combinatorial method to be efficient, the synthesis must be followed by an efficient screening method to search for desired properties. While the methods to do this depend somewhat on the property being exploited, optimal methods usually involve some sort of optical readout that allows one to view the entire library at once.

A New Combinatorial Method for Finding Anode Electrocatalysts

We proposed to search for new anode fuel cell electrocatalysts for methanol and ethanol oxidation through the use of combinatorial chemistry. However, unlike the methods described above, we produce and test thin film composition spreads of up to three elements using the method of van Dover *et. al.* due to its simplicity; no computer systems are required to produce the films and the times of deposition are relatively short (anywhere from 3 to 15 minutes). Furthermore, annealing the films is possible but not necessary. We use optically based electrocatalytic evaluation methods based on those of Reddington *et. al.* and Jayaraman *et. al.* that are relatively quick (around 15 minutes) so as to test as many compositions as possible in a short period of time. We can also evaluate the composition, surface morphology, and crystal structure of electrocatalytically active regions of each film.

Our combinatorial methods are described in detail in Chapter 2, followed by an evaluation of the methods on a Pt-Bi-Pb thin film composition spread in Chapter 3. Chapters 4 and 5 describe detailed analyses of Pt-Bi-Pb and Pt-Ru-Pb thin film composition spreads for the oxidation of methanol and ethanol. Chapters 6 through 8 describe electrochemical screenings of Pt-Ru-X, Pt-Pb-X, and Pt-Nb-X thin film

composition spreads (where X is a third element) for methanol and ethanol oxidation as well as characterization of active regions.

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CHAPTER 2 EXPERIMENTAL DESIGN OF A COMBINATORIAL SEARCH

An effective combinatorial method for finding new fuel cell electrocatalysts should meet three criteria. First, the method of synthesis should produce a wide range of compositions in a single sample. Second, the synthesis of each sample should take place in a reasonable amount of time so that one can investigate a large number of materials systems. Third, there must be a quick evaluation method to screen the compositions and compare their electrocatalytic abilities. Our method meets all of these criteria: we use physical vapor deposition to synthesize thin films of continuous composition spreads of two or three elements in a matter of hours, and we use a fluorescence electrochemical screening method to find the most effective compositions for the oxidation of a few simple fuels.

Synthesis Background

Magnetron Sputtering

Physical vapor deposition is a process by which thin films are synthesized using physical processes (such as evaporation or sputtering) as opposed to chemical processes such as chemical vapor deposition (CVD). In our combinatorial method, we deposit thin films using magnetron sputter guns. Figure 2.1 shows the cross-section of a magnetron sputter gun.

The sputter gun consists of a cathode that is in electrical and thermal contact with the material to be deposited, called the target. In close proximity to the target face (1/16 to 1/8 inches away) but electrically isolated from it is a ground shield. A ring magnet and button magnet are located behind the cathode and produce magnetic field lines that arch over the surface of the target. Along with the magnets are spaces for

cooling water to flow to prevent the target from overheating and melting. The cooling lines are sealed with o-rings so as to prevent leaking outside the sputter gun.



Figure 2.1 Cross section of a magnetron sputter gun.

Magnetron sputter guns operate inside a vacuum chamber, typically with base pressures below 10^{-5} Torr. Deposition requires introducing a sputtering gas into the chamber at pressures on the order of 1 to 10^2 mTorr, depending on the desired deposition rates.

To initiate sputtering, a power supply places a potential difference, on the order of 10^2 volts, between the cathode and the ground shield. The target is supplied with a negative potential, and the resulting electric field ionizes some of the sputtering gas atoms to a positive charge and accelerates them toward the target. The resulting collisions between sputtering gas ions and the target surface ejects atoms as well as secondary electrons from the target. These secondary electrons then proceed to ionize more sputtering gas ions and the process repeats to produce a sustained plasma, with

atoms continuously ejected from the target for deposition on a nearby substrate. The magnetic field lines arching over the face of the target serve to trap secondary electrons close to the target for greater sputtering efficiency.

The sputtering yield is the number of atoms ejected from the target per unit area per sputtering gas ion. In general, a higher sputtering yield produces a higher deposition rate. The sputtering yield is directly related to the sputter gun current (the charge per unit time carried by secondary electrons from the cathode to the ground shield). The user can manipulate the potential difference between the cathode and ground shield with a power supply, thereby changing the power and current. Power supplies typically have controls that maintain a constant power, current, or voltage.

The type of sputtering gas influences the sputtering yield. Possible sputtering gasses include He, Ne, Ar, Kr, or Xe, with Ar being a typical choice because of its relatively low cost and easy availability. Vossen and Cuomo have listed sputtering yields of different metals using these sputtering gases¹. In general, Ar produces higher sputtering yields than He and Ne by factors of 1 to 2, while Kr and Xe produce yields greater than Ar by factors of 1 to 1.5. These factors are presumably due to the relative masses of each type of gas atom. An atom with higher mass has more momentum to transfer to the target for the same kinetic energy and therefore could produce a higher yield.

Thornton and Penfold have summarized the influence of sputtering gas pressure on sputtering yield and deposition rate². The sputtering yield is optimized at a range of pressures dependent on the choice of sputtering gas. If the pressure is too low, the mean free path of the secondary electrons will be relatively large. The secondary electrons will ionize sputtering gas atoms far from the cathode, increasing the probability of losing the ions to the walls of the vacuum chamber. As a result, the plasma is unsustainable and deposition ceases. If the pressure is too high, the mean free path of the atoms ejected from the target is relatively low and the atoms will scatter before they reach the substrate. The sputtering yield is maximized at a pressure between the two extremes.

Secondary gasses intentionally introduced into the vacuum chamber can react with deposited atoms to produce compounds in the bulk of the thin film that are different from the target. This process, known as reactive sputtering, has been used to produce indium oxide photodiodes³, chromium oxide thin films⁴, and titanium nitride thin film resistors⁵ among many other examples. Residual gasses remaining in the vacuum chamber while pumping down to base pressure constitute contaminants in the system and also can react with sputtered atoms, highlighting the need for a vacuum pump capable of reducing the base pressure as much as possible. Some of the most common contaminants are oxygen and water vapor, which can produce oxides in the thin film. Such secondary gasses can react with sputtered atoms at the target surface or with the film as it is deposited, depending on the partial pressure of the reactant gas and the deposition rate¹. At low partial pressures and high deposition rates, compound formation occurs mainly by reaction with the deposited film. This is due to a high rate of compound removal and/or decomposition at the target. If the partial pressure is increased or the deposition rate is decreased, the rate of compound formation at the target surface can increase beyond that of removal, leading to "poisoning" of the target surface and deposition of a highly reacted film.

Target Material Considerations

Figure 2.2 shows a periodic table with typical elements for sputtering highlighted in color. The colors indicate any special conditions required for deposition from a magnetron sputter gun. As can be seen, almost any solid element that is



Figure 2.2 Periodic table showing typical elements deposited from magnetron sputter guns and any special conditions they require.

conducting can be sputtered using a DC power supply. This will include most of the transition metals and metals of the p-block in the periodic table.

Fe, Co, Gd, and Ni are difficult to sputter due their ferromagnetic properties. The low-reluctance path provided by ferromagnetic targets shunt the magnetic field lines from the button and ring magnets (see Figure 2.1), resulting in a weak field about the target and a poor ability to trap ionizing secondary electrons near the target face. To remedy this problem, the deposition of ferromagnetic materials requires specially designed sputter guns housed with stronger magnets and the use of thin targets (approximately 1/16-in. thick). The high magnetic flux density available from a strong magnet will saturate the target and allow a strong field over the face of the target.

The cooling water circulating through the sputter gun helps to cool targets as they absorb heat from the plasma during sputter deposition. However, elements such as In, Bi, and Pb have low enough melting points (156°C, 271°C, and 327°C, respectively) that the rate of heat transfer may be too low to prevent melting. This can also happen for targets with a low thermal conductivity (less than approximately 10 W/m-K) such as Bi. To prevent melting, the backs of targets are bonded to a thin copper plate since Cu has a high thermal conductivity and increases the rate of heat transfer to the cooling water. Another solution is to apply low-vapor pressure grease with a high loading of silver to the back of the target.

Semiconductors such as Si, insulators, and elements available only as oxides are difficult to sputter because poor electrical conductivity leads to a significant voltage drop across the target instead of the cathode dark space, where ions receive most of their energy for impact at the target. However, if RF power is supplied to the target then the impedance of the dielectric material is reduced. The voltage drop across the target is less and power is efficiently coupled to the plasma. Sputtering insulators and semiconductors therefore requires a power supply capable of producing an RF current.

Theoretical Model of the Synthesis of Thin Film Composition Spreads

Gnaedinger⁶ derived functions that describe the deposition rate from a sputtering source onto a receiver (in this case a substrate) as a function of distance from the source axis. To obtain a simple model, he made the following assumptions:

- Any gasses in the sputtering environment do not scatter the atoms or molecules ejected from the sputtering source.
- 2. All atoms or molecules, upon reaching the receiver, stick to it (i.e., the sticking coefficient is 1).
- 3. The sputtering source ejects atoms or molecules at a uniform rate at every point on its surface.
- 4. The flux of atoms or molecules from the source in a particular direction is proportional to the projected area of the source in that direction. The total flux per unit area at the source is therefore

$$\frac{\Delta G}{\Delta A_s} = \pi F_o \text{ molecules/cm}^2\text{-s}, \qquad (1)$$

where ΔG is the flux of atoms (in molecules/s) from the source in all directions, ΔA_S is a unit area on the source, and F_o is the flux density of molecules from the source in units of molecules/cm²-s/sr.

Figure 2.3 shows a diagram of the source, receiver, and associated variables that appear in Gnaedinger's derivation. Given the above assumptions, the flux of molecules at the receiver $\Delta H/\Delta A_R$ (in molecules/s-cm²) as a function of the distance *r* from the sputter source axis is

$$\frac{\Delta H}{\Delta A_R} = \frac{\pi}{2} F_o \left[1 - \frac{\left(d^2 + r^2 - r_s^2\right)}{\sqrt{r_s^4 - 2r_s^2\left(r^2 - d^2\right) + \left(r^2 + d^2\right)^2}} \right].$$
 (2)

Figure 2.4 shows a plot of this function with d = 3.8 cm (1.5 in.) and $r_s = 1.5$ cm. These values correspond to the features of the sputtering deposition chamber that we use to produce thin films of composition spreads of electrocatalyst materials. Note that the radius of the source (i.e. the target) is actually 2.54 cm (1 in.). However, nearly all of the material from a 2-in diameter target in a magnetron sputter gun comes from within a radius of 1.5 cm. The flux of molecules per unit area at the receiver is normalized to the flux per unit area at the source.



Figure 2.3 Diagram showing variables used in Gnaedinger's derivation of deposition rate on a receiver as a function of distance from the source axis. The source axis passes through the center of the source and receiver. d is the distance from the source to the receiver, r_s is the radius of the source, and r is the distance from the point of interest on the receiver to the source axis.

From Figure 2.4 we can see that the deposition rate from a sputtering source will be at a maximum at the source axis (13.5% of the flux of molecules per unit area from the source), with lower rates at points further from the axis. The flux per unit area decreases slowly with radial distance up to around r = 0.5 cm, then decreases more rapidly beyond 0.5 cm, with an inflection point around r = 2.1 cm. At the far

edge of the receiver (i.e. the substrate) upon which we deposit films (r = 10.2 cm), the flux per unit area is calculated to be 0.2% of that from the source, or just over 1% of that at the center of the substrate.



Figure 2.4 Graph of the theoretical flux per unit area deposited at the receiver (normalized to the flux of molecules per unit area at the surface of the source) as a function of distance from the sputter gun axis.

We can use this relationship between flux per unit area at the receiver and distance from the sputtering source axis to create thin films of continuous composition spreads of two or three elements. Figure 2.5 shows the arrangement of three magnetron sputter guns that we used in our vacuum deposition chamber. Each gun, held in place by a flange, is positioned at the vertices of an equilateral triangle, 2.5 in. from the center of the triangle and 120° apart from each other. The substrate is 1.5 in. from the plane of the sputter gun targets and centered on an axis passing through the center of the gun triangle.



Figure 2.5 The arrangement of three magnetron sputtering guns for the deposition of thin films of continuous composition spreads. Reused with permission from Mark Prochaska, Review of Scientific Instruments, 77, 054104 (2006). Copyright 2006, American Institute of Physics.

If each gun sputters a different material with the same flux per unit area from the target, then each source will deposit its material onto the substrate with the deposition profile shown in Figure 2.4. Due to the arrangement of the sputter guns, the molar ratios of each material deposited depend on the position on the substrate. We can use equation (2) to predict how these ratios will map onto the substrate. Figure 2.6 shows a contour plot of the results of this calculation for material sputtered at the same flux per unit area from guns 1 and 2. The contours show the molar ratio of material from gun #1 to material from gun #2. The area inside the circle indicates the region of the plot that would deposit on a 3-in. diameter substrate, the kind used in our depositions.



Figure 2.6 Contour plot of the theoretical molar ratio of materials (material #1 to material #2) sputtered from guns 1 and 2 in Figure 2.5. The circle indicates the ratios that would be "captured" by a 3-inch diameter substrate.

As expected, the molar ratio of material sputtered from gun #1 to material sputtered from gun #2 varies with position on the substrate. Positions that are closer to gun #1 have a higher ratio of material #1 than positions farther from gun #1. Due to the mirror symmetry of the configuration of the guns and their sputtering rates, the molar ratio of the two materials is 1 across the mirror plane. Using the three-fold symmetry of the sputter guns and sputtering rates, the ratio map of any other two materials can be found by rotating the contour plot by 120° in the appropriate direction.

Figure 2.7 shows a ternary phase diagram for materials sputtered from guns 1, 2, and 3. The shaded region indicates the calculated compositions that would deposit on a 3-in. diameter substrate given the deposition profile of Figure 2.4 for each gun. From the diagram we can see that approximately 75% of the compositions of the ternary phase diagram would be deposited, given the assumption of Gnaedinger's model. We can easily shift the coverage of the phase diagram by adjusting the sputtering rates of each gun.



Figure 2.7 Ternary plot showing the theoretical coverage of a ternary phase diagram for a single deposition onto a 3-inch diameter substrate.

The validity of our theoretical map and ternary plot must be weighed against each of Gnaedinger's initial assumptions. Each assumption is violated in the following ways and may change the results of a real sputtering system.

- 1. Atoms or molecules ejected from the sputtering source are likely to be scattered. At standard temperature (298 K) and a typical sputtering gas pressure (10 mTorr), the mean free path of the sputtering gas is on the order of 1 cm. This is less than the distance between the sputtering source and substrate (3.81 cm), and therefore some of the atoms or molecules ejected from the source are likely to scatter off of sputtering gas atoms. The degree of scattering will depend on the velocity and mass of the ejected atoms or molecules relative to the sputtering gas atoms or molecules. Lighter metals such as Ni (atomic mass 58.69 g/mol) will scatter significantly more in Ar (atomic mass 39.948 g/mol) than will Pt (atomic mass 195.08 g/mol), assuming similar ejection velocities.
- 2. Not all atoms or molecules that reach the receiver stick to it. This is especially true of depositions in which the receiver is heated and for materials with low melting points. In this case, higher temperatures increase the vapor pressure of deposited materials and increase the probability that the atoms and molecules will escape the surface.
- 3. *The rate of ejection of atoms or molecules from the source is not uniform across its surface.* This assumption is especially false for magnetron sputter guns, where magnetic fields concentrate secondary electrons toward specific regions of the source for the ionization of the sputtering gas. Since the sputtering gas is not ionized uniformly, it is unreasonable to assume it will eject atoms or molecules from the source uniformly. This is evidenced by the fact that during the lifetime of a magnetron-sputtered target, most of

the atoms or molecules are ejected from a ring around the center, leaving behind an indentation. Another cause of non-uniformity, although perhaps to a lesser degree, is the shape of the surface of the source. The aforementioned indentation erodes the flat surface of a new target, changing its sputtering rate across the surface.

Although a real sputtering system may violate the assumptions of Gnaedinger's model, we should still be able to produce thin films of composition spreads that cover a significant portion of the ternary phase diagram of any three phases that can be sputtered. Furthermore, we should be able to deposit each film in a matter of hours. Two criteria of an effective combinatorial method for finding new fuel cell electrocatalysts are thus met.

Electrochemical Testing Background

Methods of evaluating large arrays of materials in combinatorial experiments can be classified in two ways: parallel evaluation and serial evaluation. Parallel evaluation involves testing all the materials in an array simultaneously. It is usually the fastest method but provides fewer details of the desired characteristics. Parallel methods have been used to evaluate photoluminescence⁷, transport across biological membranes⁸, and water oxidation catalysts⁹. Serial methods evaluate materials in a combinatorial array one at a time. They are slower than parallel evaluation methods, but provide more information about the desired properties of each composition. Serial methods have been used to evaluate dielectric properties^{10, 11} and transmission spectra¹².

Electrochemical Testing by Fluorescence

Reddington *et. al.* developed an optical screening method for testing a large number of anode fuel cell electrocatalysts in parallel¹³. They manually pipetted a Pt-Rh-Os array of precursor metal salts in different molar ratios onto Toray carbon paper followed by borohydride reduction. To test the array for electrocatalytic activity toward methanol oxidation, they placed it in a three-electrode cell in which the carbon paper serves as the working electrode. The cell contained an aqueous mixture of 6 M methanol (pH 6) and the fluorescent indicator quinine. They then incrementally stepped up the potential of the working electrode to beyond the oxidation potential of methanol. As the potential increased, the quinine began to fluoresce over the composition of Pt, Rh, and Os with the lowest onset of activity. They identified the best anode electrocatalyst in the array for methanol oxidation as $Pt_{62}Rh_{25}Os_{13}$. This composition was much better than Pt and slightly worse than $Pt_{50}Ru_{50}$ at oxidizing methanol.

Reddington *et. al.* subsequently tested a "five-pick-four" quaternary array of 220 different Pt, Ru, Os, Ir, and Rh compositions using an ink-jet printing synthesis method. In this experiment, they used the Ni²⁺ complex of 3-pyridin-2-yl-(4, 5, 6)-triazolo-(1, 5a)-pyridine as a fluorescence indicator to identify the best methanol oxidation electrocatalyst in their array as $Pt_{44}Ru_{41}Os_{10}Ir_5$.

The parallel screening method above relies on the fact that oxidation reactions of potential fuels produce protons in solution. The oxidation of methanol is an example of such a reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

As the potential applied to a combinatorial array increases (typically at a constant rate on the order of 1 to 10 mV/s), the compositions with the best electrocatalytic ability will oxidize methanol to protons before compositions with less electrocatalytic ability.

This decreases the pH in a region of the electrolyte over the good composition before it does over less efficient compositions. The pH indicator begins to fluoresce when the local pH decreases to a particular value, thus indicating the compositions with the best electrocatalytic ability.

The advantage of the fluorescence screening method in a combinatorial experiment is its ability to differentiate between electrocatalytically active and inactive compositions quickly. One can determine the relative effectiveness of each composition simply by how soon in the potential scan the electrolyte above it begins to fluoresce. The disadvantage of the method is that it does not directly determine any potential-current relationship that would quantitatively show the reaction rates of a particular electrocatalyst, although the total working electrode current can be monitored. The method is best used as a preliminary screening tool.

Electrochemical Testing by Scanning Electrochemical Microscopy

Bard *et. al.* have described the operation of the scanning electrochemical microscope (SECM) in detail and have used it for the investigation of surfaces immersed in a liquid¹⁴. The instrument has also been used for investigations of living cells¹⁵ and polymer film surfaces¹⁶. Figure 2.8 shows a diagram of the parts of a SECM.

The SECM consists of a working electrode, tip electrode, counter electrode, and reference electrode (not shown in Figure 2.8). The substrate surface to be studied, immersed in electrolyte, serves as the working electrode. A bipotentiostat, connected to both the tip and working electrodes, controls the potential of each electrode. The tip is usually an ultramicroelectrode of Pt (diameter of approximately 10 μ m) that piezoelectric controllers can move in any direction. The counter electrode is also

immersed in the electrolyte and completes the electrical circuit to the working electrode.



Figure 2.8 Diagram of a scanning electrochemical microscope.

Jayaraman *et. al.*^{17, 18} have used a SECM in a serial evaluation method for screening electrocatalysts in combinatorial experiments. They produced arrays of Pt_xRu_y and $Pt_xRu_yMo_z$ electrodes of different composition on a substrate using pulsed electrochemical deposition followed by poisoning by CO. To test the compositions for electrocatalytic activity toward hydrogen oxidation in the presence of CO, they placed the arrays in acidic electrolyte in a SECM then lowered the tip electrode close to the electrocatalyst surface. The working electrode (in this case, the substrate containing the arrays of different compositions) is biased at a positive potential while the tip is biased at a negative potential sufficient to reduce protons in solution to hydrogen. They subsequently rastered the tip over the surface of the electrocatalysts and measured the tip current as a function of position. Compositions with good electrocatalytic activity would produce higher currents through the tip than compositions with poor electrocatalytic activity.

The method of Jayaraman *et. al.* is based on the reversibility of the reduction of H^+ ions to H_2 . Hydrogen produced at the tip diffuses down to the working electrode, as shown in Figure 2.8. Active electrocatalysts on the working electrode oxidize the hydrogen back to protons that diffuse back to the tip. A composition on the working electrode that served as a good electrocatalyst for hydrogen oxidation would produce protons at a higher rate than a poor electrocatalyst, resulting in a higher tip current. The technique showed that the best electrocatalysts in the Pt_xRu_y array had 20 to 30 atomic % Ru, while the best electrocatalyst in the $Pt_xRu_yMo_z$ array had 10 to 20 atomic % Mo and 6 to 7 atomic % Ru.

The SECM method described above allows one to obtain more detailed information than the fluorescence testing method. Current measurements at the tip, in conjunction with manipulations of the working electrode potential, provide information about the current-voltage relationship for a set of electrocatalysts. However, the method can require more time, depending on the desired resolution and the size of the area to be scanned. The SECM is best suited for scanning over portions of a combinatorial sample and for determining the current-voltage characteristics of active regions revealed by a parallel screening method.

We now have methods that meet all three criteria of an effective combinatorial search for fuel cell electrocatalysts. We applied the background information described above to implement a general procedure for finding new anode electrocatalysts for methanol and ethanol oxidation.

Thin Film Composition Spread Synthesis

Deposition System Design

We deposit all thin films in a cylindrical vacuum chamber with the arrangement of three magnetron sputter guns (US Gun II, US Inc., San Jose, CA)

shown in Figure 2.5. Each sputter gun holds a 2-inch diameter target and is connected to a DC power supply (US Gun II, US Inc., San Jose, CA; or MDX 500, Advanced Energy, Fort Collins, CO). The ternary gun arrangement is mounted on the side of the chamber. A fourth sputter gun (referred to as gun #4), an S-gun (Sputtered Films, Inc., Santa Barbara, CA), is also mounted on the side of the chamber but at 135° around the chamber's axis from the ternary gun arrangement. The S-gun is positioned so as to produce uniform thickness thin films of a single composition onto substrates.

The substrate holder in the middle of the vacuum chamber can rotate between facing the ternary gun arrangement and facing the S-gun. This allows the user to presputter from each gun without depositing on the substrate and to alternate between depositions from the S-gun and ternary gun arrangement. During depositions from the ternary gun arrangement, the substrate is approximately 1.5 inches away. During depositions from the S-gun, the substrate is 5 inches away. The substrate holder contains a resistance heater for heating thin films up to 600°C during or after deposition. The user can control the temperature of the substrate by varying the voltage across the heater with an adjustable transformer. A type K thermocouple, inserted into the side of the substrate holder, allows the user to monitor the holder temperature during heating. The presumption is that the substrate temperature is close to that of the holder, but in any case is reproducibly set by monitoring the holder temperature.

Three types of vacuum pumps are connected to the vacuum chamber. A mechanical "rough" pump reduces the pressure down to approximately 800 mTorr. Below this pressure, a cryopump that can reduce the pressure below $4x10^{-6}$ Torr is used. A pair of sorption pumps can also rough pump the chamber and cryopump down to 400 mTorr, but without the risk of oil contamination. This is especially important

during cryopump regeneration, in which trapped gasses must be released from the cryopump approximately every month.

Several pressure gauges allow the user to monitor the chamber during pumpdowns and depositions. A thermocouple gauge monitors the pressure down to 50 mTorr while rough pumping the chamber. Ion gauges connected to the side of the cryopump and to the chamber indicate pressures in the 10^{-8} to 10^{-4} Torr range. A capacitance monometer connected to the vacuum chamber allows the user to monitor sputtering gas pressure in the range of 1 to 1000 mTorr during depositions.

We chose to use Ar as the sputtering gas. Ar flows into the chamber through a mass flow controller that the user can adjust to change the flow rate and therefore the pressure. When feeding in Ar gas, the cryopump evacuates the chamber through a throttle valve to reduce the pumping speed and allow Ar to remain longer in the chamber during sputtering. The user can also adjust the throttle valve to manipulate the sputtering gas pressure.

Deposition Rate Calibrations

To determine the deposition rate desired from each sputter gun in the synthesis of thin film composition spreads, we measure the deposition rate for a particular target and gun at the center of the substrate. A convenient way of doing this is to replace the substrate holder with a crystal deposition rate monitor whose position corresponds with the center of a mounted substrate. The crystal deposition rate monitor measures changes in the resonant frequency of a crystal as sputtered material is deposited on it. Since the resonant frequency is linearly related to the mass of deposited material, the total film thickness deposited on the face of the crystal can be calculated if the density of the material is known¹⁹.

With the crystal deposition rate monitor in place, we load each sputter gun with the desired targets and pump down the system. We then measure the thickness of material deposited in 20 s for several different currents through each gun individually. From these measurements we determine the relationship between average deposition rate (in Å/s) at the substrate center and gun current (in mA). An example graph is shown in Figure 2.9 for a Pt target sputtered from gun #1.



Figure 2.9 Sample plot of deposition rate vs. gun current for a Pt target loaded in gun #1. The Ar sputtering gas pressure was 10.0 mTorr.

The relationship between deposition rate and gun current is dependent on the target, sputtering gas pressure, and the particular gun in use. Any changes to any of these variables require new measurements. The relationship between deposition rate and gun current can also shift over time, requiring new measurements approximately every six months.

To determine the gun currents needed to deposit a composition spread, we first choose the deposition rate at the center of the substrate from one of the sputter guns. Using the density and molar mass of the element in the chosen gun, we calculate the equivalent molar deposition rate (in mol/cm²-s) at the substrate center. We typically choose to deposit thin film composition spreads with 1:1:1, 1:2:1, or 1:3:1 molar ratios of the three elements at the center. This ratio determines the deposition rates from the other guns. We then use the deposition rate/gun current calibrations we previously measured to determine the constant current to supply to each sputter gun during thin film synthesis. Typical gun currents, gun voltages, and deposition rates are 50 to 500 mA, 150 to 600 V, and 1.0 to 5.0 Å/s, respectively. This procedure is approximate and assumes that the sputter rates of a particular element at a particular spot on the substrate are reproducible and independent of the sputtering conditions set by the other sputtering guns. This assumption may be better in some cases than others.

Thin Film Composition Spread Deposition

Once we determine the gun currents, we load a 3-inch diameter Si substrate onto the substrate holder and pump the chamber down to pressures on the order of 10⁻⁶ Torr (this usually takes several hours). If we desire to heat the films during deposition ("hot sputtering"), we adjust the voltage across the heater at this time to increase the substrate temperature. The introduction of Ar sputtering gas into the chamber and subsequent deposition begins once the temperature reaches approximately 20°C below the desired temperature. All temperatures recorded for hot sputtering are the temperatures indicated by the thermocouple at the end of deposition. The typical sputtering gas pressure is 10.0 mTorr.

In our first tests, we found that a thin film composition spread deposited directly onto a Si substrate would delaminate during electrochemical testing. To promote adhesion, we now first deposit a uniform layer of Ta from gun #4. With the substrate holder turned toward the ternary gun arrangement, we pre-sputter from gun

#4 for 1 to 2 minutes then turn the substrate holder toward gun #4 and deposit the underlayer to a thickness of 1000 Å to 1200 Å.

To deposit the composition spread layer, we leave the substrate holder facing gun #4 while pre-sputtering from guns 1, 2, and 3 for 1 to 2 minutes. We then turn the substrate holder toward the ternary gun arrangement. The sputtering time is usually such that the thickness of the composition spread at the center of the substrate is approximately 2500 Å, neglecting changes in density from the formation of compounds.

For hot sputtering, we shut off the voltage across the heater and allow the substrate to cool down to at least 70°C before opening the chamber to reduce oxidation of the films. If we desire to do post-deposition annealing, we adjust the voltage across the heater and allow the temperature to reach the desired range. We typically anneal the films for two hours at the desired temperature, then shut off the voltage across the heater and allow the substrate to cool down below 70°C before opening the chamber.

For identification purposes, each thin film sample is named according to the date we synthesize it. If we make more than one film in a day, the film name includes an alphabetic suffix (a, b, or c) according to the order in which it is made for that date.

Electrochemical Screening

Electrochemical Cell Design

After synthesis, we screen the composition spreads for electrocatalytic activity using fluorescence testing or in some cases scanning electrochemical microscopy. All tests utilize the electrochemical cell show in Figure 2.10.



working electrode

Figure 2.10 Diagram of the electrochemical cell used in each electrochemical test.

The cell, made of polytetrafluoroethylene (Teflon), holds down the sample with an O-ring close to the edge of the substrate. The O-ring prevents electrolyte from leaking out of the compartment above the sample. The cell has three electrodes to measure and control potentials and currents. The working electrode connects to the edge of the sample and does not come in contact with the electrolyte. The counter electrode, a coiled wire of Pt or Au that runs along the rim of the sample compartment, is submerged in the electrolyte. The reference electrode is a Ag wire coated with AgCl inserted into a vial of saturated KCl solution. The tip of the vial is submerged into the electrolyte.

A bipotentiostat connected to all three electrodes controls the potential of the working electrode (i.e. the entire thin film and substrate) while measuring the current through the counter electrode. We measure all potentials relative to the Ag/AgCl reference electrode.

Fluorescence Screening

We chose to use a fluorescence test as the primary screening method for finding active electrocatalysts in our thin films. The electrolyte for this test is typically 5 M fuel (methanol or ethanol), 0.1 M supporting electrolyte (typically NaCF₃SO₃), and 0.5 mM quinine, the fluorescence indicator. Quinine has excitation wavelengths of 317 nm and 347 nm and an emission wavelength of 448 nm for pH $< 5^{20}$. An ultraviolet light placed over the electrochemical cell provides the necessary radiation for excitation. A Nikon D100 controlled by Nikon Capture 4 software automatically takes images of the sample every few seconds during the fluorescence screening. A profile of fluorescence screening images shows that this setup provides a resolution of active regions on the order of 0.1 mm.

The fluorescence test is first completed without fuel in the electrolyte. This is to eliminate the possibility of a false positive indicator, where the pH in areas of the electrolyte could drop due to chemical processes other than fuel oxidation. Such processes may or may not be potential dependent. If no fluorescence is seen at open potential, we scan the working electrode at a negative potential (typically -500 mV). We then linearly increase the potential at a rate of 5 mV/s toward positive values. If the sample exhibits no fluorescence without fuel, we repeat the test with fresh electrolyte containing fuel.

To quantitatively describe the best electrocatalyst with the fluorescence screening method, we take the initial image of the film under the ultraviolet light (before scanning the potential) and subtract it from every image captured during the scan. We then make contour plots of the fluorescence intensity for each transformed image and plot the intensity of the brightest regions vs. potential. The intensity is measured with an arbitrary linear scale from 0 to 255. Since the typical background fluorescence intensity is 50, we define the onset potential for any active electrocatalyst
to be the potential at which the intensity first increases above this value. The error in the measurement of onset potential is ± 25 mV. An ideal electrocatalyst in the typical electrolyte described above would have an onset potential of approximately -500 mV vs. Ag/AgCl.

Scanning Electrochemical Microscopy

Scanning electrochemical microscopy (SECM) is a serial screening method used to determine electrocatalytic activity with high local resolution. A fine Sb tip electrode (around 10 μ m in diameter) is fashioned and used to measure the local pH of the electrolyte over different areas of the composition spreads. This is possible since the potential of an Sb tip is linearly dependent on pH, with a slope of approximately $-59 \text{ mV/pH unit}^{21}$. While applying a constant potential to the substrate, we rastered the tip electrode over regions of the composition spread that had shown fluorescence activity while measuring the pH to produce a map of the tip electrocatalysts since such compositions would oxidize fuel efficiently, produce protons at a higher rate, and therefore induce a higher potential at the tip.

Thin Film Characterization

We use several instruments to characterize the regions containing the best electrocatalysts on our thin films. We acquire X-ray diffraction (XRD) spectra using a Bruker AXS general area diffraction detector system (GADDS) to determine crystal structure characteristics²². The system has a laser to pinpoint the location at which X-rays strike the composition spread and indicate the correct height for mounting. The X-ray beam (wavelength 1.54 Å), generated with a voltage of 40 kV and current of 40 mA, is approximately 1 mm in diameter. A crossed-wire detector counts x-rays at each

angle and sends them to a computer to generate an XRD spectrum. We match the spectra to those of known compounds taken from a powder diffraction file (pdf) database²³, referenced by pdf number in this dissertation. All spectra are collected for a period of 5 minutes.

We use a LEICA 440 scanning electron microscope or a JEOL 8900 EPMA electron microprobe to determine surface morphology of interesting areas of the films with scanning electron microscopy (SEM). An electron beam, typically 10 keV to 25 keV in energy with currents of 0.1 nA to 15 nA, rasters over the surface of the film and produces X-ray emissions and secondary electrons. A computer uses the secondary electrons to produce images of the surface. Each instrument can resolve surface features of the films down to approximately 1 µm in size.

The electron microprobe also serves as an instrument for measuring bulk compositions of areas of the films. The X-rays generated from the incident electron beam as it strikes the film have energies that are characteristic of the film's composition. With energy dispersive spectroscopy (EDS), a detector measures the intensity of x-rays over a range of energies. The atomic percentages of elements in the film are calculated from the energy spectrum using either ZAF²⁴ or Proza²⁵ matrix corrections. EDS is a semi-quantitative analysis method that measures bulk composition with an error of $\pm 10\%$. We typically use EDS with a beam energy of 10 keV and current of 15 nA over an area 2.3 mm x 1.6 mm in size. For a more quantitative measurement of bulk composition, we sometimes use wave dispersive spectroscopy (WDS). A detector measures the intensity of emitted X-rays at specific wavelengths. For each film we use a set of elemental or compound standards containing elements found in the film. WDS utilizes the electron beam's "spot mode", where the beam strikes only one spot on the film instead of rastering over a particular area. The electron beam has a diameter of approximately 1 µm, with a typical energy

of 10 keV and current of 100 nA. A computer collects the X-ray emission data and calculates the atomic composition assuming that the sample is thick (many times the penetration depth of the electron beam) instead of a thin film. We use the GMRFILM software to make corrections to the composition measurement for thin films.

It should be noted that a 10 keV microprobe electron beam generates X-rays in the top 5000 Å of the film. This means that some of the X-ray emission data may be associated with the Ta underlayer and not just the composition spread layer, contributing to errors in any composition measurement (especially when measuring oxygen content). However, the X-rays originating from the Ta sublayer may still not be able to penetrate out of the film. According to Monte Carlo simulations of electron trajectories performed by the Win X-ray software, the majority of detectable X-rays originate from the top 2000 Å of a film, which is less than the thickness of the composition spread layer in the majority of our samples.

To obtain surface composition of areas of the films, we use X-ray photoelectron spectroscopy (XPS) on two different machines: a Surface Science SSX-100 and a VG Escalab 220i-XL. X-rays strike the surface of the sample, ejecting electrons at energies characteristic of the surface composition. XPS methods produce information on the top 5 to 10 nm of the film. The measurements are also semiquantitative with an error of $\pm 10\%$.

Rutherford back-scattering (RBS) provided data on composition and thickness of the different layers of the film. A 1 MeV Tandetron accelerated a 30 nA beam of He²⁺ ions toward interesting areas of the films. The energy spectrum of the scattered ions and analysis by the program RUMP²⁶ gave information about the films' composition and thickness. However, films that contain elements with close atomic number are difficult to analyze with RBS. The RBS machine has been decommissioned, and we no longer use this method. In the next chapter we will evaluate these methods and show their suitability for discovering active electrocatalysts in a Pt-Bi-Pb composition spread.

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CHAPTER 3 TESTS OF THE EXPERIMENTAL DESIGN

In this chapter we describe tests of the experimental design by depositing a Pt-Bi-Pb thin film composition spread and compare the results to the theoretical model described in Chapter 2. The tests included synthesizing a film, determining the actual portion of the Pt-Bi-Pb ternary phase diagram included in the film, mapping the compositions, screening for electrocatalytic activity, and characterizing active regions.

We chose to test the Pt-Bi-Pb system based on previous studies of the intermetallic compounds PtBi and PtPb. Casado-Rivera *et. al.* have found bulk PtPb to be an active electrocatalyst for methanol oxidation, with a higher peak current density and lower onset potential than bulk Pt¹. In contrast, bulk PtBi showed no activity for methanol oxidation. We therefore hypothesized that if our experimental methods are valid for finding new fuel cell anode electrocatalysts, we should find an active PtPb phase in a Pt-Bi-Pb composition spread and our electrochemical tests should indicate better electrocatalytic activity for the PtPb phase than for Pt. Furthermore, it may be for a particular fuel that the optimal composition exhibiting the highest activity is in fact a ternary composition.

Synthesis of a Pt-Bi-Pb Thin Film Composition Spread

To synthesize a Pt-Bi-Pb thin film composition spread, we loaded Pt, Bi, Pb, and Ta targets into guns 1, 2, 3, and 4, respectively. We began by sputtering a uniform underlayer from gun #4 with 730 mA of current, for a deposition rate of 5.4 Å/s according to calibrations performed at the time (see Chapter 2 for information on calibration methods). The time of sputtering from gun #4 was around 440 ± 2 s for a Ta underlayer film thickness of approximately 2400 Å.

We wanted a 1:1:1 molar ratio of Pt:Bi:Pb at the center of the composition spread layer. To accomplish this, we chose the Pt deposition rate from gun #1 to be 1.3 Å/s at the center of the substrate, corresponding to a gun current of 135 mA. Since Pt has an atomic volume of 9.10 cm³/mol, the molar deposition rate was 1.4 nmol/cm²-s. Bi and Pb must have the same molar deposition rate to produce a 1:1:1 molar ratio at the center. The atomic volumes of Bi and Pb are 21.3 cm³/mol and 18.30 cm³/mol, respectively. We therefore required deposition rates of 3.0 Å/s for Bi and 2.4 Å/s for Pb at the center of the substrate. This corresponded to a gun #2 current of 110 mA and a gun #3 current of 76 mA. To determine the time of deposition, we chose a target composition spread layer thickness of approximately 2700 Å at the center. By assuming that the thickness deposition rate at the substrate center is simply the sum of all three elemental deposition rates (a total of 6.7 Å/s), we calculated a deposition time of 400 s.

After depositing the composition spread layer, we turned on the heater and annealed the sample at 260°C for two hours. Table 3.1 summarizes the synthesis parameters for this sample, named 2006-04-09.

sample	gun #	1	2	3	4
2004-04-09	targets	Pt Bi Pb Ta		Та	
	gun currents (mA)		110	76	730
	deposition rates at center (Å/s)	1.3	3.0	2.4	5.4
	deposition time (s)	400 440		440	
	molar ratio at center (Pt:Bi:Pb)	1:1:1			
	annealing temperature (°C)	260			
	annealing time (h)	2			

Table 3.1 Synthesis parameters of sample 2004-04-09.

Experimental Determination of Compositions Produced in a Single Film

Wax Deposition Method

A "wax deposition method" allows one to experimentally map the compositions synthesized on sample 2004-04-09 and compare them to the theoretical composition maps and the ternary phase diagram coverage derived in Chapter 2. We painted a narrow line of wax (2 to 3 mm wide) from a solution of black wax and trichloroethylene across the center of a Si substrate and allowed it to dry. The substrate was placed in the chamber so that the line was oriented toward the axis of gun #1. We then deposited a film of Pt from gun #1 onto the substrate. The gun current and deposition time matched those used to synthesize sample 2004-04-09. The film was not annealed at any point during deposition, and there was no Ta underlayer.

After removing the substrate from the chamber, we removed the wax and film on top of it by soaking the substrate in trichloroethylene. The result was a film with the Si substrate exposed along a line directly toward the axis of gun #1, as shown in Figure 3.1. We then used a profilometer (Tencor Instruments Alpha-Step 200) to measure the thickness of the film at six different distances from the gun axis, starting at 1 cm from the thickest edge of the substrate and every 1 cm thereafter. Using the atomic volume (in cm³/mol), we could calculate the molar surface density of the material from gun #1 (in mol/cm²) as a function of distance from the gun axis.



Figure 3.1 A Pt film with the wax line removed.

We repeated the procedure above for Bi from gun #2 and Pb from gun #3 to obtain the dependency of molar surface density on distance from the gun axis for all three elements. The gun currents and times of deposition matched those listed in Table 3.1. We then used the molar surface density functions to map the compositions that appear on sample 2004-04-09 and calculate the coverage of the Pt-Bi-Pb ternary phase diagram.

Determination of Pt-Bi-Pb Ternary Phase Diagram Coverage and Composition Maps

The graph in Figure 3.2 shows the results of the wax deposition measurements and analysis corresponding to sample 2004-04-09. The plot shows the molar surface densities of Pt from gun #1, Bi from gun #2, and Pb for gun #3 vs. distance from the corresponding sputter gun axis. The data points were fitted to an exponential function of the form Ae^{-br} , where r is the distance from the sputter gun axis and A and b are fitting constants. The values of the constants for each sputtering source are shown in Table 3.2. The R^2 ("goodness of fit") values of the functions for Pt, Bi, and Pb were 0.97, 0.98, and 0.98, respectively, showing an excellent fit to the experimental data. Note that Pt deposited with the highest surface density at each distance shown, followed by Bi then Pb.

Figure 3.3 shows the extent to which sample 2004-04-09 covers the Pt-Bi-Pb ternary phase diagram. In comparing the experimental coverage to the theoretical coverage shown in Figure 2.7, we see that the set of compositions is not centered on the ternary plot, but is shifted toward Pt and away from Pb. The coverage of the Pt-Bi-Pb phase diagram is approximately 70%, compared to the theoretical coverage of 75%.



Figure 3.2 A plot showing the experimental molar surface density as a function of distance from the sputter gun axis for Pt from gun #1, Bi from gun #2, and Pb from gun #3. The plot applies to sample 2004-04-09.

Table 3.2 Values of constants for the exponential functions fitted to experimental deposition profiles for sample 2004-04-09.

Source	$A (\mu \text{mol/cm}^2)$	$b (\mathrm{cm}^{-1})$
Pt gun #1	12.7	0.363
Bi gun #2	16.0	0.435
Pb gun #3	19.8	0.534

We also used the molar surface density functions to map the compositions on sample 2004-04-09. Figure 3.4 shows the maps of the ratios of Pt:Bi, Pt:Pb, and Bi:Pb. The circle indicates the portion of the map that the substrate captured during deposition. Notice that the 1:1 ratio contour is not a straight line between any two sputtering sources as it is in the theoretical ratio map of Figure 2.6. Instead, the line is shifted away from the Pt gun in (a) and (b), while it is shifted away from Bi in (c). The sample favors compositions with higher atomic fractions of Pt, followed by Bi then Pb. The ratio of Pt:Bi is as high as 15:1, but the ratio of Bi:Pt reaches only 10:1. The

highest Pt:Pb ratio is over 20:1, while the highest Pb:Pt ratio is only 10:1. The Bi:Pb map is also shifted, although to a lesser degree: The Bi:Pb ratio is 25:1 close the Bi gun, while the Pb:Bi ratio reaches approximately 20:1. This is consistent with the shift in coverage of the ternary phase diagram toward Pt in Figure 3.3, as well as the higher Pt molar surface densities plotted in Figure 3.2.



Figure 3.3 Ternary plot showing the experimental coverage of the Pt-Bi-Pb phase diagram for sample 2004-04-09.

The shift of the compositions away from those that are richer in Pb may be accounted for by its difficulty in sputtering. The particular Pb target we used in the depositions around this time required as much as 5 minutes of pre-sputtering, sometimes with the loss of the plasma. This suggests that the deposition rate from the target fluctuated with time. The difference in the molar surface densities may also reflect violations of the assumptions put forth by Gnaedinger in his model of deposition profiles (see Chapter 2). The atoms from each target are scattered by different amounts, the elements have different sticking coefficients, and there is no reason to assume that the profile of the rate of ejection of atoms is uniform across the surface of each target or the same for different targets. However, the coverage of the ternary phase diagram is adequate for our purposes.



Figure 3.4 Maps of the experimental ratios of (a) Pt:Bi, (b) Pt:Pb, and (c) Bi:Pb for sample 2004-04-09. The circle indicates the ratios that were captured by the substrate. Also indicated are the orientations of the elemental sputtering sources.

Electrochemical Tests of the Pt-Bi-Pb Thin Film Composition Spread

Fluorescence Screening

We first tested the fluorescence screening method (see Chapter 2) on a series of nanoparticle electrocatalysts. We prepared Pt, PtBi, PtPb, and PtRu nanoparticle suspensions by mixing 4 mg of nanoparticles with 3.98 mL of distilled water, 1 mL of isopropanol, and 20 μ L of 5% w/w Nafion solution in alcohols and water. Each mixture was sonicated for 4 h then spotted in pairs on a Pt foil that had been polished with 1 μ m diamond paste.

The results of the fluorescence screening, using the typical electrolyte with methanol described in Chapter 2, are shown in Figure 3.5. Panel (a) shows the location of each pair of nanoparticle spots in images taken at 0 mV, 200 mV, and 300 mV (vs. Ag/AgCl), shown in panels (b) through (d). The images show the electrolyte fluorescing above the PtRu nanoparticles first, followed by PtPb then Pt. The PtBi nanoparticles show no electrochemical activity up to 300 mV. The test leads us to conclude that the PtRu nanoparticle electrocatalysts have the lowest onset potential, followed by PtPb then Pt, while PtBi is inactive for methanol oxidation up to 300 mV. This is consistent with tests on bulk Pt, PtBi, and PtPb electrocatalysts¹ as well as tests on nanoparticle Pt, PtPb, and PtRu electrocatalysts².

We also performed the fluorescence screening on sample 2004-04-09, the composition spread described in Table 3.1, for methanol oxidation. At the time of the screening, we used an electrolyte of 5 M methanol, 0.1 M KNO₃, and 0.5 mM quinine. However, because NO₃⁻ is strongly oxidizing toward our films, we replaced it with 0.1 M NaCF₃SO₃ in all screenings of subsequent samples, as described in Chapter 2. The potential was scanned from 0 to 400 mV (vs. Ag/AgCl) at 5 mV/s. Figure 3.6 shows the results of the fluorescence screening, with the relative orientation of the sputtering sources labeled and three regions of interest labeled 1, 2, and 3 in panel (d).



Figure 3.5 Results of the fluorescence screening of a series of nanoparticle electrocatalysts for methanol oxidation at various potentials. (a) The position of each type of nanoparticle pairs in the fluorescence images. (b) 0 mV. (c) 200 mV. (d) 300 mV. All potentials are relative to a Ag/AgCl reference electrode. Reused with permission from Mark Prochaska, Review of Scientific Instruments, 77, 054104 (2006). Copyright 2006, American Institute of Physics.

The electrolyte exhibits no fluorescence until a potential of 150 mV, where there is an initial onset of activity in region 2. The fluorescence becomes brighter and other regions begin to fluoresce with increasing potential. It is interesting to note the sharp boundary between regions 1 and 2, running between the Pb and Pt sources. The boundary coincides with a line between different surface morphologies on the film. Note also that there is no activity in region 3, close to the Pt sputtering source, up to 300 mV. This is expected since pure Pt is known to be a poor electrocatalyst for methanol oxidation.





Figure 3.6 Results of the fluorescence screening for methanol oxidation of sample 2004-04-09. The images show the composition spread at potentials of (a) 0 mV, (b) 150 mV, (c) 250 mV, and (d) 300 mV vs. Ag/AgCl. Also shown are the orientations of the elemental sputtering sources and number labels for regions of interest. Reused with permission from Mark Prochaska, Review of Scientific Instruments, 77, 054104 (2006). Copyright 2006, American Institute of Physics.

SECM pH Mapping with an Sb Tip

We compared the fluorescence screening results with those of SECM using an Sb tip electrode to map electrolyte pH as described in Chapter 2. Sample 2004-04-09 was immersed in the usual electrolyte of 5 M methanol, 0.1 M NaCF₃SO₃, and 0.5 mM quinine. The SECM scanned the tip over regions 1 and 2 of the composition spread, indicated in Figure 3.6(d). The scan started in region 1 and progressed toward region 2.

Figure 3.7 shows the results of the tip electrode scan at substrate potentials of -100 mV, 100 mV, 200 mV, and 300 mV vs. Ag/AgCl. The graphs show the tip



Figure 3.7 Graphs of the tip electrode potential (relative to a Ag/AgCl reference electrode) over regions 1 and 2 of sample 2004-04-09 (labeled in Figure 3.6(d)). The substrate potentials for each scan were (a) -100 mV, (b) 100 mV, (c) 200 mV, and (d) 300 mV vs. Ag/AgCl. Reused with permission from Mark Prochaska, Review of Scientific Instruments, 77, 054104 (2006). Copyright 2006, American Institute of Physics.

electrode potential, relative to a Ag/AgCl reference electrode, vs. position. Region 1 is located toward lower y-values of position, while region 2 is toward higher values of y. At -100 mV, there is little change in tip potential across the entire scanned region. At 100 mV, region 2 of the scan reveals a higher tip potential, indicating a lower pH and therefore more oxidation of methanol to protons. The difference in tip potentials across the scanned region becomes especially noticeable at substrate potentials above 200 mV. Note that the substrate potential at which we begin to detect activity is within a reasonable range (± 50 mV) of the onset potential indicated by the fluorescence screening. The results from the SECM identify activity in the same region as the fluorescence screening, but with greater resolution. The difference in tip potential shown in Figure 3.7 occurs over a distance of approximately 60 µm, suggesting that this is the minimum resolution. In contrast, the resolution of the fluorescence screening is on the order of 0.1 mm. It is expected, according to the phase rule, that many regions of the film contain two or three phases in equilibrium. The variations seem in Figure 3.7 are presumably due to scanning over one phase that shows little activity followed by a second with good activity.

Other Screening Methods

It should be briefly noted that we attempted to use other screening methods to detect active compositions. This included the SECM in feedback mode, used by Jayaraman *et. al.*^{3, 4} for hydrogen oxidation (see Chapter 2). However, we found that hydrogen bubbles form at the Pt tip electrode and adsorb to its surface, preventing further reduction of H^+ to hydrogen gas.

We also tried using thermal imaging as a parallel screening method to detect electrochemical activity. This method is similar to the fluorescence screening method, except that there is no fluorescence indicator in the electrolyte and an infrared camera captures images of the composition spread during potential scans. We hypothesized that an active electrocatalyst exhibits a thermal signature detectable by the camera, revealing its location. Yamada *et. al.* have used this method to evaluate combinatorial libraries of electrocatalysts for hydrogen gas oxidation and CO poisoning⁵. Our method differs in that the reactants are in aqueous solution, which proved to be its downfall. The amount of heat generated from the electrochemical oxidation of fuel in solution is insufficient to produce a detectable thermal gradient. Characterization of Active and Inactive Regions in a Pt-Bi-Pb Composition Spread XRD

We used GADDS to perform XRD measurements on regions 1, 2, and 3 of sample 2004-04-09 after electrochemical screenings. The XRD spectra for regions 1 (inactive) and 2 (active) are shown in Figure 3.8, with vertical lines indicating the peaks of known compounds that might be present in the regions. The corresponding compound and powder diffraction file (pdf) number⁶ are listed in the legend of each graph.

The strongest peaks in the spectrum for region 2 are close to those of PbPt (pdf #6-374). BiPt has a very similar spectrum since both compounds adopt the NiAs structure type and Bi and Pb have very similar atomic sizes. In region 1, the spectrum also contains peaks that are close to those of PbPt, but they are weaker in intensity relative to peaks that match to PbPt_x (pdf #6-574). The PbPt_x spectrum is the same as that for the compound PbPt₃.

Figure 3.9 shows the XRD spectrum for region 3 (inactive), whose location is shown in Figure 3.6(d). The spectrum is clearly that of pure Pt.

SEM and Microprobe

We captured images of the surface with SEM and performed composition measurements with EDS for selected regions of sample 2004-04-09 before electrochemical screenings. Figure 3.10 shows a surface image that is near region 2 (active). The film in this location contains easily visible granules and hillocks of material approximately 10 μ m in size. The granules may have formed during annealing since this particular region was close to the Pb source and the annealing temperature (260°C) was within 70°C of the melting point of Pb (328°C).



Figure 3.8 The XRD spectra, taken after electrochemical screenings, of (a) region 2 and (b) region 1 of sample 2004-04-09, indicated in Figure 3.6(d). The vertical lines indicate the location of peaks of known compounds that could match the spectrum. The legend in each graph indicates the compound and powder diffraction file number.



Figure 3.9 XRD spectrum of region 3, indicated in Figure 3.6(d).



Figure 3.10 SEM image, taken before electrochemical screenings, of an area close to region 2 in Figure 3.6(d).

EDS semi-quantitative analysis suggests a composition of $Pt_{0.26}(Bi/Pb)_{0.74}$ in region 2. Since the emission energies of Bi Ma (2.423 keV) and Pb Ma (2.342 keV) are within 81 eV of each other, a measurement of their individual atomic percentages is likely to have a large error (at least ±20%). It should be noted that we analyzed the

EDS spectrum without subtracting the Ta M α emission peak (1.712 keV) originating in the underlayer. The peak is wide enough that it can also contribute to the emission peaks of Pt, Bi, and Pb and therefore increase the measurement error above the usual 10%. In all subsequent EDS measurements, we subtracted Ta peaks from the emission spectrum to obtain more accurate results. The ratio maps of each element (see Figure 3.4) suggest a composition of Pt_{0.50}Bi_{0.16}Pb_{0.35} in region 2.

The 1:1 ratio of Pt:(Pb/Bi) in region 2 indicated by the ratio maps is consistent with the XRD spectra showing the presence of only the PbPt structure type. Since Bi and Pb have similar atomic radii, they can easily substitute for each other in the crystal lattice while maintaining the NiAs structure type. Although the PbPt structure type is also present in region 1, it may be covered or surrounded by the more prevalent PbPt_x structure type, preventing its exposure to electrolyte and preventing electrochemical activity from the PbPt component.

The composition of region 3 is approximately $Pt_{0.82}Bi_{0.14}Pb_{0.04}$ according to the ratio maps in Figure 3.4. Note that this region is rich in Pt and inactive below 400 mV vs. Ag/AgCl, as we hypothesized.

Conclusions

We successfully synthesized a thin film composition spread of Pt, Bi, and Pb using the sputtering deposition chamber described in Chapter 2. According to deposition profiles obtained using a wax deposition method, the film contains compositions covering approximately 70% of the Pt-Bi-Pb ternary phase diagram. The fluorescence screening method successfully reveals the location of active electrocatalysts for methanol oxidation below 400 mV vs. Ag/AgCl and is consistent with a SECM screening using a pH-sensitive Sb tip electrode. The electrocatalyst with the lowest onset potential in the Pt-Bi-Pb composition spread is of the NiAs structure

type according to XRD, the same as the intermetallic compound PbPt. The deposition profiles show a composition of $Pt_{0.50}Bi_{0.16}Pb_{0.35}$, consistent with the structure type found. Regions of the film that are rich in Pt exhibit no fluorescence below 400 mV vs. Ag/AgCl. The results are consistent with those of Casado-Rivera *et. al.*¹, supporting our conclusion that our combinatorial method is a reliable method for finding new fuel cell anode electrocatalysts.

In the next chapter we will investigate the Pt-Bi-Pb system in more detail, including how the regions of the composition spread change with electrochemical testing and how deposition temperature affects electrochemical activity.

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CHAPTER 4 A STUDY OF THE Pt-Bi-Pb SYSTEM

In this chapter we describe the characterization and screening of several Pt-Bi-Pb thin film composition spreads for determination of the most electrocatalytically active composition in this ternary system. We "hot sputtered" (as opposed to postdeposition annealing as in Chapter 3) the films at different temperatures to explore the effect of deposition temperature on electrocatalytic activity. We also characterized selected regions of each sample and examined how their composition, crystal structure, and surface morphology change during electrochemical screening.

Pt-Bi-Pb Background

Ordered Intermetallic Compounds

There has been much research in recent years on various phases in the Pt-Bi-Pb system as fuel cell electrocatalysts. Smith *et. al.* studied the oxidation of formic acid on Pt surfaces modified by Bi on various step sites. They found enhanced current densities on such surfaces compared to bare Pt¹ and a reduction in the amount of CO poisoning², an intermediate in formic acid oxidation. The amount of poisoning decreased linearly with the fraction of Bi coverage on the (100) and (110) step sites. The discoveries led to an investigation by Casado-Rivera *et. al.*, mentioned in Chapter 1, of the oxidation of formic acid by the ordered intermetallic compound PtBi³. The compound had an onset potential 300 mV lower than Pt and a steady state current density almost 40 times higher than Pt. The investigation continued with additional experiments on PtBi and other ordered intermetallic compounds as electrocatalysts for the oxidation of several fuels, including methanol on PtPb and PtBi⁴. PtPb is able to oxidize methanol with an onset potential 100 mV less than Pt and a peak current

density approximately 40 times higher than Pt. In contrast, PtBi was inactive for methanol oxidation. Alden *et. al.* made nanoparticle electrocatalysts of PtPb and also found enhanced activity for formic acid and methanol oxidation compared to nanoparticles of Pt and PtRu⁵.

Volpe *et. al.* investigated the effects of various surface treatments of PtPb and PtBi electrocatalysts on the oxidation of formic acid⁶. The surfaces of both electrocatalysts become rough during cyclic voltammetry when the potential increases above 400 mV vs. Ag/AgCl. Polishing the surface of PtBi with alumina is one of the best methods of enhancing its electrocatalytic activity since it is less likely to change the structure and composition of its surface. Surface treatments of PtPb in air do little to enhance its activity.

Blasini *et. al.* studied the surface composition of PtPb and PtBi electrocatalysts after cyclic voltammetry in sulfuric acid electrolyte⁷. They found that oxides of Pb or Bi form on the surface of the intermetallic compounds upon air exposure and leach from the electrocatalysts at more positive potentials in the electrolyte. Surface Bi remains a part of the PtBi electrocatalyst up to a potential of 400 mV vs. Ag/AgCl, while surface Pb remains a part of the PtPb electrocatalyst up to a potential of 800 mV vs. Ag/AgCl (perhaps as a PbSO₄ precipitate).

Binary Phase Diagrams of Bi-Pt, Pb-Pt, and Bi-Pb

We expected to synthesize some of the phases appearing in binary phase diagrams of Bi-Pt, Pb-Pt, and Bi-Pb in our Pt-Bi-Pb thin films. However, it must be remembered that phase diagrams show compositions synthesized with heating and cooling rates slow enough that the system is always in equilibrium. The films described in this chapter were heated during deposition, and equilibrium conditions have not been established. The cooling rate of a substrate immediately after turning the heater off is on the order of 10°C/min. Some of the phases encountered may therefore not correspond to those of the phase diagram, and some new phases may be synthesized by quenching.

The Bi-Pt phase diagram shows three ordered phases⁸. BiPt congruently melts at 765°C, while Bi₂Pt incongruently melts to liquid and Bi₃Pt₂ at 660°C. Bi₃Pt₂ undergoes a eutectoid reaction when cooled below 570°C, decomposing into Bi₂Pt and BiPt, and incongruently melts at 685°C. We therefore expected only the Bi₂Pt and BiPt phases in our Pt-Bi-Pb films since none of the deposition temperatures were higher than 570°C.

The Pb-Pt phase diagram shows three ordered phases, all of which could appear in our films⁸. All three incongruently melt at different peritectic temperatures. PtPb₄ decomposes to liquid and PtPb at 360°C, PtPb to liquid and Pt₃Pb at 795°C, and Pt₃Pb to liquid and Pt at 915°C. However, there is some uncertainty about the existence and properties of phases toward the Pt-rich side of the diagram.

There are no ordered phases in the Bi-Pb phase diagram⁸. An ε -phase appears between -46°C and 125°C around the composition Bi₃Pb₇ and has a stoichiometric width that varies with the temperature. The diagram also shows the existence of Pb-rich solid solutions up to 327°C.

Ternary Phase Diagram of Pt-Bi-Pb

Figure 4.1 shows compositions reported for the ternary phase diagram of Pt-Bi-Pb⁹. Line (a) indicates compositions that have Pt:(Bi/Pb) atomic ratios of 1:2. This includes the reported compositions Bi₂Pt, Bi₇PbPt₄, Bi₃PbPt₂, Bi₁₃Pb₇Pt₁₀, BiPbPt, Bi₃Pb₅Pt₄, and Bi₂Pb₄Pt₃. Line (b) indicates compositions with the Pt:(Bi/Pb) atomic ratio of 1:4, incorporating the reported compositions Pb₄Pt, BiPb₇Pt₂, and BiPb₃Pt.



Figure 4.1 Ternary phase diagram for the Pt-Bi-Pb system showing reported compositions. Each of the compositions along line (a) have an atomic fraction of Pt of 0.33; each of the compositions along line (b) have an atomic fraction of Pt of 0.20.

Various authors have reported unique crystallographic structures of Bi₇PbPt₄, Bi₃PbPt₂, Bi₁₃Pb₇Pt₁₀, BiPb₇Pt₂, and BiPb₃Pt¹⁰⁻¹⁴. However, XRD cannot distinguish between Pb and Bi since they differ in the number of electrons only by 1 and can substitute for each other in a crystal lattice due to similar atomic radii. The crystal structures of BiPb₇Pt₂ and BiPb₃Pt are related to that of Pb₄Pt, while the crystal structures of Bi₇PbPt₄, Bi₃PbPt₂, and Bi₁₃Pb₇Pt₁₀ are related to that of PtBi₂. This is expected since compounds in each group have similar atomic ratios of Pt:(Bi/Pb). The crystallographic structures of BiPbPt, Bi₃PbPt₄, and Bi₂Pb₄Pt₃ are unknown but assumed to be related to that of PtBi₂. From inspection of the ternary phase diagram of Pt-Bi-Pb, we did not expect any ternary phases that would differ significantly in structure from the binary phases.

Synthesis and Electrochemical Screening of Pt-Bi-Pb Films

Synthesis Conditions

We synthesized six Pt-Bi-Pb thin film composition spreads at different deposition temperatures. With a Pt target loaded into gun #1, Bi in gun #2, Pb in gun #3, and Ta in gun #4, the gun currents were 100 mA, 58 mA, 57 mA, and 730 mA, respectively, for each deposition. The currents corresponded to deposition rates at the substrate center of 1.5 Å/s for Pt, 3.4 Å/s for Bi, 2.9 Å/s for Pb, and 2.7 Å/s for Ta, to produce an expected 1:1:1 molar ratio of the first three elements at the center of the composition spread layer. The times of deposition were 445 ± 2 s for Ta (producing an underlayer thickness of 1200 Å) and 320 ± 2 s for the composition spread layer (producing an estimated thickness of 2500 Å at the substrate center). The deposition temperatures were ambient chamber temperature (i.e. heating from the sputtering process itself, approximately 20°C as measured by the thermocouple in the substrate holder), 100°C, 160°C, 260°C, 400°C, and 510°C. A summary of the synthesis parameters of all six thin film ternary composition spreads are shown in Table 4.1. The names of the samples and their deposition temperatures are shown in Table 4.2.

Table 4.1 Synthesis parameters of the ternary thin film composition spreads.

six Pt-Bi-	gun #	1	2	3	4
Pb ternary	targets	Pt	Bi	Pb	Та
samples	gun currents (mA)	100	58	57	730
	deposition rates at center (Å/s)	1.5	3.4	2.9	2.7
	deposition times (s)	320 4		445	
	molar ratio at center (Pt:Bi:Pb)	1:1:1			

Sample Name	Deposition Temperature (°C)
2005-08-30	260
2005-08-31b	ambient
2005-09-10b	400
2005-10-05a	160
2005-10-11a	510
2005-10-13	100

Table 4.2 Deposition temperatures and names of the ternary thin film composition spreads.

We also synthesized two binary thin film composition spreads of Pt-Bi and Pt-Pb to ascertain the effects of Pb and Bi on the electrocatalytic activity of active compositions. The guns had the same targets as for the ternary composition spreads described above, and the deposition parameters of the Ta underlayer were similar. Both composition spreads were deposited at rates to produce a 1:1 molar ratio of the two elements at the center of the film. For the Pt-Bi film, we used currents of 112 mA in gun #1 and 57 mA in gun #2, corresponding to deposition rates of 1.7 Å/s for Pt and 4.2 Å/s for Bi at the center of the substrate. The time of deposition of the composition spread layer was 240 ± 2 s for an estimated thickness of 1400 Å at the center. The deposition rates, and deposition times as those for Pt and Pb in the ternary composition spreads. The thickness of the composition spread layer at the center was estimated to be 1400 Å, and the deposition temperature was 265°C.

A summary of the synthesis parameters of the two binary films and their names are listed in Table 4.3.

sample	gun #	1	2	4	
2005-08-02	targets	Pt	Bi	Та	
	gun currents (mA)	112	57	730	
	deposition rates at center (Å/s)	1.7	4.2	2.7	
	deposition time (s)	240		445	
molar ratio at center (Pt:Bi)		1:1			
	deposition temperature (°C)	260			
sample	gun #	1	3	4	
2005-10-05b	targets	Pt	Pb	Та	
	gun currents (mA)	100	57	730	
deposition rates at center (Å/s)		1.5	2.9	2.7	
	deposition time (s)	320 44			
	molar ratio at center (Pt:Pb)	1:1			
	deposition temperature (°C)	265			

Table 4.3 Names and synthesis parameters of the binary thin film composition spreads.

Fluorescence Screening Conditions and Results

We used the fluorescence screening method to find active electrocatalysts for methanol oxidation in all eight thin film composition spreads described above. In all tests, the electrolyte was 5 M methanol, 0.1 M NaCF₃SO₃, and 0.5 mM quinine. The initial screenings were from 0 to 400 mV vs. Ag/AgCl at 5 mV/s. If the test showed no fluorescence, we repeated it with fresh electrolyte.

Images of the fluorescence screening of sample 2005-08-30 (Pt-Bi-Pb deposited at 260°C) are shown in Figure 4.2, with the orientation of the sputtering sources indicated in panel (a). The results show no fluorescence at any point on the composition spread until 175 mV vs. Ag/AgCl. The active region is located toward the lower part of the sample, close to the Pb sputtering source. The region fluoresces with greater intensity as the potential increases to higher potentials. Notice that the active region is in a position close to the active region of sample 2004-04-09, described in Chapter 3.



Figure 4.2 Images of the fluorescence screening of sample 2005-08-30 at (a) 0 mV, (b) 175 mV, (c) 250 mV, and (d) 350 mV vs. Ag/AgCl. Also shown in (a) are the relative orientation of the elemental sputtering sources.

Figure 4.3 shows the analysis used to determine the onset potential of the active region of sample 2005-08-30 (see Chapter 2). The background-subtracted image at 350 mV in panel (a) and the corresponding contour plot of the fluorescence intensity in panel (b) more clearly indicate the location of the active region. Its position is nearly directly above the Pb sputtering source. Panel (c) shows a plot of the fluorescence intensity (and therefore assumed to be the most active), indicated by the arrow in panel (b). The intensity reaches a value of 50 at approximately 175 ± 25 mV vs. Ag/AgCl, and we therefore state this as the onset potential of the active region on sample 2005-08-30.



Figure 4.3 Analysis for the determination of the onset potential of the active region of sample 2005-08-30. (a) The background-subtracted image of fluorescence screening at 350 mV vs. Ag/AgCl. (b) A contour plot of fluorescence intensity for the image shown in (a). The arrow indicates the location of the region with the highest intensity and therefore most activity. (c) A plot of fluorescence intensity vs. potential for the most intense region.

Images of the fluorescence screening of samples 2005-09-10b (Pt-Bi-Pb deposited at 400°C), 2005-10-05a (Pt-Bi-Pb deposited at 160°C), and 2005-10-05b (Pt-Pb deposited at 265°C) at selected potentials are shown in Figure 4.4. The location of the most active region in each composition spread is similar: toward the edge of the

sample, close to the Pb sputtering source, just as it was for sample 2005-08-30. However, the area of the active region is much smaller in sample 2005-10-05a, and the shape of the active region is different in sample 2005-10-05b. Samples 2005-08-02 (Pt-Bi deposited at 260°C), 2005-08-31b (Pt-Bi-Pb deposited at ambient temperature), 2005-10-11a (Pt-Bi-Pb deposited at 510°C), and 2005-10-13 (Pt-Bi-Pb deposited at 100°C) exhibited no fluorescence below 400 mV vs. Ag/AgCl. Only samples deposited between 160°C and 400°C show any activity, and the sample without Pb is completely inactive below 400 mV vs. Ag/AgCl. A summary of the fluorescence screening results is shown in Table 4.4.



Figure 4.4 Images of the fluorescence screening of active films. (a) Sample 2005-09-10b (Pt-Bi-Pb deposited at 400°C) at 400 mV vs. Ag/AgCl. (b) Sample 2005-10-05a (Pt-Bi-Pb deposited at 160°C) at 300 mV vs. Ag/AgCl. (c) Sample 2005-10-05b (Pt-Pb deposited at 265°C) at 250 mV vs. Ag/AgCl. The relative orientations of the elemental sputtering sources are indicated in each image.

Sample	Elements Deposited	Deposition Temperature (°C)	Onset Potential of Most Active Region (mV vs. Ag/AgCl)
2005-08-31b		ambient	no activity
2005-10-13	Pt, Bi, Pb	100	no activity
2005-10-05a		160	255
2005-08-30		260	175
2005-09-10b		400	175
2005-10-11a		510	no activity
2005-08-02	Pt, Bi	260	no activity
2005-10-05b	Pt, Pb	265	210

Table 4.4 Summary of fluorescence screening results.

The fluorescence screening results suggest that deposition temperature has a significant impact on electrocatalytic activity for methanol oxidation on the Pt-Bi-Pb system. Synthesis of an active composition requires deposition temperatures that are at most between 100°C and 510°C, with the optimal temperature (in terms of lowest onset potential) being at least between 260°C and 400°C. The fact that sample 2005-08-02, containing no Pb, is completely inactive shows that Pb is necessary to synthesize an active composition for methanol oxidation. In contrast, sample 2005-10-05b, containing no Bi but having an active composition, suggests that Bi is unnecessary to synthesize active compositions. However, its presence may enhance the electrocatalytic ability of the active region; the onset potential with Bi present was lower by 35 mV, although this value is within the experimental and reproducibility errors of the fluorescence screening method.

Effects of Electrochemical Screening on Pt-Bi-Pb Composition Spread Characteristics

We investigated the effects of the fluorescence screening on the appearance, surface morphology, composition, and crystal structure of each of the films listed in Tables 4.2 and 4.3, with the exception of sample 2005-08-02 (Pt-Bi deposited at 260°C). We selected nine small areas (several millimeters on an edge) having the

same locations on each film and characterized each spot with SEM, EDS, and XRD after synthesis. We repeated the characterizations on the same spots after fluorescence screening. The locations of the nine regions, labeled 1 to 9, are shown in Figure 4.5.



Figure 4.5 Locations, relative to the elemental sputtering sources, and labels of the nine regions characterized to determine the effect of the fluorescence screening on each film.

For this dissertation, we describe the effects of fluorescence screening on sample 2005-08-30 (Pt-Bi-Pb deposited at 260°C) in detail and briefly summarize the effects on the other samples.

Appearance and Surface Morphology

Figure 4.6 shows images of sample 2005-08-30 before and after the fluorescence screening. Regions 1 and 4, close to the Pt sputtering source, show a specular surface that remains so after screening. The other regions of the composition spread, closer to the Bi and Pb sputtering sources, are dull with various textures. The appearance changes in color during fluorescence screening, turning milkier in regions close to the Bi and Pb sputtering sources and darker in the middle region.


Figure 4.6 Images of sample 2005-08-30 (Pt-Bi-Pb deposited at 260°C) (a) before and (b) after fluorescence screening, with the relative orientation of the sputtering sources shown.

Images of the nine regions before and after fluorescence screening, magnified by SEM, are shown in Figures 4.7 and 4.8, respectively. As expected, the specular surfaces of regions 1 and 4 are smooth while the dull surfaces of the other regions have textured surfaces of hillocks. The largest hillocks are approximately 2 µm across, located in regions 6, 8, and 9 where we expect a large fraction of Bi and Pb. The hillocks may be due to the fact that Bi and Pb have low melting points (271°C and 327°C, respectively) and therefore are more mobile upon deposition to form microstructures. Although the visual appearance of the dull regions changed during fluorescence screening, the SEM images show no significant changes. This may suggest that the film underwent a chemical rather than physical change at the surface in these regions.

The other Pt-Bi-Pb thin films show an appearance similar to that of sample 2005-08-30, with a specular surface close to the Pt sputtering source and dull surfaces toward the Bi and Pb sputtering sources. However, the size of the specular regions are smaller in samples 2005-08-31b (deposited at ambient temperature), 2005-10-13 (deposited at 100°C), and 2005-10-11a (deposited at 510°C). It is interesting to note



Figure 4.7 SEM images of regions 1 to 9 of sample 2005-08-30 before fluorescence screening, in order from (a) to (i).



Figure 4.8 SEM images of regions 1 to 9 of sample 2005-08-30 after fluorescence screening, in order from (a) to (i).

that these are the same samples that show no electrocatalytic activity. Fluorescence screening on the other samples also change the dull regions to a milkier color while leaving the specular regions the same.

Binary composition spread samples 2005-08-02 (Pt-Bi deposited at 260°C) and 2005-10-05b (Pt-Pb deposited at 265°C) before and after fluorescence screening are shown in Figure 4.9. Only the dull regions, located close to the Bi or Pb sputtering sources, change appearance during screening. The images show that the dull surfaces and changing appearance are probably the result of a threshold ratio of Pt to Pb or Bi.



Figure 4.9 Images of sample 2005-08-02 (Pt-Bi deposited at 265°C) (a) before and (b) after fluorescence screening and sample 2005-10-05b (Pt-Pb deposited at 260°C) (c) before and (d) after fluorescence screening, with the relative orientation of the sputtering sources shown.

In general, SEM images of the other samples show results similar to those of 2005-08-30. Regions 1 and 4 are smooth, while those closer to the Bi and Pb sputtering sources have various microstructures. Sample 2005-10-11a (Pt-Bi-Pb deposited at 510°C) is an exception to these rules, where all the regions have microstructures, probably due to the relatively high deposition temperature. On sample 2005-09-10b (Pt-Bi-Pb deposited at 400°C) region 1, there are small hillocks approximately 0.1 µm across. In each sample, SEM images before and after fluorescence screening generally show no significant changes in the surface morphology. There are exceptions on regions 5 and 8 of sample 2005-10-05a (Pt-Bi-Pb deposited at 160°C); region 5 acquired dark spots following screening, while region 8 acquired "flakes" on top of the original textured surface. Flakes also appeared over region 6 after fluorescence screening of sample 2005-10-13 (Pt-Bi-Pb deposited at 100°C). The images suggest that it may be possible for material to leach from the film and redeposit itself.

Composition

Figure 4.10 shows the compositions, measured with EDS, of all nine regions of sample 2005-08-30 before and after fluorescence testing. The highest atomic percentages of Pt, Bi, and Pb are located close to their respective sputtering sources in regions 4, 3, and 9, respectively. It is interesting to note that region 7 has a lower atomic percentage of Pb than regions 8 and 9. This may be due to the fact that Pt sputtered more efficiently than Bi or Pb, which would diminish the fraction of Pb; the atomic percentage of Pt is as high as $95 \pm 10\%$, whereas Bi and Pb have maxima of only $60 \pm 10\%$ and $70 \pm 10\%$. The data suggest that Pb may leach from the bulk of some compositions; in regions 8 and 9 the atomic percentage of Pb dropped by 40%

and 15%, respectively. The compositions of the other regions changed by less than 10%, within the experimental error of EDS as applied to these films.



Figure 4.10 Compositions, measured by EDS, of the nine regions of sample 2005-08-30 before and after fluorescence testing.

In the other samples, most post-screening atomic percentage drops greater than 10% occur for Pb in regions 6, 8, or 9, far from the Pt sputtering source. The Pb content dropped by 15% in region 6 and 20% in region 9 on sample 2005-08-31b (Pt-Bi-Pb deposited at ambient temperature); by 10% in region 6 and 35% in region 8 on sample 2005-09-10b (Pt-Bi-Pb deposited at 400°C); by 20% in region 8 on sample 2005-10-05a (Pt-Bi-Pb deposited at 160°C); and by 15% in region 6 and 20% in region 8 on sample 2005-10-05b (Pt-Pb deposited at 265°C). There were some exceptions to the above observation: the atomic percentage of Bi dropped by 10% in region 6 of sample 2005-10-13 (Pt-Bi-Pb deposited at 100°C), and region 9 of sample 2005-10-05a showed a 10% increase of Pb, perhaps due to leaching followed by

resettlement of Pb at more positive potentials during fluorescence screening. On sample 2005-10-11a (Pt-Bi-Pb deposited at 510°C), all the regions were stable in their compositions. This may suggest a certain threshold deposition temperature between 400°C and 510°C that promotes the stability of all compositions.

The maximum atomic percentage of Pb in the films decreases with deposition temperatures above 400°C. This is reasonable since these temperatures are much higher than the melting point of Pb (327°C). At the higher temperatures, the vapor pressure of Pb is higher and therefore it has a lower sticking coefficient.

The regions where there were significant changes in composition (regions 6, 8 and 9) match those regions that change physical appearance. However, a change in physical appearance does not necessarily imply that the composition changed significantly.

Crystal Structure

Figure 4.11 shows the XRD spectra of all nine regions of sample 2005-08-30 before and after fluorescence screening. Each panel shows the original spectrum in black and the spectrum after screening in light blue. The vertical lines indicate the peaks of phases that match the spectra peaks within $\pm 0.5^{\circ}$. The power diffraction file (pdf) number¹⁵ and phase are shown in the legend. The peaks at 34° correspond to the Ta underlayer.

Regions 1, 2, and 5 have the most stable XRD spectra before and after fluorescence screening. All the spectra in these regions match those of the PbPt phase (pdf #6-374, NiAs structure type), with the exception of a missing peak at 69.5° in regions 1 and 2, presumably due to microstructure in the film. The most intense peaks of region 1 match those of the Pt structure (pdf #4-802), as one would expect from the high percentage of Pt in the composition data.

Figure 4.11 XRD spectra of regions 1 to 9 of sample 2005-08-30, in order from (a) to (i). The black and light blue plots are the spectra before and after fluorescence screening, respectively. The vertical lines indicate the location of peaks of known spectra, with the phase and pdf number indicated in the legend.







(b)

Figure 4.11 (continued)







(d)

Figure 4.11 (continued)



Figure 4.11 (continued)



Figure 4.11 (continued)



Regions 3 and 6 show moderately stable spectra; in general, peaks remain at the same values of 20 after screening, but the intensities change significantly. In region 3, the largest peaks at 30° and 45.5° , corresponding to Bi (pdf #44-1246) and Bi oxide (pdf #45-1344) phases, approximately double in intensity, while the third largest peak at 27° , corresponding to the Bi phase, decreases by a factor of four. In region 6, the most intense peak at 42° , corresponding weakly to a Pb-Bi oxide phase (pdf #41-405), is stable, while the second-most intense peak at 31° split in two and decreases by a factor of approximately two during screening.

The most intense peaks of region 4, similar to those of region 1, match the structure of pure Pt. However, the intensity of the corresponding peaks decrease by a factor of two. This is surprising considering the electrochemical stability of Pt, with a standard reduction potential of 1.188 V vs. NHE (0.9657 V vs. Ag/AgCl). A PbPt

phase also appears following screening that is not present in the original spectrum. It is possible that the PbPt phase has a preferred orientation that was not detected in the original spectrum. The fact that the intensity ratios of the peaks matching the PbPt phase are different from those of the known spectrum lends credence to this hypothesis.

Region 7 shows that the PbPt phase has moderate stability during screening. Most peaks have the same intensity, with the exception of the most intense peak at 29.5°, where it decreases by a factor of 2.5. The Pb₄Pt phase (pdf #6-463) matches the spectrum only before screening, suggesting that the phase is unstable.

Regions 8 and 9 are exceptionally unstable, losing most semblance of structure to the background following screening. Region 8 shows a possible match to the Pb_4Pt phase only before screening, indicating its instability as in region 7. Region 9 shows a possible match to a Pb-Bi oxide (pdf #45-294) before screening, but the largest peak at 33.5° completely disappears afterwards.

The other samples show some similar characteristics in their XRD spectra. In general, the peaks in each spectrum are broader with lower deposition temperatures, especially in regions 8 and 9. This is to be expected since diffusion rates are lower at cooler temperatures.

The spectra match Pt in regions 1 and 4 of all the samples; the corresponding peaks are stable in position but change in intensity with fluorescence screening, with the exception of region 1 of sample 2005-10-11a (Pt-Bi-Pb deposited at 510°C). Note that this sample has the highest deposition temperature, possibly contributing to the stability of the region. Peaks matching the PbPt_x phase (pdf #6-574), which has the same structure type as Pt₃Pb, appear in regions 1 and 4 of the two samples deposited at the highest temperatures (2005-10-11a and 2005-09-10b).

The PbPt phase appears in region 2 of all samples except 2005-08-31b (Pt-Bi-Pb deposited at ambient temperature) and 2005-10-05b (Pt-Pb deposited at 265°C). The peaks are still present after screening with variations in intensity. Since region 2 is between the Pt and Bi sputtering sources, we suspect that the phase corresponds to the presence of the compound PtBi. The peaks of region 7 also match the PbPt phase in all the samples and change little during screening; since region 7 is close to the Pb sputtering source, we suspect it contains the compound PbPt. It must be remembered, however, that Bi and Pb can easily substitute for each other in their respective lattice positions, and the compounds present may actually be $Pt_{0.50}(Bi/Pb)_{0.50}$.

Regions 3 and 6 tend to maintain their spectrum during screening but change drastically in the intensity. The most drastic spectrum changes occur in regions 8 and 9, where peaks frequently disappear after screening. An exception is in sample 2005-10-11a (Pt-Bi-Pb deposited at 510°C), where regions 8 and 9 match the PbPt phase.

Stability of Regions

The characterization of samples before and after fluorescence screening show that regions 8 and 9, close to the Pb sputtering source, are the most unstable. These regions undergo the greatest changes in appearance, composition, and crystal structure. This is reasonable since these regions contain the greatest atomic percentages of Pb and show poor compound formation. Free Pb is likely to leach from the film early in the potential scan due to the relatively low standard reduction potential of the Pb²⁺/Pb couple (-0.1262 V vs. SHE, -0.3474 V vs. Ag/AgCl). Other regions, such as 1, 2, 3, or 4, that contain a large atomic percentage of Bi and especially Pt are not as likely to leach these elements since the standard reduction potentials of Bi³⁺/Bi (0.308 V vs. SHE, 0.086 V vs. Ag/AgCl) and Pt²⁺/Pt (1.18 V vs. SHE, 0.96 V vs. Ag/AgCl) are higher. Region 7 also contains high atomic percentages

of Pb but shows little change in composition. We attribute this to the presence of the PbPt phase, shown by the XRD spectra of the region. If the intermetallic compound PbPt had indeed formed, the Pb would be stabilized by virtue of its bonding with Pt. Leaching of Pb would require overcoming the free energy of the bond followed by the oxidation of two electrons. The extra free energy increases the reduction potential of the Pb²⁺/Pb couple and decreases the probability of Pb oxidation into solution. A method described by Miedema *et. al.*^{16, 17} estimates the enthalpy of bond formation for PbPt at -26.6 kJ/mol of atoms. Neglecting the entropy contribution to the Gibbs free energy of formation, the shift in the standard reduction potential of the Pb²⁺/Pb couple is +0.276 V. The stability of the PbPt phase is also in agreement with the results of Blasini *et. al.*⁷.

Characterization of Active Regions

We characterized the electrocatalytically active region of each film after fluorescence screening. As noted earlier, the active region is located at approximately the same location on each film. We also characterized the same location in each of the inactive films (with the exception of sample 2005-08-02) after screening for comparison. Our goal was to determine any characteristics that differed from the active films that might explain the dependence of electrochemical activity on deposition temperature.

Bulk Composition

Figure 4.12 shows the bulk composition, measured by WDS, of the active region of each film as well as the corresponding region in the inactive films. There is a substantial atomic percentage of oxygen in most regions (as high as 33%), with no apparent relationship to the deposition temperature. The source of the oxygen could be

from oxidation of the film during fluorescence screening, during which the potential of film reaches more positive values. Another source of oxygen could be from contaminants such as oxygen and water in the sputtering chamber during deposition. Although we evacuated the chamber down to a pressure on the order of 10^{-6} Torr, there still may be enough contaminants at this pressure to react with the film. Note also that the atomic percentage of Bi is never greater than 10%, indicating once again the possibly minor role that Bi plays in the enhancement of electrocatalytic activity.



Figure 4.12 Compositions, measured by WDS, of the active region of each film and the corresponding region on inactive films. The deposition temperature is indicated next to the sample name.

Crystal Structure

Figure 4.13 shows the XRD spectra of the active regions of films in panels (a) to (d) and the corresponding regions in the inactive films in panels (e) to (g). The locations of the peaks in each spectrum are the same. However, the background is larger and the widths of the peaks are broader for the lower deposition temperatures, notably those of samples 2005-08-31b (Pt-Bi-Pb deposited at ambient temperature)

Figure 4.13 XRD spectra of the active regions of samples (a) 2005-10-05a (Pt-Bi-Pb deposited at 160° C), (b) 2005-08-30 (Pt-Bi-Pb deposited at 260° C), (c) 2005-10-05b (Pt-Pb deposited at 265° C), and (d) 2005-09-10b (Pt-Bi-Pb deposited at 400° C), followed by the same region on inactive samples (e) 2005-08-31b (Pt-Bi-Pb deposited at ambient temperature), (f) 2005-10-13 (Pt-Bi-Pb deposited at 100° C), and (g) 2005-10-11a (Pt-Bi-Pb deposited at 510° C).



Figure 4.13 (continued)



Figure 4.13 (continued)



Figure 4.13 (continued)



and 2005-10-13 (Pt-Bi-Pb deposited at 100°C). Using the most intense peaks at 41° and the Scherrer formula¹⁸, the grain sizes in these two regions are approximately 10 nm. Compare these to the grain size in sample 2005-10-11a (Pt-Bi-Pb deposited at 510°C) of 11 nm. This is expected since deposition at a higher temperature increases the diffusion rates of sputtered material on the film, allowing larger grain formation.

All the spectra match the PbPt structure type, regardless of activity. Note that the intensity ratios of the peaks in each spectrum are different from those of the powder diffraction file, indicating once again a preferred orientation of grains in the films.

Surface Composition

Since electrocatalysis is a surface phenomenon, characteristics of the surface can better reveal the properties of the films that enhance electrocatalysts. We therefore proceeded to measure the surface composition (top 5 to 10 nm) of active regions and corresponding inactive regions with XPS. The results, shown in Figure 4.14, indicate that the surface compositions of the regions differ from their bulk compositions (see Figure 4.12). When considering metallic elements only (i.e. neglecting oxygen content), the atomic percent of Pt is lower at the surface than in the bulk on all films. The difference is greatest on the films deposited at the two lowest temperatures, samples 2005-08-31b and 2005-10-13, where the atomic percentages of Pt on the surface are less than 1% and 20%, respectively. Compare these to the Pt bulk compositions of approximately 40%.



Figure 4.14 Surface composition, measured by XPS, of the active regions of samples (a) 2005-10-05a (Pt-Bi-Pb deposited at 160°C), (b) 2005-08-30 (Pt-Bi-Pb deposited at 260°C), (c) 2005-10-05b (Pt-Pb deposited at 265°C), and (d) 2005-09-10b (Pt-Bi-Pb deposited at 400°C), followed by the same region on inactive samples (e) 2005-08-31b (Pt-Bi-Pb deposited at ambient temperature), (f) 2005-10-13 (Pt-Bi-Pb deposited at 100°C), and (g) 2005-10-11a (Pt-Bi-Pb deposited at 510°C).

We do not know at present what to attribute this difference to; in part it could be that the XPS data are un-calibrated. It could also be that the surface composition is intrinsically different, with Pb or Bi enriched at the surface due to surface thermodynamics or surface kinetics during deposition. The difference could be related to surface oxidation upon exposure to air or to the electrolyte and electrochemical cycling. The data show no apparent relationship between surface composition and electrocatalytic activity during fluorescence screening.

Relationship between Characterization Data and Electrocatalytic Activity

The bulk composition, surface composition, and crystal structure data showed no relationship with the deposition temperature and activity revealed by the fluorescence screening. However, all the active regions matched the PbPt phase (NiAs structure) in their XRD spectra. We therefore conclude that the NiAs structure must be present for electrocatalytic activity in the Pt-Bi-Pb system, but its presence does not guarantee activity. Other surface characterization techniques may be more helpful in explaining why the electrocatalytic activity only appears for a range of deposition temperatures.

Conclusions

We deposited six ternary thin film composition spreads of Pt, Bi, and Pb; one binary film of Pt and Bi; and one binary film of Pt and Pb at different temperatures. Fluorescence screening revealed electrocatalytic activity for methanol oxidation for ternary films deposited between 160°C and 400°C, with optimal onset potentials for deposition temperatures of 260°C and 400°C. The Pt-Pb binary film also showed electrocatalytic activity, but the Pt-Bi binary film was inactive. The results show that Bi is unnecessary for activity, but may lower the onset potential of active regions by a small amount. Measurements of the bulk composition, surface composition, and crystal structure show no relationship to deposition temperature (in the range of 160°C to 400°C) or electrocatalytic activity. However, the NiAs structure type was present in all active regions. The average composition of all the active ternary phases was Pt_{0.49}Bi_{0.07}Pb_{0.26}O_{0.17}. The high oxygen content is of concern in interpreting the results since it may include not only oxides that are distributed in the bulk during synthesis but also at the surface upon exposure to air.

Characterization of nine regions of the films before and after fluorescence screening showed changes in appearance, crystal structure, and bulk composition in regions that were rich in Pb. We attributed these changes to leaching of Pb due to its low standard reduction potential. However, the changes were reduced in Pb-rich regions containing the NiAs structure type.

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CHAPTER 5 A STUDY OF THE Pt-Ru-Pb SYSTEM

In March 2005, Professor Abruña of the Chemistry and Chemical Biology Department at Cornell University suggested preparation of a thin film composition spread of Pt, Ru, and Pb. PtRu alloy is the current standard for the electrocatalytic oxidation of small organic molecules such as methanol. We hypothesized that the addition of a third element such as Pb may enhance the electrocatalytic ability of PtRu. Pb turned out to be an excellent choice, and it led to extensive studies on active compositions in the Pt-Ru-Pb system.

Pt-Ru-Pb Background

Binary Phase Diagrams of Pt-Ru and Pb-Ru

The binary phase diagram of $Pt-Ru^1$ shows two alloys (solid solutions) at 1000°C of composition Pt_xRu_{1-x} : an fcc structure (same as that of Pt) for x > 0.38 and an hcp structure (same as that of Ru) for x < 0.20. For 0.20 < x < 0.38, a two-phase mixture of the fcc and hcp structures exists. Although there is no data shown below 1000°C, we assume alloys with similar compositions are present below this temperature. The width of the two-phase region is somewhat temperature dependent above 1000°C, as is typical for such partial solid solution phase diagrams. No ordered phases exist for Pt and Ru.

No binary phase diagrams of Pb-Ru are published². The two elements form no known compounds or alloys and are reported to be completely immiscible. For a description of the phase diagram of Pb-Pt, see Chapter 4.

PtRu as a Fuel Cell Anode Electrocatalyst

Researchers have investigated various forms of PtRu-type materials as fuel cell anode electrocatalysts for the oxidation of methanol, ethanol, and hydrogen. These have included bulk PtRu alloys³⁻⁵, Ru deposited on Pt surfaces⁶⁻⁸, nanoparticles of PtRu^{9, 10}, PtRu alloy clusters from reduction of oxides¹¹, and PtRu particles impregnated into carbon supports^{12, 13}. PtRu-type electrocatalysts show superiority over Pt in terms of reduced Pt loading ^{3, 10}, higher activity toward methanol^{6-8, 11, 13} and ethanol⁷ oxidation, and resistance to CO poisoning^{14, 15} (an intermediate in methanol oxidation).

Methanol oxidation on PtRu-type electrocatalysts occurs through the following bifunctional mechanism^{16, 17}:

$Pt + CH_3OH \rightarrow Pt-(CH_3OH)_{ads}$	(1)
$Pl + CH_3OH \rightarrow Pl - (CH_3OH)_{ads}$	(1)

$$Pt-(CH_3OH)_{ads} \rightarrow Pt-(CH_3O)_{ads} + H^+ + e^-$$
(2)

$$Pt-(CH_3O)_{ads} \rightarrow Pt-(CH_2O)_{ads} + H^+ + e^-$$
(3)

$$Pt-(CH_2O)_{ads} \rightarrow Pt-(CHO)_{ads} + H^+ + e^-$$
(4)

$$Pt-(CHO)_{ads} \rightarrow Pt-(CO)_{ads} + H^{+} + e^{-}$$
(5)

$$M + H_2O \rightarrow M - (H_2O)_{ads}$$
(6)

$$M-(H_2O)_{ads} \rightarrow M-(OH)_{ads} + H^+ + e^-$$
(7)

$$Pt-(CO)_{ads} + M-(OH)_{ads} \rightarrow Pt + M + CO_2 + H^+ + e^-$$
(8)

M represents a second metal alloyed with Pt, in this discussion Ru. In this multi-step mechanism, methanol molecules adsorb to surface Pt sites (step 1) and lose hydrogen atoms until CO remains (steps 2 to 5). Water molecules, adsorbed on adjacent Ru sites (step 6), also lose hydrogen atoms (step 7) and the remaining hydroxide assists in the final removal of CO from Pt (step 8). This final step is supported by several studies that show the presence of hydrous Ru oxides on the surface of PtRu alloy electrocatalysts^{4, 5, 12, 18}.

There is controversy over the exact structure of PtRu-type electrocatalysts. Many works assume the active species is a PtRu bulk alloy, with hydrous Ru oxides at the surface only as described in the bifunctional mechanism above. However, a study by Rolison *et. al.*¹⁹ showed that PtRu blacks are actually mixtures of Pt metal and Ru oxides, with lesser amounts of mixtures of Pt oxides and elemental Ru. The active species has been misidentified due to the fact that hydrous Ru oxides are amorphous and therefore only appear in the background of XRD spectra. Long *et. al.*⁹ showed that PtRu blacks that contain a mixture of Pt and hydrous Ru oxides.

Some researchers have increased the activity of PtRu-type anode electrocatalysts by adding a third metal such as $Os^{4, 17, 20}$ and Ir^{20} . A patent also exists for a PtRu anode fuel cell electrocatalysts with a separate addition of 5 mg/cm² of Pb²¹. In a fuel cell, the electrocatalyst shows a -200 mV shift in the onset of methanol oxidation compared to binary PtRu.

Initial Investigations of the Pt-Ru-Pb System

Synthesis, Screening, and Characterization of Sample 2005-03-31

We synthesized our first Pt-Ru-Pb thin film composition spread (sample 2005-03-31) with the parameters shown in Table 5.1. The sample was "hot sputtered", and the chosen parameters produced a 1:1:1 ratio of Pt:Ru:Pb at the center according to calibrations of the time. The Ta sublayer thickness is 1200 Å and the estimated thickness of the composition spread layer at the center is 1600 Å. Figure 5.1(a) shows an image of the sample after synthesis. Similar to the Pt-Bi-Pb composition spreads in Chapter 4, the regions closest to the Pt sputtering source exhibit specular reflection and those closest to the Pb sputtering source are dull. The regions close to the Ru source are also specular. There are visible structures toward the Pb sputtering source that appear to have been created by liquid running down the substrate during deposition. This may be from the Pb since the deposition temperature was greater than its melting point (327°C).

samples	gun #	1	2	3	4
2005-03-31	targets	Pt	Ru	Pb	Та
and 2005-	gun currents (mA)	112	95	48	730
05-11a	deposition rates at center (Å/s)	1.7	1.6	3.5	2.7
	deposition times (s)	240 445 1:1:1			445
	molar ratio at center (Pt:Ru:Pb)				
	deposition temperature (°C)	350			

Table 5.1 Synthesis parameters of samples 2005-03-31 and 2005-05-11a.



Figure 5.1 Images of sample 2005-03-31 (a) before and (b) after fluorescence screening for both methanol and ethanol. The relative orientation of the sputtering sources are shown in (a).

We screened sample 2005-03-31 for active electrocatalysts for methanol and ethanol oxidation with the fluorescence technique. The screening for methanol oxidation was in the standard electrolyte of 5 M methanol, 0.1 M NaCF₃SO₃, and 0.5 mM quinine. The potential scanned from 0 to 200 mV vs. Ag/AgCl at 5 mV/s. Following the methanol test, we rinsed the sample and electrochemical cell with distilled water and proceeded with screening for ethanol oxidation. The ethanol test also contained the standard electrolyte (5 M ethanol, 0.1 M NaCF₃SO₃, and 0.5 mM quinine) with the potential scanned from 0 to 200 mV vs. Ag/AgCl at 5 mV/s.

The results and analysis of the methanol screening of sample 2005-03-31 is shown in Figure 5.2. Panel (a) shows an image of the sample at 200 mV vs. Ag/AgCl. Panel (b) shows a contour plot of the background-subtracted image at 200 mV. There are two active regions, labeled 1 and 2, close to the Pt sputtering source. Panel (c) shows a plot of the fluorescence intensity vs. potential for regions 1 and 2. From the plot, one can see that the onset potentials for regions 1 and 2 are 100 and 110 ± 25 mV vs. Ag/AgCl, respectively. These values are an improvement over the methanol active regions of the Pt-Bi-Pb composition spreads, for which the lowest onset potential is 175 mV vs. Ag/AgCl (see Chapter 4).

The results and analysis of the ethanol screening of sample 2005-03-31 are shown in Figure 5.3. Panel (a) shows the fluorescent image at 200 mV vs. Ag/AgCl and (b) shows the corresponding intensity contour plot of the background-subtracted image. There is only one active region for ethanol oxidation, close to the Ru sputtering source. Panel (c) shows a plot of the fluorescence intensity vs. potential for the region, with an onset potential of 40 ± 25 mV vs. Ag/AgCl.

Figure 5.1(b) shows an image of the film after fluorescence screening. When compared to Figure 5.1(a), one can see that the regions closer to the Pt sputtering source remain reflective following screening, while there is discoloration in the other regions, especially those closer to the Pb sputtering source. This may indicate leaching of Pb, as it did with the Pt-Bi-Pb films described in Chapter 4.

The onset potentials of the active regions of sample 2005-03-31 are exceptionally low compared to those of Pt and even the intermetallic compound PtPb. According to the study by Casado-Rivera *et. al.*²², bulk Pt has an onset potential of 370 mV vs. Ag/AgCl for methanol and 250 mV vs. Ag/AgCl for ethanol. PtPb has onset potentials of 290 mV vs. Ag/AgCl for methanol and 130 mV vs. Ag/AgCl for ethanol.



Figure 5.2 Results and analysis of the fluorescence screening of sample 2005-03-31 for the oxidation of methanol. (a) Image of the screening at 200 mV vs. Ag/AgCl, with the orientation relative to the sputtering sources shown. (b) Contour plot of the background-subtracted image at 200 mV vs. Ag/AgCl. The most active regions, labeled 1 and 2, are indicated by the arrows. (c) A plot of the fluorescence intensity vs. potential for regions 1 and 2.



Figure 5.3 Results and analysis of the fluorescence screening of sample 2005-03-31 for the oxidation of ethanol. (a) Image of the screening at 200 mV vs. Ag/AgCl, with the orientation relative to the sputtering sources shown. (b) Contour plot of the background- subtracted image at 200 mV vs. Ag/AgCl. The most active region is indicated by the arrow. (c) A plot of the fluorescence intensity vs. potential for the active region.

Due to the impressive onset potential of the ethanol active region and the incentives for using ethanol as fuel (see Chapter 1), we directed our initial characterization efforts toward determining the composition and crystal structure of the ethanol active region. All characterizations were performed after fluorescence screening. EDS measured a composition of $Pt_{0.19}Ru_{0.73}Pb_{0.08}$ (error ±10%), which makes the region all the more impressive considering the low fraction of Pt. The XRD spectrum of the region is shown in Figure 5.4. The peak locations of known spectra from the powder diffraction file database²³ show possible matches to Pt (pdf #4-802), Ru (pdf #6-663), and PbPt_x (pdf #6-574, same spectrum as PbPt₃). The tallest peak, at 34°, comes from the Ta underlayer. Note that the Pt and Ru peaks from the powder



Figure 5.4 XRD spectrum of the ethanol active region of sample 2005-03-31.

diffraction files are shifted from their corresponding peaks in the spectrum. This may indicate two alloy phases in the film: one having the Pt structure type (fcc lattice) and the other having the Ru structure type (hexagonal lattice). The Pt-Ru binary phase diagram shows a two-phase region when the atomic percentage of Ru is between 62% and 80%, and the composition indicated by EDS is within this range. However, when Ru forms alloys with Pt, the lattice parameter decreases compared to pure Pt because of the smaller radius of the Ru atoms. According to LAPODS²⁴, a computer program that calculates lattice parameters using Cohen's Method²⁵⁻²⁷, the lattice parameter of the Pt phase is 3.95 ± 0.08 Å. This is greater than the lattice parameter of pure Pt (3.92 Å), and may indicate that Pb is substituting into Pt sites in the lattice since it has a larger atomic radius.

Synthesis, Screening, and Characterization of Sample 2005-05-11a

We synthesized a second film, sample 2005-05-11a, using the same parameters as those listed in Table 5.1. An image of the film after synthesis is shown in Figure 5.5(a). Similar to sample 2005-03-31, the dull regions appear closer to the Ru and Pb sputtering sources. However, this particular sample has a dark spot close to the Ru sputtering source.



Figure 5.5 Images of sample 2005-05-11a (a) before and (b) after fluorescence screening, with the relative orientation of the sputtering sources shown.

We conducted fluorescence screenings on sample 2005-05-11a for methanol oxidation followed by ethanol oxidation using the same standard electrolytes as those for sample 2005-03-31. For the screening in methanol, the potential scanned from 0 to
300 mV vs. Ag/AgCl at 5 mV/s, while the potential scanned from -100 to 200 mV vs. Ag/AgCl at 5 mV/s during the ethanol screening.

Figure 5.6 shows the results and analysis of the methanol screening. The image of the screening and the corresponding contour plot of the background-subtracted image indicate three active regions. The region with the first onset of fluorescence is



Figure 5.6 Fluorescence screening of sample 2005-05-11a for the oxidation of methanol. (a) Image of the screening at 300 mV vs. Ag/AgCl, with the orientation relative to the sputtering sources shown. (b) Contour plot of the background-subtracted image at 300 mV vs. Ag/AgCl. The region with the first onset of fluorescence is indicated by the arrow. (c) A plot of the fluorescence intensity vs. potential for the active region indicated in (b).

indicated by the arrow in panel (b), and a plot of the fluorescence intensity vs. potential for this region is shown in (c). The onset potential for methanol oxidation in the region is 110 ± 25 mV, comparable to the methanol active regions of sample 2005-03-31. However, the location of the active region is much closer to the Ru sputtering source, at the dark spot noted above in Figure 5.5.

The results and analysis of the ethanol screening are shown in Figure 5.7. Note that the location of the active region with the first onset of fluorescence for ethanol is the same as that of methanol. This is also the same approximate location as the ethanol active region in sample 2005-03-31, but the fluorescence is much sharper and intense in sample 2005-05-11a. The onset potential for ethanol oxidation is also much lower at -35 ± 25 mV vs. Ag/AgCl.

Figure 5.5(b) shows an image of sample 2005-05-11a after fluorescence screening. As usual, the dull regions changed color during the screening. Note that the dark region that is active for both methanol and ethanol is still on the film, although it is lighter in color. Figure 5.8 shows an SEM-magnified image of the dark region with randomly dispersed particles on the surface that are approximately 1 µm in size.

We performed extensive characterizations of the active region of sample 2005-05-11a. EDS suggests a composition of $Pt_{0.22}Ru_{0.74}Pb_{0.04}$ (±10% for each fraction), very similar to the composition of the ethanol active region of sample 2005-03-31. Analysis by RBS confirms a similar composition at $Pt_{0.25}Ru_{0.70}Pb_{0.05}$. We also used XPS to determine the composition of the surface (top 5 to 10 nm) at $Pt_{0.24}Ru_{0.60}Pb_{0.16}$. While the bulk and surface compositions are within the experimental errors of each other (±10%), the data may suggest that Pb is more prominent at the surface than in the bulk. This is also the case for the active regions of the Pt-Bi-Pb films in Chapter 4.



Figure 5.7 Fluorescence screening of sample 2005-05-11a for the oxidation of ethanol. (a) Image of the screening at 125 mV vs. Ag/AgCl, with the orientation relative to the sputtering sources shown. (b) Contour plot of the background-subtracted image at 125 mV vs. Ag/AgCl. The region with the first onset of fluorescence is indicated by the arrow. (c) A plot of the fluorescence intensity vs. potential for the active region indicated in (b).



Figure 5.8 SEM image of the methanol/ethanol active region of sample 2005-05-11a.

Figure 5.9 shows the XRD spectrum of the active region of sample 2005-05-11a. Similar to the ethanol active region of sample 2005-03-31, the spectrum peaks



Figure 5.9 XRD spectrum of the methanol/ethanol active region of sample 2005-05-11a.

match those of Pt (pdf #4-802), Ru (pdf #6-663), and PbPt_x (pdf #6-574). However, in this spectrum, the Ru peaks are shifted by less than 0.3° . The Pt peaks are shifted to

lower values of 2 θ compared to the ethanol active region of sample 2005-03-31; LAPODS calculates an expansion in the fcc lattice parameter to 3.94 ± 0.09 Å from 3.92 Å.

Comparison of the Activity of Pt-Ru-Pb and Pt-Ru Thin Film Composition Spreads

The active regions on samples 2005-03-31 and 2005-05-11a are impressive for their low onset potentials (especially toward ethanol) and low Pt content. While the ethanol onset potential of sample 2005-05-11a (-35 mV vs. Ag/AgCl) is among the lowest reported, it is still far from the ideal, which under these conditions is approximately -500 mV. To determine if the extraordinary properties are due to the presence of Pb, we synthesized a Pt-Ru thin film composition spread (sample 2005-07-01) and screened it for electrocatalytic activity for methanol and ethanol oxidation. The synthesis parameters are shown in Table 5.2. The parameters are the same as those of samples 2005-03-31 and 2005-05-11a, with the exception of the deposition temperature (a small difference of 35°C) and the absence of Pb. The estimated thickness of the composition spread layer at its center is 790 Å. Figure 5.10(a) shows an image of the film after synthesis. The entire film is reflective, indicating that the dull textures on the Pt-Ru-Pb films are due to Pb.

Table 5.2 Synthesis	parameters of samp	e 2005-07-01.
5	1 1	

sample	gun #	1	2	4
2005-07-01	targets	Pt	Ru	Та
	gun currents (mA)	112	95	730
	deposition rates at center (Å/s)	1.7	1.6	2.7
	deposition time (s)	24	40	445
molar ratio at center (Pt:Ru)		1:1		
	deposition temperature (°C)	385		



Figure 5.10 Images of sample 2005-07-01 (a) before and (b) after fluorescence screening, with the relative orientation of the sputtering sources indicated.

We conducted a methanol fluorescence screening with the standard methanol electrolyte (see Chapter 2) while scanning the potential from 0 to 400 mV vs. Ag/AgCl at 5 mV/s. The entire film is inactive over this range of potentials. We subsequently screened the film in the standard ethanol electrolyte (see Chapter 2) from 0 to 800 mV vs. Ag/AgCl at 5 mV/s. Figure 5.11 shows fluorescent images at selected potentials and their corresponding background-subtracted images. Since the images show fluorescence only above 400 mV vs. Ag/AgCl, the onset potential is no less than 350 mV vs. Ag/AgCl.

We completed two more screenings, each in fresh ethanol electrolyte. The second screening was from 0 to 600 mV vs. Ag/AgCl at 5 mV/s. The film was active toward ethanol oxidation in approximately the same region as the first screening, but the onset potential was lower at 250 ± 25 mV vs. Ag/AgCl. The third screening, from 0 to 400 mV vs. Ag/AgCl at 5 mV/s, showed fluorescence for the same region with an onset potential of 275 ± 25 mV vs. Ag/AgCl, within experimental error of the second screening. The lower onset potentials of the last two screenings suggest that the scan to higher potentials in the first screening altered the active region of the film by leaching one or more components. This is not surprising since the maximum potential



Figure 5.11 Images of the ethanol fluorescence screening of sample 2005-07-01 and their background-subtracted images at (a) 350 mV, (b) 400 mV, (c) 600 mV, and (d) 800 mV vs. Ag/AgCl. The relative orientation of the sputtering sources is shown in (a).

of the first scan, 800 mV vs. Ag/AgCl, is higher than the standard reduction potential of both Pb and Ru. Oxide formation on the film surface is also likely at such a high potential.

Figure 5.10(b) shows an image of sample 2005-07-01 after the fluorescence screenings. There are no apparent changes in the film surface after the screening, except for the large circular stain left by the o-ring of the electrochemical cell. When compared to similar images of samples 2005-03-31 and 2005-05-11a, one can attribute the changes in color from fluorescence screening to the presence of Pb.

A comparison of the onset potentials of sample 2005-07-01 to samples 2005-03-31 and 2005-05-11a clearly indicate that Pb enhances the electrocatalytic activity of the active regions. Electrocatalytic activity was completely absent without Pb for methanol below 400 mV vs. Ag/AgCl, and the onset potential of ethanol oxidation in the active region without Pb was higher by as much as 435 mV.

Other Pt-Ru-Pb and Pt-Ru Films

Pt-Ru-Pb Films Deposited Between 370°C and 400°C

We synthesized six other Pt-Ru-Pb thin film composition spreads at deposition temperatures from 370°C to 400°C, close to those of samples 2005-03-31 and 2005-05-11a. The synthesis parameters of each film are listed in Table 5.3. Note that many of the composition spread layers have molar ratios other than 1:1:1 at the center. We did this to shift the active region found in sample 2005-05-11a closer to the center of the film. The new films allow us to test the reproducibility of the active regions.

We used the fluorescence screening method to determine the onset potentials of electrocatalytically active regions for methanol and ethanol oxidation in the films listed in Table 5.3. For most of the films, we tested for methanol oxidation first in the standard methanol electrolyte, then tested for ethanol oxidation with fresh

sample	gun #		2	3	4
2005-10-12	targets	Pt	Ru	Pb	Та
	gun currents (mA)	66	242	42	730
	deposition rates at center (Å/s)		2.4	1.8	2.7
	deposition times (s)		490		445
	molar ratio at center (Pt:Ru:Pb)		1:3	3:1	
	deposition temperature (°C)		4(00	
sample	gun #	1	2	3	4
2006-01-25a	targets	Pt	Ru	Pb	Ta
	gun currents (mA)	55	213	50	780
	deposition rates at center (Å/s)	1.2	2.1	2.4	2.5
	deposition times (s)		440		400
	molar ratio at center (Pt:Ru:Pb)		1:2	2:1	
	deposition temperature (°C)		37	70	
sample	gun #	1	2	3	4
2006-01-25b	targets	Pt	Ru	Pb	Ta
	gun currents (mA)	55	213	50	780
	deposition rates at center (Å/s)	1.2	2.1	2.4	2.5
	deposition times (s)	440 4		400	
	molar ratio at center (Pt:Ru:Pb) 1:2:1				
	deposition temperature (°C)	380			
sample	gun #	1	2	3	4
2006-05-16	targets	Pt	Ru	Pb	Та
	gun currents (mA)	50	200	35	700
	deposition rates at center (Å/s)	0.8	1.4	1.5	3.7
	deposition times (s)		675		270
	molar ratio at center (Pt:Ru:Pb) 1:2:1				
	deposition temperature (°C)		37	70	
sample	gun #	1	2	3	4
2006-05-23	targets	Pt	Ru	Pb	Та
	gun currents (mA)	55	135	76	700
	deposition rates at center (Å/s)	1.0	0.9	4.0	3.7
	deposition times (s)	425		270	
	molar ratio at center (Pt:Ru:Pb)	1:1:2			
	deposition temperature (°C)	390			
sample	gun #	1	2	3	4
2006-06-22	targets	Pt	Ru	Pb	Та
	gun currents (mA)	55	250	43	700
	deposition rates at center (Å/s)	1.0	1.8	2.0	3.7
	deposition times (s)	520 270		270	
	molar ratio at center (Pt:Ru:Pb)		1:2	2:1	
	deposition temperature (°C)	370			

Table 5.3 Synthesis parameters of Pt-Ru-Pb films deposited between 370°C and 400°C.

standard ethanol electrolyte (see Chapter 2 for a description of standard electrolytes). However, we screened sample 2006-01-25a for ethanol only and sample 2006-01-25b for methanol only. These variations were to check if the initial test in methanol affects the activity toward ethanol and to characterize a methanol active region that had not received a screening for ethanol oxidation.

Table 5.4 shows the lowest onset potential of the active regions on each Pt-Ru-Pb film deposited at 350°C and higher. The lowest onset potentials are -20 ± 25 mV vs. Ag/AgCl for methanol (samples 2005-05-16 and 2005-05-23) and -220 ± 25 mV vs. Ag/AgCl for ethanol (sample 2005-05-16). The average methanol onset potential is 56 mV vs. Ag/AgCl, with a standard deviation of 77 mV, and the average ethanol onset potential is -77 mV vs. Ag/AgCl, with a standard deviation of 90 mV. The

somplo	methanol onset potential	ethanol onset potential
sample	(±25 mV vs. Ag/AgCl)	(±25 mV vs. Ag/AgCl)
2005-03-31	100	40
2005-05-11a	110	-35
2005-10-12	180	-20
2006-01-25a	-	-75
2006-01-25b	-5	-
2006-05-16	-20	-220
2006-05-23	-20	-60
2006-06-22	45	-170

Table 5.4 Lowest onset potential of the active regions on each Pt-Ru-Pb film.

standard deviations show a wide variation in onset potentials for both methanol and ethanol oxidation. However, all the onset potentials (with the exception of 2005-10-12) are lower than those of bulk Pt (370 mV vs. Ag/AgCl toward methanol, 250 mV vs. Ag/AgCl toward ethanol²²). Note that sample 2006-01-25a, tested only for ethanol oxidation, has an onset potential as low as most other samples, indicating that methanol screening before ethanol screening does not dampen the electrocatalytic activity of the best ethanol oxidation catalysts on the film. It should also be noted that

the methanol and ethanol active regions have the same location on sample 2005-10-12 only, just as they did on sample 2005-05-11a.

Figure 5.12 shows the composition, measured with WDS, of the methanol and ethanol active regions with the lowest onset potential for each sample listed in Table 5.3. The compositions of the methanol active regions vary widely, especially in the



Figure 5.12 Composition, measured with WDS, of the (a) methanol and (b) ethanol active regions with the lowest onset potential on each Pt-Ru-Pb sample listed in Table 5.3.

atomic percentages of Pt and Ru; the average composition is $Pt_{0.37}Ru_{0.57}Pb_{0.04}O_{0.02}$, with standard deviations of 18%, 22%, 5%, and 1% for Pt, Ru, Pb, and O, respectively. Because of the variation, it is difficult to determine if the ethanol screening changes the composition of the methanol active region of sample 2006-01-25b (tested for methanol only). The ethanol active regions show less variation in atomic percentages; the average composition is $Pt_{0.22}Ru_{0.69}Pb_{0.04}O_{0.05}$, with standard deviations of 6%, 10%, 3%, and 2% for Pt, Ru, Pb, and O, respectively. For the compositions of both methanol and ethanol active regions, there is weak correlation between the atomic percentages of each element and the onset potentials.

The XRD spectra of the methanol active regions are shown in Figure 5.13. Most of the spectra have peaks at the same approximate locations but with different intensities, matching the powder diffraction files of Pt (pdf #4-802), Ru (pdf #6-663), and PbPt_x (pdf #6-574). However, two spectra differ noticeably from the others. The spectrum from sample 2005-10-12 matches Ru only. This region had a higher onset potential than the other methanol active regions, and may suggest that the other phases typically present are necessary to achieve the low onset potentials we typically observe. Sample 2006-05-23 shows matches to only Pt and PbPt (pdf #6-374), yet the onset potential of the methanol active region is -20 mV vs. Ag/AgCl, the lowest measured of all the methanol onset potentials.

The XRD peaks matching the Pt structure type are shifted to higher values of 20, indicating that the corresponding phase has a smaller fcc lattice parameter than that of pure Pt. This is opposite the case of the methanol active region of sample 2005-05-11a. We attribute the shift in the lattice parameter to alloying between Pt and Ru. Table 5.5 shows the lattice parameters of the phases, calculated with the LAPODS program. We can also estimate the alloy composition of the phase from the lattice parameter using the relationship between lattice parameter and PtRu alloy composition

Figure 5.13 XRD spectra for the methanol active regions of samples (a) 2005-10-12, (b) 2006-01-25b, (c) 2006-05-16, (d) 2006-05-23, and (e) 2006-06-22.







Figure 5.13 (continued)



(d)





(e)

for arc-melted PtRu, as determined by Díaz-Morales *et. al.*²⁸ and based on Vegard's Law²⁹. The associated compositions are shown in Table 5.5. For lattice parameters less than 3.84 Å, we extrapolate the relationship between lattice parameter and alloy composition from the figure of Díaz-Morales *et. al.* The composition may therefore be less reliable. The alloy compositions show no apparent relationship to the onset potential.

Table 5.5 Lattice parameters of the Pt fcc phase, indicated by XRD, and the corresponding PtRu alloy composition in the methanol and ethanol active regions.

	methanol active region		ethanol active region			
sample	lattice parameter $(\pm 0.01 \text{ Å})$	composition	lattice parameter $(\pm 0.01 \text{ Å})$	composition		
2005-10-12	no Pt phase		no Pt phase			
2006-01-25a				$Pt_{0.25}Ru_{0.75}$		
2006-01-25b	3.83	$Pt_{0.26}Ru_{0.74}$				
2006-05-16	3.85	$Pt_{0.40}Ru_{0.60}$	3.85	$Pt_{0.40}Ru_{0.60}$		
2006-05-23	3.90	$Pt_{0.78}Ru_{0.22}$	no Pt phase			
2006-06-22	3.87	$Pt_{0.55}Ru_{0.45}$	3.87 Pt _{0.55} Ru _{0.45}			

The XRD spectra of the ethanol active regions, similar to those of methanol, are shown in Figure 5.14. The spectra match Pt, Ru, and PbPt_x structure types in most regions, with the exception of the active region of sample 2005-10-12. Note also that the spectrum of sample 2006-05-23 matches PbPt only. However, none of these phases indicate a relationship to the onset potentials. Just as for the methanol active regions, the ethanol active regions have peaks that are shifted from those of pure Pt. Table 5.5 lists the lattice parameter of any Pt phases and the composition of the PtRu alloy associated with it. There is no apparent relationship between the lattice parameter and ethanol onset potential.

Pt-Ru Films Deposited Between 300°C and 435°C

We also synthesized three more Pt-Ru thin film composition spreads to test for variations in their activity toward methanol and ethanol. The synthesis parameters of the films are listed in Table 5.6. The deposition temperature for sample 2006-03-03a is unknown due to a broken thermocouple following evacuation of the chamber. We estimate the temperature was 300°C to 400°C based on the voltage placed across the heater and the time of heating.

We screened each of the Pt-Ru films for active methanol and ethanol electrocatalysts using the fluorescence method. For each film, we conducted the methanol screening first using our standard methanol electrolyte followed by ethanol screening with fresh standard ethanol electrolyte (see Chapter 2 for standard electrolytes). Table 5.7 lists the onset potentials of the active regions for methanol and ethanol oxidation.

Just like the Pt-Ru-Pb films, the Pt-Ru films also show wide variations in onset potential for both methanol and ethanol oxidation, with standard deviations of 154 mV and 201 mV, respectively. The average onset potentials are 288 mV vs. Ag/AgCl and Figure 5.14 XRD spectra for the ethanol active regions of samples (a) 2005-10-12, (b) 2006-01-25a, (c) 2006-05-16, (d) 2006-05-23, and (e) 2006-06-22.



Figure 5.14 (continued)



Figure 5.14 (continued)



Table 5.6 Synthesis parameters of Pt-Ru films deposited between 300°C and 435°C.

sample 2006-	gun #	2	3	4
03-03a	targets	Pt	Ru	Та
	gun currents (mA)	145	235	700
	deposition rates at center (Å/s)	2.5	2.2	3.7
	deposition time (s)	5.	30	270
	molar ratio at center (Pt:Ru)		1:1	
	deposition temperature (°C)	unknown (estimated at 30	0°C to
			400°C)	-
sample 2006-	gun #	1	2	4
03-13a	targets	Pt	Ru	Та
	gun currents (mA)	103	220	700
	deposition rates at center (Å/s)	2.5	2.2	3.7
	deposition time (s)	530 270		
	molar ratio at center (Pt:Ru)	1:1		
	deposition temperature (°C)	435		
sample 2006-	gun #	1	2	4
05-17	targets	Pt	Ru	Та
	gun currents (mA)		200	700
	deposition rates at center (Å/s)	0.8 1.4		3.7
	deposition time (s)	1135 27		270
	molar ratio at center (Pt:Ru)	1:2		
	deposition temperature (°C)		370	

sample	methanol onset potential $(+25 \text{ mV ys} \text{ Ag/AgCl})$	ethanol onset potential $(+25 \text{ mV ys} \text{ Ag/AgCl})$
2006-03-03a	410	-10
2006-03-13a	340	310
2006-05-17	115	-60

Table 5.7 Lowest onset potential of the active regions on each Pt-Ru film.

80 mV vs. Ag/AgCl for methanol and ethanol oxidation, respectively. The values measured here are much different than those of sample 2005-07-01, where there was no activity for methanol oxidation and the initial onset potential toward ethanol oxidation was greater than 350 mV vs. Ag/AgCl. It is interesting to note that the extraordinarily low onset potentials toward ethanol oxidation found on the Pt-Ru-Pb films are also possible on the Pt-Ru films, although there is still a substantial difference between the lowest values. It should also be noted that the methanol and ethanol active regions are at the same location on sample 2006-05-17.

Figure 5.15 shows the composition, measured with WDS, of the methanol and ethanol active regions of each film. The average compositions of the methanol and ethanol active regions are $Pt_{0.36}Ru_{0.64}$ and $Pt_{0.42}Ru_{0.58}$, respectively. The methanol active regions contain a higher atomic percentage of Ru than the optimum reported by Gasteiger *et. al.*^{5, 30, 31} of 10% to 30%. The methanol active regions show more variation in their compositions compared to the ethanol active regions, although there is less variation in both compared to those of the Pt-Ru-Pb films. Note also that the atomic percent of oxygen is negligible (less than 1%) in each region. This may indicate that Pb is responsible for the higher oxygen content found in the Pt-Ru-Pb films.

Figures 5.16(a), (b), and (c) show the XRD spectra of the methanol active regions on the films listed in Table 5.6. Samples 2006-03-13a and 2006-05-17 show suitable peak matches to Pt (pdf #4-802) and Ru (pdf #6-663), while sample 2006-03-

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Figure 5.15 Composition, measured with WDS, of the (a) methanol and (b) ethanol active regions on each Pt-Ru sample listed in Table 5.6.

03a shows a match to Ru only. For both phases in each region the peaks are shifted, indicating alloying between Pt and Ru. LAPODS calculates fcc lattice parameters of 3.84 ± 0.01 Å and 3.85 ± 0.01 Å for the methanol active regions of samples 2006-03-13a and 2006-05-17, respectively. The corresponding alloy compositions are Pt_{0.33}Ru_{0.67} and Pt_{0.40}Ru_{0.60}, respectively.

Figures 5.16(d), (e), and (f) show the XRD spectra of the ethanol active regions. All the spectra show matches to Pt and Ru structure types, with peaks shifted from those of the powder diffraction files. LAPODS calculates Pt fcc lattice parameters of 3.85 ± 0.01 Å for both regions of samples 2006-03-13a and 2006-05-17, for a corresponding alloy composition of Pt_{0.40}Ru_{0.60}. The spectrum of the ethanol active region on sample 2006-03-03a indicates an fcc lattice parameter of 3.84 ± 0.01 Å, for a corresponding alloy composition of Pt_{0.32}Ru_{0.68}.

Reproducibility Issues

The active regions of all Pt-Ru-Pb and Pt-Ru films have wide variations in onset potentials and composition. While most of the onset potentials are low enough to indicate a reasonable electrocatalyst (an ideal electrocatalysts would have an onset potential of approximately -500 mV vs. Ag/AgCl in the standard electrolyte), the results make the exact nature of the active regions and their reproducibility uncertain. Several conditions may account for the variations. There are numerous Ru oxides and hydrous Ru oxides, possibly with different degrees of electrocatalytic activity. If this is the case, slight variations in the deposition conditions such as base pressure or time of deposition could change the amount of oxide present. Variations in atmospheric exposure between synthesis and screening, such as humidity or temperature, could also affect the amount of oxide. The study by Rolison *et. al.*¹⁹, described earlier, may support this hypothesis. If the hypothesis is true, more consistent deposition and

Figure 5.16 XRD spectra for the methanol active regions of samples (a) 2006-03-03a, (b) 2006-03-13a, and (c) 2006-05-17, as well as XRD spectra for the ethanol active regions of samples (d) 2006-03-03a, (e) 2006-03-13a, and (f) 2006-05-17.





Figure 5.16 (continued)





Figure 5.16 (continued)





screening procedures are needed to obtain more consistent results. Also, the surface composition and structure, which determine electrocatalytic behavior, may be different than the bulk composition and structure. Surface characterizations are necessary to more completely understand what determines activity.

Pt-Ru-Pb Films at Lower Deposition Temperatures

We deposited five Pt-Ru-Pb thin film composition spreads at deposition temperatures of 270°C and lower to determine its effect on electrocatalytic ability of active regions. Table 5.8 shows the synthesis parameters of the five films. Most of the films have the same deposition parameters, with the exception of sample 2006-08-03 for which the deposition time is larger than the others due to a miscalculation on the part of the experimenter.

We screened each film, using the fluorescence method, for methanol oxidation followed by ethanol oxidation in their respective standard electrolytes (see Chapter 2). Table 5.9 lists the lowest onset potentials for methanol and ethanol oxidation on each sample. Note that the onset potentials are some of the lowest measured in the Pt-Ru-Pb system, especially for the films deposited without deliberate heating (ambient temperature). Furthermore, the results are more consistent for the ambient deposition temperature films, with the same onset potentials for methanol oxidation and a standard deviation of only 18 mV for ethanol onset potentials. However, we found no strong relationship between onset potential and deposition temperature for all the samples discussed in this chapter.

Figure 5.17 shows the composition, measured with WDS, of the methanol and ethanol active regions described in Table 5.9. For the films deposited at ambient temperature, the average composition of the methanol active regions is $Pt_{0.64}Ru_{0.22}Pb_{0.06}O_{0.08}$, with standard deviations of 8.36%, 5.20%, 1.34%, and

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sample	gun #	1	2	3	4
2006-06-	targets	Pt	Ru	Pb	Та
23a	gun currents (mA)	55	250	43	700
	deposition rates at center (Å/s)	1.0	1.8	2.0	3.7
	deposition times (s)	520		270	
	molar ratio at center (Pt:Ru:Pb)		1:2	2:1	
	deposition temperature (°C)		27	70	
sample	gun #	1	2	3	4
2006-08-03	targets	Pt	Ru	Pb	Та
	gun currents (mA)	55	250	43	700
	deposition rates at center (Å/s)	1.0	1.8	2.0	3.7
	deposition times (s)		735		270
	molar ratio at center (Pt:Ru:Pb)		1:2	2:1	
	deposition temperature (°C)		19	90	
sample	gun #	1	2	3	4
2006-06-	targets	Pt	Ru	Pb	Та
23b	gun currents (mA)	55	250	43	700
	deposition rates at center (Å/s)	1.0	1.8	2.0	3.7
	deposition times (s)		520 2		
	molar ratio at center (Pt:Ru:Pb)		1:2	:1	
	deposition temperature (°C)	ambient			
sample	gun #		2	3	4
2006-08-30	targets	Pt	Ru	Pb	Та
	gun currents (mA)	55	250	43	700
	deposition rates at center (Å/s)	1.0	1.8	2.0	3.7
	deposition times (s)	520 270			270
	molar ratio at center (Pt:Ru:Pb)		1:2	2:1	
	deposition temperature (°C)	ambient			
sample	gun #		2	3	4
2006-10-	targets	Pt	Ru	Pb	Та
16a	gun currents (mA)	55	250	43	700
	deposition rates at center (Å/s)	1.0	1.8	2.0	3.7
	deposition times (s)	520 2			270
	molar ratio at center (Pt:Ru:Pb)1:2:1deposition temperature (°C)ambient		2:1		
			oient	t	

Table 5.8 Synthesis parameters of the five Pt-Ru-Pb films deposited at 270°C and lower.

complo	deposition	methanol onset potential	ethanol onset potential
sample	temperature (°C)	(±25 mV vs. Ag/AgCl)	(±25 mV vs. Ag/AgCl)
2006-06-23a	270	90	-170
2006-08-03	190	-30	-220
2006-06-23b	ambient	-20	-240
2006-08-30	ambient	-20	-250
2006-10-16a	ambient	-20	-215

Table 5.9 Lowest onset potentials for methanol and ethanol oxidation for Pt-Ru-Pb films deposited at 270°C and lower.



Figure 5.17 Composition, measured with WDS, of the (a) methanol and (b) ethanol active regions of the Pt-Ru-Pb films described in Table 5.9.

2.83% for atomic percentages of Pt, Ru, Pb, and O, respectively. The average composition of the ethanol active regions for films deposited at ambient temperature is Pt_{0.42}Ru_{0.45}Pb_{0.04}O_{0.09}, with standard deviations of 9.63%, 14.58%, 2.42%, and 3.08% for atomic percentages of Pt, Ru, Pb, and O, respectively. The active regions for both methanol and ethanol have higher average atomic percentages of Pt and O and a lower average atomic percentage of Ru than those of the most active regions of films deposited between 370°C and 400°C. Note also that the films deposited at ambient temperature had lower standard deviations in the Pt and Ru atomic percentages for the methanol active regions, but higher standard deviations for the ethanol active regions. For the films listed in Table 5.9, we found no strong relationship between the atomic percentages of any one element and the onset potentials.

Figures 5.18 and 5.19 show the XRD spectra of the methanol and ethanol active regions described in Table 5.9. Each spectrum matches the structure types of Pt (pdf #4-802) and PbPt_x (pdf #6-574), although the corresponding peaks of both are frequently shifted. The shifts in the Pt peaks are not consistent for all the active regions of films deposited at ambient temperature; note that the methanol active regions of samples 2006-06-23b and 2006-08-30 show negligible shifts. The Ru structure type (pdf #6-663) is a good match only for spectra of regions deposited at 190°C or 270°C. This may indicate that the presence of the Ru phase is not responsible for the low onset potentials of the active regions. Note also that the spectra of regions deposited at ambient temperature have broader peaks than those deposited at higher temperature. Using the most intense Pt peaks at approximately 40° in the methanol active regions, the Scherrer formula³² gives grain sizes of 7.3 nm for sample 2006-06-23a (deposited at 270° C) and 5.0 nm for sample 2006-06-23b (deposited at ambient temperature). This is expected since lower deposition temperatures provide

Figure 5.18 XRD spectra for the methanol active regions of the Pt-Ru-Pb films described in Table 5.9. (a) 2006-06-23a (deposited at 270° C) (b) 2006-08-03 (deposited at 190° C) (c) 2006-06-23b (deposited at ambient temperature) (d) 2006-08-30 (deposited at ambient temperature) (e) 2006-10-16a (deposited at ambient temperature).





Figure 5.18 (continued)








Figure 5.19 XRD spectra for the ethanol active regions of the Pt-Ru-Pb films described in Table 5.9. (a) 2006-06-23a (deposited at 270°C) (b) 2006-08-03 (deposited at 190°C) (c) 2006-06-23b (deposited at ambient temperature) (d) 2006-08-30 (deposited at ambient temperature) (e) 2006-10-16a (deposited at ambient temperature).





Figure 5.19 (continued)









less mobility to deposited atoms and result in the formation of smaller grains, as noted in Chapter 4 for the Pt-Bi-Pb films.

Electrochemical Pre-Treatment of a Pt-Ru-Pb Film

Volpe *et. al.*³³ and Blasini *et. al.*³⁴ conducted electrochemical pre-treatments of the ordered intermetallic compounds PtBi and PtPb. The pre-treatments included cycling the potential of the electrocatalysts from negative to positive values repeatedly, leaching oxides of the less noble metal from the surface and exposing more Pt active sites. We conducted a modified electrochemical pre-treatment of a Pt-Ru-Pb thin film composition spread to test its effect on the activity observed in methanol and ethanol electrolytes.

We synthesized the Pt-Ru-Pb film for electrochemical pre-treatment (sample 2006-10-16b) within hours of sample 2006-10-16a (see Table 5.8) and using the same synthesis parameters, listed in Table 5.10. By synthesizing both films on the same day, we reduce the chances of any unknown differences in sputtering chamber conditions. Figures 5.20(a) and (b) show images of samples 2006-10-16a and 2006-10-16b, respectively, before fluorescence screening. The films appear identical, indicating a high probability that the films have similar surface characteristics.

sample	gun #	1	2	3	4	
2006-10-	targets	Pt	Ru	Pb	Та	
16b	gun currents (mA)	55	250	43	700	
	deposition rates at center (Å/s)	1.0	1.8	2.0	3.7	
	deposition times (s)	520 270				
	molar ratio at center (Pt:Ru:Pb)	1:2:1				
	deposition temperature (°C)	ambient				

Table 5.10 Synthesis parameters of the Pt-Ru-Pb film to undergo electrochemical pretreatment.



Figure 5.20 Images of samples (a) 2006-10-16a and (b) 2006-10-16b before fluorescence screening. Image (c) shows sample 2006-10-16a after normal fluorescence screening, while (d) shows sample 2006-10-16b after a fluorescence screening with electrochemical pre-treatment.

We screened sample 2006-10-16b using the fluorescence method for both methanol and ethanol oxidation. For the electrochemical pre-treatment, conducted in the standard methanol electrolyte (see Chapter 2), we held the potential of the entire sample at -500 mV vs. Ag/AgCl (arbitrarily chosen) for 1 minute. We then proceeded to scan the potential at 5 mV/s up to 250 mV vs. Ag/AgCl. We repeated the potential scan in the same electrolyte from -300 to 25 mV vs. Ag/AgCl. Following the methanol screening, we screened for ethanol oxidation activity in fresh standard ethanol electrolyte.

Figures 5.20(c) and (d) show samples 2006-10-16a (no pre-treatment) and 2006-10-16b (pre-treatment), respectively, after fluorescence screening. Even after the screening, the films have similar appearances. Figure 5.21 shows images of the screenings of each film for both methanol and ethanol oxidation. The regions showing the lowest onset potential for both methanol and ethanol are in similar locations on the films. This was also true for the second methanol screening of sample 2006-10-16b. The onset potentials of the active regions on sample 2006-10-16b are -10 ± 25 mV and -245 ± 25 mV vs. Ag/AgCl for methanol and ethanol oxidation, respectively. Although the onset potential of the methanol active region is higher and the onset potential of the ethanol active region is lower than that of sample 2006-10-16a (no pre-treatment), the differences are within experimental error. The data suggest that our particular pre-treatment does not enhance the electrocatalytic ability of the active regions beyond the error in measurement of onset potentials. However, pre-treatment at potentials of -1000 mV vs. Ag/AgCl or lower, where hydrogen is generated, may have a noticeable effect.

The compositions, measured with WDS, of the methanol and ethanol active regions of sample 2006-10-16b (pre-treatment) are $Pt_{0.50}Ru_{0.27}Pb_{0.10}O_{0.13}$ and $Pt_{0.39}Ru_{0.37}Pb_{0.09}O_{0.15}$, respectively. The compositions of the methanol and ethanol active regions of sample 2006-10-16a (no pre-treatment) are $Pt_{0.71}Ru_{0.19}Pb_{0.04}O_{0.05}$ and $Pt_{0.50}Ru_{0.35}Pb_{0.05}O_{0.10}$, respectively. The atomic percentages of Pt are significantly different for the active regions of both samples, which is surprising considering they were synthesized within hours of each other. This may suggest that the surface composition, rather than bulk, is the determining factor of the low onset potentials for each film.

Figure 5.22 shows the XRD spectra of the methanol and ethanol active regions of sample 2006-10-16b (pre-treatment). In each spectrum, the best matches are to



Figure 5.21 Images of the fluorescence screening of samples (a) 2006-10-16a (no pre-treatment) at 238 mV vs. Ag/AgCl and (b) 2006-10-16b (pre-treatment, first scan in potential) at 250 mV vs. Ag/AgCl in methanol, as well as screenings for samples (c) 2006-10-16a at -13 mV vs. Ag/AgCl and (d) 2006-10-16b at 13 mV vs. Ag/AgCl in ethanol. The circles indicate the region with the lowest onset potential.

those of the Pt structure type (pdf #4-802), although the peaks are slightly shifted in the ethanol active region. The PbPt_x structure type (pdf #6-574) may also match, although the large shifts in peaks cast some doubt on its presence in the film. The spectra of both regions are similar to the corresponding spectra found in the active regions of sample 2006-10-16a (no pre-treatment). The lattice parameters of the Pt structure type, according to the LAPODS program, are 3.91 ± 0.01 Å for both the methanol and ethanol active regions of sample 2006-10-16b (pre-treatment), respectively, and 3.89 ± 0.01 Å and 3.88 ± 0.01 Å for the methanol and ethanol active regions of sample 2006-10-16a (no pre-treatment). Thus, the corresponding active regions of both samples have fcc lattice parameters that differ at most by 0.03 Å.



Figure 5.22 XRD spectrum of the (a) methanol and (b) ethanol active regions of sample 2006-10-16b (with pre-treatment).

Conclusions

We synthesized several Pt-Ru-Pb thin film composition spreads and tested them for electrocatalytic activity for methanol and ethanol oxidation using fluorescence screening. The deposition temperatures ranged from ambient temperature (approximately 20°C according to the thermocouple in the substrate holder) to 400°C. All the films have active regions for both methanol and ethanol, with onset potentials lower than bulk Pt and bulk PtPb. The lowest methanol onset potential is -30 ± 25 mV vs. Ag/AgCl (for a sample deposited at 190°C), and the lowest ethanol onset potential is -250 ± 25 mV vs. Ag/AgCl (for a sample deposited at ambient temperature). Furthermore, some of the active regions contain low atomic percentages of Pt, the lowest being 11% for both methanol and ethanol active regions (for a sample deposited at 400°C). The onset potentials are significantly lower than those measured for a Pt-Ru thin film composition spread. However, the onset potentials for both Pt-Ru and Pt-Ru-Pb films vary widely, with no apparent relationship to composition, deposition temperature, or crystal structure. The compositions of the active regions also vary widely, with atomic percentages of Pt as high as 71% in methanol active regions and as high as 50% in ethanol active regions (both for a sample deposited at ambient temperature). The crystal structure of the active regions usually show Pt (pdf #4-802), Ru (pdf #6-663), and possibly PbPt_x (pdf #6-574) structure types. The matches to Pt in the XRD spectra are frequently shifted, possibly indicating varying degrees of alloying with Ru. Electrochemical pre-treatment of a Pt-Ru-Pb film at -500 mV vs. Ag/AgCl did not significantly change the onset potentials of methanol and ethanol oxidation in the active regions of Pt-Ru-Pb films synthesized within a time span of several hours.

The results indicate that the bulk composition may not be the most important factor in determining the electrocatalytic ability of active regions. Surface

characteristics may play a more important role, and surface characterization techniques such as XPS may prove more useful in understanding the relationships between electrocatalyst composition and onset potentials. The results also indicate the need for consistent deposition and testing procedures. The determining factors of electrocatalytic activity may be dependent on changes in the deposition chamber such as background pressure, humidity, or the time elapsed between synthesis and screening. Such factors can alter the composition in the bulk or surface and thereby change electrocatalytic properties of the films.

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CHAPTER 6

A COMBINATORIAL SEARCH THROUGH COMPOSITION SPREADS OF TYPE Pt-Ru-X

In this chapter we use our combinatorial search method to find active electrocatalysts for methanol and ethanol oxidation in several thin film composition spreads. All the films contain Pt, Ru, and a third element that we hypothesized could enhance the active electrocatalysts found on the Pt-Ru films described in Chapter 5.

Pt-Ru-X Background

As noted in Chapter 5, methanol oxidation on Pt-based alloy electrocatalysts such as PtRu occurs through the following bifunctional mechanism^{1, 2}:

$Pt + CH_3OH \rightarrow Pt-(CH_3OH)_{ads} $ ((1))	
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$$Pt-(CH_3OH)_{ads} \rightarrow Pt-(CH_3O)_{ads} + H^+ + e^-$$
(2)

$$Pt-(CH_3O)_{ads} \rightarrow Pt-(CH_2O)_{ads} + H^+ + e^-$$
(3)

$$Pt-(CH_2O)_{ads} \rightarrow Pt-(CHO)_{ads} + H^+ + e^-$$
(4)

$$Pt-(CHO)_{ads} \rightarrow Pt-(CO)_{ads} + H^+ + e^-$$
(5)

$$M + H_2O \rightarrow M-(H_2O)_{ads}$$
(6)

$$M-(H_2O)_{ads} \rightarrow M-(OH)_{ads} + H^+ + e^-$$
(7)

$$Pt-(CO)_{ads} + M-(OH)_{ads} \rightarrow Pt + M + CO_2 + H^+ + e^-$$
(8)

M represents a second metal alloyed with Pt. The mechanism shows that adsorption and de-hydrogenation of methanol occurs on surface Pt sites of the electrocatalyst (steps 1 to 5), while water molecules adsorb to M sites and provide an oxygen atom to convert CO on Pt sites to CO_2 (steps 6 to 8). Gasteiger *et. al.*³ showed that the rate-determining step of methanol oxidation at 25°C is methanol adsorption/de-hydrogenation (steps 1 to 5); at higher temperatures, up to 60°C, the oxidation of CO (step 8) becomes the rate-determining step. The choice of M affects the reaction rates of steps 1 to 5 through electronic effects on Pt ⁴ and steps 6 to 8 through the M-O bond strength⁵. If the M-O bond strength is too low, water molecules adsorb to M sites poorly and the rate of step 6 is slow. If the M-O bond strength is too high, the M-O bond in step 8 is less likely to break and reduces the rate of this step. An intermediate value of M-O bond strengths must therefore optimize the reaction rate of methanol oxidation.

Some researchers, based on the reasoning above, investigated PtRuOs and PtRuOsIr alloys as fuel cell anode electrocatalysts for methanol oxidation^{2, 6, 7}. The alloys have superior characteristics to PtRu binary alloys, with reduced CO poisoning of the electrocatalyst surface and 30% higher current densities at 400 mV vs. RHE for an alloy of Pt_{0.65}Ru_{0.25}Os_{0.10}.

We found active regions on Pt-Ru-Pb films, described in Chapter 5, that had lower onset potentials for methanol and ethanol oxidation than active regions on Pt-Ru films. In light of the bifunctional mechanism described above and the Pt-Ru-Pb results, we hypothesized that Pt-Ru-X films, where X is an element with a similar metal-oxygen bond strength to Pb (within \pm 50 kJ/mol), would also have active regions with lower onset potentials for methanol and ethanol oxidation than Pt-Ru films. Table 6.1 lists Pb, the metals we chose for X, and their corresponding metal-oxygen bond dissociation energies⁸. If our hypothesis is correct, there should be onset potentials lower than those of Pt-Ru films for methanol and ethanol active regions of Pt-Ru-Co, Pt-Ru-Ni, Pt-Ru-Fe, and Pt-Ru-In films.

element	M-O bond dissociation energy (kJ/mol at 25°C)
Pb	374
Co	384.5
Ni	366
Ag	221
V	637
Мо	502
Fe	407.0
In	346
Sb	434

Table 6.1 Metal-oxygen bond dissociation energies at 25°C for elements chosen for Pt-Ru-X films.

Synthesis and Screening of Pt-Ru-X Films

We synthesized eight thin film ternary composition spreads of type Pt-Ru-X, where X is one of the elements listed in Table 6.1. Table 6.2 shows the synthesis parameters of all eight films. We "hot sputtered" the films at deposition temperatures within 40°C of each other, from 370°C to 410°C. The thermocouple malfunctioned during depositions of samples 2006-03-02 and 2006-03-03b; we estimate the temperatures to be 400 \pm 40°C based on voltage and time applied to the heater. All the films have an expected 1:1:1 molar ratio of the three elements at the center based on deposition calibrations at the time.

We used fluorescence screening to test all films for electrocatalytic activity for methanol and ethanol oxidation. For each film, we conducted a methanol test in the standard electrolyte first, then washed the film and electrochemical cell with distilled water, then conducted an ethanol test in fresh standard electrolyte (see Chapter 2 for standard electrolytes).

Samples 2006-02-11 (X = Ag), 2006-03-02 (X = Fe), and 2006-06-02 (X = Sb) are inactive for methanol and ethanol oxidation up to 300 mV vs. Ag/AgCl, 400 mV vs. Ag/AgCl, and 400 mV vs. Ag/AgCl, respectively. During a pre-screening potential

sample	gun #	1	2	3	4			
2006-02-	targets	Pt	Ru	Co	Та			
10a	gun currents (mA)	102	228	190	620			
	deposition rates at center (Å/s)	2.5	2.2	1.8	4.0			
	deposition times (s)		385		250			
	molar ratio at center (Pt:Ru:Co)		1:	1:1				
	deposition temperature (°C)		39	90				
sample	gun #	1	2	3	4			
2006-02-	targets	Pt	Ru	Ni	Та			
10b	gun currents (mA)	102	228	215	620			
	deposition rates at center (Å/s)	2.5	2.2	1.8	4.0			
	deposition times (s)		385		250			
	molar ratio at center (Pt:Ru:Ni)		1:	1:1				
	deposition temperature (°C)		40	00				
sample	gun #	1	2	3	4			
2006-02-11	targets	Pt	Ru	Ag	Та			
	gun currents (mA)	102	228	105	620			
	deposition rates at center (Å/s)	2.5	2.2	2.8	4.0			
	deposition times (s)		250					
	molar ratio at center (Pt:Ru:Ag)		1:	1:1				
	deposition temperature (°C)		4	10				
sample	gun #	1	2	3	4			
2006-02-	targets	V	Pt	Ru	Та			
16a	gun currents (mA)	255	135	225	620			
	deposition rates at center (Å/s)	2.1	2.3	2.1	4.0			
	deposition times (s)		385		250			
	molar ratio at center (V:Pt:Ru)		1:	1:1				
	deposition temperature (°C)		39	90				
sample	gun #	1	2	3	4			
2006-02-	targets	Pt	Ru	Mo	Та			
16b	gun currents (mA)	102	228	270	620			
	deposition rates at center (Å/s)	2.5	2.2	2.5	4.0			
	deposition times (s)	350 250						
	molar ratio at center (Pt:Ru:Mo)		1:	1:1				
	deposition temperature (°C)	400						

Table 6.2 Synthesis parameters of the Pt-Ru-X films.

Table 6.2 (continued)

-		1	1	1	1		
sample	gun #	1	2	3	4		
2006-03-02	targets	Fe	Pt	Ru	Та		
	gun currents (mA)	260	145	235	700		
	deposition rates at center (Å/s)	1.9	2.5	2.2	3.7		
	deposition times (s)		380		270		
	molar ratio at center (Fe:Pt:Ru)		1:1	1:1			
	deposition temperature (°C)		unkr	iown			
sample	gun #	1	2	3	4		
2006-03-	targets	Pt	Ru	In	Та		
03b	gun currents (mA)	46	95	85	700		
	deposition rates at center (Å/s)	0.9	0.8	1.6	3.7		
	deposition times (s)	760 270					
	molar ratio at center (Pt:Ru:Pb)	1:1:1					
	deposition temperature (°C)	unknown					
sample	gun #	1	2	3	4		
2006-06-02	targets	Sb	Pt	Ru	Та		
	gun currents (mA)	32	75	60	700		
	deposition rates at center (Å/s)	1.5	0.7	0.7	3.7		
	deposition times (s)	860 2					
	molar ratio at center (Sb:Pt:Ru)	1:1:1					
	deposition temperature (°C)	370					

scan in electrolyte without fuel (i.e. 0.1 M NaCF₃SO₃, 0.5 mM quinine – see Chapter 2) for samples 2006-02-16a (X = V) and 2006-02-16b (X = Mo), there is fluorescence on approximately half of the film, toward the regions rich in element X. This indicates the production of protons in solution without fuel, and therefore any screening for methanol or ethanol is unreliable. We attribute the production of protons to the formation of isopolymetallates, long chains of oxidized metal complexes. Both V and Mo form these types of compounds in water⁹ and are therefore unstable as electrocatalysts.

Samples 2006-02-10a (X = Co), 2006-02-10b (X = Ni), and 2006-03-03b (X = In) have active regions for both methanol and ethanol oxidation, shown by the screening images in Figure 6.1. The methanol and ethanol active regions with the



Figure 6.1 Images of the fluorescence screenings of samples 2006-02-10a for (a) methanol at 400 mV and (b) ethanol at 195 mV vs. Ag/AgCl; 2006-02-10b for (c) methanol at 400 mV and (d) ethanol at 145 mV vs. Ag/AgCl; and 2006-03-03b for (e) methanol at 245 mV and (f) ethanol at 20 mV vs. Ag/AgCl. The orientation of the sputtering sources is shown in each image. The circles indicate the regions with the lowest onset potentials for each fuel.

lowest onset potential are at approximately the same location on each film, separated by no more than 1 cm. Note that this is the same approximate location as the active region in sample 2006-05-11a, a Pt-Ru-Pb film with a 1:1:1 ratio at the center. Table 6.3 lists the lowest onset potentials for methanol and ethanol oxidation for each sample. Table 6.4 lists characteristics of the methanol and ethanol active regions of Pt-Ru films for comparison. Only sample 2006-03-03b has a methanol active region with an onset potential lower than that of a Pt-Ru film (sample 2006-05-17) by more than the experimental error. This is also true for the ethanol active region of sample 2006-03-03b. It appears that of the three active films, only In enhances the electrocatalytic ability over Pt-Ru. The active regions of sample 2006-03-03b have onset potentials for both methanol and ethanol oxidation comparable to the lowest corresponding onset potentials of the Pt-Ru-Pb films (-30 mV and -250 mV vs. Ag/AgCl for methanol oxidation on sample 2006-08-03 and ethanol oxidation on sample 2006-08-30, respectively). The data show that our hypothesis concerning metal-oxygen bond strengths and onset potentials is either incomplete or false.

Table 6.3 Lowest onset potentials for methanol and ethanol oxidation on each active Pt-Ru-X film.

sample	element X	methanol onset potential (±25 mV vs. Ag/AgCl)	ethanol onset potential (±25 mV vs. Ag/AgCl)
2006-02-10a	Со	245	-45
2006-02-10b	Ni	95	-70
2006-03-03b	In	-30	-160

Table 6.4 Onset potentials and compositions, measured by WDS, of active regions of Pt-Ru films.

	methanol act	ive region	ethanol active region			
sample	onset potential		onset potential			
	$(\pm 25 \text{ mV vs.} \text{ composition})$		(±25 mV vs.	composition		
	Ag/AgCl)	_	Ag/AgCl)			
2006-03-03a	115	$Pt_{0.20}Ru_{0.80}$	-60	Pt _{0.38} Ru _{0.62}		
2006-03-13a	410	$Pt_{0.40}Ru_{0.59}$	-10	$Pt_{0.40}Ru_{0.59}O_{0.01}$		
2006-05-17	340	$Pt_{0.47}Ru_{0.53}$	310	$Pt_{0.47}Ru_{0.53}$		

Characterization of Active Regions

We characterized the composition with WDS and crystal structure with XRD of the methanol and ethanol active regions of samples 2006-02-10a, 2006-02-10b, and 2006-03-03b following fluorescence screening.

Sample 2006-02-10a (X = Co)

Figures 6.2 (a) and (b) show images of sample 2006-02-10a before and after fluorescence screening. The film changes little in physical appearance from screening, being reflective over the entire surface. The compositions, measured by WDS, of the methanol and ethanol active regions are $Pt_{0.26}Ru_{0.50}Co_{0.23}$ and $Pt_{0.29}Ru_{0.39}Co_{0.32}$, respectively. The atomic percentage of Pt in the methanol active region is comparable to that of sample 2006-03-03a (Pt-Ru film; see Table 6.4), where the atomic percentage of Pt is 20%. However, the atomic percentage of Ru in the methanol active region of sample 2006-02-10a is lower, apparently replaced by Co. The ethanol active region has a lower atomic percentage of Pt than any of the ethanol active regions of the Pt-Ru films. Note also that the active regions of sample 2006-02-10a do not contain significant amounts of oxygen (i.e. below the noise limits of detection, about 1%).

Figures 6.2 (c) and (d) show the XRD spectra of the methanol and ethanol active regions of sample 2006-02-10a. The peaks of both spectra show matches to the Ru (pdf #6-663) and Co (pdf #5-727) structure types, although some of the corresponding Ru peaks are shifted to varying degrees within the same spectrum. This may be due in part to alloying with Pt; the spectrum shows no indication of an fcc Ptrich phase. The Co phase shows no corresponding shift in peaks. The peaks at 34° and 65° correspond to the Ta underlayer.



Figure 6.2 Characterization of sample 2006-02-10a: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

Sample 2006-02-10b (X = Ni)

Figures 6.3 (a) and (b) show images of sample 2006-02-10b before and after fluorescence screening. The film mostly maintains a reflective surface after screening, with the only exception being a small area less than 2 mm across where the film delaminated. The compositions of the methanol and ethanol active regions are $Pt_{0.30}Ru_{0.51}Ni_{0.19}$ and $Pt_{0.24}Ru_{0.46}Ni_{0.30}O_{0.01}$, respectively. The atomic percentages of Pt and Ru differ from those of the corresponding active regions of 2006-02-10a by no more than 7%. Only the ethanol active region contains a lower atomic percentage of Pt than the best ethanol active region of the Pt-Ru composition spreads (sample 2006-03-03a; see Table 6.4). There are no significant amounts of oxygen in the active regions, as is the case for sample 2006-02-10a.

Figures 6.3 (c) and (d) show the XRD spectra of the methanol and ethanol active regions of sample 2006-02-10b. Both regions show excellent matches to the Ni structure type (pdf #45-1027). The peaks corresponding to the Ru structure type (pdf #6-663) are shifted and may indicate alloying with Pt or Ni, both of which form alloys with Ru¹⁰.

Sample 2006-03-03b (X = In)

Figures 6.4 (a) and (b) show images of sample 2006-03-03b before and after fluorescence screening. The film has a dark color on half of the film toward the In sputtering source and on a region close to the Ru source; note that the latter is in the same location as the active region. The film shows no signs of leaching from screening. The compositions of the methanol and ethanol active regions are $Pt_{0.47}Ru_{0.47}In_{0.04}O_{0.03}$ and $Pt_{0.59}Ru_{0.36}In_{0.03}O_{0.02}$, respectively. While these regions have the lowest onset potentials of the Pt-Ru-X films, they have higher atomic percentages of Pt. The percentages even exceed those of the best corresponding active regions on



Figure 6.3 Characterization of sample 2006-02-10b: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

the Pt-Ru films. The atomic percentage of In in each region is lower than the percentages of Co and Ni in samples 2006-02-10a and 2006-02-10b, respectively.

The XRD spectra of the active regions of sample 2006-03-03b, shown in Figures 6.4 (c) and (d), have peaks corresponding to an fcc Pt-like structure type (pdf #4-802). The peaks are shifted, most likely from alloying with Ru. According to calculations with the LAPODS program¹¹ and Cohen's method¹²⁻¹⁴, the Pt fcc lattice parameter in both the methanol and ethanol active regions is 3.87 ± 0.01 Å. Using the relationship between lattice parameter and PtRu alloy composition^{15, 16} (see Chapter 5), the corresponding PtRu alloy composition is expected to be Pt_{0.57}Ru_{0.43}. The ratio of Pt to Ru is similar to those measured with WDS: 0.50:0.50 for the methanol active region and 0.62:0.38 for the ethanol active region. The data give evidence that the active phase is a PtRu alloy. XRD shows no In-containing phases, although this is expected since the atomic percentage of In is low according to WDS measurements. Other characterizations, especially those that probe the surface, are necessary to determine the role played by In in the improved electrocatalytic activity over the PtRu films.

Conclusions

We synthesized several thin film composition spreads containing Pt, Ru, and either Co, Ni, Ag, V, Mo, Fe, In, or Sb. The films with Ag, Fe, and Sb showed no electrocatalytic activity for methanol and ethanol oxidation below 300 mV vs. Ag/AgCl. The films with V and Mo are unstable and fluoresce during screenings without fuel.

We hypothesized that films containing Pt, Ru, and elements with metal-oxygen bond strengths similar to those of Pb have regions with onset potentials lower than those of Pt-Ru films. The data disprove the hypothesis, as only the film containing In



Figure 6.4 Characterization of sample 2006-03-03b: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

shows lower onset potentials for methanol and ethanol oxidation than the best Pt-Ru film. However, the active compositions of the Pt-Ru-In film contain higher atomic percentages of Pt. XRD spectra show the presence of fcc PtRu-like alloys in the active regions. In contrast, the films containing Co and Ni show no significant improvements in onset potentials for methanol and ethanol oxidation but contain lower fractions of Pt than the Pt-Ru films.

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CHAPTER 7

A COMBINATORIAL SEARCH THROUGH COMPOSITION SPREADS OF TYPE Pt-Pb-X

In this chapter we apply our combinatorial methods to synthesize thin film composition spreads containing Pt, Pb, and a third element. We test the films for active regions for methanol and ethanol oxidation.

Pt-Pb-X Background

In light of the extraordinary electrocatalytic activity discovered in Pt-Ru-Pb films (see Chapter 5), we chose to test films containing Pt, Pb, and a third element (X) to replace Ru. We hypothesized that since Pb enhances the electrocatalytic activity of Pt-Ru films for methanol and ethanol oxidation, a third element may do the same for Pt-Pb films.

As reviewed in Chapter 1, several studies show that certain ordered intermetallic compounds have superior characteristics over Pt as fuel cell anode electrocatalysts for fuels such as formic acid, methanol, and ethanol¹⁻⁵. We therefore planned to use elements for X in Pt-Pb-X films that formed binary intermetallic compounds with both Pt and Pb. The choice of elements would allow us to synthesize numerous binary and possibly ternary intermetallic compounds. Table 7.1 lists several elements that from intermetallic compounds with Pt or have an ordering dome with Pt in their binary phase diagrams⁶. The *gray* squares indicate elements that also form intermetallic compounds with Pb or have an ordering dome with Pb. However, at the time of choosing X, the author confused the meaning of the gray and white squares and chose the elements Sn, Mo, Co, Cr, Fe, Nb, Ni, Si, Ta, and In. Each of these elements are either immiscible with Pb or form an alloy (solid solution) with it.

Despite the confusion, we found electrocatalytic activity for methanol and ethanol oxidation in most of the films.

Table 7.1 List of elements that form intermetallic compounds with Pt. Elements in gray squares also form intermetallic compounds or have an ordering dome with Pb.

Ag	Al	В	Be	Bi	Ca	Nb	Co	Cr	Dy	Er	Fe	Gd	Ge	In
Мо	Nd	Ni	Pr	Sb	Sc	Si	Sn	Та	Tb	Ti	V	Y	Yb	

Synthesis and Screening of Pt-Pb-X Films

Table 7.2 lists the synthesis parameters of the Pt-Pb-X films deposited. The films have deposition temperatures between 350° C and 415° C, with the exception of two of them. The thermocouple malfunctioned during deposition of sample 2006-03-16a (X = Sn); we estimate its deposition temperature to be at least 450° C based on the time and power supplied to the heater. We chose a lower deposition temperature for sample 2006-06-14 (X = In) due to the low melting point of In (157° C). Most of the films have an expected 1:1:1 molar ratio of the three elements at the center, based on calibrations at the time. However, sample 2006-06-13a has a lower fraction of Si since the element proved difficult to sputter. To sputter Si more effectively requires an AC power supply (see Chapter 2), but we used a DC power supply. While we were able to sputter the Si target, the maximum obtainable gun current was lower than that needed for a 1:1:1 molar ratio at the center.

We used the fluorescence method to screen each sample for methanol oxidation first, then ethanol oxidation after rinsing the film and electrochemical cell with distilled water. We used the standard electrolytes for methanol and ethanol screenings (see Chapter 2).

Table 7.2 Synthesis parameters of films of type Pt-Pb-X.

sample	gun #	1	2	3	4			
2006-02-17	targets	Pb	Pt	Sn	Та			
	gun currents (mA)	60	70	85	620			
	deposition rates at center (Å/s)	2.4	1.2	2.1	4.0			
	deposition times (s)		440	I	250			
	molar ratio at center (Pb:Pt:Sn)		1:1	1:1				
	deposition temperature (°C)		4	15				
sample	gun #	1	2	3	4			
2006-03-	targets	Pb	Pt	Sn	Та			
16a	gun currents (mA)	60	70	85	700			
	deposition rates at center (Å/s)	2.4	1.2	2.1	3.7			
	deposition times (s)		440		270			
	molar ratio at center (Pb:Pt:Sn)		1:1	1:1				
	deposition temperature (°C)		unkr	nown				
sample	gun #	1	2	3	4			
2006-03-	targets	Pb	Pt	Sn	Та			
16b	gun currents (mA)	60	70	85	700			
	deposition rates at center (Å/s)	2.4	1.2	2.1	3.7			
	deposition times (s)		440 27					
	molar ratio at center (Pb:Pt:Sn)		1:1	1:1				
	deposition temperature (°C)	400						
sample	gun #	1	2	3	4			
2006-03-	targets	Pb	Pt	Mo	Та			
17b	gun currents (mA)	83	100	195	700			
	deposition rates at center (Å/s)	3.5	1.7	1.8	3.7			
	deposition times (s)		270					
	molar ratio at center (Pb:Pt:Mo)		1:1	1:1				
	deposition temperature (°C)	395						
sample	gun #	1	2	3	4			
2006-05-	targets	Pb	Pt	Со	Та			
24a	gun currents (mA)	72	130	95	700			
	deposition rates at center (Å/s)	2.7	1.4	1.0	3.7			
	deposition times (s)		490		270			
	molar ratio at center (Pb:Pt:Co)	1:1:1						
	deposition temperature (°C)	375						
sample	gun #	1	2	3	4			
2006-05-	targets	Pt	Cr	Pb	Та			
24b	gun currents (mA)	73	195	53	700			
	deposition rates at center (Å/s)	1.3	1.0	2.6	3.7			
	deposition times (s)		510		270			
	molar ratio at center (Pt:Cr:Pb)		1:	1:1				
	deposition temperature (°C)	365						

Table 7.2 (continued)

sample	gun #	1	2	3	4			
2006-05-25	targets	Fe	Pt	Pb	Та			
	gun currents (mA)	100	95	43	700			
	deposition rates at center (Å/s)	0.8	1.0	2.0	3.7			
	deposition times (s)		660		270			
	molar ratio at center (Fe:Pt:Pb)		1:1	1:1				
	deposition temperature (°C)		35	50				
sample	gun #	1	2	3	4			
2006-05-	targets	Pt	Nb	Pb	Та			
26a	gun currents (mA)	40	240	37	700			
	deposition rates at center (Å/s)	0.9	1.0	1.7	3.7			
	deposition times (s)		695		270			
	molar ratio at center (Pt:Nb:Pb)		1:1	1:1				
	deposition temperature (°C)		37	75				
sample	gun #	1	2	3	4			
2006-05-	targets	Pb	Pt	Ni	Та			
26b	gun currents (mA)	57	95	80	700			
	deposition rates at center (Å/s)	2.0	1.0	0.8	3.7			
	deposition times (s)	660 27						
	molar ratio at center (Pb:Pt:Ni)	1:1:1						
	deposition temperature (°C)		40	00				
sample	gun #	1	2	3	4			
2006-06-	targets	Pt	Si	Pb	Та			
13a	gun currents (mA)	50	250	36	700			
	deposition rates at center (Å/s)	0.8	0.9	1.6	3.7			
	deposition times (s)		715		270			
	molar ratio at center (Pt:Si:Pb)		1:0.	74:1				
	deposition temperature (°C)		410					
sample	gun #	1	2	3	4			
2006-06-	targets	Та	Pt	Pb	Та			
13b	gun currents (mA)	95	80	36	700			
	deposition rates at center (Å/s)	1.0	0.8	1.6	3.7			
	deposition times (s)		735		270			
	molar ratio at center (Ta:Pt:Pb)		1:	1:1				
	deposition temperature (°C)	405						

Table 7.2 (continued)

sample	gun #	1	2	3	4		
2006-06-14	targets	Pb	Та				
	gun currents (mA)	38	64	36	700		
	deposition rates at center (Å/s)	1.2	0.6	1.0	3.7		
	deposition times (s)		270				
	molar ratio at center (Pb:Pt:In)	1:1:1					
	deposition temperature (°C)	260					

The three films containing Sn (samples 2006-02-17, 2006-03-16a, and 2006-03-16b) produced inconsistent results. Sample 2006-02-17 fluoresced across approximately half the film, toward the Sn and Pb sputtering sources, during prescreening in an electrolyte without fuel (0.1 NaCF₃SO₃, 0.5 mM quinine; see Chapter 2). Furthermore, the appearance of the film after screening showed evidence of leaching in the same regions that show fluorescence during pre-screening. We proceeded with screenings for methanol and ethanol oxidation and found active regions outside of the leaching area and close to the Pt sputtering source, with onset potentials of -62 mV and -103 mV vs. Ag/AgCl, respectively. However, the results were not reproducible; neither sample 2006-03-16a nor 2006-03-16b showed any active regions up to 0 mV vs. Ag/AgCl for methanol or up to 200 mV vs. Ag/AgCl for ethanol.

Sample 2006-03-17b (X = Mo), when placed in electrolyte without fuel for pre-screening, had an open-circuit potential of -400 mV vs. Ag/AgCl. The extremely low potential indicates that the film oxidizes easily, is susceptible to leaching at very low potentials, and is therefore not likely to contain good electrocatalysts. This observation is not surprising given that sample 2006-02-16b (Pt-Ru-Mo; see Chapter 6) fluoresced during pre-screening.
The other samples listed in Table 7.2 did not fluoresce during pre-screening and have active regions for methanol and ethanol oxidation. The lowest onset potentials for each fuel on each sample are listed in Table 7.3. Note that all the methanol onset potentials are lower than that of sample 2005-10-05b (Pt-Pb deposited at 265°C, methanol onset potential of 210 mV vs. Ag/AgCl; see Chapter 4) by more than the experimental error. Samples 2006-06-13b (X = Ta) and 2006-06-14 (X = In) have methanol active regions with onset potentials lower than that of sample 2006-08-03 (Pt-Ru-Pb deposited at 190°C, methanol onset potential of -30 mV vs. Ag/AgCl; see Chapter 5), although not by more than the experimental error. None of the ethanol active regions have onset potentials lower than that of sample 2006-08-30 (Pt-Ru-Pb deposited at ambient temperature, ethanol onset potential of -250 mV vs. Ag/AgCl; see Chapter 5). As noted in Chapter 2, the ideal (theoretical) potential for the oxidation of methanol or ethanol in the standard electrolytes is approximately -500 mV vs. Ag/AgCl. In all cases, there is a significant overpotential for the oxidation of these fuels. However, such overpotentials are smaller than those found for PtPb for the same fuels.

comple	element	methanol onset potential	ethanol onset potential
sample	Х	(±25 mV vs. Ag/AgCl)	(±25 mV vs. Ag/AgCl)
2005-10-05b	none	210	-
2006-05-24a	Со	90	40
2006-05-24b	Cr	50	-105
2006-05-25	Fe	50	-55
2006-05-26a	Nb	-20	-170
2006-05-26b	Ni	150	80
2006-06-13a	Si	80	-50
2006-06-13b	Та	-50	-145
2006-06-14	In	-35	-85

Table 7.3 Lowest onset potentials for methanol and ethanol oxidation on active films of type Pt-Pb-X.

Figure 7.1 shows images of the films listed in Table 7.3 during fluorescence screening for methanol and ethanol oxidation. For many of the films, the regions with lowest onset potentials are located closer to the Pt or Pb sputtering sources than they are to the source of element X. Exceptions are found for both active regions of sample 2006-05-24a (X = Co), the ethanol active region of sample 2006-05-25 (X = Fe), the ethanol active region of sample 2006-05-25 (X = Fe), the ethanol active region of sample 2006-06-13b (X = Ta), and the ethanol active region of sample 2006-06-14 (X = In).

Characterization of Active Regions of Pt-Pb-X Films

We characterized the methanol and ethanol active regions with lowest onset potentials on each film, indicated in Figure 7.1 and described in Table 7.3, after fluorescence screening. We used WDS to estimate bulk composition and XRD to determine crystal structure.

Sample 2006-05-24a (X = Co)

Figures 7.2(a) and (b) show images of sample 2006-05-24a before and after fluorescence screening. The film has a reflective surface toward the Pt sputtering source and but becomes more dull closer to the Co and Pb. The regions close to the Pb source darken considerably after screening, which include the location of the methanol active region (see Figure 7.1). The compositions of the methanol and ethanol active regions are $Pt_{0.39}Pb_{0.03}Co_{0.57}O_{0.01}$ and $Pt_{0.15}Pb_{0.12}Co_{0.52}O_{0.24}$, respectively. There is a relatively high fraction of Co in both regions, and the ethanol active region contains a substantial fraction of oxygen.

Figures 7.2(c) and (d) show the XRD spectra of each region. Both spectra match the PbPt phase (pdf #6-374, NiAs structure type), while the methanol active region may also contain the CoPt phase (pdf #29-498), although the match is less

Figure 7.1 Images of the fluorescence screenings of samples 2006-05-24a (X = Co) for (a) methanol at 250 mV and (b) ethanol at 200 mV vs. Ag/AgCl; 2006-05-24b (X = Cr) for (c) methanol at 300 mV and (d) ethanol at 150 mV vs. Ag/AgCl; 2006-05-25 (X = Fe) for (e) methanol at 300 mV and (f) ethanol at 150 mV vs. Ag/AgCl; 2006-05-26a (X = Nb) for (g) methanol at 250 mV and (h) ethanol at 145 mV vs. Ag/AgCl; 2006-05-26b (X = Ni) for (i) methanol at 400 mV and (j) ethanol at 300 mV vs. Ag/AgCl; 2006-06-13a (X = Si) for (k) methanol at 360 mV and (l) ethanol at 245 mV vs. Ag/AgCl; 2006-06-13b (X = Ta) for (m) methanol at 215 mV and (n) ethanol at 190 mV vs. Ag/AgCl; and 2006-06-14 (X = In) for (o) methanol at 200 mV and (p) ethanol at 170 mV vs. Ag/AgCl. The orientation of the sputtering sources is shown in each image. The circles indicate the regions with the lowest onset potentials for each fuel.











(d)







Figure 7.1 (continued)





Figure 7.2 Characterization of sample 2006-05-24a: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

certain. The lack of a phase containing Co in the ethanol active region is surprising considering the large fraction of Co measured by WDS. It is possible that the Co leached from the sample during screening, which may explain the change in coloration of the ethanol active region. The methanol active region has a relatively large XRD spectrum background, with wider peaks than the ethanol active region and therefore smaller grain sizes. The Scherrer formula⁷ and the PbPt peaks at 41.2° give grain sizes of 5.0 Å and 11.4 Å for the methanol and ethanol active regions, respectively. The grain sizes of both regions are very small and likely the result of a relatively low deposition temperature. Oxides, especially in the ethanol active region, can form at grain boundaries and also prevent larger grain formation.

Sample 2006-05-24b (X = Cr)

The images of sample 2006-05-24b before and after fluorescence screening in Figures 7.3(a) and (b) show predominantly dull surfaces close to the Pb and Cr sputtering sources. These same surfaces darken after screening, especially toward the Pb source. The shape of the methanol fluorescent area in Figure 7.1(c) matches that of the reflective region, while the shape of the ethanol fluorescent area in Figure 7.1(d) matches part of the dark regions. The compositions of the methanol and ethanol active regions are $Pt_{0.72}Pb_{0.01}Cr_{0.20}O_{0.07}$ and $Pt_{0.55}Pb_{0.17}Cr_{0.23}O_{0.04}$, respectively. Pt is the predominant element in both regions, consistent with their locations on the film.

The XRD spectra in Figures 7.3(c) and (d) show matches to the Pt structure type (pdf #4-802) in the methanol active region and the PbPt structure type (pdf #6-374) in the ethanol active region. Both regions also show matches to the Pt₃Cr structure type (pdf #34-1080). The Pt and Pt₃Cr peaks in the methanol active region are slightly shifted; according to calculations by the computer program LAPODS⁸, the lattice parameter of the fcc Pt phase is 3.88 ± 0.01 Å, compared to 3.92 Å for pure Pt.



Figure 7.3 Characterization of sample 2006-05-24b: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

The decrease is expected since Cr has a smaller atomic radius than Pt. Although Pb has a larger atomic radius than Pt, the Pb content is low and the binary phase diagram of Pb-Pt shows no alloys⁶. The appearance of the PbPt structure type in the ethanol active region but not in the methanol active region is consistent with the low fraction of Pb in the methanol active region.

Sample 2006-05-25 (X = Fe)

Images of sample 2006-05-25 before and after fluorescence screening in Figures 7.4(a) and (b) show dull regions toward the Pb and Fe sputtering sources. These regions become darker following screening, while the reflective region close to the Pt source remains so. The region that fluoresces during the methanol screening covers the entire reflective region along with a small dark region between the Pt and Fe sources; the ethanol active region covers only the dark region (see Figure 7.1). The compositions of the methanol and ethanol active regions are Pt_{0.72}Pb_{0.01}Fe_{0.25}O_{0.02} and Pt_{0.38}Pb_{0.06}Fe_{0.39}O_{0.17}, respectively. As expected from their locations on the film, the methanol active region contains a high fraction of Pt, while the ethanol active region contains approximately equal fractions of Pt and Fe and a significant amount of oxygen.

The XRD spectra in Figures 7.4(c) and (d) show excellent matches to two different Fe-Pt alloy phases (pdf #29-717, composition $Pt_{0.8}Fe_{0.2}$, in the methanol active region; and #29-718, composition $Pt_{0.46}Fe_{0.54}$, in the ethanol active region). Note that the Pt to Fe ratio of the compositions of both phase matches is similar to that of the corresponding WDS measurements. One can see the shift in the peaks from the Pt phase (pdf #4-802), indicating alloying with Pt. The LAPODS program calculates fcc Pt lattice parameters of 3.86 ± 0.01 Å and 3.80 ± 0.01 Å for the methanol and ethanol active regions, respectively, compared to 3.92 Å for pure Pt. No Pb-containing phases



Figure 7.4 Characterization of sample 2006-05-25: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

are detectable in the spectra, consistent with the low fraction of Pb from the WDS measurements.

Sample 2006-05-26a (X = Nb)

Figures 7.5(a) and (b) show images of sample 2006-05-26a before and after fluorescence screening. The appearance of the film is different from other films of type Pt-Pb-X; the dull region is located between the Pt and Pb sputtering sources and opposite the Nb source. Most of the film is reflective, and there is little change in appearance after screening, with the exception of a thin streak approximately 5 mm wide in the dull region. The methanol and ethanol active regions, located at the same place on the film, coincide with the dull region (see Figure 7.1). The composition of the active region is Pt_{0.70}Pb_{0.07}Nb_{0.15}O_{0.07}. The composition has a higher fraction of Nb than expected considering its location relative to the Nb sputtering source. It is possible that the Nb deposition rate decreases slowly with distance from the sputter gun axis. This would explain the small size of the dull regions on the film and the greater fraction of Nb than Pb at the active region.

Figure 7.5(c) shows the XRD spectrum of the active region, with matches to the Pt (pdf #4-802) and PbPt_x (pdf #6-574) structure types, although the latter is shifted by as much as 2.3°. The Pt peaks are shifted only slightly; LAPODS calculates an fcc Pt lattice parameter of 3.93 ± 0.01 Å, an increase of only 0.01 Å from that of pure Pt and less than the calculated error. It is possible that the increase in lattice parameter is due to Nb or Pb substituting into Pt sites in the lattice; both have larger atomic radii than Pt, and the Nb-Pt phase diagram shows an fcc Pt-like phase for low amounts of Nb ⁶. There is no evidence of any Nb or Pt-Nb structure types in the spectrum.



Figure 7.5 Characterization of sample 2006-05-26a: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; (c) XRD spectra of the region active toward both methanol and ethanol.

Sample 2006-05-26b (X = Ni)

Figures 7.6(a) and (b) show images of sample 2006-05-26b before and after fluorescence screening. Over half the film has a dull surface toward the Pb and Ni sputtering sources, with a gradual transition to a reflective surface toward the Pt source. The film changes color as a result of screening, becoming darker closer to the Pb source. The shape of the color pattern appears to match that of the fluorescence in Figures 7.1(i) and (j). The compositions of the methanol and ethanol active regions are $Pt_{0.32}Pb_{0.40}Ni_{0.19}O_{0.09}$ and $Pt_{0.26}Pb_{0.31}Ni_{0.34}O_{0.09}$, respectively. Both regions have low fractions of Pt, with comparable amounts of Pb.

The XRD spectrum of Figure 7.6(c) contains numerous peaks that may match the Pb (pdf #4-686), PbO (pdf #5-561), or Pb₄Pt (pdf #6-463) structure types, although many peaks are shifted. It is surprising to find the Pb₄Pt structure type in the spectrum since the phase is unstable in region 7 of sample 2005-08-30 (Pt-Bi-Pb deposited at 260°C; see Chapter 4), although the intensities of the corresponding peaks are quite low and the phase may have partially corroded during screening. The XRD spectrum of the ethanol active region in Figure 7.6(d) matches the PbPt structure type (pdf #6-374), although some of the peaks are shifted, especially toward higher values of 20.

Sample 2006-06-13a (X = Si)

The images of sample 2006-06-13a in Figures 7.7(a) and (b) show a predominantly dull and dark film, with an abrupt change to a reflective surface closer to the Pt sputtering source. The film acquires a milkier color at the center of the film following screening. The methanol fluorescent area includes the reflective surfaces as well as part of the dull region; the ethanol fluorescent area includes the dull region and is faint in a small part of the reflective region (see Figure 7.1). The methanol and ethanol active regions with the lowest onset potential have the same location on the



Figure 7.6 Characterization of sample 2006-05-26b: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

film. The composition of the active regions is $Pt_{0.30}Pb_{0.16}Si_{0.16}O_{0.38}$. The oxygen content is some of the highest measured for any samples due to the presence of Si, a highly oxophilic element.

Figure 7.7(c) shows the XRD spectrum of the active region. The peaks show matches to the PbPt_x (pdf #6-574), Pt₂Si (pdf #17-683), and Pt₆₄Si₃₆ (pdf #39-1295) structure types. Note that the ratios of Pt to Si in the last two structure types are close to that of the Pt to Si ratio measured by WDS.



Figure 7.7 Characterization of sample 2006-06-13a: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; (c) XRD spectra of the region active toward both methanol and ethanol.

Sample 2006-06-13b (X = Ta)

Figures 7.8(a) and (b) show images of sample 2006-06-13b before and after fluorescence screening. Dull surfaces are located toward the Ta and Pb sputtering sources, and those closest to Pb are darkest in color. Changes in the film surfaces are limited to these same regions. The fluorescent region of methanol screening is located mostly in the reflective region, while the fluorescent region of ethanol screening includes the reflective region and a line (approximately 5 mm wide) along a reflective/dull boundary between the Pt and Pb sources (see Figure 7.1). The compositions of the methanol and ethanol active regions are $Pt_{0.65}Pb_{0.02}Ta_{0.24}O_{0.09}$ and $Pt_{0.50}Pb_{0.02}Ta_{0.36}O_{0.12}$, respectively. However, there is a larger uncertainty in the atomic percentage of Ta than normal (at least ±10%) since some of the X-rays analyzed in WDS may have originated in the Ta underlayer. Both regions have a significant fraction of Pt and minor fractions of Pb.

The XRD spectra of the methanol and ethanol active regions are shown in Figures 7.8(c) and (d). Both spectra show matches to the Pt structure type (pdf #4-802) with peaks shifted toward lower values of 2 θ indicating an increase in the lattice parameter from that of pure Pt. The lattice parameter of the fcc Pt phase in both regions, calculated with the LAPODS program, is 3.96 ± 0.01 Å, up from 3.92 Å for pure Pt. Substitution of either Ta or Pb into the Pt lattice could account for the increase since both Pb and Ta have larger atomic radii than Pt. The Pt-Ta binary phase diagram shows an fcc Pt-rich phase⁶. The active regions may also contain the PbPt_x structure type (pdf #6-574), although the extreme shift in the peaks by as much as 1.9° and the low atomic fraction of Pb make this unlikely.



Figure 7.8 Characterization of sample 2006-06-13b: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

Sample 2006-06-14 (X = In)

Sample 2006-06-14, shown before and after fluorescence screening in Figures 7.9(a) and (b), has a narrow reflective region close to the Pt sputtering source and a larger reflective region close to the In source. As seen in most of the other films, the regions close to the Pb source are dull and change color the most from screening. The fluorescent areas during screening (see Figure 7.1) are located over a dull region close to the Pt source, and the ethanol active region with the lowest onset potential appears over a reflective region close to the In source. The compositions of the methanol and ethanol active regions are $Pt_{0.65}Pb_{0.19}In_{0.13}O_{0.02}$ and $Pt_{0.26}Pb_{0.01}In_{0.65}O_{0.08}$, respectively. The ethanol active region contains a relatively low fraction of Pt.

The XRD spectrum of the methanol active region in Figure 7.9(c) shows peaks corresponding to the PbPt_x (pdf #6-574) and PbPt (pdf #6-374) structure types, although the latter is shifted by less than 1°. In and Pb differ in their atomic radii by only 0.09 Å, and it may be possible for In to substitute for Pb in the PbPt structure. The ethanol active region in Figure 7.9(d) shows matches to the most intense peaks of the PbPt_x and In₃Pt₄ (pdf #31-598) structure types. The smaller peaks in the latter may be hidden in the background. The Pt structure type (pdf #4-802) may also be present, although the peaks are shifted by significantly different amounts.

Conclusions

We synthesized ten different thin film composition spreads containing Pt, Pb, and a third element X. For X, we chose Sn, Mo, Co, Cr, Fe, Nb, Ni, Si, Ta, and In. Of the three films of Pt-Pb-Sn, only one had active regions for both methanol and ethanol oxidation, although this particular film showed fluorescence during pre-screening without fuel. The Pt-Pb-Mo film has an extremely negative open circuit potential indicating electrochemical instabilities. Of the remaining films, all have active regions





(d)

Figure 7.9 Characterization of sample 2006-06-14: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

for methanol and ethanol oxidation. The Pt-Pb-Ta film has the lowest methanol onset potential (-50 mV vs. Ag/AgCl), but the corresponding active region contains a significant fraction of Pt, with a composition of $Pt_{0.65}Pb_{0.02}Ta_{0.24}O_{0.09}$ and a Pt structure type. The Pt-Pb-Nb film has the lowest ethanol onset potential (-170 mV vs. Ag/AgCl) and the corresponding active region also has a significant fraction of Pt with a composition of $Pt_{0.70}Pb_{0.07}Nb_{0.15}O_{0.07}$. The region also contains the Pt structure type.

The methanol active regions of all the films had lower onset potentials than that of sample 2005-10-05b (Pt-Pb deposited at 265°C, methanol onset potential of 210 mV vs. Ag/AgCl). It is therefore apparent that the addition of certain third elements enhances the electrocatalytic activity in the film, although the reason for the enhancement is unknown and requires further study.

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CHAPTER 8

A COMBINATORIAL SEARCH THROUGH COMPOSITION SPREADS OF TYPE Pt-Nb-X

In this chapter we describe the synthesis and screening of several thin film composition spreads containing Pt, Nb, and a third metal. Each film was tested for active regions for methanol and ethanol oxidation.

Pt-Nb-X Background

In Chapter 7, we describe the synthesis and screening of a thin film composition spread containing Pt, Nb, and Pb (sample 2006-05-26a) deposited at 375° C. The onset potentials of the methanol and ethanol active regions are -20 mV and -170 mV vs. Ag/AgCl, respectively. The onset potential of the ethanol active region is the lowest of the Pt-Pb-X films tested and is lower than the average of the Pt-Ru-Pb films, but the atomic fraction of Pt is significant (70% according to WDS). We therefore chose to test composition spreads containing Pt, Nb, and a third element in order to achieve lower onset potentials and lower Pt content in active regions.

A literature search on fuel cell anode electrocatalysts containing Pt and Nb (or Cb, Columbium, an older name for Nb) shows that few have performed studies on them. Papageorgopoulos *et. al.* investigated the inclusion of Nb in Pt and PtRu carbon-supported anode electrocatalysts in hydrogen PEMFCs¹. Cyclic voltammetry showed that a Pt₃Nb alloy at 80°C partially oxidizes CO at potentials close to 0 mV vs. RHE, lower than that of pure Pt. However, when used in a fuel cell with a hydrogen fuel stream and up to 200 ppm CO, the current density was approximately half that of a PtRu alloy electrocatalyst. A Pt₉Ru₉Nb₂ alloy showed no improvement over Pt-Ru alloys in a fuel cell operating with similar H₂/CO streams.

O.J. Adlhart and K.O. Hever hold a patent on a fuel cell with Pt-Nb alloy anode electrocatalysts². The fuel cell, operated between 50°C and 200°C, has an acid electrolyte and uses hydrocarbons as fuel. When the weight percent of Pt in the Pt-Nb alloy electrocatalyst is between 50% and 90%, the overpotential of the anode at a current density of 50 mA/cm² is 100 mV lower than that of pure Pt.

In depositing films of type Pt-Nb-X, we chose elements for X that form intermetallic compounds or have ordering domes with both Pt and Nb. We expected the formation of several binary and possibly ternary compounds with such choices. As reviewed in Chapter 1, several studies show that ordered intermetallic compounds are superior to pure Pt as fuel cell anode electrocatalysts³⁻⁷. We hypothesized that addition of a third metal that forms intermetallic compounds with both Pt and Nb produces active regions for methanol and ethanol oxidation in our films. Furthermore, we hypothesized that the active regions have lower onset potentials than those of sample 2006-05-26a (Pt-Nb-Pb deposited at 375°C) or a Pt-Nb film.

The elements Al, Be, Co, Cr, Fe, Ge, In, Ni, Sb, and Si all form intermetallic compounds or have ordering domes with Pt and Nb⁸. We chose Co, In, Ni, Sb, and Fe for element X due to their ease of sputtering.

Synthesis and Screening of Pt-Nb-X Films

We deposited five thin film ternary composition spreads containing Pt, Nb, and a third element X (Co, In, Ni, Sb, or Fe). The synthesis parameters are listed in Table 8.1. We also deposited a thin film binary composition spread containing only Pt and Nb for comparison, with the synthesis parameters listed in Table 8.2. All the films have expected equal atomic fractions of each element at the center of the film according to calibrations at the time. The deposition temperatures of most of the films are close to each other, from 395°C to 440°C. However, since In has a low melting point (157°C), we deposited sample 2006-10-03a (X = In) at a lower temperature of 325° C.

sample	mple gun #		2	3	4
2006-10-02	targets	Pt	Nb	Со	Та
	gun currents (mA)	70	350	90	700
	deposition rates at center (Å/s)	1.3	1.5	0.9	3.7
	deposition times (s)	675			270
	molar ratio at center (Pt:Nb:Co)	1:1:1			
	deposition temperature (°C)	430			
sample	gun #	1	2	3	4
2006-10-	targets	Pt	Nb	In	Та
03a	gun currents (mA)	45	240	53	700
	deposition rates at center (Å/s)	0.8	1.0	1.4	3.7
	deposition times (s) 780				270
	molar ratio at center (Pt:Nb:In)	1:1:1			
	deposition temperature (°C)	325			
sample	gun #	1	2	3	4
2006-10-	targets	Pt	Nb	Ni	Та
03b	gun currents (mA)	75	370	100	700
	deposition rates at center (Å/s)	1.4	1.6	1.0	3.7
	deposition times (s)	625			270
	molar ratio at center (Pt:Nb:Ni)	Nb:Ni) 1:1:1			
	deposition temperature (°C)		42	20	
sample	gun #	1	2	3	4
2006-10-04	targets	Sb	Pt	Nb	Та
	gun currents (mA)	49	135	280	700
	deposition rates at center (Å/s)	2.9	1.5	1.7	3.7
	deposition times (s) 410			270	
	molar ratio at center (Sb:Pt:Nb) 1:1:1				
	deposition temperature (°C)	395			
sample	gun #	1	2	3	4
2006-10-12	targets	Fe	Pt	Nb	Та
	gun currents (mA)	120	120	250	700
	deposition rates at center (Å/s)	1.0	1.3	1.5	3.7
	deposition times (s)	700			270
	molar ratio at center (Fe:Pt:Nb) 1:1:1				
	deposition temperature (°C)	435			

Table 8.1 Synthesis parameters of the thin film ternary composition spreads of type Pt-Nb-X.

sample	gun #	1	3	4
2006-10-11	targets	Pt	Nb	Та
	gun currents (mA) deposition rates at center (Å/s)		250	700
			1.5	3.7
deposition time (s)		89	270	
	molar ratio at center (Pt:Nb)	1:1		
	deposition temperature (°C)	440		

Table 8.2 Synthesis parameters of the Pt-Nb thin film binary composition spread.

We tested each film for electrocatalytic activity using fluorescence screening (see Chapter 2). We conducted the methanol oxidation screening first using the standard methanol electrolyte and then rinsed the film and electrochemical cell with distilled water before conducting a screening for ethanol oxidation in the standard ethanol electrolyte. However, we conducted two consecutive methanol screenings of sample 2006-10-03a (X = In) since the active region in the first screening had a high onset potential of 290 mV vs. Ag/AgCl. The region with the lowest onset potential for methanol oxidation had the same location in both screenings.

All the films have regions that are active for methanol and ethanol oxidation. Although sample 2006-10-02 (X = Co) fluoresces in a region not more than 2 to 3 mm wide in electrolyte without fuel (0.1 M NaCF₃SO₃, 0.5 mM quinine) during prescreening, the region is not located over any other active region and so should not affect any analyses of onset potentials. Figure 8.1 shows images of the fluorescence screening of each fuel for each film. The methanol and ethanol regions are within 1 cm of each other on most films, except for samples 2006-10-03b (X = Ni) and 2006-10-11 (binary composition spread). None of the methanol active regions have the same location as the methanol active region of the Pt-Nb binary spread (sample 2006-10-11). Only on samples 2006-10-02 (X = Co) and 2006-10-03a (X = In) are the ethanol active regions close the location of the ethanol active region of the Pt-Nb binary

Figure 8.1 Images of the fluorescence screenings of samples 2006-10-02 (X = Co) for (a) methanol at 350 mV and (b) ethanol at 200 mV vs. Ag/AgCl; 2006-10-03a (X = In) for (c) methanol (second screening) at 400 mV and (d) ethanol at 190 mV vs. Ag/AgCl; 2006-10-03b (X = Ni) for (e) methanol at 400 mV and (f) ethanol at 240 mV vs. Ag/AgCl; 2006-10-04 (X = Sb) for (g) methanol at 400 mV and (h) ethanol at 290 mV vs. Ag/AgCl; 2006-10-12 (X = Fe) for (i) methanol at 400 mV and (j) ethanol at 300 mV vs. Ag/AgCl; and 2006-10-11 (binary composition spread) for (k) methanol at 400 mV and (l) ethanol at 190 mV vs. Ag/AgCl. The orientation of the sputtering sources is shown in each image. The circles indicate the regions with the lowest onset potentials for each fuel.





spread. These observations suggest that the addition of a third element to a Pt-Nb film does indeed affect the electrocatalytic activity. Sample 2006-10-12 has two fluorescent regions for both methanol and ethanol oxidation. However, the brighter regions in Figures 8.1(i) and (j) are unstable and therefore unsuitable for electrocatalysts.

Table 8.3 lists the lowest onset potentials for methanol and ethanol oxidation on each film. For the methanol active regions, only three of the films have onset potentials lower than those of the Pt-Nb binary spread (sample 2006-10-11) by more than the experimental error: samples 2006-10-02 (X = Co), 2006-10-03a (X = In), and 2006-10-04 (X = Sb). None of the films have ethanol onset potentials that are lower than that of the Pt-Nb binary spread by more than the experimental error. For oxidation of both methanol and ethanol, sample 2006-10-03a has the lowest onset potential. However, both values are considerably greater than that of sample 2006-05-26a (Pt-Nb-Pb deposited at 375°C), where the lowest onset potentials are -20 mV and -170 mV vs. Ag/AgCl for methanol and ethanol oxidation, respectively.

complo	element	methanol onset potential	ethanol onset potential
sample	Х	(±25 mV vs. Ag/AgCl)	(±25 mV vs. Ag/AgCl)
2006-10-02	Со	190	45
2006-10-03a	In	155	40
2006-10-03b	Ni	255	75
2006-10-04	Sb	190	50
2006-10-12	Fe	380	290
2006-10-11	none	270	80

Table 8.3 Lowest onset potentials for methanol and ethanol oxidation on each Pt-Nb-X film.

Characterization of Active Regions of Pt-Nb-X Films

We characterized the active regions described in Figure 8.1 and Table 8.3 following fluorescence screening. We measured compositions with WDS and crystal structure with XRD.

Sample 2006-10-02 (X = Co)

Figures 8.2(a) and (b) show images of sample 2006-10-02 before and after fluorescence screening. The film is mostly reflective, with a faint dark color between the Pt and Nb sputtering sources that could indicate the formation of particular phase. Following fluorescence screening, the film acquires a slightly darker color toward the Co source, perhaps because of oxidation of the film. The areas of fluorescence in the methanol and ethanol screenings include this darkened region (see Figure 8.1). The Pt_{0.84}Nb_{0.04}Co_{0.11}O_{0.01} compositions of the active regions are and Pt_{0.80}Nb_{0.05}Co_{0.13}O_{0.02}. Both regions have similar compositions, as expected given their close proximity to each other. The atomic fraction of Pt is relatively high, and the regions did not oxidize extensively.

The XRD spectra of both active regions in Figures 8.2(c) and (d) have sharp Pt peaks, most of which are shifted from those of the Pt structure type (pdf #4-802). This structure type is expected given the significant atomic percentage of Pt. The shift in the peaks toward higher values of 20 may be the result of Nb or Co atoms inserted in the Pt lattice; the Nb-Pt binary phase diagram shows an fcc Pt-rich alloy⁸. However, Co has a similar atomic radius as Pt, while that of Nb is greater than Pt and would cause a shift in the peaks toward lower 20. The lattice parameters of the fcc Pt phase in the methanol and ethanol active regions, calculated by the computer program LAPODS⁹ using Cohen's method¹⁰⁻¹², are 3.91 ± 0.01 Å and 3.90 ± 0.01 Å, respectively. The lattice parameter of pure Pt is 3.92 Å.



Figure 8.2 Characterization of sample 2006-10-02: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

Sample 2006-10-03a (X = In)

Figures 8.3(a) and (b) show images of sample 2006-10-03a before and after fluorescence screening. The film has several texture boundaries toward the In sputtering source that do not change as a result of screening. The compositions of the methanol and ethanol active regions are $Pt_{0.94}Nb_{0.04}In_{0.01}O_{0.01}$ and $Pt_{0.91}Nb_{0.06}In_{0.01}O_{0.02}$, respectively. Just as for the active regions of sample 2006-10-02 (X = Co), the atomic fraction of Pt is relatively high and there is little bulk oxidation of the film.

Figures 8.3(c) and (d) show the XRD spectra of the methanol and ethanol active regions. Both regions show matches to the Pt structure type (pdf #4-802), as expected from the high atomic fraction of Pt according to WDS. The fcc Pt lattice parameters of the methanol and ethanol active regions are 3.95 ± 0.01 Å and 3.92 ± 0.01 Å, respectively, according to calculations by LAPODS. Insertion of In or Nb into Pt lattice sites could cause the lattice parameter to increase in the methanol active region. Both the In-Pt and Nb-Pt binary phase diagrams have fcc Pt-like phases⁸.

Sample 2006-10-03b (X = Ni)

Figures 8.4(a) and (b) show images of sample 2006-10-03b before and after fluorescence screening. The film has a faint dark region between the Pt and Nb sputtering sources, similar to that of sample 2006-10-02 (X = Co). It also has a darker region between the Nb and Ni sources. The film shows no change in appearance after screening. The compositions of the methanol and ethanol active regions are $Pt_{0.80}Nb_{0.05}Ni_{0.14}O_{0.01}$ and $Pt_{0.63}Nb_{0.21}Ni_{0.03}O_{0.13}$, respectively. Only the ethanol active region has a fraction of Pt lower than the active regions of samples 2006-10-03a (X = In) and 2006-10-02. It also shows substantial bulk oxidation, possibly from oxygen and water contaminants in the sputtering chamber.



Figure 8.3 Characterization of sample 2006-10-03a: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.



Figure 8.4 Characterization of sample 2006-10-03b: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

Figures 8.4(c) and (d) show the XRD spectra of the methanol and ethanol active regions. The peaks match those of the Pt structure type (pdf #4-802), just as they do in the active regions of samples 2006-10-03a (X = In) and 2006-10-02 (X = Co) but with greater shifts from pure Pt. The fcc Pt lattice parameters calculated by LAPODS are 3.96 ± 0.01 Å and 3.95 ± 0.01 Å, respectively. Nb in the lattice sites can account for the increase in the lattice parameter from that of pure Pt since Nb has a larger atomic radius than Pt.

Sample 2006-10-04 (X = Sb)

The images of sample 2006-10-04 in Figures 8.5(a) and (b) show few changes in appearance as a result of screening. The darkest regions of the film are located close to the Sb source and between the Pt and Sb sources. When compared to samples 2006-10-02 (X = Co) and 2006-10-03b (X = Ni), it appears that the presence of Sb darkens the faint spot between the Pt and Nb sputtering sources. The methanol and ethanol active regions are over this spot, having the same location on the film. The composition of the active region is $Pt_{0.41}Nb_{0.36}Sb_{0.06}O_{0.18}$, with a relatively low atomic fraction of Pt and high fractions of Nb and oxygen.

The XRD spectrum of the active region, shown in Figure 8.5(c), is the only one of the Pt-Nb-X films that shows evidence of an intermetallic phase, in this case the Pt₅Sb structure type (pdf #46-1065). The peaks are very broad, indicating small grains. The spectrum may also match the Pt structure type (pdf #4-802), although the peaks at 46.2° and 67.5° may be hidden in the background of the Pt₅Sb peaks.

Sample 2006-10-12 (X = Fe)

Figures 8.6(a) and (b) show images of sample 2006-10-12 before and after fluorescence screening. The film has faint colored textures toward the Fe sputtering



Figure 8.5 Characterization of sample 2006-10-04: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; (c) XRD spectra of the region active toward both methanol and ethanol.

source that show significant corrosion following screening, as mentioned above. The compositions of the methanol and ethanol active regions are $Pt_{0.69}Nb_{0.07}Fe_{0.18}O_{0.07}$ and $Pt_{0.76}Nb_{0.04}Fe_{0.15}O_{0.05}$, respectively. The high atomic percentages of Pt are reasonable in terms of their locations on the film (see Figure 8.1).

The XRD spectra of the active regions are shown in Figures 8.6(c) and (d). Both spectra match the structure type of a Pt-Fe alloy (pdf #29-717, composition $Pt_{0.8}Fe_{0.2}$), although the actual composition is probably somewhat different since the peaks are slightly shifted. The peaks are also shifted from the Pt structure type (pdf #4-802), giving further evidence for a Pt-Fe alloy. Note that the shift in the peaks from


Figure 8.6 Characterization of sample 2006-10-12: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

the Pt structure type is in the same direction of 2 θ as pdf #29-717. The lattice parameter of the fcc Pt structure type calculated by LAPODS is 3.89 ± 0.01 Å for both active regions.

Sample 2006-10-11 (binary composition spread)

Figures 8.7(a) and (b) show images of sample 2006-10-11 before and after fluorescence screening. The appearance of the film does not change as a result of screening. The faint, dark region between the Pt and Nb sputtering sources, common to most of the Pt-Nb-X films, is also present in the binary spread. The compositions of the methanol and ethanol active regions are $Pt_{0.89}Nb_{0.06}O_{0.06}$ and $Pt_{0.89}Nb_{0.06}O_{0.05}$, respectively. Each region has approximately the same composition even though they have different locations on the film (see Figure 8.1); however, this is reasonable since uniform compositions on a binary spread lie along contour lines between the sputtering sources (see Figure 2.6). In fact, the texture patterns on the film and the shape of the fluorescent regions shown in Figure 8.1 also appear to follow the calculated contours for a binary composition spread. With the exception of sample 2006-10-03a (X = In), the other films of type Pt-Nb-X have lower fractions of Pt, indicating that the third element X, while not reducing the onset potential, may reduce the fraction of Pt necessary for the active regions.

The XRD spectra of the methanol and ethanol active regions in Figures 8.7(c) and (d) match the Pt structure type (pdf #4-802), having nearly the same peak locations. This observation further supports the idea that both active regions lie along the same composition contour. The fcc Pt lattice parameter of both regions is 3.92 ± 0.01 Å, the same as that of pure Pt, indicating no alloying between Pt and Nb. The structure types indicated in the XRD spectra are also found in the active regions of the other Pt-Nb-X films. The lack of shift in lattice parameter of the binary film is not



Figure 8.7 Characterization of sample 2006-10-11: Images of the film (a) before and (b) after fluorescence screening, with the orientation of the sputtering sources shown; XRD spectra of the (c) methanol and (d) ethanol active regions with the lowest onset potentials.

found in the Pt-Nb-X films, with the exception of the ethanol active region of sample 2006-10-03a (X = In). Note that this film has the lowest ethanol onset potential. The data may suggest that the addition of a third element reduces the fraction of Pt needed for an active electrocatalyst in the Pt-Nb-X system. However, it is not conclusive whether or not the third element reduces the onset potential of ethanol oxidation.

Conclusions

We synthesized five thin film composition spreads containing Pt, Nb, and a third element X (Co, In, Ni, Sb, or Fe), as well as a binary composition spread of Pt and Nb. Each of the elements chosen for X form intermetallic compounds or have ordering domes with both Pt and Nb. While all of the films have electrocatalytically active regions for methanol and ethanol oxidation, only those containing Co, In, or Sb have methanol onset potentials that are lower than the active region of the binary spread by more than the experimental error. The addition of the third element does not reduce the ethanol onset potentials that not be more than the experimental error. None of the films have lower onset potentials that not of sample 2006-05-26a (Pt-Nb-Pb deposited at 375°C, methanol and ethanol onset potentials of -20 mV and -170 mV vs. Ag/AgCl, respectively).

Characterizations of the active regions of each film show the Pt structure type, possibly alloying with Nb or element X. Only the XRD spectrum of the active region of the Sb-Pt-Nb film shows the possible presence of an intermetallic compound, Pt₅Sb. The methanol and ethanol active region of the same film also contains the lowest atomic fraction of Pt, with onset potentials 80 mV and 30 mV lower than those of the binary film for methanol and ethanol oxidation, respectively.

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CHAPTER 9 SUMMARY

In this dissertation, we investigated new anode electrocatalyst materials for direct methanol and direct ethanol polymer electrolyte fuel cells (PEMFCs). Using traditional one-at-a-time synthesis and testing methods would have taken an inordinate amount of time for such an investigation. We therefore designed a combinatorial method to make the search more efficient. Our method involves depositing thin film composition spreads of two to three elements by magnetron sputtering on a suitable substrate. The theoretical model developed in Chapter 2 shows that a film of three elements contains approximately 75% of the compositions on a ternary phase diagram. We can deposit the films within a few hours and at temperatures up to 600°C. We test the films for active methanol and ethanol oxidation electrocatalysts using a parallel fluorescence screening method. The method is useful for determining the onset potential of the most active composition. We can characterize the surface morphology (with SEM), bulk (with EDS and WDS) and surface (with XPS) compositions, and crystal structure (with XRD) of interesting regions of the films.

We used our combinatorial method to investigate the methanol and ethanol oxidative properties of over 50 thin film composition spreads containing Pt-Pb-X, Pt-Ru-X, or Pt-Nb-X (where X is either a third element or an undeposited component, i.e. a binary film). The methanol oxidation electrocatalyst with the lowest onset potential, described in Chapter 7, was a composition containing Pt, Pb, and Ta. An electrocatalyst containing Pt, Ru, and Pb, described in Chapter 5, had the lowest onset potential for ethanol oxidation. While each of these compositions had lower onset potentials than Pt, they were still far from that expected for an ideal electrocatalyst.

Our investigation revealed that deposition temperature affects the electrocatalytic ability of compositions in some systems. For example, an active methanol electrocatalyst in the Pt-Bi-Pb system, described in Chapter 4, had an optimal onset potential for deposition temperatures between 260°C and 400°C. Other active compositions, such as those in the Pt-Ru-Pb system described in Chapter 5, show no dependence on deposition temperature (for the range of temperatures tested).

Tests of films containing Pt, Ru, and Pb showed that films deposited under apparently similar conditions (including deposition temperature) can vary in their activity. Such active compositions for methanol and ethanol oxidation varied widely in their onset potentials and bulk compositions. The variations, however, may be less significant for other systems such as Pt-Bi-Pb. At present we do not understand the source(s) of these variations, but note that the electrochemical activity of films is determined by their surfaces, not by their bulk (or average) structure and composition.

It must be kept in mind that the particulars of the synthesis and testing procedures are likely to influence results. The time between synthesis and testing, deposition conditions in the sputtering chamber, and atmospheric conditions (temperature, humidity, etc.) during film storage may change characteristics of the film. We suspect such conditions greatly influence the amount of oxygen in the films. The content of oxygen can influence properties of the film such as grain sizes, surface morphology, and the formation of particular phases. Such observations show the need for consistent synthesis and testing procedures.

Surface characterization techniques are needed to more completely determine the relationship between electrocatalytic ability and electrocatalyst characteristics. Most of the active compositions showed no strong relationship between bulk properties and onset potential. We therefore suspect that the surfaces of the films studied are more variable than the bulk of the films. More measurements with XPS,

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SIMS (secondary ion mass spectroscopy), or other surface techniques would be helpful.

We concluded that our combinatorial method is an effective tool for efficiently searching for new PEMFC anode electrocatalysts. We expect the techniques to enable discoveries of new materials and help make the use of fuel cells more feasible. However, determining the active species on the film surface may be more difficult than we initially assumed.

APPENDIX

An interesting issue that arises from our combinatorial method for synthesizing thin film composition spreads is whether or not the phases produced on the film correspond to those predicted by a phase diagram. We investigated this issue for a Pt-Ru thin film composition spread. We chose the Pt-Ru system because of its relative simplicity; the Pt-Ru binary phase diagram contains only two different alloy phases with different structure types. The phases should therefore be easy to identify with XRD.

The synthesis parameters of the Pt-Ru film tested (sample 2006-11-06b) are listed in Table A.1. The film has an underlayer of Ta much like other films used for electrocatalytic screening. Also note that the film has an expected Pt:Ru molar ratio at the center of 1:2. We chose this ratio to produce compositions high in Ru since such compositions tended to be electrocatalytically active for ethanol oxidation. However, we never tested the film for activity prior to the characterization described below.

sample	gun #	1	2	4
2005-07-01	targets	Pt	Ru	Та
	gun currents (mA)	55	250	700
	deposition rates at center (Å/s)	1.0	1.8	3.7
	deposition time (s)	895 2		270
	molar ratio at center (Pt:Ru)	1:2		
	deposition temperature (°C)	ambient		

Table A.1 Synthesis parameters of sample 2006-11-06b.

We characterized the crystal structure (using XRD) and composition (using EDS) at seven points on the film. The points are 1 cm apart along a horizontal line through the center of the film, labeled as shown in Figure A.1. The first point is 1 cm from the edge of the film, closer to the Pt source than to the Ru source.



Figure A.1 Location of the seven points of sample 2006-11-06b that were characterized. The relative positions of the Pt and Ru sputtering sources are also shown.

Figure A.2 shows the XRD spectra, measured with GADDS, for points 1 through 7. As expected, the regions closest to the Pt sputtering source have spectrum peaks that match the fcc Pt structure type (pdf #4-802 at points 1 through 4), while those closer to the Ru sputtering source have peaks that match the hcp Ru structure type (pdf #6-663 at points 3 through 7). Notice that the peaks corresponding to the Pt structure type are shifted toward greater values of 2θ as one moves from point 1 to point 4. The shifts indicate a decrease in the lattice parameter that we attribute to increasing amounts of Ru alloying with fcc Pt. Similarly, as one moves from point 7 to point 3, the peaks corresponding to the Ru structure type are shifted toward lower values of 2θ , indicating an increase in the lattice parameter that we attribute to increasing amounts of Pt alloying with hcp Ru.

Table A.2 shows the lattice parameters of any fcc Pt phases present at the seven points, calculated using the LAPODS program¹ and Cohen's Method²⁻⁴. Compare these to the lattice parameter of the pure Pt phase, 3.92 Å. Also shown are

Figure A.2 XRD spectra (a) through (g) of points 1 through 7, respectively, on sample 2006-11-06b.





Figure A.2 (continued)



Figure A.2 (continued)



Figure A.2 (continued)



Table A.2 Lattice parameters of the fcc Pt phase, compositions of the fcc Pt phase, and compositions measured by EDS at points 1 through 7 of sample 2006-11-06b.

point	fcc Pt phase lattice	composition of fcc Pt	composition measured
	parameter (Å)	phase	with EDS (±10 atomic %)
1	3.90	$Pt_{0.78}Ru_{0.22}$	$Pt_{0.85}Ru_{0.15}$
2	3.89	$Pt_{0.71}Ru_{0.29}$	$Pt_{0.78}Ru_{0.22}$
3	3.86	$Pt_{0.48}Ru_{0.52}$	$Pt_{0.57}Ru_{0.43}$
4	3.85	$Pt_{0.40}Ru_{0.60}$	$Pt_{0.38}Ru_{0.62}$
5	-	-	$Pt_{0.20}Ru_{0.80}$
6	-	-	$Pt_{0.10}Ru_{0.90}$
7	-	-	$Pt_{0.05}Ru_{0.95}$

the compositions of the fcc Pt phase according to the relationship between lattice parameter and PtRu alloy composition^{5, 6} (see Chapter 5), as well as the compositions measured with EDS. As noted above, the lattice parameter of the fcc Pt phase decreases at increasing distance from the Pt source, and therefore the associated composition of the fcc Pt phase contains increasing amounts of Ru. As expected, the

amount of Pt decreases with increasing distance from the Pt sputtering source, while the amount of Ru increases with decreasing distance from the Ru sputtering source.

The Pt-Ru binary phase diagram is described in detail in Chapter 5 and reproduced in Figure A.3. According to composition and crystal structure measurements on the film, fcc Pt is the lone phase for compositions containing 78 to 100 atomic % Pt. The hcp Ru phase is the lone phase for compositions containing at most 38 atomic % Pt or lower. Both phases are observed between 38 and 78 atomic % Pt. Note that this result differs from the Pt-Ru binary phase diagram, where both phases are present only between 20 and 38 atomic % Pt. In our thin film, the hcp Ru phase is favored.



Figure A.3 The Pt-Ru binary phase diagram⁸.

Several reasons could account for the difference between the equilibrium phase diagram and the results of the film. These include the low deposition temperature relative to the melting points of Pt and Ru (and relative to the temperature region shown in the Pt-Ru phase diagram), the expected stress in the deposited film⁷, and the possible inclusion of oxygen in the film.

The results indicate that the phases synthesized on a thin film composition spread may not correspond to those indicated on a phase diagram. This is not surprising since phase diagrams indicate phases present under equilibrium conditions. Clearly, synthesis by sputtering does not guarantee equilibrium conditions in films. Meta-stable and amorphous phases are possible, especially at low deposition temperatures. This property of films should be kept in mind when using our combinatorial approach.

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