COMBINATORIAL SCREENING OF FUEL CELL CATALYSTS

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Abstract

by

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Improved low temperature fuel cell catalyst compositions were pursued by constructing and screening thin film combinatorial libraries. The discrete composition combinatorial libraries were fabricated by plasma sputtering through shadow masks and then annealed in a vacuum furnace. Multichannel cyclic voltammetry was used to examine these libraries for short term catalytic activity. The oxidation of methanol and the reduction of oxygen were the reactions of interest. For the methanol oxidation reaction, compositions were ranked based on the potential defined at the onset of the reaction and the current density at the peak of the reaction. For the oxygen reduction reaction, compositions were ranked based on the onset potential of the oxygen reduction reaction.

Results from the Pt-Ru, Pt-Ru-W, Pt-Ru-WC, Pt-Ru-(WC-Ta), Pt-Ta-WC, Pt-Ru-C, Pt-Ru-Cr, Pt-Ru-Ni, Pt-Ni-Cr, Pt-Ru-Co, Pt-Ti-Co, Pt-Co-Cr, Pd-Cr-Co, Pt-Co-Cu, Co-Cr-Cu, Pt-Ru-Cu, Pt-Ru-Mg₄Ti, Pt-Fe-Ru, Pt-Fe-C and Pt-Fe-Cr systems are discussed. It was found that the optimum composition changed from initial to final tests. Cycling the potential at 60 °C conditioned the libraries and altered the
performance of most compositions. Usually the compositions that were initially active,
were also unstable and would corrode away with the conditioning process.

Systems that did not contain Pt (Pd-Cr-Co and Co-Cr-Cu) showed no activity for
either methanol oxidation or oxygen reduction. Methanol oxidation testing revealed that
the Pt-Ru-W, Pt-Ru-C, Pt-Ru-Ni and Pt-Ru-Co systems had compositions that could
outperform the best Pt-Ru compositions. Overall the best methanol oxidation
composition was Pt$_{12}$Ru$_{44}$Co$_{44}$ with double the peak current density and an onset potential
142 mV lower than the average Pt response. The activity of this composition
diminished in the presence of oxygen; the best composition to reduce methanol in
saturated oxygen was Pt$_{44}$Ru$_{12}$W$_{44}$. Strong oxygen reduction responses were observed
from compositions in the Pt-Ni-Cr, Pt-Ti-Co, Pt-Co-Cr and Pt-Fe-Cr systems. The best
oxygen reducing composition was Pt$_{27}$Co$_{36}$Cr$_{37}$ with an onset potential of 0.673 V-SCE,
107 mV better than the standard, pure Pt. Another Pt-Co-Cr composition (Pt$_{30}$Co$_{40}$Cr$_{30}$)
was the best oxygen reducing catalyst in the presence of methanol. Powder forms of
these compositions may replace the current anode and cathode catalysts of all types of
PEMFC in the near future.
For my family
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CHAPTER 1:  
LITERATURE SURVEY

1.1 Fuel Cells

1.1.1 History

The concept of a fuel cell has existed for over a hundred years and has played a role in several energy related issues of world history [1]. The first reported approximation of a fuel cell was envisaged by Sir William Grove [2] in 1839 when he published his paper on a “gas battery”. For some perspective of the time this was merely 50 years after the first fleet landed in Australia and three years before the University of Notre Dame was founded in the United States. But a fuel cell would only be as useful as the fuel put into it and the principal energy source of that time period was coal. Mond and Langer [3] contrived a process where hydrogen could be derived from coal and coke and then generate electricity in a scaled up Grove gas battery. Unfortunately impurities mixed in with hydrogen poisoned the cell and the high cost of the Pt Black catalyst made the project unfeasible. It should be noted that these are two challenges that are still faced by the fuel cell industry today. Mond and Langer had made huge improvements to Grove’s gas battery by using a porous matrix and powdered electrocatalysts. Other groups pushed to achieve a direct coal fuel cell but were plagued with seemingly insurmountable problems [1]. It wasn’t until 1933 that direct coal fuel cells were principally abandoned in favor of the now named “Bacon Cell”.

Bacon has written many interesting accounts of his and others early work with fuel cells [4-6]. As a curious side note he believed the first electrochemical cell that generated electricity was constructed by an Italian in 1790 when he touched a dissimilar pair of electrodes to certain nerves in a frog’s leg [4]. The electricity generated from this experiment would have been a dribble in comparison to the Bacon’s cell, an alkaline fuel cell that achieved 1.1 A cm\(^{-2}\) at 0.6 V and 240 °C. Unfortunately this power diminished rapidly with use due to corrosion of the nickel cathode catalyst. This problem was overcome in 1959 by using a lithium doped nickel oxide cathode catalyst that made the alkaline fuel cell a reliable and very expensive power source [1]. The alkaline fuel cell was so expensive that there was no commercially feasible application for it on the face of the earth.

The sputnik launches of 1957 and the following “space race” spurred a need for a lightweight, reliable power source and thankfully for fuel cell development, money was not an issue. At this time William Grubb of General Electric was looking for applications for ion exchange membranes. From these polymer electrolyte membrane fuel cells (now commonly referred to as proton exchange membrane fuel cells) were developed and deployed in the Gemini program in 1962. The AFC wasn’t necessarily worse than the PEMFC; the AFC used cheaper catalysts and required higher operational temperatures and pressures. The AFC was more efficient and is still used in space shuttles today [1]. The PEMFC and its brother the direct methanol fuel cell (DMFC) are more suited to terrestrial activities and are believed to be the future replacements of batteries and combustion engines.
McNicol [7] reviewed direct methanol fuel cell research from the previous decade in 1981. At this early time techniques like FTIR had not been used and the reaction intermediates that were poisoning the surface were still unknown. Despite this many researchers had already recognized the best way to improve a Pt catalyst was to alloy it with other elements. As of 2006 several different types of fuel cell have been developed but they still have not achieved widespread commercial adoption. The high efficiency and low emissions of fuel cells over traditional power sources make them an attractive alternative. The main obstacle to common commercial use has been the cost of the technology. Research has focused on lowering the cost of fuel cells and improving their performance so that they will become common place in the near future [8].

1.1.2 Basic Principles

The fuel cell is a device that directly and continuously converts the chemical energy of a reaction into electricity. This is different from a battery that consumes its limited supply of chemical reactants as it produces electricity where as a fuel cell can operate indefinitely. Typically a fuel cell will oxidize a fuel (e.g. hydrogen) at its anode and reduce oxygen at its cathode. The fuel oxidation will liberate electrons and a charged species, usually protons for low temperature fuel cells. The electrons pass through an external circuit doing the electrical work that the fuel cell was meant to power. The charged species is mobile and diffuses internally through the fuel cell to the cathode where it is reduced with oxygen. The direct liberation of chemical energy into electrical power means that the fuel cell is more efficient than the combustion engine that is limited by the Carnot cycle [9].
Fuel cells are classified by either their fuel or their mobile charged species into one of six categories [10]. Alkaline Fuel Cell (AFC) uses hydroxide ions and operates between 50 °C and 200 °C, they are still used in space vehicles. Proton Exchange Membrane Fuel Cells (PEMFC) use protons as their mobile ions and oxidize hydrogen, they are very similar in construction and operation to Direct Methanol Fuel Cells (DMFC) but the latter oxidizes methanol. Phosphoric Acid Fuel Cells (PAFC) also use protons but operate at higher temperatures (~220 °C) than the PEMFC or DMFC. Typical PAFC units are large stationary power generators which preprocess natural gas into hydrogen that is then consumed by the cell. The Molten Carbonate Fuel Cell (MCFC) and the Solid Oxide Fuel Cell (SOFC) operate at temperatures over 500 °C and use CO$_3^-$ and O$_2^-$ respectively. This study has been concerned with the catalysts of the two low temperature fuel cells, the PEMFC and the DMFC.

When the current drawn from a fuel cell increases the potential decreases as shown in figure 1.1.1 [11]. This leads to no power being possible at either high or low potentials and limited power at median potentials that is below perfect efficiency. The inefficiencies that constrain a fuel cell’s maximum power have been divided into four groups [11, 12]. The first inefficiency is the activation losses, which refers to the energy required to just drive the reaction. The PEMFC has an activation loss of ~ 300 mV due to the energy required to overcome the sluggish reduction of oxygen at the cathode. The oxidation of hydrogen is fairly efficient with only a few mV lost but the oxidation of methanol at the anode of a DMFC can cause another ~ 100 mV of loss. The second inefficiency is fuel crossover. As the name implies fuel permeates through the porous membrane and oxidizes at the cathode wasting the electrons it would have generated at
the anode. Fuel that crosses over to the cathode can also poison the catalyst with intermediate oxidation products further reducing the efficiency. The third inefficiency is the ohmic loss which refers to the power required to push the electrons through the poorly conducting interfaces within the cell. Anything that hinders or slows the charged species through the electrolyte is also considered an ohmic loss. Mass transport losses are the fourth inefficiency and refer to the concentration gradients of the reactants that occur on the surface of the electrodes. At high potentials when the reaction is required to proceed quickly the electrode surface becomes starved of reactants that can’t diffuse to the surface fast enough. This investigation was principally concerned with overcoming was the activation losses of low temperature fuel cells.

Figure 1.1.1, Potential (black line) and power density (blue line) plotted against current density for a typical low temperature fuel cell. Regions of potential that are affected by the different losses are shaded appropriately to show the contributing factors that keep the fuel cell from achieving its theoretical potential (dotted line) [11].
The environmental cleanliness and the simplicity of refueling make the low
temperature PEMFC and DMFC attractive power sources. Unfortunately both types of
fuel cell currently have poor power densities, cannot be operated above 100 °C and are
built from this planet’s most expensive and rarest elements. There are additional
problems for the cells that are specific to the fuels they each utilize. Compressed
hydrogen has a much higher energy density than methanol. Unfortunately the storage of
hydrogen requires a strong, heavy, composite containment unit in comparison to the
storage of methanol which can be kept in simple plastic containers. When the
containment weight is added to energy density calculations methanol becomes the
superior fuel [13]. Unfortunately the methanol oxidation reaction has a higher over
potential than the hydrogen oxidation reaction, meaning that the DMFC has higher
activation losses and worse performance than the PEMFC. On top of this methanol that
crosses through the proton exchange membrane is not only wasted but it will also poison
the catalyst reducing the cathode’s efficiency. The crossover effect can be reduced by
altering the membrane, improving the anode catalyst activity or improving the cathode
catalysts selectivity so it does not oxidize methanol or become poisoned [14].

Another solution to the crossover problems of the DMFC is the Mixed Reactant
Fuel Cell (MRFC). Just like the PEMFC, the MRFC operates at low temperatures on a
hydrogen or light alcohol fuel. In a MRFC the fuel and oxygen are mixed together in a
single feedstream that first passes over an anode catalyst that selectively reduces the fuel
and ignores the oxygen. The feedstream now with protons from the reduced fuel then
passes through a porous but electrically insulating membrane to the cathode. At the
cathode the protons and oxygen are selectively reduced completing the chemical reaction.
The key to the MRFC is the selectivity of the anode and cathode catalyst; it will not work if oxygen is reduced at the anode or if the fuel is oxidized at the cathode [15]. The prime advantages stem from the simplified design; only one pump is required to control the one fuel/oxidant stream and a more robust design that won’t fail from a breached membrane [16]. The disadvantages come from the poor performance and efficiency losses that occur because there is no perfectly selective catalyst. If a MRFC could generate the same power density as a DMFC then its simplicity would easily make it the more desirable power source [17].

Shukla [15] reviewed work done on methanol resistant oxygen reduction catalysts. Amongst the many compositions, helpfully categorized into four structural groups, two show potential for a MRDMFC; Iron-tetramethoxyphenylporphyrin for the anode and RuSe/C for the cathode. Cyclic voltammetry experiments confirmed the compositions selectivity and a fuel cell test with Pt-Ru and RuSe catalysts succeeded in generating 50 mWcm$^2$. Though this is still low in comparison to current DMFC standards, the obvious path for improvement is to refine the catalyst selectivity.

1.2 Reactions
1.2.1 Methanol Oxidation Reaction

Iwasita [18] reported that the thermodynamic potential for methanol oxidation to CO$_2$, is very close to the equilibrium potential for hydrogen, eqn (1). However compared to hydrogen oxidation it is quite slow.

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad \quad E^o = 0.02 \text{ V-SHE} \quad \quad (1)$$
The simplest oxidation path would be for the methanol to adsorb and then undergo successive dehydrogenation steps [19].

\[
CH_3OH \rightarrow (CH_3O)_{ads} + H^+ + e^- \quad (2)
\]

\[
(CH_3O)_{ads} \rightarrow (CH_2O)_{ads} + H^+ + e^- \quad (3)
\]

\[
(CH_2O)_{ads} \rightarrow (CHO)_{ads} + H^+ + e^- \quad (4)
\]

\[
(CHO)_{ads} \rightarrow (CO)_{ads} + H^+ + e^- \quad (5)
\]

The adsorption of methanol to a catalyst’s surface eqn. (2) is not simple; it is a large atom that requires multiple sites [20]. On top of that, methanol cannot displace adsorbed protons. At low pH, adsorption cannot begin until the potential is raised enough for neighboring catalyst sites to become free of protons, which would be above 0.2 V-SHE for Pt. Once methanol has adsorbed the removal of the first three hydrogen groups is assumed to be quick eqn. (2), (3) and (4) [21]. The removal of the last hydrogen group eqn. (5) is considered slow [21] but not as slow as oxidation of the remaining CO group. The simplest model to oxidize CO includes the sequential dehydrogenation of water and then the combination of the water’s oxygen group with the adsorbed CO to form of CO\(_2\) [22].

\[
(H_2O)_{ads} \rightarrow (OH)_{ads} + H^+ + e^- \quad (6)
\]

\[
(OH)_{ads} \rightarrow O_{ads} + H^+ + e^- \quad (7)
\]

\[
(CO)_{ads} + O_{ads} \rightarrow CO_2 \quad (8)
\]
But eqn. (8) assumes complete dehydrogenation from both CH$_3$OH and H$_2$O takes place before the adsorbed CO and O form CO$_2$. But it is possible for the methanol and water to react before they have both fully dehydrogenated for example [21]

$$\text{(CO)}_{\text{ads}} + \text{(OH)}_{\text{ads}} \rightarrow \text{(COOH)}_{\text{ads}} \rightarrow +\text{CO}_2 + H^+ + e^-$$  \hspace{1cm} (9)

Partially dehydrogenated products recombining could also produce H$_2$CO, HCOOH, HCOOCH$_3$, and CH$_2$(CH$_3$O)$_2$ which have been experimentally observed [23-25]. Factors that affect the yield of intermediates are methanol concentration, temperature, electrode roughness and time. The desired formation of CO$_2$ was found to be favored at high temperatures on a high surface area electrode [22]. This was confirmed by Honma and Toda [26]; they reported that the onset potential of methanol oxidation decreased with increasing temperature on Pt and Pt alloys.

Identifying these intermediates and their interactions has been filled with discrepancies and controversy [22]. The differences are probably due to experimental approach. For example, trace amounts of oxygen would be simultaneously reduced on a Pt surface and form H$_2$O$_2$ intermediates that act as oxidizing agents. Additionally the methanol oxidation reaction is very complex and sensitive. Electrodes made from differently orientated single crystals of Pt have shown very different methanol oxidation cyclic voltammetry curves [27]. With the difficulties that surround this complex reaction it is little wonder that the reaction mechanism is still far from being precisely defined.
Current density measurements are especially sensitive to experimental conditions [28]. For example, current densities measured in half cells with perchloric acid as the electrolyte can be as much as $20 \times$ higher than a similar setup with sulphuric acid electrolyte [29-31]. When an electrode of high surface area nanoparticles is measured, the current density can be more than $100 \times$ higher than a similar composition flat surface electrode [12]. Shen and Tseung [32] tested the same Pt-WO$_3$ catalysts in different concentrations of sulphuric acid. They observed that at low pH varying the methanol concentration had no effect, but at high pH (yet still acidic) increased methanol concentration increased the reaction rate. They hypothesized that the rate limiting step changed from the adsorption of water to the adsorption of methanol in dilute sulphuric acid solutions. Unfortunately our group’s unique combinatorial experiments were dissimilar to other reported fuel cell catalysis work. This meant that the comparison of current density results from this work to those in literature could only be performed qualitatively.

There is a reasonable consensus regarding the general mechanisms at different potentials on Pt surfaces. At low potentials, less than 0.4 V-SHE (0.16 V-SCE), the rate determining step for a pure Pt electrode is the adsorption of methanol [33]. Above 0.4 V-SHE (0.16 V-SCE) CO$_2$ is generated, implying that the rate determining step would now be the oxidation of CO and other methanol residues. Bagotzky and Vassilyev [34] performed fairly exhaustive testing on Pt surfaces. They performed potential step experiments, observing the instantaneous ($t=0$) non steady state current and the steady state current after 2 – 20 minutes. From their experiments they were able to deduce that the slow adsorption of methanol became the rate limiting step at higher potentials. The
The tafel slope they determined for pure Pt was 0.06 V at potentials below 0.55 V-DHE (~0.31 V-SCE) and 0.11 V above that potential. They also reported that the electrooxidation of methanol on pure Pt experiences a maximum at 1 M and decreases at higher concentrations. Bagotzky and Vassilyev [34] observed many unusual results that highlighted the complex nature of the methanol reaction. For example, after holding the potential at 0.5 V-DHE (~0.26 V-SCE) for 5 minutes and achieving a steady state current they stepped the potential up to 0.8 V-SHE (~0.56 V-SCE). Counter-intuitively the current instantly decreased after the potential was increased. After dropping, the current slowly returned back up to its steady state value.

The most important potential regime for a fuel cell is ~ 0.4 SHE (~0.16 V-SCE) and the consensus agreement is that at this potential the RDS is the oxidation of CO [35]. Unfortunately a catalyst composition with excellent CO oxidizing performance is not always also a good methanol oxidizing catalyst [36]. For example, Pt$_3$Sn has shown extraordinary CO oxidation activity but is nearly useless when it comes to methanol oxidation. There are several reasons for this, but the principle reason is that the adsorbed CO remaining from methanol oxidation tends to be tightly bound to a few Pt sites and CO adsorbed directly from CO in solution tends to be weakly bound to many Pt sites. The two different forms of CO require two different catalysts to be efficiently oxidized [37].

Work done to improve catalytic efficiency of the methanol oxidation reaction can be divided into three groups; the particle size and dispersion of Pt$_{50}$Ru$_{50}$ catalysts, novel carbon structures used to support catalysts and the exploration of new catalyst compositions [38]. The search to enhance Pt’s methanol oxidation catalysis with
another element started several decades ago. Anderson [39] summarized some very early work [40] that examined basic catalytic performance of some alloys. Pt alloyed with Ru and Sn excelled and interestingly it was speculated that the Ru and Sn helped the catalytic process via different mechanisms. Pt alloyed with Ti, V, Cr, Mn, Rh, Re and Mo showed some enhancement, but Fe, Co, Ni and Cu did not improve platinums base performance. There was no reported improvement when a third element (W, Ta, Zr or Mo) was substituted into Pt-Ru. Ru-Rh was reported to have worked quite well but binary combinations of Ru or Os with Pd, Ir or Rh did not do better than pure Pt.

Today the list of compositions that have been tested for enhanced methanol oxidation is becoming near limitless. Many binary and ternary catalysts have been investigated, mainly based on Pt with one or two additional elements [41]. Investigated binary combinations include Pt with Co, Cr, Fe, Ir, Mn, Mo, Ni, Pd, Rh and Ru [41-43]. Ternary combinations include Pt and Ru with Al, Mo, Cr, Ir, Mn, Co, Nb, Ni, Pd, Rh, W and Zr [44, 45-47] additionally there exists a ternary (Pt-Re-(MgH2)) that doesn’t contain Ru [48]. Not all functioning catalysts need to contain Pt; WC [49, 50], Au-Pd [51] and Pd-Co [52, 53] are examples of non Pt binary compounds that have had some success as catalysts. Out of all these catalysts, carbon supported Pt50Ru50 is still considered the optimum methanol oxidation catalyst [38].

The method used to measure the catalytic activity of these different compositions can be another source of confusion. Usually a catalyst’s activity will be reported as a current density based on its active area, where the active area is the number of atomic sites that participate in the reaction. For a simple reaction like the hydrogen oxidation reaction where for each Pt site a single hydrogen is reduced, the active area would be
based on the number of Pt sites [54]. This allows for comparison between the catalytic activity of high surface area powders and smooth flat electrodes. Unfortunately, for more complicated reactions that require multiple sites of differing composition, the active area cannot be defined as simply. Hughes and Miles [55] performed cyclic voltammetry on a few high surface electrodes, examining methanol oxidation and monitoring changes to active area by following the adsorption of $H^+$. They admitted that it was impossible to accurately determine the active area of their Pt$_{70}$Ru$_{30}$ electrode because $H^+$ does not adsorb to Ru sites. Saffarian et al. [56] concur that measurements of surface area by hydrogen adsorption is only feasible for pure Pt samples. Lakshminarayanan et al. [57] compared roughness and area measurements made by a STM to those derived from electrochemical studies of adsorbed hydrogen. Though there was a reasonable correlation for pure Pt, the surface area of a Pt-Ru alloy could not be accurately measured electrochemically. The principle reason for the electrochemical technique failing was because the Pt-Ru had no double layer in sulphuric acid and was under partial activation control at all potentials [57].

Currently the best catalyst with the highest activity used in direct methanol fuel cell anodes is Pt$_{50}$Ru$_{50}$ and it is frequently stated that the two elements work via a bi-functional mechanism. The term implies that Pt adsorbs and dissociates methanol and Ru adsorbs and dissociates water to oxidize the residue. This is a little misleading; at slightly higher potentials Pt can absorb and dissociate H$_2$O [22] and at reasonable temperatures ($60 – 80 \,^\circ C$) ruthenium can also adsorb methanol [58]. Ru has also been observed affecting the dissociative adsorption of methanol on Pt [59 , 60]. Aside from these details the consensus believes that on a Pt-Ru catalyst the methanol adsorption
mainly occurs on the Pt and water adsorption mainly occurs on the Ru sites, they “bi-functionally” strip hydrogen and then combine the CO with the O.

Gojkovic et al. [61] examined the kinetics of methanol oxidation on a carbon supported Pt-Ru catalyst and semi-empirically derived a rate law based on their experimental observations. They found that the current density was directly proportional to the root of methanol concentration and inversely proportional to root of the H\(^+\) concentration. They also observed Arrhenius behavior between 27 °C and 40 °C and determined the activation energy to be 70 kJmol\(^{-1}\). Unfortunately this was only applicable for a half cell tested with perchloric acid and their treatment becomes inadequate when applied to more complex environments that more accurately simulate a fuel cell [61].

1.2.2 Oxygen Reduction Reaction

The oxygen reduction reaction is very important for many practical systems, but is of special interest because its necessity in all fuel cells [62]. Oxygen reduction is fundamentally complex and very sensitive to electrode surfaces and the presence of other adsorbed species. The biggest issue with the oxygen reduction reaction is its high overpotential. It is estimated that the best cathode platinum catalysts still have an overpotential of 300 mV. This overpotential is calculated by first determining the equilibrium potential based on the gibbs free energy. For the 4 electron reduction of oxygen to water at low pH, eqn. (10), it is 1.229 V-SHE. The overpotential is then determined by experimentally measuring the open circuit potential and subtracting it from the theoretical equilibrium potential. The open circuit potential for the ORR on a Pt electrode this has been difficult to measure with values rarely exceeding 1.1 V-SHE in
careful experiments and usually about 0.9 V-SHE in fuel cells. This is much lower than the 1.229 predicted by the theoretical calculation from the Gibbs free energy of reaction [63].

\[ O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad E_0 = 1.229 \text{ V-SHE} \quad (10) \]

The reaction however, involves a variety of intermediates, electron transfers and reaction steps. Figure 1.2.1 shows the possible intermediates and their chemical potentials [62]. From figure 1.2.1 it is easy to see that there are many possible paths by which the reaction could proceed. But the true situation is even more complex because the behavior of each intermediate will depend on the type of catalyst site it is adsorbed to and the adsorbed species that are about it. Note that figure 1.2.1 also doesn’t show the activation energies required to change from one intermediate to another.

Figure 1.2.1, Intermediates of the oxygen reduction reaction and their chemical potentials, reproduced from [62].
ORR Literature has tended to break down its examination of oxygen reduction into two paths. The parallel path where oxygen is dissociated and reduced to water is different from the series path where oxygen is reduced to hydrogen peroxide and then further reduced to water. The parallel path involves an atomic oxygen intermediate (O at 230 kJmol\(^{-1}\) in figure 1.2.1) and requires a catalyst surface that drastically reduces this intermediate’s chemical potential. The only materials considered feasible are Pt, Pd, Ag and the (100) face of Au. Other materials have tended to follow the series path which takes two steps and generates hydrogen peroxide as intermediate.

\[
O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad E_O = 0.67 \text{ V-SHE} \quad (11)
\]

Continuation of this reaction (the series path) ends with the generation of water

\[
H_2O_2 + 2e^- + 2H^+ \rightarrow 2H_2O \quad E_O = 1.77 \text{ V-SHE} \quad (12)
\]

Fuel cells desire maximum efficiency and can irreversibly degrade in the presence of too much hydrogen peroxide. In a fuel cell cathode the parallel path 4-electron reduction is the preferred reaction.

The most thoroughly studied oxygen reducing catalyst is platinum. The oxygen reduction reaction is very sensitive to the Pt surface structure. Very different oxygen reduction voltagrams have been recorded for the different single crystal surfaces of Pt and for polycrystalline Pt. At the potentials above the oxygen reduction reaction many oxide and hydroxide forms are stable on the Pt surface and these too can affect the
The reduction of oxygen on platinum occurs predominantly via the 4-electron path and is susceptible to influence from many possible surface species. The reverse reaction (oxygen evolution from water) occurs at a high potential where the platinum surface is dominated by an oxide species. This oxygen evolution behavior of this Pt oxide structure is not comparable to the oxygen reduction behavior of a more metallic Pt surface. There is little benefit studying the reverse reaction as it sheds little insight on the oxygen reduction reaction [64].

Work done rotating ring disk electrodes (RRDE) to determine the relation between the parallel and series pathways has had some success. This was not initially the case, as early work used simplified models and some broad assumptions that grossly altered the conclusions. In contrast, more complicated models could not determine enough experimental data to determine all of the rate constants of their more convoluted processes. Wroblowa [65, 66] was the first to establish a reaction scheme that did not over simplify the reaction but could still expand the results gained from RRDE experimental work. It was found for polycrystalline Pt in phosphoric acid that the rate of reaction of the parallel path ($k_P$) was double that of the series path ($k_S$). On gold electrodes $k_p$ could be easily determined as close to zero but in a 0.55 M H$_2$SO$_4$ the reaction rates varied with potential and could not be as simply calculated. An even more complex model accounted for the non-linear behavior in sulphuric acid and found that initially at high potentials $k_P \gg k_S$. As the potential dropped $k_S$ and $k_P$ both
increased until 0.6 V-SHE at which point $k_P$ remained constant but $k_S$ continued to increase.

There also exists a theory that the parallel path and the series path use different sites. The principal evidence for the “separate paths, separate sites” theory has come from experiments that use under potential deposition (UPD) metals [67-71]. These experiments usually take a single crystal of Pt, deposit a fraction of a monolayer of a second material on the surface and then test the oxygen reduction properties. The majority of these surfaces have a reduced oxygen reduction activity; interestingly it is the parallel path that is strongly affected while the rate of reaction of the series path is unchanged. One explanation hypothesizes that the parallel path requires two sites for adsorption while the series path requires only one. This makes the parallel path second order in available sites and more sensitive to surface perturbations.

Gas phase adsorption studies of oxygen on Pt at cryogenic temperatures have broadened the understanding of how oxygen dissociates [62]. Below 90 K oxygen will be truly physisorbed, lying parallel to the surface. At higher temperatures other bonding is seen; weakly bound $O_2^-$ with one electron in its $\pi$ antibonding orbital and $O_2^{2-}$ with two electrons from the platinum surface. Even higher temperatures will see the oxygen dissociate to atomic oxygen sitting in the threefold hollow sites. Curiously, atomic oxygen distributes across a Pt surface in a non-uniform pattern, forming clusters and chains across the surface. The core of the adsorption is the interaction between the oxygen’s antibonding orbital and the metal d-band. The metals d-band is influenced by interatomic spacing, and the height of the metal d-band relative to the Fermi level. While gas phase adsorption studies aid in understanding oxygen adsorption, the
electrochemical case is more complicated with adsorbed water and ions also interacting with the process [62].

Modelling can provide more information about the oxygen reduction reaction but it too must simplify the complex reaction to remain feasible. Norskov et al. [72] created a model for the oxygen reduction reaction based on the simplified version of the parallel path.

\[
\frac{1}{2} O_2 + Pt_v \rightarrow Pt - O
\]  
\[Pt - O + H^+ + e^- \rightarrow Pt - OH\]  
\[Pt - OH + H^+ + e^- \rightarrow H_2O + Pt_v\]

Where Pt\(_v\) is a vacant platinum site and Pt-X is the same site but now with X species adsorbed there. With a few assumptions the binding energies for (14) and (15) can be considered in terms of the reaction energies of

\[
Pt_v + H_2O \rightarrow Pt - OH + \frac{1}{2} H_2
\]  
\[Pt_v + H_2O \rightarrow Pt - O + H_2\]

The assumptions are that the electrolyte pH is 0, the gas phase has 1 bar of H\(_2\) at 298 K, the reaction energy of (16) is equal to the reverse of (15) and the reaction energy of (17) is equal to the summed reverse of (14) and (15) combined. Norskov et al. [72] solved these equations with density functional theory to predict the free energy of the different reaction steps at different potentials and different coverage’s of O\(_2\). At a
potential of 0 (ie a short circuited cell) all of the steps are strongly exothermic but at higher potentials the free energies for the reactions are reduced. Above potentials of 0.78 V-SHE reactions (14) and (15) become endothermic and one of the two becomes the rate limiting step. In other words, this simplified reaction is slowed by adsorbed oxygen and hydroxide which are thermodynamic sinks. Norskov et al. [72] calculated that the overpotential at the thermodynamically maximum cell potential of 1.23 V was at least $\Delta G = 0.45$ eV which was close to the experimentally observed overpotential.

Norskov et al. [72] went on to apply the same calculations to other metals and identify an interesting trend. Their calculations recognized Pt and Pd as having the lowest overpotential, in agreement with experimental data, but misidentified Cu, Au and Ag as even better than Pt. The problem was that these materials have an exothermic proton transfer and should therefore have a fast reaction rate, but oxygen bonds poorly to these surfaces so proton transfer is impossible and basic dissociation is very unfavorable. Taking the bonding of the oxygen into account and determining the relative activity of different metal surfaces again shows Pt as the best element. When this relative activity is plotted against the M-O and the M-OH bond strength as shown in figure 1.2.2, a volcano shape becomes apparent.

In figure 1.2.2, although Pt is near the peak it is not at the absolute maximum. Metals with a slightly lower oxygen binding energy should have a higher rate of oxygen reduction. DFT calculations of Pt with a sub-monolayer of Ni, Co, Fe and Cr should be closer to the desired oxygen binding energies. Unfortunately those same calculations imply that the OH bonding will be too high for these alloys, pushing them down the other
Figure 1.2.2, Trends in the oxygen reduction activity plotted as a function of both the O and the OH binding energy, reproduced from [72].

But it is an enticing explanation for the improved oxygen reduction performance seen by alloys with a Pt skin [73, 74].

Norskov et al. [72] then increased the complexity of their model including possible intermediates and alternate reaction paths. They found that the more complex model made little to no difference to the trend of activity shown in figure 1.2.2. Disturbingly this implies their calculated activity is almost independent of the mechanism. But they are not the only group to determine a volcano like relation between the oxygen reduction activity and a structural parameter. There is a long list of features that have
been related to the oxygen reduction reaction, including many other physical parameters; interatomic distance, crystal structure, grain size, concentration and types of defects. There are just as many electronic parameters that have been correlated, including; %d character, d-band vacancies, work function and heats of sublimation. When oxygen reduction activity is plotted against one of these parameters there is usually a maximum with linear correlations to either side, yielding a volcano shape [60, 75-77]. Researchers have then designed a new composition to tweak the parameter in question up to the peak.

Another example of trend mapping was reported by Jalan and Taylor [78] who theorized that the critical parameter for the oxygen reduction reaction was the inter-atomic spacing of Pt. If the Pt-Pt distance was too wide then dissociation would have to occur before adsorption and if the Pt atoms were too close then repulsive forces would retard dual site adsorption. They conceded other factors such as altered surface structures, surface free energy, oxidation potential, and interactions between O₂ and the alloying element may also affect the Pt upon alloying. That said, they did observe an excellent straight line correlation between interatomic spacing and activity that they hypothesized would peak with a Pt-Ni, Pt-Co or Pt-Ni-Co alloy. The interatomic trend reported by Jalan and Taylor [78] was disputed by Stonehart [79], who stated that the trend was too neat and clean to be believable and even if true, would not translate to carbon supported nanocrystals.

Since Stoneharts dismissal of the trend two subsequent investigations have repeated the work of Jalan and Taylor and confirmed the benefit of manipulating the interatomic distance of Pt. Alloys of Pt with Cr, Mn, Fe, Co and Ni were studied [75] with promising results leading to a further investigation of Pt with Cr, Co and Ni [80].
The alloys that performed 4-fold better than a commercial pure Pt catalyst were studied with XANES resulting in a determination of an altered Pt-Pt bond distance and higher d-orbital vacancies [80]. Min et al [81] fabricated Pt$_{75}$X$_{25}$ (X=Cr, Co, Ni) nanoparticles and tested their oxygen reduction activities under PAFC conditions (190 °C, near pure H$_3$PO$_4$). They found improved performance from the alloys that was also attributed to shorter Pt-Pt bond distances. The trend was debunked by Xu et al. [82], they used DFT calculations to compared a Pt$_3$Co alloy to a pure Pt sample that had been physically compressed to match the alloys interatomic spacing. They did not observe the same performance and concluded that the benefit gained from alloying Co into Pt was not from the altered interatomic spacing.

Stamenkovic et al [74] examined Pt$_{75}$X$_{25}$ alloys (X = Ti, V, Fe, Co and Ni) by RRDE in HClO$_4$ and found that they all outperformed Pt. Pt$_{75}$Co$_{25}$ in particular had an oxygen reduction onset potential 50 mV higher and twice the current density at 0.9 V-RHE of a Pt standard. When the activity was plotted against either the oxygen binding energy or the relative d-band, then a volcano relationship could be seen. The peak activity of the volcano when predicted by a model and DFT calculations would be Pt$_{75}$Ni$_{25}$ which was slightly at odds with the experimentally determined optimum, Pt$_{75}$Co$_{25}$. They concluded that the best catalyst would have slightly weaker oxygen binding than Pt, probably an alloy with a Pt skin.

The normal way of improving performance has been to alloy a second element into Pt. A thorough review of the reported combinations of elements and their performance follows in section 1.6. Fundamentally, the second (third and fourth) element will alter Pt’s interatomic spacing and increase the Pt 5-d orbital vacancies or
possibly take a direct role through interactions with oxygen or as a redox mediator.
Initial studies of many of these alloys was for use in a phosphoric acid fuel cells (200 °C and 100 % H₃PO₄) where preferential leaching and surface roughening was not always accounted for. Controversy has also risen between different groups regarding the state of the alloying element. Under normal cathode conditions the non-platinum element would be most stable as an oxide or hydroxide, electrically insulating and nearly useless. Although the exact mechanism of how the alloying element enhances Pt has not been definitively proven it is accepted that further fine tuning is still possible.

1.3 Modelling

1.3.1 Methanol Oxidation Models

There are many possible catalysts so it would be beneficial to filter obvious duds from the initial search. This refining can be done by finding a relevant pattern of behavior across the periodic table and then testing the elements that peak within the trend. Gurau et al. [83] attempted to explain the catalyst mechanism by examining relevant bond strengths between gas phase diatomic molecules. There does appear to be some correlation between a catalyst’s methanol oxidation activity and that same catalysts bond strength to either carbon or oxygen. Gurau et al. [83] used these trends with bond strength to determine the likely catalyst sites fuel components would bond too. They examined trends across group 5 and 6 noble metals predicting and experimentally confirming that a Pt-Ru-Os-Ir alloy would be superior to Pt-Ru. Smotkin and Morales [84] reported that Ley et al. [85] extended the examination of metal to carbon (M-C) and metal to oxygen bonding (M-O) to recommend V, Mo, Ru, Os, Ge and Sn as candidates
for alloying. This simple theory could be applied further and predict likely elements outside the noble metals that fall into the same pattern. In this way Cr, Mn, Fe, Ni, Cu, As, Se, Rh, Sb, Te, Nd, Sm, Ho, Ir and Au have been determined as a good starting field of elements.

Data regarding a relevant surface property does not always exist for every element or alloy of interest. This can be solved by using DFT calculations to estimate the properties of a non-existent alloy’s surface. Anderson et al [39] modeled 18 molecule Pt clusters modified with one of 42 other elements shown in figure 1.3.1. They examined the variation of a possibly relevant property across the periodic table. Unfortunately alloys that have been experimentally recognized as good catalysts (e.g. Pt-Ru) did not have a single characteristic that singled them out of the doss. Their study did conclude that the early first and second transition metals should dissociate water as well as if not better than Ru and further study of alloys with these elements was warranted.

![Periodic Table](image)

Figure 1.3.1, The highlighted elements were alloyed with Pt in a model that estimated their surface properties [39].
Following select properties of elements across the periodic table can be taken a step further by modeling the actual reaction. This would be the best way to avoid lengthy experiments and determine possible catalysts. The latest work by Greeley and Mavrikakis [86] highlights the benefits and shortcomings of the modeling method. They considered near surface alloys composed of a close packed monolayer of solute atoms (Cu, Pt, Pd, Ni, Mo, Cu, Re, Fe, Au, W, Ta, Rh, Ir or V) either laying on top of a bulk lattice of solvent atoms (Pt, Pd, Ir, Rh, Ru) or segregating 1 layer below. They performed calculations on this huge field of elements determining optimum fuel cell compositions with weak H\textsubscript{2} binding energy and low dissociation energy. From their calculations they were able to determine trends across compositions that could lead to an optimum catalyst.

However, Greeley and Mavrikakis [86] failed to delve into any of the complications that exist in real systems. Firstly, they restrain their model to a horizontally homogenous, atomically smooth surface. To physically reproduce such surfaces would require costly molecular beam epitaxy or blind luck with bulk fabrication. Even if a true surface could be generated that matched the model surface its performance would not be optimal. Molecularly smooth surfaces have helped explain the function of catalysts but it has long been recognized that irregular sites like kinks and steps are usually the active areas of most catalysts [87]. The interaction of Pt and Ru has been shown to be optimum in a nanoscale heterogeneous structure [37]. Modeling is helpful in showing possible paths to experimental success, but is still currently limited to the analysis of unobtainable surfaces in implausible environments.
Other models fail similarly due to the necessity to simplify the problem to remain computable. Shubina and Kruper investigated Pt alloys of Ru, Mo and Sn by discussing the bonding energies of the common fuel cell reactants with atomically smooth surfaces [88]. They concluded that PtRu was better than Pt due to altered adsorption energies. Cristofferson et al. investigated the competition between CO and H for active sites of Pt alloyed with transition metals [59]. Though thorough, their work was limited to reactions not involving H₂O. Though easy to pick at the shortcomings of models, they do give valuable insights into possible compounds that may work.

Comparison between experimental work and theoretical predictions does correlate, with the model usually explaining the mysterious benefit from the alloyed component. For example, the work of Norskov tends not to use models not to predict possible new materials but to confirm that DFT calculations can replicate experimentally established systems [89]. Model’s backing up the experimental observations of the same group occurs frequently, but not always. Strasser et al. [90] simultaneously performed experiments and theoretical screening on many binary and ternary Pt alloys. Unfortunately the theoretical screening predicted Pt₃₃Ru₃₃Fe₃₃ alloy would be the optimum but their experiments found Pt₂₀Ru₂₀Co₆₀ to be the best. Though the theoretical screening matched some experimentally observed trends it probably deviated because it was unable to account for corrosion of unstable compositions. Gu and Balbuena [91] performed DFT calculations and found that alloys of most transition metals with Pt would have a lower corrosion resistance than pure Pt.

Greeley and Mavrikakis [86] do fall short of recreating the real system but their work does show that Pd alloys may possibly replace Pt alloys for methanol oxidation [51,
This follows the vision Wasmus had to find a new catalyst [93]; start with theoretical modeling that eliminated absurd possibilities and then follow that up with a modern combinatorial screening method.

1.3.2 Oxygen Reduction Models

Models of oxygen reduction catalysts provide insights but should be considered with caution as they also fall short in the same areas discussed in the previous section. Kitchin et al [94] performed DFT calculations on a Pt (111) surfaces modified by a sublayer of V, Cr, Mn, Fe, Co or Ni. Based entirely around a shift in the Pt d-band they calculated that Pt-Cr should have the lowest oxygen dissociation energy. The failure to reproduce this experimentally led to Norskov et al [72] making more complex model that could account for strain effects. When examining the catalytic activity of different materials vs the binding energy of oxide or hydroxide groups they found a volcano like relationship that has been experimentally verified (see figure 1.2.2 and surrounding discussion). The volcano relationship seen when comparing activity against binding strength has been expanded by Greeley et al [95]. If an intermediate binds too weakly then the surface will not activate it, but if it binds too strongly then it will irreversibly occupy catalyst sites and poison the reaction. Thus, when binding energy is plotted against an indicator of catalytic activity, the resultant curve would be volcano shaped with the optimum binding energy at the peak. Taking this a step further, defects and steps would not be expected to improve a Pt cathodes activity because oxygen has a stronger bond on those sites than on a flat surface [72]. For example on Pt (1 1 0) oxygen is bound 0.5 eV stronger than on Pt (1 1 1) displacing it away from the optimum.
The thorough oxygen reduction modeling work of Norskov was discussed in section 1.2.2. Norskov et al. [96] later stirred up controversy when they assessed the activity of the hydrogen evolution reaction a wide range of metallic surfaces with DFT. The model they used in their calculations was simpler than much earlier works [97]. Further work with the simplified model [98, 99] dismayed Schmickler and Trasatti [100] who published their contempt for the simple model and required Norskov et al. [101] to defend the shortcomings of the simplified model.

Other groups have come up with simple models to help predict an alloy’s properties. Greeley and Norskov [102] developed a model that estimated oxygen binding energies to an unknown alloys surface. They verified the models predictions against more thorough density functional theory calculations but did not go further and report what the optimum catalytic composition would be.

1.4 Combinatorial Studies
1.4.1 Combinatorial Methodology

A suitable experimental method to deal with the vast number of potential catalysts that modeling suggests as promising is the combinatorial technique [84]. A combinatorial study consists of a few defined steps [103]. Firstly, there is the generation phase where elements of interest are methodically combined in various combinations, permutations and concentrations [104]. An improved fuel cell catalyst has already been determined using the combinatorial process [83]. With the discovery of Pt$_{44}$Ru$_{41}$Os$_{10}$Ir$_5$ it was noted that all of the binary compounds of similar composition were completely ineffective in the reaction. Thus, classic methods of mapping a trend
of positive activity to an optimum composition would have failed to examine this compositional area. The final composition was only found through a thorough investigation of all possible combinations.

Janssen and Moolhuysen [105] performed what could arguably be the first combinatorial investigation into methanol oxidation catalysts. They made a rapid assessment of Pt catalysts whose top monolayer had been modified by another element via the immersion method. They performed fairly standard electrochemical tests on these modified catalysts and noted some interesting results summarized in table 1.4.1. As expected, Pt-Ru and Pt-Sn were the best. Little known Pt-Os and Pt-Re systems also did well, but the surprise was that Pt-Ti also showed a strong promotion of methanol oxidation. Further testing of “Raney” Pt-Ti catalysts showed they were unstable in the acidic environment (4M H₂SO₄).

Depending upon the complexity of the system, a combinatorial process can generate an enormous number of samples. Reddington et al. used an inkjet to deposit 220 compositional elements that defined various quaternary systems and went on to define the Pt/Ru/Os/Ir/Rh system with 645 different compositions [106]. Barkhouse et al. created a continuous Ni/Pt system that varied composition and layer thickness. This was sampled at 100 different positions by x-ray diffraction and electron microprobe [107]. Choi, Kim and Woo used an inkjet to deposit 275 different compositions that covered the quaternary phase space of Pt/Ru/Mo/W [108]. Other investigations into photoluminescent and superconducting materials [109-111] have generated even more complicated libraries with thousands of samples [112]. These large samples required clever ways to sort and isolate valuable library members.
TABLE 1.4.1
METHANOL OXIDATION PERFORMANCE OF SYSTEMS EXAMINED BY JANSSEN AND MOOHLUYSSEN [105].

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Methanol Oxidation</th>
<th>No.</th>
<th>System</th>
<th>Methanol Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pt-Ag</td>
<td>Decrease</td>
<td>14</td>
<td>Pt-Zr</td>
<td>Unchanged</td>
</tr>
<tr>
<td>2</td>
<td>Pt-Au</td>
<td>Decrease</td>
<td>15</td>
<td>Pt-V</td>
<td>Increase, 2 x</td>
</tr>
<tr>
<td>3</td>
<td>Pt-Hg</td>
<td>Increase, 7 x</td>
<td>16</td>
<td>Pt-Nb</td>
<td>Increase, 2-3 x</td>
</tr>
<tr>
<td>4</td>
<td>Pt-Ge</td>
<td>Increase, 4 x</td>
<td>17</td>
<td>Pt-Mo</td>
<td>Increase, 2-3 x</td>
</tr>
<tr>
<td>5</td>
<td>Pt-Sn</td>
<td>Increase, 50-100 x</td>
<td>18</td>
<td>Pt-W</td>
<td>Unchanged</td>
</tr>
<tr>
<td>6</td>
<td>Pt-Pb</td>
<td>Decrease</td>
<td>19</td>
<td>Pt-Re</td>
<td>Increase, 30-40 x</td>
</tr>
<tr>
<td>7</td>
<td>Pt-As</td>
<td>Increase, 3 x</td>
<td>20</td>
<td>Pt-Ru</td>
<td>Increase, 25 x</td>
</tr>
<tr>
<td>8</td>
<td>Pt-Sb</td>
<td>Increase, 2 x</td>
<td>21</td>
<td>Pt-Rh</td>
<td>Insignificant</td>
</tr>
<tr>
<td>9</td>
<td>Pt-Bi</td>
<td>Decrease</td>
<td>22</td>
<td>Pt-Pd</td>
<td>Decrease</td>
</tr>
<tr>
<td>10</td>
<td>Pt-S</td>
<td>Decrease*</td>
<td>23</td>
<td>Pt-Os</td>
<td>Increase, 25 x</td>
</tr>
<tr>
<td>11</td>
<td>Pt-Se</td>
<td>Decrease*</td>
<td>24</td>
<td>Pt-Ir</td>
<td>Insignificant</td>
</tr>
<tr>
<td>12</td>
<td>Pt-Te</td>
<td>Decrease*</td>
<td>25</td>
<td>Pt-Dy</td>
<td>Decrease*</td>
</tr>
<tr>
<td>13</td>
<td>Pt-Ti</td>
<td>Increase 5-25x</td>
<td>26</td>
<td>Pt-U</td>
<td>Increase, 5 x</td>
</tr>
</tbody>
</table>

Those marked with * mainly showed decreased performance except for a 2-3 × increase at very specific optimal compositions.

1.4.2 Combinatorial Screening

The method chosen to determine whether a new catalyst composition is “better” is a complex issue [113]. There are many variables that affect the performance of a fuel cell catalyst including composition [84], fabrication method [114, 115], particle size distribution [36, 116], loading [117, 118], support material [113], degradation [119], etc. Comparing catalysts requires a method that carefully considers the many combinations and permutations of variables [113]. Smotkin et al. [120] recently set out 4 criteria that a combinatorial investigation should strive for. They were 1. Inclusion of a relevant control: this would be a commercially available industry standard (e.g. Pt$_{50}$Ru$_{50}$ for methanol oxidation). 2. Catalyst fabrication by a scalable method: there is little point testing a catalyst that can’t be reproduced or mass produced if successful. 3. Separation of catalyst screening and fabrication, and 4. Realistic fuel cell conditions: obviously the
test should closely match the desired application. Unfortunately 90% of combinatorial fuel cell investigations, including this study, fail at least three criteria. Coincidently the only group that passes the criteria is the same group that set them (Smotkin et al. [120]). These criteria are excellent for keeping an investigation focused and returning meaningful data, but they apply to investigations that have already identified promising candidates and are performing a final confirmation. Initial screening work, like this study, that sifts through thousands of possibilities must fail some criteria to remain feasible.

Investigations that have used the combinatorial technique to screen thousands of possible catalysts have had some success. Combinatorial libraries have been fabricated via a variety of methods, including physical vapor deposition techniques such as sputtering [90, 121-126], or less commonly by techniques such as electro-deposition [127, 128], sol-gel [103], or gel transfer [129, 130]. Screening of samples has been performed by a variety of techniques including fluorescence imaging [108, 129, 131-134], scanning electrochemical microscope [135-139], rotating disk electrode [140, 141], multi-array half cell [90, 116, 122] and multi-array fuel cell [113, 142-144]. It should be noted that many of these fabrication techniques generate libraries of samples that do not have the same form as an actual fuel cell catalyst. High surface nanoparticles embedded on a conductive support (carbon) are generally avoided to facilitate efficient screening of the libraries. But it has long been cautioned [79] that bulk properties cannot be presumed for nanoparticles of the same composition.
1.4.2.1 Screening by Fluorescence

The work of Reddington et al. [106] has been the most famous and most cited combinatorial fuel cell catalyst investigation [145]. They were the first to successfully apply the fluorescence method to a combinatorial array of fuel cell catalysts. The method works by soaking the catalyst array with methanol and a fluorescent indicator (usually quinine) that becomes luminescent at low pH. Then the potential of the array is biased upwards and until a catalyst starts to oxidize methanol. Catalysts that oxidize methanol will generate protons that effectively lower the local pH and causes the site to glow. Reddington et al. [106] screened the quarternary Pt-Ru-Os-Ir system and determined that Pt$_{44}$Ru$_{41}$Os$_{10}$Ir$_{15}$ was the optimum composition. This was successfully confirmed in a single cell test [106].

The work of Reddington et al. was expanded by Chen et al. [132] with a huge fluorescence library (715 different samples) comprised of combinations of Pt, Ru, Os, Ir and Rh. Chen et al. were perhaps too ambitious with there being no way to concisely and unambiguously map the activity across a five element system. In the long run it didn’t really matter as they found the optimum composition from the system, Pt$_{50}$Ru$_{44}$Ir$_{6}$ did not contain Os or Rh. Unfortunately when they refabricated the best sample as a bulk alloy its ORR performance was not significantly different from pure Pt. Choi et al. [108] also performed fluorescence testing on a combinatorial array of compositions from the Pt-Ru-W-Mo system. The strongest response was from Pt$_{77}$Ru$_{17}$Mo$_{4}$W$_{2}$ which also outperformed Pt$_{50}$Ru$_{50}$ and Pt$_{82}$Ru$_{18}$ in longer term polarization tests. The work of Chen et al. and Choi et al. implied that Pt-Ru binary compositions could be further optimized by the addition of a small concentration of another element.
Gruber et al. [134] also did fluorescence testing but with Pt-Sn binary phase field using metal salts on toray paper. Pure Pt up to Pt\textsubscript{70}Sn\textsubscript{30} showed strong activity and the optimum was Pt\textsubscript{90}Sn\textsubscript{10}. Surprisingly there was very little sign of the pure Pt being poisoned in the 4 M Methanol environment. Chu et. al. [146] while examining fuel cell catalysts created 55 combinations of platinum-ruthenium-Nafion elements. Chu et al. determined that the most active composition was (Pt\textsubscript{50}Ru\textsubscript{50}):(Nafion) = (63.6):(36.4) Wt\%. Chu et al. [133] also used the fluorescence method to determine if Au/TiO2 additions improved the efficiency of a Pt-Ru catalyst. Sullivan et. al. [147] examined organo-sulfur monolayers of different chain lengths in an identical manner to Chu et al. They found the fluorescence method was limited in that it was influenced by background fluorescence and couldn’t accurately distinguish slight differences in activity. They applied a more accurate electrochemical technique to areas of the library that showed fluorescent potential. The technique was equivalent to that of a rudimentary electrochemical microscope and discerned subtle differences in the monolayers that were unnoticed from fluorescence.

Liu et al. [131] used the fluorescence method to combinatorially screen a wide range of alloys for ORR activity. They found that Pt\textsubscript{67}Bi\textsubscript{33}, Pt\textsubscript{89}Cu\textsubscript{11}, Pt\textsubscript{78}Se\textsubscript{22} were superior to pure Pt in clean oxygen saturated electrolyte. They also tested non-Pt catalysts and found that Ru\textsubscript{56}Fe\textsubscript{44} and Ru\textsubscript{67}Co\textsubscript{33} had a better ORR activity than pure Pt. Ru-Cu, Ru-Ni and other compositions of Ru-Fe and Ru-Co failed to outperform Pt. The catalysts they identified as being active were also good oxygen reduction catalysts in the presence of methanol. Jayerman and Hillier used a gel transfer technique to fabricate a continuous combinatorial library of Pt-Ru-Rh [129] and Pt-Ru-Mo [130] compositions.
They then screened these libraries by the fluorescence method for various oxidation reactions. They found that the optimum composition was Pt$_{40}$Ru$_{30}$Rh$_{30}$ for methanol oxidation. They extended this study by using SECM to examine the hydrogen oxidation reaction on these libraries in the presence of CO [130].

1.4.2.2 Screening by Scanning Electrochemical Microscope (SECM)

Jayaraman and Hillier used scanning electrochemical microscope to probe a combinatorial libraries with different compositions [130, 148] or different loadings of Pt [149]. The experimentation was not aimed at discerning new catalysts, but was to assess the suitability of the SECM as a fuel cell catalyst screening tool. The scanning electrochemical microscope was set at a bias so that a diffusion limited proton reducing redox reaction was occurring at its tip. When the tip was brought near an insulating surface the diffusion of protons were hindered and the tip current reduced. In contrast, when the tip scanned above an active catalyst that was producing protons, the current increased at a rate proportional to the catalyst-influenced rate constant for hydrogen oxidation. The performances of eight catalysts were characterized by SECM and then they were tested in actual fuel cells. They found that activity information gained from the scanning electrochemical microscope had an accurate correlation to the same catalyst’s fuel cell performance [148].

Prochaska and Jin et. al. [136] combined the fluorescence imaging and SECM methods to examine a continuous Pt-Pb-Bi library formed by co-sputtering. With fluorescence they quickly determined small compositional pockets that were active in the methanol oxidation reaction. The SECM was then focused solely in these pockets greatly reducing the time required to characterize the library. Unfortunately the active
Pt$_{50}$Pb$_{15}$Bi$_{35}$ identified by fluorescence was not examined with the SECM, possibly due to a composition-space correlation issue.

Our group has also investigated fuel cell catalysts with a scanning electrochemical microscope. Early investigations examined the hydrogen oxidation performance of discrete Pt-Ru libraries but were fraught with difficulties [139, 150]. Later studies used the deposition phenomena of overspray to fabricate micro scaled continuous gradient libraries that were perfect for SECM analysis. The hydrogen oxidation performance of Pt-Ru-W [137, 151] and Pt-Ru-Co [137] libraries were determined to an extremely fine compositional detail. An unusual SECM method [138] has also made it possible to examine the oxygen reduction performance of our continuous combinatorial libraries [152]. Fernandez et al. [52, 53] who developed the ORR SECM technique examined activity of a combinatorial array of non platinum catalysts.

1.4.2.3 Screening by Multiple Rotating Disk

He et al. [153, 154] perform Rotating Disk Electrode (RDE) studies that can be considered combinatorial in nature. They didn’t fabricate libraries but simultaneously generate individual samples by physical vapor deposition. Each sample was then tested in one of sixteen rotating disk electrode apparatus that ran simultaneously. From this work they identified some promising catalyst combinations. After the initial RDE screening they went on to carefully fabricate powder versions of the optimum compositions. They found that the best oxygen reduction composition with reasonable stability and high activity was Pt$_{75}$Co$_{25}$. The next best performance came from Pt$_{50}$Ni$_{50}$ Pt$_{75}$Zn$_{25}$ Pt$_{50}$Cu$_{50}$. Finally Pt$_{35}$W$_{65}$, Pt$_{75}$Ti$_{25}$, Pt$_{15}$Se$_{85}$ did not perform better than pure Pt but their excellent corrosion resistance may make them suitable for stabilizing other
active and unstable compositions [155]. He et al. further addressed the issue of correlating thin film screening against nanoparticles fuel cell catalyst testing. They carefully fabricated several Pt-Ti and Pt-W nanoparticles and observed the same activity trends previously achieved with thin films [141].

He et al. [156] continued their study of Pt binary alloys and reported many more interesting observations. They found that Pt_{78}Co_{22} was the optimum oxygen reducing Pt-Co alloy because it was stable, had the highest mass fraction specific activity and a half wave potential 110 mV higher than Pt. The next best alloys were from the Pt-Ni, Pt-Cu and Pt-V systems, but they never specified the exact compositions. It is worth noting that their results implied there were no active stable compositions from the following systems; Pd-Co, Pt-Cr, Pt-Nb, Pt-Pd, Pt-Sn, Pt-Ta or Pt-Zr. From this work on Pt alloys they divided the base metals into two groups: The first was corrosive and active metals such as Fe, Co, V, Mn, Cu, Mo and Ni; and the second was stable but less active metals like Cr, Ta, Nb, W and Ti. By combining Pt with elements from the two groups they claimed to have achieved alloys that were active and stable, but never specified the compositions. All of this work establishing the merit of their combinatorial has led to the discovery of a Pt-V-Fe catalyst that has never been considered before [140].

1.4.2.4 Screening by Multiarray Testing

Multiarray cells are similar to half cells except they have multiple working electrodes. There are two basic categories of multiarray: the serial automated multiarray and the parallel multiarray. Each working electrode in a serial automated multiarray is addressed sequentially by the potentiostat while the others remaining electrodes are idle.
This is ideal if the system is coupled with another analysis technique like DEMS [25, 157]. The working electrodes of a parallel multiarray are all biased simultaneously through the same experiment by the potentiostat [135, 151, 158]. This method has the advantage of being more efficient, but caution must be taken such that neighboring electrodes do not interfere with each other. Multiarrays are an ideal tool for use in a combinatorial investigation.

Sullivan et al. [147] performed experiments with a combinatorial multiarray that addressed each electrode sequentially. Though their work did not focus upon fuel cell catalysis it was recognized that the technique could be readily extended to do so.

Strasser et al. [90] did focus on fuel cell catalysts, using a multielectrode microarray consisting of 64 titanium pads (each 1.7 mm in diameter) formed lithographically on a 3” quartz wafer. The catalyst members were deposited in wedges by moving shutters and achieved in situ atomic mixing. They simultaneously investigated ternary compositions of Pt-Ru-M (M=Co, Ni, W) in methanol solutions. They combined their work with density functional theory to build a model to explain the positive and negative performances they encountered. They physically found that Pt_{20}Co_{60}Ru_{20} was much more electrochemically active than Pt_{50}Ru_{50}. Their modeling went on to recommend an alloy of Pt, Co, Ru and Fe as possibly being even better [90]. Strasser et al. [159] have also used their multiarray system to examine oxygen reduction. They found a Pt-Co-Cr composition with very favorable activity and continued to perform well when fabricated as a high surface area powder and tested with a rotating disk electrode.
Guerin et al. [116] fabricated a multiarray with 64 working electrodes and used it to investigate particle size effects on the ORR. These first libraries were labor intensive and since then they have changed their library fabrication method to co-sputtering [160]. The advantage with co-sputtering was that it was easier to ensure that the bulk and the surface of their alloys were homogenous as no annealing was required. The benefit of skipping an annealing step was praised by Whiteacre et al. [122] who also co-sputtered onto a combinatorial array. In their discussion of deposition techniques they are quite critical of inter-layer depositions that are annealed, but skip over the whether a co-sputtered surface could be reproduced by another technique.

1.6 Catalyst Compositions

1.6.1 Platinum – Ruthenium

Pt-Ru compositions have been the most intensely studied catalysts with regard to methanol oxidation for fuel cells. The best Pt-Ru composition for methanol oxidation reported in the literature varies depending on several factors. Tests on carbon supported high surface area catalyst nanoparticles tend to show Pt$_{50}$Ru$_{50}$ as the best composition [161, 162]. This conflicts with electrochemical surface studies of relatively flat metallic surfaces that tend to report a Pt rich optimum composition between Pt$_{00}$Ru$_{10}$ - Pt$_{80}$Ru$_{20}$ [23, 122, 163, 164]. However, even this “flat surface optimum” has been seen to shift to higher Ru concentrations (~Pt$_{70}$Ru$_{30}$) at higher temperatures [58, 157]. Why the results from nanoparticles differ from flat surfaces has remained an open question.

There exists a variety of theories that explain the discrepancy between surface studies and nanoparticles, ranging from surface segregation during nanoparticle
fabrication [165] to empirically derived reaction mechanisms [166], but nothing definitive has been established. Another explanation for the discrepancy between the optimum Pt-Ru composition for nanoparticles and flat alloy surfaces is based on the oxidation of state of the ruthenium [166]. Metallic Ruthenium is not stable in a fuel cell environment and would quickly oxidize to a RuO$_x$H$_y$ form capable of conducting electrons and protons. A Pt-Ru nanoparticle catalyst with metallic ruthenium was reported as having orders of magnitude less activity than a mixed phase oxide. The ruthenium oxide theory is contradicted by Babu et al. [167], who annealed commercially available Pt-Ru nanoparticle catalysts in different atmospheres and were surprised to find that 24 hours at 220 °C in a hydrogen atmosphere improved the Pt-Ru catalyst activity 3 fold. A simultaneous NMR study revealed that the ruthenium in the extra-active catalyst had been reduced to a metallic form and this was believed to be responsible for the improved performance. This also contradicts the very early work of McNicol and Short [168] who found decreased activity from Pt-Ru catalysts annealed in hydrogen at 300 °C for 24 hours. They did not report the state of the ruthenium but did mention that the catalysts had an enriched Pt skin.

Gasteiger et al. [163, 169] believed that the electrochemical cleaning of nanoparticles stripped Ru and electrochemically annealed the surface. This could potentially leave a Pt$_{50}$Ru$_{50}$ nanoparticle with a surface composition enriched up to Pt$_{85}$Ru$_{15}$. They raise the point that methanol is a large molecule which during oxidation strips its H groups to neighboring Pt sites, but still requires at least one Ru neighbor for the bifunctional mechanism. This makes the optimum methanol adsorption site three Pt atoms neighbored by one Ru atom and another 8 Pt atoms as shown in figure 1.6.1 (a).
Comparison of the (111) of a Pt$_{90}$Ru$_{10}$ and Pt$_{50}$Ru$_{50}$ surfaces, figure 1.6.1 (b), both being near ideal solid solution with no ordering or clustering [169], then obviously Pt$_{90}$Ru$_{10}$ has many more optimum adsorption sites. Gasteiger et al. [163] went on to calculate the probability of the optimum adsorption site occurring at different concentrations as shown in figure 1.6.1 (c). From the distributions they determined the composition that would have the most sites suitable for methanol adsorption would be ~Pt$_{90}$Ru$_{10}$, in agreement with their experiments [163].

![Figure 1.6.1](image)

Figure 1.6.1, (a) Three Pt atoms neighbored by one Ru atom and another eight Pt atoms is the optimum methanol adsorption site. (b) Schematic comparison of a Pt$_{90}$Ru$_{10}$ (111) surface with a Pt$_{50}$Ru$_{50}$ (111) surface. (c) probability distribution of the optimum adsorption site occurring on different low index geometries as a function of Ru mole fraction. After [163].

Not all groups report contrary results: in long term, steady state polarization tests Choi et al. [108] saw identical performances from Pt$_{50}$Ru$_{50}$ and Pt$_{82}$Ru$_{18}$. Green and Kucernak [170] used electrodeposition to synthesize samples and found the optimum composition was Pt$_{60}$Ru$_{40}$ ± 10 At%. Iwasita [171] used several techniques to modify the Ru surface concentration of Pt crystal and determined a broad range of compositions about Pt$_{75}$Ru$_{25}$ ± 15%Ru were active catalysts. Essentially the only fact that 99% of
researchers agree upon is that Pt-Ru alloys with more Ru than Pt$_{50}$Ru$_{50}$ will perform poorly. For the record, Sasaki et al. [172] is the one group that dissents; they fabricated a Pt-Ru catalyst with the lowest reported Pt content by depositing 1/8 of a monolayer of Pt onto Ru Nanoparticles. This catalyst had an overall composition of approximately Pt$_{10}$Ru$_{90}$ and was reported as being very active and stable during long term testing. Of course, if the bulk was ignored and just the surface composition was considered that could be considered as high as Pt$_{40}$Ru$_{60}$.

Saffarian et al. [56] performed a methanol oxidation surface study comparing three arc melted alloys and surprisingly found the Pt rich composition was not the best. Based on the tafel slopes, the catalyst ranking was Pt$_{44}$Ru$_{56}$ > Pt$_{68}$Ru$_{32}$ > Pt. Hoster et al. [173] saw similar short term responses from smooth Pt$_{75}$Ru$_{35}$ and Pt$_{85}$Ru$_{15}$ electrodes but after 30 minutes the performance of Pt$_{85}$Ru$_{15}$ diminished more so than Pt$_{75}$Ru$_{25}$. Both Pt$_{75}$Ru$_{25}$ and Pt$_{85}$Ru$_{15}$ outperformed Pt$_{50}$Ru$_{50}$ in the short (< 5 minutes) and long term (> 30 minutes). Beden et al. [174] examined several binary Pt electrodes and reported that the Ru on the surface of the Pt-Ru electrode was unstable, oxidizing and dissolving during cyclic voltammetry in 0.5 M H$_2$SO$_4$. This would be in agreement with studies that see the dissolution of Ru from fuel cell anodes [175].

Page et al. [176] reported that a commercially available carbon membrane electrode with 0.5 mgcm$^{-2}$ pure Pt catalyst had an onset potential of 385 mV-SCE for the methanol oxidation reaction at 25 °C in 0.5 M H$_2$SO$_4$ electrolyte. This improved, decreasing to 320 mV-SCE, when tested at 75 °C. Page et al. [176] also tested other carbon membrane electrodes (CME) with different catalyst compositions. The CME with 0.5 mgcm$^{-2}$ Pt$_{50}$Ru$_{50}$ catalyst had an onset potential of 300 mV-SCE for the
methanol oxidation reaction at 25 °C. This was 85 mV lower than the pure Pt CME they tested under the same conditions. Upon testing at higher temperatures the potential was reduced further, reaching 250 mV-SCE at 75 °C. Hughes and Miles [55] found that methanolic residues where more easily oxidized at 90 °C than at 22 °C. They also found that the Pt70Ru30 could achieve similar current densities to pure Pt catalysts at potentials 60 mV lower. Vidakovic et al. [177] also examined commercially available Pt-Ru catalysts of the same composition and concluded that the most important factor was the surface distribution of Pt and Ru atoms.

Desai and Neurock [178] performed DFT calculations to determine how alloying Ru into Pt changes the oxidation of CO. They found the reaction was energetically unfavorable on a pure Pt (111) surface with the required water desorbing before it would react. They calculated that the addition of Ru to the alloy lowered the reactions activation barrier by 80% and may even have changed the rate limiting step.

Lee et al. [179] used cyclic voltammetry to investigate methanol oxidation on microporous Pt/C and Pt40Ru60/C electrodes. For the Pt electrode they reported that the MOR onset potential was 0.405 V-SCE at 25 °C and 0.305 V-SCE at 80 °C. The Pt40Ru60 electrode had a MOR onset potential of 0.291 V-SCE at 25 °C and 0.180 V-SCE at 80 °C. The authors also noted that for both electrodes the peak current density increased with both scan rate and temperature. Their results confirmed that at 25 °C methanol oxidation is irreversible and that the rate limiting step is a charge transfer process. One more interesting point was that Lee et al. saw the onset potential increase with increasing scan rate when testing at 80 °C; they had no explanation for this counterintuitive result.
Pt-Ru is of such catalytic interest it has been subjected to several surface structure investigations. Gasteiger et. al. have used LEIS and AES to determine circumstances that could cause the surface composition to vary from the bulk [169]. Surprisingly they found that annealing in a vacuum caused extreme enrichment of Pt in the surface layer. An alloy that consisted of 9.5At% Pt had achieved a nearly pure monolayer of Pt after annealing at 800 °C for 5 minutes. Further work where they calculated the thermodynamics revealed that Pt was very favorably the equilibrium surface phase in that atmosphere. They went on to show that under reducing conditions (ie in the presence of hydrogen) the surface composition more closely resembles the bulk [58, 163, 180-183]. Continuing their work Greeley and Mavrikakis calculated the stable equilibrium surfaces of alloys finding that usually pure monolayers tended to dominate the surface of their alloys regardless of composition, rarely did they see a mixed layer of both atoms [86].

There are no reports of a Pt-Ru catalyst being deliberately used on the cathode of a low temperature fuel cell. There are some reports of Ru diffusing from the anode to the cathode where it pollutes and diminishes the performance of the previously pure Pt catalyst [184, 185]. The only positive report of a Pt-Ru oxygen reducing catalyst was by chen et al. [132]. Their combinatorial screening identified Pt_{50}Ru_{44}Ir_{6} as being superior to other compositions from the Pt-Ru-Os-Ir-Rh system. Unfortunately Pt_{50}Ru_{44}Ir_{6} was not significantly different to pure Pt in follow up single cell tests. They also noted in their study that Pt_{50}Ru_{50} and other Pt-Ru compositions were not stable and corroded during ORR testing [132].
1.6.2 Platinum – Carbon

Pt and C are believed to form a simple eutectic system with no stable intermediate compounds below the eutectic [186]. Other researchers have reported the formation of metastable compounds. Witcomb et al has isolated and identified the platinum carbide phase Pt$_2$C [187]. Unfortunately the carbide only existed in the form of a precipitate that developed when a quenched platinum sample was aged. Lamber et al found that Pt would react with graphite at high temperatures and form Pt$_{3+\alpha}$C$_{1-\alpha}$ [186]. Unfortunately this phase was also metastable and would disassociate at lower temperatures under vacuum or reducing atmospheres [186]. Carbon has a very low solubility in the Pt matrix. The small amount of dissolved carbon is predominantly found on interstitial sites [188]. Interestingly at the regions of disorder within a Pt sample (grain boundaries for example) carbon will move from being interstitial to pseudo-substitutional by filling in vacancies. This changes these small regions of disorder to ordered structures with a Pt$_7$C FCC structure [188].

As discussed in the above Pt-Ru, section carbon supported Pt-Ru alloys behave differently than Pt-Ru bulk alloys, but other compositions also behave differently when on a carbon support. McNicol [7] performed cyclic voltammetry of Pt on different carbon supports and reported curves that were drastically different to unsupported pure Pt. He did not determine how the different carbon supports were causing the different outcome or even suggest if atomic carbon may be involved with the surface reactions. Paulus et al. [189] compared the ORR performance of some bulk alloys to carbon supported nanoparticles with the same composition. The carbon supported alloy nanoparticles all behaved the same as carbon supported Pt but the bulk alloys were 2 ×
better. Jalan and Taylor [78] found the same compositional trend existed across carbon supported nanocatalysts as for bulk alloys. Choi et al. [190] examined the performance of Pt on different carbon supports and concluded that commercially made Vulcan XC-72 was the best. Surprisingly Vulcan XC-72 had a mediocre surface area but made up for this with superior conductivity.

Carbon has been involved in a Pt free oxygen reduction cathode catalyst. Mukherjee [191] investigated the oxygen reduction reaction of surfaces of nickelised graphite in alkaline solutions. They performed some intricate calculations on fairly weak cyclic voltammetry data to finally conclude that the advantage gained from the modified surfaces was principally from increased roughness. Mukherjee and Basumallick [191] modified nickelised graphite with polypheneleneoxide and enhanced the ORR by altering the surface roughness or adsorption properties, but they only tested with alkaline media. Easton et al. [125] investigated sputter deposited Pt free catalysts for the ORR. They deposited and annealed compositions from the Fe-C-N system and did find some active compositions. The bulk of these samples were carbon with less than 3.5 At% Fe. Samples with a higher iron concentration tended to corrode in the 0.5 M H₂SO₄ electrolyte.

1.6.3 Platinum – Iron

There are very few reports of Pt-Fe catalysts being used for methanol oxidation. The most recent work tested thin films of PtFePO₄ and claimed enhanced methanol oxidation activity [192]. Xu et al. [193] incorporated Pt-Fe nanoparticles into multi-walled carbon nanotubes (MWNT) and tested it by cyclic voltammetry. They found the Pt-Fe/MWNT outperformed a similar Pt/MWNT catalyst, but they believed
that the Fe merely altered the particle size and Pt utilization and did not contribute directly to the reaction. Lima et al. [194] tested several alloys including a Pt-Ru-Fe composition that wasn’t specified. The Pt-Ru-Fe alloy outperformed Pt-Ru but was overshadowed by the superior activity of Pt-Ru-Mo, Pt-Ru-W and Pt-Ru-Co compositions. Page et al. [176] reported that a commercially available carbon membrane electrode with a 0.5 mgcm\(^{-2}\) Pt\(_{50}\)Fe\(_{50}\) catalyst had an onset potential of 375 mV-SCE for the methanol oxidation reaction at 25 °C. This was similar to the pure Pt CME they tested under the same conditions that recorded an onset potential of 385 mV-SCE. Upon testing at higher temperatures the Pt\(_{50}\)Fe\(_{50}\) catalyst continued to behave like the pure Pt sample, reducing its potential to 330 mV-SCE at 75 °C. Shukla and Raman [15] while looking for MRFC catalysts performed cyclic voltammetry on a carbon supported Pt-Fe catalyst. They reported that the Pt-Fe catalyst had the same MOR onset potential but a much weaker peak current density.

The majority of work examining Pt-Fe alloys was concerned with the oxygen reduction reaction. Toda et al. [73] sputter deposited several Pt-Fe alloys and reported that all of the alloys outperformed Pt in the oxygen reduction reaction. The best composition, Pt\(_{51}\)Fe\(_{49}\), had 150 mV less over potential and a current density 25 x higher than pure Pt. They confirmed this result 6 months later [195] with a study that also covered Pt-Ni and Pt-Co alloys. They postulated that compositions with more Pt than Pt\(_{50}\)Fe\(_{50}\) had a weak adsorption of O\(_2\) and compositions with less Pt than Pt\(_{50}\)Fe\(_{50}\) became inactive due to a strong OH bond. This agreed with DFT calculations of Pt\(_{80}\)Fe\(_{20}\) performed by Hirschl et al. [196]. With careful consideration of Fe’s magnetic moment, they concluded that Fe did not affect the adsorption energies; instead it altered the surface
geometries and strained the Pt into alternate electronic configurations. Curiously Toda et al. also observed that all of the alloys had pure Pt skins after testing and thus the alloying element was indirectly altering the way Pt interacted with the reaction components. This confirmed the previous calculations of Xu et al. [82], who reported that Pt$_{75}$Fe$_{25}$ with a skin would be less active than pure Pt but would more importantly be less susceptible to deactivation from oxide formation.

When examining the oxygen reduction reaction of Pt-Fe compositions the majority of researchers tend to report a particular Pt rich composition ~Pt$_{75}$Fe$_{25}$. Teliska et al. [77] studied the formation of poisonous hydroxide groups on several Pt binary alloys. They found that Pt$_{72}$Fe$_{28}$ was the second best composition; worse than Pt$_{73}$Cr$_{27}$ but better than Pt$_{74}$Co$_{26}$, Pt$_{71}$Ni$_{29}$ and pure Pt. Xiong and Manthiram [197] examined the ordering in Pt-M (M = Fe, Co, Ni and Cu) alloys and its effect on the oxygen reduction reaction. From their results it was possible to rank the alloys in terms of current density. One of the best alloys was Pt$_{80}$Fe$_{20}$ which had twice the activity of pure Pt. Baglio et al. [198] claimed Pt$_{75}$Fe$_{25}$ had a better oxygen reduction performance than pure Pt, but the single cell curves they presented did not appear significantly different. The premise of Pt rich alloys being better agrees with the work of Bonakdarpour et al [199, 200], who examined the corrosion resistance of Pt-Fe thin films and found that samples with less than 75% Pt were soon leached of the alloying element until the bulk composition was >70% Pt. Similar to other Pt alloys all of the compositions had a Pure Pt skin after immersion in the 80 °C acid [200].

Not all groups found the optimum Pt-Fe alloy was Pt rich. Xiong et al. [201] performed a study on Pt alloys that were primarily made up of a transition metal for the
oxygen reduction reaction. In a polarization test Pt\textsubscript{17}Fe\textsubscript{83} had an onset potential that was just better than pure Pt (5 mV difference) but pure Pt had a vastly superior current density at the same potentials. Strasser et al. [159] examined oxygen reduction on a combinatorial array of Pt-Fe compositions and empirically determined that Pt\textsubscript{40}Fe\textsubscript{60} ± 10 At\% was the best catalyst composition. Liu et al. [131] combinatorially screened many alloys with fluorescence and found that Ru\textsubscript{56}Fe\textsubscript{44} had a better ORR activity than pure Pt. Lyons et al. [202] reported that Pt doped FeO\textsubscript{X} had ~20 times the oxygen reduction activity of a standard Pt/C catalyst. X-Ray analysis revealed that disordered FeO\textsubscript{X} contributed to the enhancement but ordered FeO\textsubscript{X} phases were inert. Though promising, the group still needed to perform stability measurements.

Sun and Tseung [203] examined the oxygen reducing properties of a Pt/C catalyst in H\textsubscript{2}SO\textsubscript{4} solutions that also contained dissolved Fe. They saw an enhancement that they attributed to the Fe catalytically improving the decomposition of H\textsubscript{2}O\textsubscript{2}. This was disputed by Ye [204] who claimed that they were merely seeing an iron reduction peak over the top of the oxygen reduction peak, and the two simultaneous reactions were responsible for the enhanced current density. This was refuted by Tseung and Sun [205], who expressed that Ye was unable to grasp the simple science they had presented. In the defense of Ye they did not conclusively rule out iron reduction by performing the same tests again in an oxygen free environment, but used a vague derivation of faradays law to imply that the Fe reduction could not be maintained at a steady state[205].

1.6.4 Platinum – Cobalt

Pt-Co alloys have been the subject of a substantial number of investigations shown and some success as methanol oxidation catalysts. Many different fabrication
techniques have seen differing results. Zhang et al. examined Pt-Co particles made by a micro-emulsion technique [206]. They reported that Pt_{41}Co_{59} showed a catalytic activity that was 1.6–2.2 times higher than that of pure Pt over a wide potential range for methanol oxidation in an alkaline electrolyte. In a later study they reported an optimum carbon supported composition of Pt_{66}Co_{33} for room temperature methanol oxidation [207]. Zeng and Lee [208] prepared Pt_{45}Co_{55} by several different routes to achieve catalysts with different particle sizes. They tested these catalysts in an acidic environment and surprisingly, Pt-Co catalysts with particle sizes greater than 3.7 nm failed to perform better than pure Pt at the methanol oxidation reaction.

Other groups have reported that ~Pt_{50}Co_{50} was the optimum composition. Zeng, et al [208] examined a Pt-Co catalyst’s oxidation of methanol they found a Pt_{50}Co_{50} alloy showed enhanced activity relative to pure Pt, with performance being better than twice that for pure Pt after extended periods (4 hrs). Okada et al. reported methanol oxidation activity by mixtures of Pt with Co-based organic complexes (Pt_{60}Co_{40}, Pt_{50}Co_{50} and Pt_{40}Co_{60}), that for some complexes was “several tens of times” larger than that of pure Pt [209]. Page et al. [176] tested several commercially available carbon membrane electrodes with 0.5 mg cm^{-2} Pt_{50}X_{50} catalysts (X = Ru, Ni, Cu, Fe and Co) and out of all of them the Pt-Co CME was the worst. It had an onset potential of 395 mV-SCE for the methanol oxidation reaction at 25 °C. Upon testing at higher temperatures the Pt_{50}Co_{50} catalyst did redeem itself slightly with an onset potential of 270 mV-SCE but this was still not better than Pt_{50}Ru_{50} and Pt_{50}Cu_{50}. Despite the onset potential falling short, the Pt-Co CME made up for it by recording the strongest peak methanol oxidation current density, even stronger than the Pt-Ru CME.
Other compositions away from Pt_{50}Co_{50} have not done as well. Salgado et al. [210] tested the methanol oxidation of some Pt-Co alloys and observed a performance worse than pure Pt. Despite all this, the Pt_{75}Co_{25} catalyst slightly outperformed pure Pt in a single cell test. On the other hand, neither Gojkovic [211] nor Beard et al. [212] observed enhanced activity in Pt_{75}Co_{25} bulk alloys relative to pure Pt. However, Gojkovic [211] commented that this might not be the case for nanoscale alloy particles.

In contrast, Pt_{75}Co_{25} has been reported as being a superior oxygen reduction catalyst. Mukerjee and Srinivasan [213] studied Pt_{75}Co_{25} in single cell tests and found that the alloy had a better ORR activity than pure Pt. They reported that the ORR onset potential for the Pt-Co alloy was 52 mV higher than pure Pt at 40 °C and 28 mV higher at 80 °C. Mukerjee et al. [80] also performed single cell tests on a commercially available ORR Pt-Co cathode catalyst and found it performed better than Pt. Markovic and Ross [36] performed RDE work on Pt, Pt_{75}Co_{25} and Pt_{75}Ni_{25} alloys and reported that in perchloric acid electrolyte the Pt-Co alloy was superior to both the pure Pt and the Pt-Ni alloy. Unfortunately in sulphuric acid the Pt-Ni alloy was better. Ross and Markovic [214] went on to compare oxygen reduction activity of a Pt_{75}Co_{25} catalyst that had an enriched Pt skin against a Pt_{75}Co_{25} catalyst that had been sputtered so that the surface matched the bulk. Both catalysts outperformed Pt but the skin catalyst was more active than the sputtered catalyst. In contrast Xu et al. [82] calculated that an enriched skin was detrimental to performance and ranked the catalysts Pt_{75}Co_{25}(skin) < Pure Pt < Pt_{75}Co_{25}(skinless). This did not match experimental observations so they concluded that alloys with skins were less active but also less susceptible to being poisoned by oxygen groups. Teliska et al. [77] examined several Pt binary alloys and although Pt_{74}Co_{26} was
not the best catalyst it did perform better than pure Pt. Xiong and Manthiram [197] compared the ORR activity of four Pt binary alloys to Pt and found that one of the best alloys was Pt$_{80}$Co$_{20}$ with twice the activity of pure Pt.

Other groups have examined Pt-Co alloys hoping to find an improvement but end up with nothing beneficial to report. Salgado et al. [215] examined Pt$_{70}$Co$_{30}$ nanoparticles that were annealed at different temperatures and found no improvement in the ORR over pure Pt. Later they expanded their investigation [210] and found Pt$_{75}$Co$_{25}$ and Pt$_{85}$Co$_{15}$ had identical onset potentials to pure Pt in 0.5 M H$_2$SO$_4$. Their data showed a marginal improvement from the alloys when the current density was normalized by the specific area calculated by hydrogen adsorption (a flawed assumption as mentioned in section 1.2.1). Xiong et al. [201] performed a study on binary alloys that had a low concentration of Pt for the oxygen reduction reaction. Despite their upbeat text, careful perusal of the data could not help but reveal that all of their alloys were worse than pure Pt. Pt$_{13}$Co$_{87}$ for example had the same ORR onset potential as pure Pt but the pure Pt had an exchange current density 50x higher than the Pt-Co alloy. The authors then carefully selected a potential to measure the current density and then reported it based on the Pt content. This artificially boosted the poorly performing Pt$_{13}$Co$_{87}$ to make it appear 4x more catalytically active than pure Pt. The Pt-Co was so bad that when they performed the same artificially inflating calculation to the results of a Pt vs Pt$_{13}$Co$_{87}$ single cell test the alloy still came out looking worse.

Really spectacular results seem to come from studies that look at current densities in perchloric acid. Toda et al. [195] co-sputtered and tested the ORR activity of Pt$_{90}$Co$_{10}$, Pt$_{71}$Co$_{29}$, Pt$_{49}$Co$_{51}$, Pt$_{38}$Co$_{62}$ and Pt$_{22}$Co$_{78}$. They reported that the activity
followed a volcano like trend with composition, peaking at Pt$_{40}$Co$_{60}$ with an activity $15 \times$ that of pure Pt. Similar to what they reported for Pt-Fe and Pt-Ni systems, after testing all of the alloys had developed a pure Pt skin. Stamenkovic et al [74] recently tested the oxygen reduction activity of Pt$_{75}$X$_{25}$ (X = Ti, V, Fe, Co and Ni) with a RRDE in HClO$_4$ and also found a volcano like relationship peaking at the Pt-Co alloy. They went on to examine the same Pt-X compositions but with different surface structures [216]. They found that samples were sputtered clean so that the surface matched the bulk would lose the transition metals in the HClO$_4$ electrolyte anyway. Regardless of the final surface structure, the optimum composition at the peak of the trend was always Pt$_{75}$Co$_{25}$ [216].

Soderberg et al. [217] fabricated and tested the ORR activity of a Pt$_{50}$Co$_{50}$ and a Pt$_{75}$Co$_{25}$ catalyst. Though both had a better activity than the pure Pt standard, the Pt$_{50}$Co$_{50}$ was slightly more active than Pt$_{75}$Co$_{25}$. All of these studies base the activity on a current density measurement made at a specific potential. This is not always a fair comparison; the current is exponentially proportional to the potential so a small difference in onset potential can become a staggeringly different current density.

A number of studies examined the trend of ORR activity against the lattice parameter usually peaking at a Pt-Co alloy [75, 80, 81], see section 1.3.2. The lattice parameter of Pt$_{75}$Co$_{25}$ bulk alloy [212] has been reported to have been lower than that of carbon supported Pt$_{75}$Co$_{25}$ nanoparticles [75, 213]. The discrepancy between the two lattice parameters could be merely from stress or a different concentration of defects, but of more speculative interest the difference could be from a small concentration of carbon infiltrating the interstitial sites of the alloy.
Beard and Ross [212] believed that the Pt-Co catalysts were initially unstable with the Co leaching from the surface until a corrosion resistant Pt₃Co phase dominated. This agrees with Bonakdarpour et al [199]who found that Pt-Co thin films would preferentially dissolve Co until the bulk concentration was greater than 70% Pt. Antolini et al [218] was also interested in the corrosion resistance of Pt alloys. They performed a thorough literature survey and some experiments, concluding that the degree of alloying was critical. Pt with Co or Cr naturally alloyed to a higher degree than Pt with V, Ni or Fe and thus Co and Cr alloys had a better corrosion resistance. They also raised the interesting point that base metal leaching can be beneficial as it can cause a rougher more active Pt surface, but this must be balanced against the loss of the base metal’s beneficial surface modification.

There have been a few ternary alloy studies that included Pt and Co. A discussion of Pt-Cr-Co and Pt-Ni-Co compositions is presented in sections 1.6.5 and 1.6.6 respectively. Lima et al. examined Pt-Ru-W and Pt-Ru-Co catalysts electrodeposited onto a carbon support and reported that a Pt-Ru-Co alloy had at least two times improvement over Pt-Ru, but they were vague about actual compositions [194]. Strasser and co-workers discovered a ternary Pt-Ru-Co alloy with promising electrocatalytic characteristics. They identified Pt₃₀Ru₂₀Co₆₀ as being superior to the widely used Pt₆₀Ru₄₀ or Pt₅₀Ru₅₀ compositions [90]. They found that there was 4-7 times the current drawn from the cobalt containing catalyst compared to the Pt-Ru binary catalysts during the methanol oxidation. They went on to fabricate a library that had many more compositions that were close to Pt₃₀Ru₂₀Co₆₀ and discovered that Pt₁₄Ru₂₃Co₆₃ and Pt₁₈Ru₂₀Co₆₂ had even better performances [219]. In a patent [220] of
the Pt-Ru-Co system they reported an optimal composition of Pt$_{27}$Ru$_{10}$Co$_{63}$. This composition showed an improvement of 180 x over their thin film Pt$_{52}$Ru$_{48}$ standard. When this composition was made in bulk form as a powder, they still saw a 5-10x improvement from this alloy.

1.6.5 Platinum – Chromium

There has been one investigation that focused solely on Pt-Cr alloys being used to oxidize methanol. After determining the best support, Choi et al. [190] examined the methanol oxidation properties of several Pt alloy compositions and found that Pt$_{50}$Cr$_{50}$/C was more active than an equivalent Pt/C catalyst. Yang et al. [221] were principally interested in the oxygen reduction properties of several Pt-Cr alloys but also gave a cursory examination of their methanol oxidation properties. From some cyclic voltammetry data they reported that Pt$_{75}$Cr$_{25}$, Pt$_{66}$Cr$_{33}$, and Pt$_{50}$Cr$_{50}$ had much weaker methanol oxidation peaks than pure Pt. In the presence of oxygen and methanol the alloy compositions would ignore the methanol and reduce oxygen 200 mV higher than pure Pt. When the electrolyte was clean the alloys had the same ORR performance as pure Pt [221].

The second composition ever to be patented as a new fuel cell cathode catalyst was a Pt-Cr alloy (the first patent was for a Pt-V alloy) [79]. Though the patent mentioned that the Pt-Cr catalyst was more stable than the Pt-V it still lost 37 Wt% of Cr after 36 hrs of operation [79]. Tamizhmani and Capuano [222] investigated one Pt-Cr alloy and several Pt-Cr-Cu alloys for the oxygen reduction reaction. They reported the Pt$_{90}$Cr$_{10}$ alloy had an ORR onset potential that was 20 mV higher than that of pure Pt. They also reported that Pt$_{25}$Cr$_{15}$Cu$_{60}$ was the best catalyst with an ORR onset potential 50
mV higher than pure Pt. Mukerjee and Srinivasan [213] studied several alloys to use in the cathode of a PAFC. Single cell tests with a Pt$_{75}$Cr$_{25}$ cathode showed a better ORR activity than a similar pure Pt cathode. The Pt-Cr alloy had an initially promising ORR onset potential 34 mV higher than pure Pt at 40 °C but this diminished with higher temperature testing to a 1 mV difference at 80 °C. Antolini et al. [223] examined carbon supported Pt-Cr electrocatalysts and found that Pt$_{75}$Cr$_{25}$ and Pt$_{90}$Cr$_{10}$ had ORR onset potentials that were higher than Pt by 60 and 35 mV respectively. But in a follow up single cell test all of the Pt-Cr alloys performed the same as pure Pt.

Not all reports have been positive, Glass et al. [224] characterized and tested several Pt-Cr alloys and found no improvement to the ORR from alloying Cr into Pt. They reported a slight decrease in activity for low concentrations of Cr and a dramatic drop for concentrations higher than Pt$_{50}$Cr$_{50}$, hypothesizing that the Cr could no longer remain soluble in the Pt matrix and passivated the surface. Beard et al. [212] also scoffed at the incredible oxygen reduction performances of Pt-Cr nanoparticles claimed in the patent of Landsman and Luczak [225]. Beard et al. [212] reported that Cr could only enhance the catalytic activity of Pt by 20% at most. Stonehart [79] reviewed the thorough work and several papers from the Los Alamos laboratories investigating Pt-Cr alloys as cathode catalysts. The conclusion of the studies was that Cr was preferentially leached from the surface leaving a rougher more active Pt structure. This disagrees with the work of Antolini et al [218] who found that Pt-Cr alloys were more stable than other binary Pt alloys. They also mentioned that some preferential leaching can be desired due to the beneficial increase in active surface area.
Teliska et al. [77] believed that an OH group was the principal poisoning factor that diminished the catalytic activity of Pt. They used XANES to study OH adsorption on several Pt binary alloys. The result of their study ranked Pt$_{73}$Cr$_{27}$ as the catalyst that most inhibited poisoning by an OH group. The next best catalyst was Pt$_{72}$Fe$_{28}$ then Pt$_{74}$Co$_{26}$, Pt$_{71}$Ni$_{29}$ and finally pure Pt was the worst. Mukerjee et al. [80] performed single cell tests on a commercially available ORR cathode Pt-Cr catalyst, and found it performed better than the control Pt catalyst.

Ternary alloys of Pt-Cr-Co have also been investigated. Early work [79, 226, 227] examining Pt-Cr-Co catalysts was primarily for use in phosphoric acid fuel cells cathodes. Later work considered Pt-Cr-Co as a possible cathode catalyst in a PEMFC. Shukla et al. [228] found that at low current densities Pt$_{51}$Co$_{22}$Cr$_{27}$ achieved a potential 40 mV higher than pure Pt as a DMFC cathode catalyst. Analysis with XPS determined the alloy had an altered crystal structure and a Pt enriched surface [229]. Seo et al. [230] more recently performed PEMFC tests and found Pt$_{76}$Cr$_{13}$Co$_{11}$ had an open circuit potential 54.3 mV higher than Pt. They went on to test other compositions from the Pt-Cr-Co system, but nothing outperformed Pt$_{76}$Co$_{13}$Cr$_{11}$. Strasser et al. [159] performed a combinatorial investigation of many Pt-Co-Cr alloys and determined that Pt$_{47}$Co$_{23}$Cr$_{30}$ was the optimum. To confirm this they fabricated Pt$_{50}$Co$_{25}$Cr$_{25}$ as a powder and tested it in a RDE rig. Unfortunately the powder performed worse than the pure Pt standard, this fact was glossed over by reporting the current density based on the Pt content. This doubled the current density of Pt$_{50}$Co$_{25}$Cr$_{25}$ and made it appear better than the Pt.
1.6.6 Platinum – Nickel

Nickel was the catalyst used in Bacon’s original alkaline fuel cell [5]. Nickel and lithium doped nickel oxide are still used in the cathodes of alkaline fuel cells today [231], but nickel alloys used in the more acidic PEMFC and DMFC have been less successful. Page et al. [176] reported that a commercially available carbon membrane electrode with a 0.5 mg cm$^{-2}$ Pt$_{50}$Ni$_{50}$ catalyst had an onset potential of 370 mV-SCE for the methanol oxidation reaction at 25 °C. This was just 15 mV lower than the pure Pt CME they tested under the same conditions. At 75 °C the Pt$_{50}$Ni$_{50}$ catalyst had an onset potential of 280 mV-SCE which was 40 mV better than the pure Pt CME but still 30 mV behind the Pt-Ru CME. Wang et al. [232] compared the ethanol oxidation performance of Pt$_{60}$Ru$_{30}$Ni$_{10}$ to Pt$_{50}$Ru$_{50}$ alloys supported on carbon. During cyclic voltammetry scans both catalysts had the same ethanol oxidation onset potential, but during steady state measurements the Pt-Ru-Ni alloy achieved a current density 20% higher than the Pt-Ru control.

Shen et al. [233] examined Pt electrodes that were modified with NiO and reported the optimum methanol oxidation composition was Pt$_{60}$(NiO)$_{40}$. Nickel alloys with platinum and ruthenium have also shown better methanol oxidation activity than pure Pt. Park et al. [234] saw Pt$_{50}$Ru$_{40}$Ni$_{10}$ give a two-fold better performance than pure Pt in methanol oxidation chronoamperometry experiments. The Pt-Ru-Ni alloy also had an onset potential 0.261 V lower than the onset for pure Pt but only 0.04 V lower than the onset of a Pt-Ru catalyst. Lima et al. [194] observed that an unspecified Pt-Ru-Ni composition just outperformed an equivalent Pt-Ru catalyst.
A platinum free nickel catalyst has also been reported. Tharamani and Mayana [235] electrodeposited a Ni-Cr alloy on to a carbon support and examined its methanol oxidation properties. They reported an incredible onset potentials and high current densities especially when compared to nearly inert pure Ni. Unfortunately they did not compare their results to pure Pt. They postulated the improved performance was because the alloy had ~ 800 × more surface area than pure Ni.

Pt-Ni alloys have also been considered as replacement oxygen reduction catalysts. Mukerjee and Srinivasan [213] studied several alloys to use in the cathode of a PAFC and amongst all of the alloys the Pt75Ni25 gave the most promising results. The Pt-Ni alloy had an ORR onset potential 49 mV higher than a similar pure Pt electrode at 40 °C. This diminished at higher temperatures, coming down to 18 mV at 80 °C but was still encouraging. Teliska et al. [77] performed an oxygen reduction surface study of several Pt binary alloys, amongst the alloys Pt71Ni29 was the worst but it still out performed pure Pt. Stamenkovic et al [74] also compared Pt alloys and found that the oxygen reduction activity of Pt75Ni25 was better than Pt but worse than Pt75Co25. Atanassova et al. [236] developed a combinatorial method to fabricate and test oxygen reduction catalyst powders. They didn’t specify the exact composition but did report that a carbon supported Pt-Ni-Co catalyst had 40% higher activity than a pure Pt standard. This improvement should be taken with a grain of salt as they were using gPtkW⁻¹ as a metric. If the new catalyst consisted of less than 30% Pt content then it would have actually performed 50% worse than the standard.

Xiong et al. [201] performed a study on Pt-M (M= Cu, Ni, Co and Fe) alloys for the oxygen reduction reaction. Pt73Ni27 had an ORR onset potential that was 10 mV
higher than Pt but the current densities it generated were 10% poorer than pure Pt. Mukerjee et al. [80] performed single cell tests on a commercially available ORR cathode Pt-Ni catalyst and reported that it outperformed the equivalent Pt catalyst.

Xiong and Manthiram [197] characterized the atomic structure of some Pt binary alloys and its effect on the oxygen reduction reaction. They found that Pt$_{80}$Ni$_{20}$ had 1.5 x more activity than pure Pt. Markovic and Ross [36] performed some RDE work on Pt, Pt$_{75}$Co$_{25}$ and Pt$_{75}$Ni$_{25}$ alloys and reported that in sulphuric acid the Pt-Ni alloy was a superior ORR catalyst to both pure Pt and the Pt-Co alloy. They went on to test the oxygen reduction of a Pt$_{75}$Ni$_{25}$ catalyst that had an enriched Pt skin and a Pt$_{75}$Ni$_{25}$ catalyst that had been sputtered so that the surface matched the bulk [214]. Interestingly the sputtered catalyst had twice the activity of Pt but the skin catalyst was close to inert. This contradicted the work of Toda et al. [195], they co-sputtered six Pt-Ni alloys and tested them for ORR activity. The best Pt-Ni composition from this study was Pt$_{70}$Ni$_{30}$ which had a kinetic current density 10 x that of Pt. Interestingly after testing the surface of all of the Pt-Ni alloys, even Pt$_{20}$Ni$_{80}$, had an enriched into a pure Pt skin. The Pt skin phenomena was also observed by Bonakdarpour [200].

Changes to the surface composition during tests have been reported by other groups. Bonakdarpour et al [199] examined the corrosion resistance of Pt-Ni thin films and also found that Ni rich samples would preferentially lose Ni until the bulk composition was greater than 70% Pt. Antolini et al. [218] found that Ni did not alloy into the Pt matrix as well as Co or Cr and as a result had a poorer corrosion resistance. This contradicts the DFT calculations of Gu and Balbuena[91], they predicted that Ni would not change the corrosion resistance of Pt.
1.6.7 Platinum – Copper

Page et al. [176] tested several commercially available carbon membrane electrodes with 0.5 mg cm\(^{-2}\) Pt\(_{50}X_{50}\) catalysts (X = Ru, Ni, Cu, Fe and Co) and out of all of them the Pt-Ru was the best and the Pt-Cu the second best. The Pt-Cu CME had an onset potential of 345 mV-SCE for the methanol oxidation reaction at 25 °C. Upon testing at higher temperatures the Pt\(_{50}Cu_{50}\) catalyst performed even better with an onset potential of 260 mV-SCE but it was still just outperformed by Pt\(_{50}Ru_{50}\) which had an onset potential of 250 mV-SCE. Unfortunately this lower onset potential of the Pt\(_{50}Cu_{50}\) CME was offset by a complete failure to sustain a reasonable current density. Page et al believed the Cu component was either dissolving or oxidizing and leaving an inert catalytically useless surface. Cu has also been considered to benefit platinum and palladium’s oxidation of carbon monoxide [103], but as mentioned before a good CO catalyst is not necessarily a good methanol catalyst. Finally Pt and Pt-Ru on a Cu\(_{70}Ni_{30}\) substrate were found to have enhanced ethanol oxidation properties, but in alkaline conditions [237].

The majority of researchers tend to report disappointing oxygen reduction activity for Pt-Cu catalysts. Initially under potential deposition (upd) of Cu on Pt was believed to help the oxygen reduction reaction [70, 238], but this was later refuted in more accurate RRDE studies [36]. Xiong et al. [201] performed a study on alloys with a low Pt content for the oxygen reduction reaction. Amongst the alloys they examined Pt\(_{17}Cu_{83}\) performed well with a promising ORR onset potential 20mV higher than Pt. Unfortunately Pt\(_{17}Cu_{83}\) had an exchange current density two orders of magnitude worse than Pt. Liu et al. [131] combinatorially screened many alloys with fluorescence and
found that Pt$_{80}$Cu$_{11}$ had a better ORR activity than pure Pt. Xiong and Manthiram [197] examined the ORR activity of some Pt binary alloys and found that Pt$_{80}$Cu$_{20}$ was the same as pure Pt.

1.6.8 Platinum – Titanium

Lai et al. [239] deposited Pt onto Ti substrates and reported an improved methanol oxidation performance. They implied the improvement was due to the alloy having more (110) and fewer (100) and (111) planes than the Pt standard. Tammeveski [240] also found that titanium substrates altered the properties of Pt thin films that were deposited on them. They found that even though the Ti substrate was inert they could still cause a shift in the potential of oxide formation and oxide reduction of thin (< 200 Å) Pt films. Ti has also shown improved methanol oxidation when incorporated into a carbon nanotube with a Pt [241] or Pt-Ni [242] catalyst. A Pt free methanol oxidation catalyst was made by alloying Ni and Ti [243]. The Ti in Ni$_{50}$Ti$_{50}$ improved the poor corrosion resistance of Ni. Methanol oxidation on Ni$_{50}$Ti$_{50}$ shifted erratically between non-existent and poor. At best it achieved peak current densities two orders of magnitude lower than Pt. Other groups have reported [218] that Pt-Ti alloys are generally stable.

Stamenkovic et al [74] tested the oxygen reduction activity of a Pt$_{75}$Ti$_{25}$ alloy and found that it had a better performance than an equivalent Pt sample. Beard and Ross [244] found a favorable ORR performance from Pt$_{75}$Ti$_{25}$ but noted there were many parameters (particle size, annealing temperature, annealing atmosphere, etc.) that could worsen the performance of Pt$_{75}$Ti$_{25}$. Kokkinidos et al. [245] found that the ORR activity of Pt was enhanced when deposited on a Ti substrate. The best performance was seen
from the thinnest layer of Pt with subsequently thicker layers diminishing in ORR activity. Unfortunately the best Pt/Ti catalyst still had an onset potential 200 mV poorer than a pure Pt bulk electrode. Other groups [246, 247] have touted improvements from Pt-TiO₂ catalysts but their single cell test results show no significant difference between their alloys and pure Pt at low current densities.

1.6.9 Platinum – Tungsten

Tungsten has long been known to improve platinum’s methanol oxidation performance. Shen and Tseung [32] showed that co-deposited Pt-WO₃ electrodes outperformed pure Pt and Pt-Ru alloys. They found the strongest activity occurred in a Pt₅₄(WO₃)₄₆ composition with an onset potential of 0.24 V-SCE in 1 M CH₃OH and 0.5 M H₂SO₄. Shukla et al. [248] also saw an improved performance from Pt-WO₃ catalysts. Their testing determined the optimum composition to be Pt₇₅(WO₃)₂₅. However, not all researchers agree, Choi et al [108] used the fluorescence technique to examine methanol oxidation over a wide range of Pt-Ru-W-Mo compositions. Included were some binary Pt-W catalysts but these failed to elicit a strong response and were easily outperformed by binary Pt-Ru compositions. Götz and Wendt [249] were vague about specific compositions but their testing also saw a better performance from a Pt-Ru alloy than from a Pt-W alloy. Jayaraman et al. [127] used a library of Pt and WO₃ compositions to demonstrate there combinatorial technique. Pure Pt outperformed the other compositions (Pt₉₀(WO₃)₁₀ to Pt₇₅(WO₃)₂₅) but they admitted that the loading and particle size of the Pt-WO₃ alloys was not equivalent to the pure Pt sample.

Arico et al. [250] examined the methanol oxidation catalysis properties of arc-melted quaternary combinations of Pt, Ru, W and Sn. They found that these alloys
showed promising performance in half cell tests even though the Ru, W and Sn were oxidized and created an uncompensated resistance. The resistance was more significant in single cell tests where the performance was poorer than pure Pt due to the ohmic loss.

Götz and Wendt [249] were the first group to take the promising works that had been done on the Pt-WO$_x$ [32, 251] system and expand it to consider Pt-Ru-W. They used the Bönnemann method to prepare colloid catalysts and tested them in a single cell test stand. They were vague about specific compositions but found a Pt-Ru-W alloy had a better performance than any Pt-Ru alloy. In contrast Lasch et al. [252] combined Pt and Ru with WO$_x$ and reported no significant difference between the methanol oxidation onset potential of Pt$_{55}$Ru$_{45}$ and Pt$_{54}$Ru$_{39}$(WO$_x$)$_7$. At the same time Holleck et al. [46] examined CO tolerant H$_2$ catalysts and reported that Pt$_{82}$W$_{18}$ was better than pure Pt, but that Pt$_{53}$Ru$_{22}$W$_{15}$ was the best. Götz [253] also prepared catalysts by the Bönnemann method maintaining a constant ratio of Pt and Ru but varying the W concentration. They found that the optimum composition was Pt$_{28}$Ru$_{28}$W$_{44}$ but acknowledged this would probably change with a differing synthesis method.

Choi et al. [108] performed fluorescence testing on a combinatorial array of compositions from the Pt-Ru-W-Mo. They noted that there was little response from the ternary systems Pt-Ru-W or Pt-Ru-Mo. The strongest response was from Pt$_{77}$Ru$_{17}$Mo$_4$W$_2$ which also outperformed Pt$_{50}$Ru$_{50}$ and Pt$_{82}$Ru$_{18}$ in longer term polarization tests. This implied that Pt-Ru binary compositions could be further optimized by the addition of small concentrations of other elements. Jusys and Schmidt [254] looked at a single composition and found the activity of Pt$_{54}$Ru$_{39}$W$_7$ similar to the PtRu produced commercially by E-TEK. Umeda, et al. [255] found
Pt$_{65}$Ru$_{20}$W$_{15}$ to be far superior to pure Pt and somewhat better than Pt$_{80}$W$_{20}$, but their investigation was not focused on finding an optimum composition. Tanaka et al. [256] found a Pt$_{80}$Ru$_{20}$ composition was favorable, but Pt$_{65}$Ru$_{20}$W$_{15}$ was an even better performer. In other studies, our group [151] investigated composition spread thin film libraries in the Pt-Ru-W system with a scanning electrochemical microscope and determined that Pt$_{30}$Ru$_{35}$W$_{35}$ was the optimum composition to oxidize hydrogen in the presence of carbon monoxide. However it has also been recognized that the long term functionality of tungsten alloys may be limited. Most groups have reported a degradation of catalytic activity due to the corrosion of the tungsten. Strong current densities for tungsten alloys have been previously reported as being due to preferential dissolution that leaves a rougher surface [90].

There are very few reports of Pt-W being used for oxygen reduction. Savadogo and Beck [257] tested Pt-WO$_3$ cathode catalysts under PAFC conditions and concluded that the tungsten increased the active area (probably by preferentially leaching away). Sun et al. [258] touted improved performance from carbon supported Pt-WO$_3$ catalysts but their single cell results show no difference at low current densities. The Honda research group [141, 154] discovered some promising Pt-W compositions for oxygen reduction. They found that Pt$_{39}$W$_{61}$ had the best mass specific activity, approximately triple that of pure Pt, but its actual performance was not significantly different. No group has conclusively reported that W directly interacts with oxygen during the oxygen reduction reaction. At best it seems that W may alter the catalyst structure to increase the Pt electroactive area.
1.6.10 Platinum – Tungsten Carbide

Early work examining WC as a catalyst for methanol oxidation is fairly rare. Gasteiger et al. [259] cited an old proceeding [260] that had shown the natural CO resistance of WC and its poor performing overpotential (e.g. 0.2 V at ~1.1 mA cm\(^{-2}\)). McNicol [7] wrote that although pure WC can oxidize formic acid or formaldehyde, it is conspicuously inert in the presence of methanol. He postulated this was because WC electrosorbs H\(_2\)O too strongly and does not adsorb methanol in competition to water.

Nie et al. [261] deposited Pt onto a WC/C support by direct reduction and intermittent microwave heating to finally form the catalyst composition Pt\(_{33}\)WC\(_{66}\). They saw an ORR onset potential 150 mV higher than a similar commercial Pt catalyst. Lee et al [262] improved the stability of WC by adding Ta. They found that the WC-Ta had better oxygen reduction properties than pure WC but did not compare to pure Pt.

1.6.11 Platinum – Tantalum

There are only a few reports on Pt-Ta compositions in a fuel cell environment. The first positive work [263] reported an increase in the oxidation of CO for Pt-TaO\(_X\) compositions but didn’t look at stoichiometry other than Pt\(_{66}\)(TaO\(_X\))\(_{33}\). Yamada et al. [264] also reported that TaO\(_5\) improved the CO resistance of Pt, but their gas phase experiments were quite dissimilar to the electrochemical oxidation of methanol. The other report by Bonakdarpour et al [126] performed a combinatorial investigation into Pt-Ta alloys and found that though stable, Ta did not aid in the oxygen reduction reaction. He et al. [156] mentioned testing Pt-Ta alloys but did not report any positive results, implying that no improvement had been observed.
1.6.12 Platinum – Palladium

There are no experimental reports of Pd alloys being used to oxidize methanol. One group has performed a simulation and found that Pd can adsorb and dehydrogenate methanol but would be poor at dehydrogenating water to complete the reaction [19]. Though theoretically Pd with a second element could be a bifunctional methanol oxidation catalyst, there is still no experimental work that confirms this.

Experimental work that used Pd-Pt and Pd-Co catalysts has principally been for oxygen reduction studies. Guerin et al. [160] co-sputtered Pd, Pt and Au onto a microarray of 100 electrodes and tested them for oxygen reduction activity. They found that Pt and Pd were principally responsible for the activity with almost no benefit from Au. This was reflected in the optimum composition Pt\textsubscript{68}Pd\textsubscript{28}Au\textsubscript{4} being nearly Au free. Pt modified with a pseudomorphic film of Pd enhanced its oxygen reduction activity by a factor of two in alkaline electrolyte. But this enhancement was not seen for tests in acid electrolyte, possibly due to Pd being susceptible to anion poisoning [36]. Shao et al. [265] examined the oxygen reduction activity of several Pd alloys and ranked Pd-Ru as the worst, then Pd-Ir, Pd-Au and Pd-Pt as the best. Performing DFT calculations they found the activity followed a volcano trend across the alloys theoretical d-band center. They went on to fabricate a Pd\textsubscript{66}Co\textsubscript{33} catalyst with an activity that they reported was comparable to Pt.

Fernandez et al. [52, 53] performed a SECM analysis of a combinatorial array of Pd-Co catalysts and reported that Pd\textsubscript{90}Co\textsubscript{10} had a lower ORR onset potential than pure Pd. They confirmed this with RRDE experiments with pure Pd and Pd\textsubscript{80}Co\textsubscript{20} outperforming pure Pt. Unfortunately the pure Pt they used for comparison had one of the worst
performances ever reported and throws the wonderful Pd and Pd-Co alloy properties that they claim into doubt. Pd has also been incorporated into carbon nanotubes and admirably reduced oxygen in this form [266], though under slightly biased conditions that didn’t use a Pt standard.
CHAPTER 2:

OBJECTIVES

There are many studies that have mapped a trend of catalytic activity against compositional parameter and seen a volcano like relationship. These trends typically place platinum, or a Pt alloy, near the peak of the volcano, but frequently leave the actual peak vacant. These works imply that there are unknown, catalyst compositions that can perform better than the platinum alloys currently accepted as the best. The hypothesis of this study is that these superior catalyst compositions could be discovered and developed.

To discover these catalysts a method that objectively considered catalytic activity had to be developed. The best way to sift through the multitude of samples and identify those with a superior property is to use a combinatorial technique. The first step of this study was to create a combinatorial process capable of generating libraries with combinations and permutations of compositions. Many previous catalyst studies have changed the composition of a catalyst but simultaneously altered some other structural characteristic, often unintentionally. The conclusions of those studies were weakened because the change in performance could not be confidently attributed solely to the changed composition. The first focus in fabricating the combinatorial libraries of this study was to control the process such that variables like roughness, grain size and surface structure did not vary between samples or libraries.
This study’s goal is to compare the catalytic activity of different samples based solely on their composition. This placed an emphasis on synthesizing samples in a manner that held other variables constant. A classic fuel cell catalyst is a high surface area carbon supported nanoparticle, which is impossible to consistently reproduce with different compositions. The best technique to construct combinatorial libraries with comparable samples is thin film deposition. Thin films can be deposited with precise control of composition and consistent surface characteristics. Caution needs to be applied to the interpretation of the results because thin film properties are not necessarily replicated by a compositionally equivalent nanoparticle. The library synthesis also needs to incorporate a standard composition into every library to facilitate comparison between libraries. The final goal of the fabrication process is for the handling and testing of the libraries to be straightforward.

After fabrication the libraries need to be screened. The screening of the libraries will test them to assess the relative catalytic activity of the different compositions in a simulated fuel cell environment. Screening in an actual fuel cell environment (e.g. Nuvant System) is not compatible with a rapid combinatorial evaluation regime; however the alternative screening technique needs to maintain some similarity with the fuel cell environment. For example, a low temperature fuel cell catalyst is usually hydrated and positioned at the interface between a fuel/oxygen stream and a Nafion membrane. The surface of the Nafion membrane is acidic with bound sulfate chains and the conditions during testing need to mimic this environment. A catalyst that has a high activity at room temperature is desirable but operation at higher temperatures also needs to be considered. Finally the catalytic activity is an electrochemical property and thus the
screening test needs to be an electrochemical test. Such a screening test needs to control the potential of a combinatorial library’s samples and measure the consequential reaction occurring on the library samples. To meet all of these needs we developed a multi-array screening approach utilizing parallel potentiostatic measurements. This enables us to perform cyclic voltammetry characterization in an appropriate electrolytic environment and acquire data from all of all library members simultaneously. The criteria used to judge and rank catalysts was based upon electrochemical parameters derived from the cyclic voltammetry curves, like the potential defined at the start of the reaction and the current densities achieved during the reaction.

There are many different types of fuel cells, each with different requirements of their catalysts. This study is concerned with low temperature fuel cells and the catalysts of interest are

1. A methanol oxidation catalyst that could outperform the optimum Pt-Ru composition.
2. A methanol oxidation catalyst that was selective and not affected by the presence of oxygen.
3. An oxygen reducing catalyst that could outperform pure Pt.
4. An oxygen reducing catalyst that was selective and not affected by the presence of a methanol poison.

The suitability of any catalyst was based on the criteria of catalytic activity and long term stability. The process of finding superior catalysts used a screening technique
developed as part of this work, that also identified and eliminated poor performing compositions. From this, future work could ignore inferior compositions and focus on developing a superior catalyst.
CHAPTER 3:  
EXPERIMENTAL

3.1 Library Synthesis

An AJA plasma deposition system with five plasma guns and a carousel of twelve masks has been used to create combinatorial libraries. The system achieved and maintained a vacuum below $10^{-6}$ Torr. Samples up to 2” in diameter were loaded through a complementary load lock. During deposition the flow of two gases and the pressure in the chamber were remotely controlled. Three of the five guns operated on DC power limiting them to the deposition of metals, the other two guns used an RF power source allowing the deposition of both conductive and non conductive materials. The entire system was computer controlled running off operator created programs. The steps in a typical program are shown in table 3.1.1. On the carousel there are typically two sets of masks; one for the generation of discrete combinatorial libraries the other for the calibration of the sputter guns.

The first step of the fabrication process was to make a silicon wafer suitable for a combinatorial library. Batches of 50mm silicon wafers were first RCA cleaned and then annealed at 1100 °C in flowing oxygen to form a 0.3 μm thick oxide layer. A clean oxidized wafer from the batch was loaded into the plasma deposition system and 1000 Å of titanium was deposited through the mask shown in figure 3.1.1 (a) leaving a ring spots and a non symmetrical marker on the periphery of the wafer. The wafer was removed
TABLE 3.1.1

STEPS THAT OCCUR DURING DEPOSITION THROUGH A MASK

<table>
<thead>
<tr>
<th>Step</th>
<th>Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carousel rotates to bring desired mask to the sample station</td>
</tr>
<tr>
<td>2</td>
<td>Sample loads on to the carousel</td>
</tr>
<tr>
<td>3</td>
<td>Carousel rotates aligning the sample above the desired gun</td>
</tr>
<tr>
<td>4</td>
<td>Controlled flow of gas introduced into the chamber (usually 20 sccm Ar)</td>
</tr>
<tr>
<td>5</td>
<td>Turbopump is partially blocked to increase pressure (usually 5 mTorr)</td>
</tr>
<tr>
<td>6</td>
<td>Gun powers up pre-sputtering into a closed shutter</td>
</tr>
<tr>
<td>7</td>
<td>Shutter opens allowing sputtered material to deposit on the sample</td>
</tr>
<tr>
<td>8</td>
<td>After a set time the shutter closes and the gun powers down</td>
</tr>
<tr>
<td>9</td>
<td>Carousel rotates back to sample station and the sample is unloaded</td>
</tr>
<tr>
<td>10</td>
<td>Carousel resets its position ready to bring another mask around if further deposition steps are desired – start at step 1 again</td>
</tr>
</tbody>
</table>

from the plasma deposition system coated with a 2 μm thick layer of 1813 photoresist. The mask depicted in figure 3.1.1 (b) was aligned with the spots and exposed upon the photoresist with a Karl Suss photolithography unit. The wafer was subsequently washed with 913 developer and baked overnight at 90 °C. The wafer was then loaded back into the plasma deposition system and a 2000 Å blanket layer of titanium nitride

![Figure 3.1.1](image)

Figure 3.1.1, Masks used to prepare a wafer for a combinatorial library. (a) sputter deposition alignment spots, (b) photoresist network traces and (c) combinatorial substrate holder mask.
(TiN) was deposited across the wafer’s entire surface. The wafer with photoresist and TiN was then transferred into the combinatorial sample holder that had a special face plate shown in figure 3.1.1 (c). The hexagons defined by the photoresist pattern were aligned with the hexagons in the combinatorial sample holder. The wafer was now ready to build a combinatorial library upon.

The discrete compositions that make up the combinatorial library on the array of hexagonal pads were formed by depositing through six binary shadow masks depicted in figure 3.1.2 (a). The 32 black hexagons in each mask indicate the openings through which material deposition would occur. The holes in the masks were aligned in a geometric pattern above 63 positions on the substrate. The combinations and permutations of overlapping holes is based on a binary masking strategy [267] similar to the scheme reported by Xiang et al. [268]. A well designed program could select mask and target combinations and generate 63 compositionally individual specimens. Typically these masks were used in a sequence that built up 49 unique ternary compositions. This common deposition sequence resulted in reasonable coverage of a ternary phase field. Other special deposition sequences could concentrate more samples around a composition of interest, for example to re-examine part of a ternary system. Outside of the combinatorial pattern were twelve composition pads that were captured with a seventh mask depicted in figure 3.1.2 (b). A fixed reference composition, usually Pt, was deposited at these twelve locations to permit easy comparison between libraries. After deposition, 75 of the 76 hexagonal pads contained multilayer thin films, each one a sample of a specific catalyst composition.
Figure 3.1.2, (a) Six combinatorial shadow masks that each have 32 hexagonal holes, each hole is aligned above the array of hexagonal pads on a 2” wafer. (b) The 12 periphery pads are captured by a 7th shadow mask usually with a control composition like pure Pt.

After the combinatorial library was deposited the wafer was ultrasonically cleaned in acetone and ethanol. This process removed all of the remaining photoresist and left the network of electrical leads and the array of combinatorial library pads. The leads electrically isolated the catalyst members from each other and traced a path between each hexagonal combinatorial member and its respective circular contact pad. After cleaning the wafer was annealed in a furnace that maintained a $10^{-6}$ Torr vacuum. The annealing process consisted of two steps: In the first the wafer was slowly heated up to 550 °C and dwelled for four hours before slowly cooling again. This initiated interdiffusion but primarily helped relieve some of the stresses that developed in the thin films during deposition. In the second step the wafer was pushed from a room temperature atrium into the 900 °C hot zone of the furnace. The wafer held for 5 minutes in the hot zone before being pulled back into the room temperature atrium. Care was taken during the second step such that the movement of the sample did not cause the vacuum to exceed $3 \times 10^{-6}$ Torr. This annealing step completed the interdiffusion of the lamina structure of
the combinatorial members and homogenized them. Interdiffusion has been confirmed by Auger Electron Spectroscopy (AES) on some early libraries and by electrochemical testing some special libraries.

Annealing to interdiffuse the deposited layers could also lead to Si diffusing into the thin film structure and contaminating the compositions. Two diffusion barriers slowed the migration of Si into the film; the first was the 0.3 μm thick SiO₂ layer thermally grown on the wafer before any processing. The second was the patterned, inert TiN base that has also been recognized as a diffusion barrier [269-271]. AES analysis has confirmed that the surface remained free of Si or Ti after annealing.

After annealing a final photoresist coating was applied that covered the network of TiN traces but left the hexagonal combinatorial pads and the contact points exposed. A composite micrograph image of an example library is shown in figure 3.1.3. The gold titanium nitride traces run from the periphery (where the blue oxidized silicon wafer is also visible) under the brown photoresist coating to the multi-colored hexagonal combinatorial library members.

Figure 3.1.3, Example combinatorial library that shows the circular contact points, network traces and array of hexagonal combinatorial library pads. The silicon wafer has a diameter of ~ 50 mm.
3.2 Electrochemical Characterization

Electrochemical testing was performed with a commercial multielectrode potentiostatic system (Scribner Associates Model 900B Multichannel Microelectrode Analyzer (MMA)) in conjunction with a specially designed electrochemical cell. This system controlled the potential and measured the respective currents from the 76 combinatorial library members. A cutaway schematic drawing of the cell is shown in figure 3.2.1. Leads run from the MMA to a ring assembly of gold pogo probes (Everett Charles Inc.) that are pressed down on the matching ring of circular TiN contact pads. A 38 mm diameter glass cylinder and silicone o-ring press down on the wafer, separating the catalyst library pads and the electrolyte from the contact pads. A plastic lid with a Teflon gasket (not shown in figure 3.2.1) screws down on the assembly and fixes the entire cell in place. Once the wafer, pogo pins, glass cylinder and Pt coated Nb counter

Figure 3.2.1, Schematic drawing of the assembled electrochemical cell. Note that a simple 16 member library is shown for clarity.
electrode (that runs completely around the periphery of the cell) were assembled, the interior of the cell was triple rinsed with 18 milli-q water and then filled with 40 mL 0.5 M H$_2$SO$_4$ (made from 96.6% pure H$_2$SO$_4$, Fisher Scientific). A type J stainless steel thermocouple, calomel reference electrode (Cole-Palmer Inc.) and type C air stone (Ace Glass Inc.) were inserted into the lid and suspended in the electrolyte. The counter electrode and the junction of the reference electrode were 17 mm above the wafer, while the thermocouple tip was ~ 2 mm from the wafer surface.

Extensive characterization of the cell design was performed prior to the reported experiments. For example, measurements were made on special libraries with the same composition at every location. With these libraries it was found that the electrolyte and contact lead resistances were negligible. Ternary libraries were examined only after verifying the reliability of the data.

This screening test is only designed to recognize promising compositions. This is a simple test that compares methanol oxidation properties in an environment that avoids complex fuel cell testing issues mentioned in the previous literature survey. Confirmation that these compositions are good DMFC catalysts would be a separate work based on powder synthesis and different testing techniques. A thin film composition that gives a strong response to the following short term tests may excel in a fuel cell. If it does, then further analysis should be carried out on high surface area powders with an equivalent composition to confirm this. These thin film libraries were only intended to quickly identify compositions that may work well in a fuel cell.
3.2.1 Methanol Oxidation Testing

For the methanol oxidation reaction dry nitrogen was passed through the air stone until a stable open circuit potential was achieved, which usually required at least 10 minutes. The cell potential at all of the catalyst pads was then set and held at -0.2 V-SCE for an additional 10 minutes before testing. Testing began by acquiring cyclic voltammograms at room temperature between -0.3 V-SCE and + 1.1 V-SCE, ramping at 10 mV/sec, until a stable curve was reproducibly measured from all of the catalyst pads. This usually required 10 – 20 cycles. A sample cyclic voltammetry curve in clean electrolyte is shown in figure 3.2.2 (a). Note that the reported current density is based on the geometric area of the sample pad (0.026 cm²) and not the active area.

![Current Density vs Potential](image)

Figure 3.2.2, Sample cyclic voltammetry curves recorded from a Pt₉₂Ru₈ catalyst pad that show the current-potential response in (a) clean electrolyte and (b) with 0.5 M methanol. Scan rate was 10 mVs⁻¹ in 0.5 M H₂SO₄ cycled 10 times at 20 °C.

For screening of methanol oxidation activity, the potential was again held at -0.2 V-SCE while 0.82 mL methanol (99.9% pure, Fisher Scientific, equivalent to 0.5 M in 40 mL solution) was introduced into the electrolyte. The potential was maintained at -0.2
V-SCE for a further 270 seconds to allow the solution to homogenize and the measured currents to stabilize. Following the introduction of the methanol, the potential was again swept from -0.3 to 1.1 V-SCE at 10 mVs⁻¹ until reasonably stable curves were again measured from all of the catalyst pads. Figure 3.2.2 (b) shows the cyclic voltammogram of an active catalyst with the methanol oxidation reaction beginning at 0.3 V-SCE and peaking at 0.58 V-SCE. Constructions that show how the two important data points taken are from a curve are shown in figure 3.2.3. The onset potential was defined at the intercept of the curve with a specific current density, usually $5 \times 10^{-5}$ Acm⁻². The current density at the peak of the methanol reaction is fairly self explanatory. For the methanol oxidation reaction an improved catalyst would have a lower onset potential but maintain a strong peak current density.

Figure 3.2.3, Example sweep from a methanol oxidation cyclic voltammetry curve with constructions that show the peak current density and the potential defined at the onset of the methanol oxidation reaction.

The current density measured at the peak of methanol oxidation was used because it was found to have a good correlation to a chronoamperic test, but is subject to less error.
The problem with the peak methanol oxidation current density, or the chronoamperic test, is that the current density is a function of surface composition and electrochemical area. It is possible for a thin film sample surface to partially corrode and change into a structure that has more active sites available (increased electrochemical area). This could lead to a false positive, that is a catalyst with average properties and a roughened surface may be misidentified as superior and worthy of further investigation. Worse still, a catalyst that is roughened by corrosive dissolution would have questionable long term stability if used in a fuel cell.

The active area of platinum surfaces is usually determined by examining a monolayer adsorption during a potential sweep [54, 170, 272-275]). This technique is based on the principle that as the potential is swept in the negative direction a monolayer of protons are adsorbed onto every active Pt Site. The total current drawn during this adsorption is directly proportional to the number of active Pt sites, or the electrochemical area. Unfortunately our MMA system is not well suited for this method. Firstly we have a fairly strong acid as an electrolyte, so when the potential was swept in the negative direction the current generated during the hydrogen reduction reaction quickly exceeded the measurable limits of the MMA. Also going past the potential limit of -0.4 V-SCE has been noted to accelerate the deterioration of the films. As such the potential is scanned to -0.3 V-SCE and we can only assume that the hydrogen reduction reaction only proceeds far enough to form a partial monolayer. The current drawn during the desorption of this partial hydrogen layer cannot be confidently used to estimate the electrochemical surface area.
It would be possible to alter the electrolyte and scan rate to optimize the test for hydrogen desorption, but this would reduce the quality of methanol oxidation data. In addition, there is another fundamental flaw. The hydrogen desorption integral defines the area as the number of Pt sites that adsorb hydrogen. The hydrogen reduction/adsorption/desorption reactions are very sensitive to the surface with even different planar faces of Pt recording very different curves [27]. All non Pt metals have an overpotential for the hydrogen reduction reaction. Mercury for example will not reduce hydrogen until an overpotential of almost 0.9 V. If the electrochemical area of a Hg electrode was determined by the normal hydrogen integral technique it would be 0. Now if that same electrode oxidizes 1 atom of methanol then the electroactive current density would be infinite. Though the example of mercury is slightly extreme, it bears repeating that all non Pt metals have an overpotential for the hydrogen reduction reaction. The parameters necessary to determine the proper hydrogen desorption test would have to be determined for each specific composition. The same test could not be confidently applied to all the samples simultaneously; each one would need to be examined individually, thus losing the combinatorial advantage [55]. Other methods to determine roughness, such as DEMS [254] or STM [56] are also not compatible with the present combinatorial testing approach.

There is a way to side step this issue by examining a property that is not proportional to the electrochemical area, the onset potential. The onset potential is normally calculated by determining the potential that corresponded to 10% of the peak current density. Figure 3.2.4 shows sample curves from Pt\textsubscript{12}Ru\textsubscript{60}Co\textsubscript{38} (black) and Pt\textsubscript{25}Ru\textsubscript{75}Co\textsubscript{0} (red). Also marked are the 10% peak current density with a horizontal blue
line for Pt$_{12}$Ru$_{60}$Co$_{38}$ and a horizontal purple line for Pt$_{25}$Ru$_{75}$Co$_{0}$. The intersection of the blue and black lines is the onset potential for Pt$_{12}$Ru$_{60}$Co$_{38}$ and similarly the intersection of the red and purple lines defines the onset potential for Pt$_{25}$Ru$_{75}$Co$_{0}$. This method has failed in this case because the standardization of the curve (subtracting the clean electrolyte scan from the scan with methanol) does not perfectly eliminate the double layer charging current. At $E = 0.1$ V-SCE the standardized current drawn should be 0 but instead it is $+ 2 \times 10^{-5}$ Acm$^{-2}$. This did not matter when we were measuring peak methanol current densities, $3 \times 10^{-3}$ Acm$^{-2} \pm 2 \times 10^{-5}$ Acm$^{-2}$ ($\sim 0.5\%$) was an acceptable error. But the process of determining the onset potential requires more accuracy. Unfortunately the shape variety amongst different cyclovoltammetry curves doesn’t facilitate an automated method to smooth and reduce this error. A different method was necessary.

![Figure 3.2.4](image.png)

Figure 3.2.4, Examples of the methanol oxidation peak and the calculation of $V_{onset}$ for Pt$_{12}$Ru$_{60}$Co$_{38}$ (black) and Pt$_{25}$Ru$_{75}$Co$_{0}$ (red)

Defining the onset based on a single current density for all the curves achieves more realistic data. Selecting a current density that is well above the baseline variation,
5 x 10^{-5} \text{Acm}^{-2} intersects the various curves as shown in figure 3.2.5. By using the one line there is a clear advantage in that curves with a strong peak current density will have a low error. Unfortunately peaks with a low current density will have a much higher error. This is apparent in the curves to the right of figure 3 that are intercepted close to their FWHM. Furthermore some especially weak peaks will not even intercept the defined current density line and will thus fail to register an onset potential. This is not necessarily bad. The error in these poor performing catalysts will always be positive. That is the measured onset potential in weak peaks will always be higher than true. This will essentially stretch the bottom of the scale of poor performing compositions but the overall ranking will remain unchanged. It should be noted that all compositions that were so weak they failed to intercept 5 x 10^{-5} \text{Acm}^{-2} were plotted with the same value as the worst performing composition (usually E = \sim 0.47 \text{V-SCE}).

Figure 3.2.5, Methanol oxidation curves from one library intercepted by a line at 5 \times 10^{-5} \text{Acm}^{-2} to define the methanol oxidation onset potential.
Compositions were therefore ranked based on two parameters, their onset potentials and peak methanol oxidation current densities. The onset potential was examined because it is not strongly influenced by any change in the surface roughness. Previous testing we have performed showed there was a strong correlation between the peak current density and the current density observed after a five minute chronoamperic experiment at 0.5 V-SCE. This corroborates reports of a reasonable connection between short term performance measured in an electrochemical cell environment and results from longer steady state tests [108, 116, 157, 194, 256] or from actual fuel cells [106, 113]. A longer chronoamperic experiment would measure the current under steady state conditions and would theoretically be closer to fuel cell operating conditions. Unfortunately the decay of the current with time increases the possibility of systematic errors misleading the results. The peak methanol oxidation current densities have less systematic error than the chronoamperic currents making them the better measurement to judge relative catalyst performances.

3.2.2 Oxygen Reduction Testing

The method to screen catalyst compositions for oxygen reduction was similar to the methanol oxidation screening test with the following alterations. Instead of nitrogen, extra dry oxygen was bubbled through the air stone. The cell was maintained at open circuit potential (OCP ~ 0.6 V-SCE) for 30 min while oxygen saturated the solution and the current stabilized. The potential was swept at 10 mV/s from OCP down to -0.3 V-SCE, up to 1.1 V-SCE and back to OCP. During the downward scan the oxygen reduction reaction would start at 0.5 – 0.6 V-SCE and quickly become diffusion
Figure 3.2.6, Example potential sweep at 10 mV/s in oxygen saturated 0.5 M H₂SO₄ at 20 °C that shows how the onset potential was calculated limited in the unstirred solution. A sample curve for pure Pt with an onset of 0.57 V-SCE and the constructions used to define the onset potential are shown in figure 3.2.6.

The performances of compositions were ranked based on the potential defined by the onset of the oxygen reduction reaction. The potential that defined the onset of the oxygen reduction reaction was calculated automatically using the intercept of two straight lines that bound the curve. The first line was calculated at 0.8 V-SCE and accounts for any deviations from the base current density due to charging or transient oxide species. The second line is defined at the point of inflection when the oxygen reduction reaction is increasing at its maximum rate. As can be seen in figure 3.2.6, this method underestimates the point where the current starts to flow for the oxygen reduction reaction. However, it was found that the underestimation was consistent for any composition in a library, so if all samples are considered relative to Pt then an accurate comparison could
be made between all libraries. To facilitate this every library had several Pt samples that were used to standardize the comparison.

It was possible for compositions to have a weak response and a poorly defined point of inflection that in turn was miscalculated as a high onset potential. To stop these compositions misleading the results a limit was set such that unless the current density at the point of inflection was more negative than $-1 \times 10^{-4}$ A cm$^{-2}$ the results would be disregarded. Compositions that failed to achieve a strong enough current density were plotted with the same onset potential as the worst measurable member of that library; usually ~0.4 V-SCE.

### 3.3 Additional Characterization

#### 3.3.1 Microscopy

Immediately before and after electrochemical testing every combinatorial library was photographed (Olympus BX-61 microscope with an Olympus DP70 camera). These images were used to determine the corrosion resistance of the thin film catalysts. Table 3.3.1 details the scoring criteria used to judge each library member, with 5 being perfect corrosion resistance and 0 being complete failure. Some example micrographs from a Pt-Ru-W library that correspond to the different levels of degradation are shown in figure 3.3.1.

Durable samples that were not perturbed by their immersion in 0.5 M H$_2$SO$_4$ retained their shiny metallic sheen as seen in figure 3.3.1 (a). Discoloration usually occurred when an oxide species dominated the surface and varied dramatically depending on composition, for example chromium rich samples turned blue and nickel rich samples
### TABLE 3.3.1

**CORROSION RESISTANCE SCORES**

<table>
<thead>
<tr>
<th>No.</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>No difference before and after testing</td>
<td>Fig. 3.3.1(a)</td>
</tr>
<tr>
<td>4</td>
<td>Some discoloration</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Spalled, ragged patches flaking off</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Perimeter is shrinking</td>
<td>Fig. 3.3.1(b)</td>
</tr>
<tr>
<td>1</td>
<td>Spalled and shrinking</td>
<td>Fig. 3.3.1(c)</td>
</tr>
<tr>
<td>0</td>
<td>Vanished, no trace of the catalyst remains</td>
<td>Fig. 3.3.1(d)</td>
</tr>
</tbody>
</table>

turned green. Spalled samples would lose patches of material as it flaked and peeled away. Spalling may have been accelerated by the presence of H₂SO₄ but was generally considered to be caused by fabrication stresses placed on the thin film. A shrinking perimeter as seen in figure 3.3.1 (b) was indicative of outright corrosion. The manner in which the perimeter of the sample dissolved implied that the TiN beneath the catalyst

![Figure 3.3.1](image)

Figure 3.3.1, The different degrees of corrosion afflicting Pt-Ru-W test pads after four days testing. (a) unaffected, (b) partial corrosion, (c) partial corrosion and spalling, (d) complete failure.
galvanically accelerated the corrosion. Samples that failed in this manner were considered unsuitable for the more demanding fuel cell environment. Samples that had multiple symptoms after testing were given the lowest applicable score; for example, the sample in figure 3.3.1 (c) discolored, shrank and spalled and was given a score of 1. Samples that were completely removed after testing (figure 3.3.1 (d)) may have failed from either extreme corrosion or severe spalling. Either way catalysts that scored 0 were excluded from further consideration or testing.

Several tests were performed on each library, some at elevated temperatures. The higher temperatures were achieved with a foil-type resistive heater (Minco) positioned under the wafer. The cell was deaerated and the potential was held at -0.2 V SCE for 10 minutes before any heating procedure started. The total time to complete a test at one temperature was approximately 4 hours. An average library would follow a schedule that first focused on methanol oxidation properties with five runs (at 20, 40, 20, 60 and 20 °C again). After the methanol oxidation testing, a library’s oxygen reduction properties would be tested with one run at room temperature. Thus the average library was immersed in 0.5 M H₂SO₄ for approximately 24 hours. It should be noted that if testing was paused for a significant period of time (i.e. over night) then the library would be immersed in deaerated 18 milli-Q water.

3.3.2 X-Ray Diffraction

Structure characterization was performed with a modified Scintag X1 advanced diffraction system. Capillary optics (XOS Inc.) focused the Cu-Kα radiation to a spot size of 5 mm² at the specimen surface. A homemade computer controlled stage moved the specimen, sequentially aligning library compositions with the beam. Typically a
theta-theta scan was performed on each catalyst sample from $2\theta = 32^\circ$ to $46^\circ$ at $0.01 \text{ °s}^{-1}$. With these specifications an entire library was characterized in a total of 33 hours. X-Ray diffraction was done before and after annealing, confirming that heat treatment altered the initially laminate structure.

3.3.3 Atomic Force Microscopy

The surface topography of selected catalyst pads was characterized using a Digital Instruments Multimode III atomic force microscope. The measurements sampled 1 $\mu\text{m}^2$ in air with the AFM operating in the tapping mode.

3.4 Data Analysis

Data from the electrochemical measurements was processed in Excel using visual basic. A copy of the macros that were used to organize the raw data and to plot the ternary diagrams is presented in Appendix A.
4.1 Sputter Rates

Controlling the thickness of deposited layers was critical, so careful attention was made to calibrate the deposition rate. A special set of eight masks was designed to deposit material onto a special substrate that held a set of quartz crystal oscillators. Each quartz crystal received a deposition from a particular target under specific conditions (e.g. varying power, time, background pressure, etc). The oscillation frequency of each quartz crystal was determined ex-situ in a home-made apparatus. The mass of the deposited material was calculated from the measured frequency change with the Saurbrey equation [276]. From this a calibration curve for thickness vs. deposition time was established. A picture of the quartz crystal sample holder and an example of the curve for deposition of Cu are shown in figure 4.1.1.

The exact sputter rate of a target would change with time but general parameters can be described. Typical deposition conditions were 75 W of direct power 20 sccm of argon and 5 mTorr background pressure. Under these conditions different metals would deposit at rates between 0.5 – 3.0 Ås\(^{-1}\). The deposition of a combinatorial library required the sequential deposition of different elements in alternating layers. The deposition was timed so that each layer contained 30 x 10\(^{-9}\) mol\(\text{cm}^{-2}\) of the appropriate element. This gave deposition times of 10 to 50 seconds for each inter layer.
Depending on the composition a combinatorial library sample would consist of ~8 layers and be 200 Å thick. Wear of the target altered the sputter rate and required the guns to be recalibrated frequently.

Figure 4.1.1, Calibration curve establishing the film thickness versus deposition time for Cu. Inset, 5 cm diameter quartz crystal sample holder with seven quartz crystals.

4.2 X-Ray Diffraction

The annealing regime promoted interdiffusion with each composition changing from a laminate nanostructure to a homogenous alloy. The electrochemical
performance of the Pt-Ru-Co system led to a more in depth appraisal of the system’s structure. Data from this system is presented here as an example of the common structural information that was gleaned from x-ray analysis of other systems. Figures 4.2.1 (a) and (c) depict the spectra of representative Pt-Co and Ru-Co binary compounds respectively. TiN (111) and (200) peaks from the substrate were present in all of the scans at $2\theta = 36.58^\circ$ and $42.59^\circ$. The strong relative intensity for the majority of samples made the TiN peaks barely discernable from the background. However Co rich samples had a relatively low intensity, so in these samples the TiN peaks are quite prominent and labeled appropriately in figures 4.2.1 (a) and (c).

![Figure 4.2.1, (a) X-ray diffraction scans of the binary combinations of Pt and Co. (b) Ternary plot with the $2\theta$ distortion of the strongest peaks Pt(111), Ru(002) and Co(002). (c) X-ray diffraction scans of the binary combinations of Ru and Co.](image)

The $2\theta$ peak shift across the entire phase field is depicted in figure 4.2.1 (b). Each circle in figure 4.2.1 (b) indicates the $2\theta$ measured for that specific composition with the dark to light shading indicative of the value from $40.0^\circ$ to $44.2^\circ$ respectively.
The background has been shaded using an averaging function to highlight the trend. The majority of samples appear to have formed alloys with no sign of the intermediate compounds CoPt₃ or CoPt. The ternary representation in figure 4.2.1 (b) shows that the change in 2θ is linearly proportional to the composition, consistent with expectations from Vegard’s law for a perfectly homogenous solid solution. Between Pt₂₀Ru₈₀Co₀ and Pt₇₇Ru₂₃Co₀ there were some signs of a Pt structure coexisting with Ru and Pt-Ru alloy phases. This is partially consistent with the binary phase diagram [277] that predicts a two phase region between Pt₃₈Ru₆₂ and Pt₂₀Ru₈₀. Note that it is only the 2θ of the alloy phase that is replotted in figure 4.2.1 (b).

A spectrum for a pure Pt sample can be seen at the top of figure 4.2.1 (a) with only the (111) peak discernable at 2θ = 40.048° which was higher than the expected value (Pt_pdf(111) 2θ = 39.764°). The simplest explanation for this 0.28° shift would be thermal strain compressing the lattice. Pt and TiN have incompatible coefficients of thermal expansion (α_{TiN} = 9.4 x 10⁻⁶ °C⁻¹, α_{Pt} = 8.8 x 10⁻⁶ °C⁻¹) [278, 279] so during cooling the Pt thin film would be gradually compressed. The pure ruthenium samples also had a compressed lattice (2θ_{exp} = 42.249°, 2θ_{pdf} = 42.153°), but in contrast the pure cobalt samples had a stretched lattice (2θ_{exp} = 44.236°, 2θ_{pdf} = 44.763°). These results are also consistent with thermal strain as the coefficients of thermal expansion varied appropriately (α_{Co} = 13 x 10⁻⁶ °C⁻¹) > (α_{TiN} = 9.4 x 10⁻⁶ °C⁻¹) > (α_{Ru} = 6.4 x 10⁻⁶ °C⁻¹) [278, 279].

It is believed that this strain would not affect the electrochemical characteristics of the surface. The strain is strongest at the interface between the two dissimilar materials and weakest at the surface. The top few surface layers of atoms are responsible for any
catalytic effect and these are the least effected by the strain. Thus measurements on these surfaces should still be consistent with measurements on bulk alloy systems.

4.3 Atomic Force Microscopy

The strong intensity of a single peak raised another concern, texturing. The x-ray diffraction patterns all show a single peak but none of the other peaks that would be expected from a polycrystalline bulk sample. The thin films were probably textured, that is they had a structure that was consistent with a single crystallographic orientation being aligned with the substrate. This meant that the surface consisted of a single oriented plane and would not be representative of a polycrystalline bulk sample.

Atomic Force Microscopy (AFM) was performed on the surface of bare TiN with the results shown in figure 4.3.1 (a). The TiN then had a typical catalyst layer (300 Å of Pt-Ru) deposited on it and was scanned again as shown in figure 4.3.1 (b). The roughness of the TiN is quite pronounced, with hill like grains that crest ~200 Å above the valley like grain boundaries. The average grain size of the bare TiN is

![Figure 4.3.1](image)

Figure 4.3.1, (a) AFM scan of unannealed TiN. Average grain size is approximately 400 – 1000 Å (40 -100 nm). (b) AFM scan of unannealed TiN coated by 300 Å of Pt-Ru. Large Grains are still approximately 1000 Å but small grains less than 500 Å are no longer discernable.
approximately 400 - 1000 Å across. When 300 Å of catalyst was deposited onto this surface the roughness was not significantly different with a crest to valley distance still ~ 200 Å. The catalyst film appeared to have “filled in” around the smaller grains such that nothing less than 500 Å wide was discernable.

This does show that the surface of the catalyst was not a textured single orientated plane. A single plane would require that the roughness of its surface not vary more than 2 Å for it to present a homogenous surface structure. There is so much variation in the height of the film it would be impossible to maintain a single crystal structure upon the surface. Although the x-ray diffraction shows that the bulk of the film is of a single orientation, an equilibrium surface would have multiple orientations to follow the rough contours of the substrate. A surface that exposes multiple orientations would be representative of the surface of a polycrystalline sample.

4.4 Library Design

The earliest library design as shown in figure 4.4.1 (a) had excellent symmetry with identical leads and consistent positioning of the samples around the periphery of the cell. Unfortunately to pack the samples into the symmetric pattern the pad size would have been reduced to 1.5 mm² and the nearest neighbor distance would have been 0.3 mm. The smaller size of the pad would reduce the signal generated during electrochemical experiments. But the pad size was of little concern compared to the small nearest neighbor distance. During deposition of the catalyst a small amount of material lands outside of the sample pad. The flux can travel as far as 0.6 mm away from the edge of the mask [135]. This would lead to contamination between neighboring
Figure 4.4.1, Initial mask designs using the (a) symmetric daisy ring pattern and (b) hexagonal spread pattern.

libraries. The design shown in figure 4.4.1 (b), although it is not nearly as symmetric as the design shown in figure 4.4.1 (a) it has much better spacing between the samples. Unfortunately the design in figure 4.4.1 (b) had issues with aligning the perimeter contact points with the pogo probes. The final library design (figure 3.1.1 (b)) combined the hexagonal layout of figure 4.4.1 (b) with the circular contact pads of figure 4.4.1 (a).

The hexagonal pattern created a new issue. The geometry and natural resistance of the TiN leads meant that the distance between the pogo pin and the contact electrode was affecting the potentiostat’s performance. Basic measurements showed that the resistance along the shortest leads was 40 Ω and this linearly increased to a resistance of 200 Ω for the longest leads. Figure 4.4.2 shows a clear example of how the resistance increased with the length of the lead. The multiarray potentiostat measured extremely small changes in current and was affected by this variance in resistance.

The solution was to increase the thickness of the titanium leads. The resistances shown in figure 4.4.2 were for leads that were 500 Å thick. Increasing the thickness
increased the cross sectional area and lowered the resistance of all the leads. There was still a difference between the long and the short leads. To examine the severity of the difference a special library that had pure Pt on every hexagonal pad and 2000 Å TiN base was tested. The results showed that the resistance difference between long and short leads was now negligible. Unfortunately there were upper limits to the thickness of TiN that could be used, films thicker than 2000 Å would tend to spall and peel off the silicon wafer.

The next concern was geometry of the electrochemical cell. The pads in the centre of the library would be closer to the reference electrode than the pads at the periphery. To establish whether this was an issue another special all-Pt library was used. Cyclic voltammetry tests were performed with the reference electrode close to the wafer (~2mm above the surface) and further away (~30 mm above the surface) but still in the solution. The performance of each catalyst pad was consistent regardless of the reference electrodes position. A similar experiment that varied the counter electrodes position also saw consistent performance from the catalysts. This was verification that
the conductivity of the 0.5 M H₂SO₄ electrolyte was high enough such that resistance drop in the solution was negligible.

4.5 Electrochemical Consistency

A set of experiments were devised in an effort to further understand the annealing of a multilayer nanostructure. Perfect annealing would create a homogenous structure and it would not matter what the last deposited “green” layer was. However the last layer, or capping layer, deposited will be present on the surface in excess in a sample that was not fully annealed. To see if the capping layer influenced surface activity a special library was fabricated. It consisted of 64 members that all had the same composition Pt₅₀Co₅₀; 32 of which were capped with Pt and the remainder capped with Co.

The common annealing schedule used for most libraries previously was 550 °C for 4 hours in a 10⁻⁷ Torr Vacuum. This temperature and time was established from SECM work. Higher temperature and longer annealing times had been performed on identical SECM libraries with no changes occurring to the activity maps. It was concluded that this regime was enough to bring the surface of the SECM library to equilibrium and further annealing merely increased the risk of TiN failure.

The standard temperature was tested first with poor results. There was a significant difference between the Pt₅₀Co₅₀ that was capped in Pt and the library members that were capped with cobalt as shown in figure 4.4.3 (a). This implied that the regime though suitable for SECM samples was inadequate for MMA samples. In retrospect the SECM crosses spread out during deposition and simultaneously thin. MMA samples do
not thin during deposition and would have interlayer thicknesses at least double that of SECM samples.

Figure 4.4.3, (a) Current generated from identical library members with different structures, annealed, 500 °C for 4 hours. (b) Consistent performance achieved after additional flash anneal, 700 °C for 20 minutes.

Further work examined whether an additional flash anneal could homogenize the surface without dilapidating the titanium nitride was performed. After annealing at 550 °C for 4 hours an additional rapid anneal for 20 minutes at 700 °C was administered. The rapid anneal did promote a homogenous surface regardless of the capping layer as shown in figure 4.4.3 (b). It was simultaneously determined that 300 Å was the minimum stack height required to achieve a consistent result. Samples below this thickness either performed poorly (40% lower currents than the average) or erratically with up to 30% variance between identical structures.

Though the rapid anneal did give a consistent result for the Pt50Co50 composition, the current density was 50% lower than the average current density of samples that were not flash annealed. This may have been from the low-temperature annealed samples having their compositions skewed into the more catalytically active regions. A more
likely explanation is that the surface of the flash annealed sample was fundamentally changed into a less active form, possibly from the promotion of a “dead” structure (like an oxide) or from removal of some active sites by partial atomic smoothing. Further annealing observations performed concurrently with regular catalyst library testing determined that the optimum annealing schedule was 4 hours at 550 °C followed by 5 minutes at 900 °C.

The deposition and annealing regime is similar to that used in the work of Johnson and co-workers [280-282] Johnson investigated the formation of intermetallic compounds from thin film precursors. For example they determined that for the Mo-Si system there is a critical interlayer thickness. Interlayers that were thinner than a critical thickness formed a homogenous glassy matrix after a low temperature anneal and then crystallized with a quick high temperature anneal. In contrast when films were deposited thicker than this critical thickness the process became diffusion limited with undesirable intermediates forming. The x-ray diffraction results described in section 4.4.2 indicate that there were no intermediates formed in any of our systems implying that the interlayer thickness was below the critical thickness determined by Johnson (~40 Å).
CHAPTER 5:
RESULTS AND DISCUSSION

5.1 Platinum – Ruthenium

5.1.1 Pt-Ru: Methanol Oxidation Reaction

Pt₅₀Ru₅₀ is the most commonly used direct methanol fuel cell anode catalyst composition. The first step in the development of the screening process was to establish the performance of Pt-Ru compositions and thus set the bar for future testing. Unfortunately initial methanol oxidation testing of Pt-Ru libraries failed to show the expected strong performance from any of the compositions. Figure 5.1.1 shows the

Figure 5.1.1, Typical peak methanol oxidation current densities of a Pt-Ru library with no pretreatment. Measurements taken during the 10th potential sweep in nitrogen saturated 0.5 M H₂SO₄, 0.5 M CH₃OH at 10 mV/s and 20 °C.
typical performance exhibited by early libraries of Pt-Ru compositions. The current density was measured at the peak of the methanol oxidation reaction. Where there were multiple data points for the same composition the average was plotted with the standard deviation used to define the error bars.

The majority of compositions failed to respond with the exception of a few Pt rich compositions (Pt\textsubscript{100}Ru\textsubscript{0}, Pt\textsubscript{83}Ru\textsubscript{17} and Pt\textsubscript{80}Ru\textsubscript{20}). The current densities of these compositions were poor and statistically insignificant from the non-responsive samples. Many variables were considered as being responsible for the poor performance but it was not until testing was performed at higher temperatures that some positive results were seen. Testing at higher temperatures “conditioned” some samples, resulting in improved peak current densities that remained regardless of the subsequent testing temperature. A library that had been previously tested at 60 °C was retested at room temperature with the resultant current density at the peak of the methanol oxidation reaction plotted in figure 5.1.2. Again, where there were multiple data points for the same composition the average was displayed with error bars determined by the standard deviation. The line in figure 5.1.2 is a Gaussian fit that highlights the trend and helps define an optimum composition at ~ Pt\textsubscript{90}Ru\textsubscript{10}. The trend of near zero activity continues from Pt\textsubscript{50}Ru\textsubscript{50} all the way to pure Ru. The previous unconditioned current densities from figure 5.1.1 have been replotted in figure 5.1.2 to highlight the dramatic improvement.

Our study found the optimum composition at all temperatures was Pt\textsubscript{90}Ru\textsubscript{10} ± 5 at\%, in agreement with most of the “flat surface” studies [23, 122, 163, 164]. Our results and the other flat surface studies conflict with the Pt\textsubscript{50}Ru\textsubscript{50} optimum defined by
Figure 5.1.2, Peak methanol oxidation current densities of a Pt-Ru library before (■) and after conditioning (●). Measurements taken during the 10th potential sweep in nitrogen saturated 0.5 M H₂SO₄, 0.5 M CH₃OH at 10 mV/s and 20 °C.

studies on carbon supported high surface area nanoparticle catalysts [161, 162]. As mentioned in the literature survey, the discrepancy between the two different studies remains an open question. The trend we see was identical to the results of Strasser et al. which is the only study that had similar experimental conditions [219]. They found that Pt₈₇Ru₁₃ outperformed pure Pt, but beyond this composition the activity decreased proportionally to the increasing Ru content. In our study the peak current density generated by Pt₉₀Ru₁₀ was 3.5 Acm⁻² ± 0.2 Acm⁻², but as discussed in the literature survey, many variables affect current measurements that makes comparison difficult. Even when the experiments were similar, the 3.5 Acm⁻² value was still higher than some groups (2 × 10⁻³ Acm⁻² [163], 0.7 × 10⁻³ Acm⁻² [23]) and lower than others (40 × 10⁻³ Acm⁻² [122]).
The potential defined at the onset of the methanol oxidation reaction also showed an interesting trend within the Pt-Ru system as shown in figure 5.1.3. The compositions with strong current densities (Pt$_{100}$Ru$_0$ to Pt$_{80}$Ru$_{20}$), also had a low onset potential of $\sim$ 0.33 V-SCE. This was followed by a steep increase in the MOR onset potential to $\sim$0.43 V-SCE for compositions with more Ru than Pt$_{70}$Ru$_{30}$. The highest recorded onset potential of 0.48 V-SCE was not surprisingly for pure Ru. Pt$_{71}$Ru$_{29}$ recoded the lowest (or best) onset potential of 0.29 V-SCE, but this was not statistically different from the other Pt rich compositions. The MOR onset potential of pure Pt was a little higher than the $\sim$0.26 V-SCE that is commonly reported by other flat surface studies [23, 163, 283]. The onset potential of the best Pt-Ru catalyst was even harder to compare to literature, with reports of compositions between Pt$_{80}$Ru$_{20}$ and Pt$_{50}$Ru$_{50}$ achieving onset potentials

![Graph](image_url)

Figure 5.1.3, Onset potential of the methanol oxidation reaction for the Pt-Ru system after conditioning. Measurements taken during the 10$^{th}$ potential sweep in nitrogen saturated 0.5 M H$_2$SO$_4$, 0.5 M CH$_3$OH at 10 mV/s and 20 °C.
0.02 – 0.18 V-SCE [21, 122, 283-286]. It was mentioned in the method description that the technique used to define the onset potential underestimated values in a manner that was consistent between libraries. But even with under-estimation the 11 mV difference achieved between Pt$_{29}$Ru$_{71}$ and pure Pt was not as high as the ~200 mV improvement seen from a good Pt-Ru catalyst [61].

There are several possible explanations for the discrepancy between our results and literature reports. The strong current densities in figure 5.1.2 show that Ru has improved the methanol oxidation of Pt in our system. Despite this activity the lack of change from the onset potential implies that the mechanism and rate determining step has not changed. At low potentials the RDS can be either the adsorption of methanol or the oxidation of CO$_{\text{ads}}$. Experiments with different concentrations of methanol saw no difference to the onset potential implying that the oxidation of CO$_{\text{ads}}$ was the RDS. Ru should have been adsorbing H$_2$O and oxidizing CO$_{\text{ads}}$ as per the bifunctional method at ~0.1 V-SCE, but this did not happen. The Ru was probably in a form that hindered its normal performance, existing either as an oxide phase or buried below an enriched Pt skin. Either way, the strong current densities match what has been reported, including some reports that have seen strong performances without major onset potential shifts [23, 163, 283].

One group that saw a similar performances was Page et al. [176]. They reported an onset potential of 0.385 V-SCE at 25 °C for a commercially available carbon membrane electrode (CME) with 0.5 mgcm$^{-2}$ pure Pt catalyst. Page et al. [176] also tested a CME with 0.5 mgcm$^{-2}$ Pt$_{50}$Ru$_{50}$ catalyst that had an onset potential of 0.300 V-SCE for the methanol oxidation reaction at 25 °C. This was 85 mV lower than the
pure Pt CME they tested under the same conditions. The onset potential of the Pt-Ru matches the performance of our best composition, Pt$_{71}$Ru$_{29}$. This is slightly at odds with our results where pure Pt outperformed Pt$_{50}$Ru$_{50}$, but there were differences between this work and that of Page et al. Most notably the surface structure of our thin film catalyst samples and their commercial nanoparticle catalysts would be different. Another issue would be the inclusion of carbon in the nanoparticles composition which, with later testing, we found to be an important variable.

Our work also contradicts the results of other groups. Hughes and Miles [55] found that the Pt$_{70}$Ru$_{30}$ could achieve similar current densities to pure Pt catalysts at potentials 60 mV lower, but we found no significant difference between pure Pt and Pt$_{70}$Ru$_{30}$. Choi et al. [108] saw identical performances from Pt$_{50}$Ru$_{50}$ and Pt$_{82}$Ru$_{18}$ but we observed Pt$_{50}$Ru$_{50}$ to be poorer than Pt$_{82}$Ru$_{18}$. Green and Kucernak [170] found the optimum composition was Pt$_{40}$Ru$_{60}$ $\pm$ 10 At% which was again no where near similar to our findings. Unfortunately there are so many factors like particle size, distribution, annealing or oxidation state that can improve or hinder any composition’s performance that comparison is very difficult [113]. The absence of these factors is a strength of our thin film synthesis route.

The performance improvement that occurred after elevated temperature testing seen in this work is not fully understood. Proton exchange fuel cells are generally conditioned before testing but this is principally to ensure the membranes are hydrated [287]. There have been some reports of the conditioning process altering the catalyst, usually with ruthenium oxide being reduced [288]. There are many possible processes that could occur in our thin film libraries at the elevated temperatures. There could be a
corrosion effect [218], an acid induced surface modification [27], reduction [288] or formation [166] of an oxide or the removal of stubborn organic contaminants [27]. The exact mechanism remains an open question.

5.1.2 Pt-Ru: Oxygen Reduction Reaction

The catalyst commonly used on the cathodes of fuel cells is pure Pt. There has been no reported benefit doping Ru into Pt in regards to the oxygen reduction reaction. Ru has only ever been reported as being present in the cathode of a fuel cell after it undesirably diffused there from the anode [184, 185]. These studies consider Ru in the cathode as one of the irreversible degradations mechanisms that diminishes the power output of a fuel cell. In general, a clean Pt cathode has always outperforms a clean Pt-Ru cathode. Our study confirmed this, as shown in figure 5.1.4. Again, where multiple measurements existed for the same composition, the average was plotted with error bars defined by the standard deviation. The Pt-Ru phase diagram [277] shows the regions of one and two phase stability, which are indicated with black arrows and dotted lines in Figure 5.1.4. The average onset potential for the oxygen reduction reaction of pure Pt was $0.568 \pm 0.008$ V-SCE. Theoretically an onset potential of $1.229$ V-SHE ($1.055$ V-SCE) [289] should be possible for a perfect catalyst. Pt has a high overpotential for this reaction; so the majority of researchers [154, 195, 290] report an onset of $0.58 \pm 0.02$ V-SCE for polycrystalline Pt in various solutions. The onset potential we measured agrees well with the other reports and provides confidence in the data generated by our system.
Figure 5.1.4, Average onset potential of Pt-Ru compositions measured during the 10th sweep at 10 mV/s in oxygen saturated 0.5 M H₂SO₄ at 20 °C. Dotted vertical lines indicate boundaries between equilibrium phases.

Increasing the concentration of Ru only worsened the catalyst's performance. From Pt₉₀Ru₁₀ up to Pt₄₀Ru₆₀ the onset potential remained fairly consistent at 0.54 V-SCE. The x-ray diffraction analysis found that these compositions were single phase solid solutions with the Pt fcc structure, consistent with the Pt-Ru phase diagram. The onset potential of compositions with less Pt than Pt₃₈Ru₆₂ dropped dramatically until finally settling at the pure Ru value of 0.46 V-SCE. This is 30 mV lower than the 0.49 V-SCE reported by Inoue, [291] but their electrolyte was 0.1 M HClO₄. X-Ray measurements revealed that compositions in the poorly performing Ru-rich region had a structure that was either partly or totally made up of the Ru phase. Ru was detrimental to the oxygen reduction reaction which agrees with the early work of Appleby [292] and has not been
disputed since. Indeed Ru would only be present on the cathode of a DMFC that had suffered from an undesired Ru migration.

5.2 Platinum – Ruthenium – Tungsten

5.2.1 Pt-Ru-W: Methanol Oxidation Reaction

The first test on an unconditioned Pt-Ru-W library showed a weak response from a wide range of compositions. The best performing composition was \( \text{Pt}_{25}\text{Ru}_0\text{W}_{75} \) with a current density of \( 5.7 \times 10^{-4} \text{ Acm}^{-2} \). The majority of the other compositions had a current density less than \( 2 \times 10^{-4} \text{ Acm}^{-2} \) with the exception of the W-Ru compositions which showed no response. Figures 5.3.1 (c) and 5.3.2 (c) in the next section show the performance of unconditioned Pt-Ru-W system compared to the Pt-Ru-WC system. Testing at 40 °C and 60 °C conditioned the Pt-Ru-W library and resulted in a strong response from a few compositions. Figure 5.2.1 (a) shows the peak methanol oxidation current density for a conditioned library tested again at 20 °C. Extremely high

Figure 5.2.1, (a) Peak current densities and (b) onset potentials of methanol oxidation for the Pt-Ru-W system. Measurements taken during the 10\textsuperscript{th} forward scan at 10 mV/s in 0.5 M \( \text{H}_2\text{SO}_4 \), 0.5 M methanol at 20 °C. Black rings in (a) indicate compositions that lost more than 50% of their surface area during testing.
conversion occurred in a narrow composition range, with the best composition Pt$_{44}$Ru$_{12}$W$_{44}$ achieving a current density of 1.9 x 10$^{-3}$ A cm$^{-2}$. This is 1.5 x more than the average Pt catalyst current density of 1.2 x 10$^{-3}$ A cm$^{-2}$. Note that to cover the ternary field, a library with reasonably wide steps between compositions was required. For this reason Pt$_{90}$Ru$_{10}$ could not be represented and the ternary performance is compared to either pure Pt or Pt$_{80}$Ru$_{20}$.

The best performing composition observed in the present work, Pt$_{44}$Ru$_{12}$W$_{44}$, doesn’t agree with the optimum compositions found by other groups. Holleck et al. [46] reported Pt$_{53}$Ru$_{32}$W$_{15}$ was better than pure Pt, while Tanaka et al. [256] found Pt$_{65}$Ru$_{20}$W$_{15}$ was the optimum Pt-Ru-W catalyst. Umeda, et al. [255] found Pt$_{65}$Ru$_{20}$W$_{15}$ to be far superior to pure Pt, while Jusys and Schmidt [254] found the activity of Pt$_{54}$Ru$_{39}$W$_{7}$ similar to the PtRu produced commercially by E-TEK. Goetz [253] found that the optimum composition was Pt$_{28}$Ru$_{28}$W$_{44}$ and in other studies, our group [151] determined by SECM testing that Pt$_{30}$Ru$_{35}$W$_{35}$ was the optimum composition to oxidize hydrogen in the presence of carbon monoxide. A summary figure of the optimum composition reported by other groups and optimum composition determined by this study is shown in figure 5.2.2.

Preferential dissolution of tungsten ions creating a rougher surface and misleadingly high current densities have also been reported [90]. To distinguish whether the superior performance of the active Pt-Ru-W compositions was due roughening, the onset potential was also considered. The most active composition in our libraries also had a 225 mV lower onset potential than the best Pt-Ru binary composition as shown in figure 5.2.1 (b). This implies that the improved performance
was due to an altered reaction mechanism and not merely a change in electroactive area. This does not mean that all tungsten alloys are perfectly stable. Some pads showed signs of deterioration after testing; those that had less than 50% surface area after testing are indicated with black rings in figure 5.2.1 (a). Obviously, tungsten rich compositions were unstable in the acidic environment. The mechanism of corrosion could have been galvanic, spalling due to a thin film stress issue, or simply electrochemical dissolution at the extreme test potentials. It is possible that that these types of corrosion would not be an issue in a true fuel cell environment, but their poor performance has eliminated these compositions from further investigation. The complete deterioration of samples with more than 75% tungsten partially confirms that corrosion affects tungsten alloys. On the other hand, the onset potential of Pt\textsubscript{44}Ru\textsubscript{12}W\textsubscript{44} was substantially lower, and that is a parameter that would not be unduly affected by a changed electroactive area.

The methanol oxidation reaction was also examined with oxygen saturated electrolyte (figure 5.2.3). Again Pt\textsubscript{44}Ru\textsubscript{12}W\textsubscript{44} was the best performing composition and achieved an even higher current density of $3.9 \times 10^{-3}$ Acm\textsuperscript{-2}. The compositions that neighbored Pt\textsubscript{44}Ru\textsubscript{12}W\textsubscript{44} that performed quite well with nitrogen were now close to inert
for the methanol oxidation reaction. These compositions would preferentially adsorb and dissociate oxygen rather than methanol. The performance of Pt$_{44}$Ru$_{12}$W$_{44}$ however was not diminished but enhanced by the presence of O$_2$. The most likely explanation would be that it was a stoichiometric oxide (probably WO$_3$) that plays a beneficial role in the reaction, and up until this test the tungsten had less oxygen than the stoichiometric optimum. Pt$_{44}$Ru$_{12}$W$_{44}$ has behaved like an ideal MRFC anode catalyst.

Figure 5.2.3, Peak current densities of methanol oxidation for the Pt-Ru-W system. Measurements taken during the 10$^{th}$ forward scan at 10 mV/s in oxygen saturated 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 °C.

5.2.2 Pt-Ru-W: Oxygen Reduction Reaction

There were no compositions in the Pt-Ru-W system that excelled at promoting the oxygen reduction reaction as shown in figure 5.2.4 (a). In the absence of methanol Pt$_{44}$Ru$_{12}$W$_{44}$ had the highest onset potential of 0.59 V-SCE, but this was merely 43 mV higher than the average Pt onset potential of 0.55 V-SCE. With the exception of the Ru-W compositions that had no Pt, most compositions responded favorably, with onsets
higher than 0.50 V. Despite this good average performance, overall there was no
exceptional fuel cell cathode catalyst worthy of further study in the Pt-Ru-W system.
This agrees with the literature reports [141, 154, 257, 258] that there is little difference
between the ORR activity of roughened pure Pt and Pt-W compositions.

Figure 5.2.4, Onset potential of oxygen reduction for the Pt-Ru-W system.
Measurements taken during the 10th backward scan at 10 mV/s in oxygen saturated 0.5 M
H2SO4 that was (a) initially clean and then with (b) 0.5 M methanol at 20 °C.

During the ORR test with methanol poison there was a dramatic change in
performance as shown in figure 5.2.4 (b). In the presence of methanol the W rich
compositions were dramatically poisoned. This is not to say that they were all inert, as
figure 5.2.3 shows that Pt44Ru12W44 had a very strong anodic current density as it
oxidized methanol and ignored the oxygen. The best composition was pure Pt, with an
onset of 0.53 V-SCE. The next best compositions with onset potentials of ~0.50 V-SCE
all had ~ 40% W with varying concentrations of Pt and Ru. This study found no
methanol resistant cathode catalyst in the Pt-Ru-W system that outperformed Pt. This
was not unsurprising, as there has been no literature suggesting that Pt-Ru-W
compositions are poison resistant.
5.3 Platinum – Ruthenium – Tungsten Carbide

5.3.1 Pt-Ru-WC: Methanol Oxidation Reaction

The Pt-Ru-WC system initially behaved in a similar manner to the Pt-Ru-W system. Figure 5.3.1 shows the initial MOR peak current densities for (a) the unconditioned Pt-Ru-WC and (c) the unconditioned Pt-Ru-W systems. The best performing composition from these two systems were the tungsten rich Pt_{25}Ru_{0}WC_{75} and Pt_{25}Ru_{0}W_{75}. The best unconditioned Pt-Ru-W composition (Pt_{75}Ru_{0}W_{25}) generated a current density of $1.1 \times 10^{-3} \text{Acm}^{-2}$ which is almost 2 times the $7.6 \times 10^{-4} \text{Acm}^{-2}$ peak current density of Pt_{25}Ru_{0}WC_{75} generated. The optimum composition from the Pt-Ru-W system changed after the library was conditioned, but Pt_{25}Ru_{0}WC_{75} remained the best composition after conditioning as shown in figure 5.3.1 (b). This is probably more of an indication of WC’s durability as Pt_{25}Ru_{0}W_{75} corroded away with the conditioning process. Although Pt_{25}Ru_{0}WC_{75} did not corrode with conditioning, its performance did diminish, generating a current density of $1.4 \times 10^{-4} \text{Acm}^{-2}$, $1/5^{th}$ of its unconditioned performance. Another observation to take from this data is that the active compositions had very low current densities and very low Pt content. This implies that

![Figure 5.3.1](image)

Figure 5.3.1, Peak current densities of methanol oxidation measured during the 10th forward scan at 10 mV/s in 0.5 M H_2SO_4, 0.5 M methanol at 20 °C. Pt-Ru-WC system (a) before and (b) after conditioning compared to a (c) Pt-Ru-W library before conditioning.
the Pt sites were still the locations where the reaction was occurring. A Pt site that was surrounded by WC could oxidize methanol at a lower potential but the presence of so much WC on the surface reduced the number of active Pt sites, reduced the active area and reduced the peak current density. These results contradict literature that tends to paint a bleak picture for Pt-WC MOR catalysts [7, 259, 260]. It wasn’t great but Pt$_{25}$WC$_{75}$ did out perform the average Pt response.

Figures 5.3.2 (a) and (c) show a surprisingly poor onset potential for Pt$_{25}$Ru$_{0}$WC$_{75}$ and Pt$_{25}$Ru$_{0}$W$_{75}$. The best unconditioned composition based on onset potential was Pt$_{13}$Ru$_{51}$WC$_{36}$ at 0.35 V-SCE which was a good deal poorer than the unconditioned Pt$_{17}$Ru$_{17}$W$_{66}$ with an MOR onset of 0.17 V-SCE. The carbon that appears to be stabilizing the tungsten also appears to be removing some of its beneficial catalytic properties. After conditioning as shown in figure 5.3.2 (b), Pt$_{12}$Ru$_{44}$WC$_{44}$ had the lowest onset potential of 0.31 V-SCE, but was still worse than the optimum Pt-Ru-W composition.

![Figure 5.3.2](image)

Figure 5.3.2, Onset potential for the methanol oxidation reaction measured during the 10$^\text{th}$ forward scan at 10 mV/s in 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 $^\circ$C. Pt-Ru-WC system (a) before and (b) after conditioning compared to a (c) Pt-Ru-W library before conditioning.
As the temperature increased the center of the Pt-Ru-WC system came alive. Figure 5.3.3 shows the (a) peak current densities and (b) onset potentials for the Pt-Ru-WC system at 60 °C. Now Pt_{30}Ru_{30}WC_{40} showed the best current density of $6.5 \times 10^{-4}$ A cm$^{-2}$, while Pt$_{12}$Ru$_{44}$WC$_{44}$ has the best onset potential of 0.16 V-SCE. Unfortunately the onset potential is a function of temperature and the excellent 0.16 V-SCE is not honestly comparable to measurements made at room temperature. The promising result from this is that at higher temperatures the composition with the best current density has moved closer to the composition with the best onset potential. If testing to even higher temperatures were possible then maybe a composition around Pt$_{30}$Ru$_{40}$WC$_{40}$ would achieve the best of both parameters. Unfortunately the overall performance of the Pt-Ru-WC system was poorer than the Pt-Ru-W system eliminating it from further testing.

Figure 5.3.3, (a) Peak current densities and (b) onset potentials of methanol oxidation for the Pt-Ru-WC system. Measurements taken during the 10$^{th}$ forward scan at 10 mV/s in 0.5 M H$_2$SO$_4$, 0.5 M methanol at 60 °C.
Completely corroded samples are marked with black rings in figure 5.3.3 (a) and define an unstable composition region. In general, the corrosion resistance of the Pt-Ru-WC system was fairly similar to the Pt-Ru-W system, with both the Ru-WC and Ru-W compositions failing. This implied that the WC was no longer stoichiometric after deposition and susceptible to acid attack. The only difference being that the compositions $\text{Pt}_{75}\text{Ru}_{0}\text{WC}_{25}$ and $\text{Pt}_{10}\text{Ru}_{45}\text{WC}_{45}$ survived and the Pt-Ru-W equivalents corroded. This shows that the presence of carbon did partially stabilize $\text{Pt}_{75}\text{Ru}_{0}\text{WC}_{25}$ and $\text{Pt}_{10}\text{Ru}_{45}\text{WC}_{45}$.

In summary, the Pt-Ru-WC showed some promise; $\text{Pt}_{25}\text{Ru}_{0}\text{WC}_{75}$ was the optimum composition at 20 °C and $\text{Pt}_{30}\text{Ru}_{30}\text{WC}_{40}$ was the optimum composition at 60 °C. Unfortunately there are no ternary Pt-Ru-WC catalysts reported in literature to compare with these compositions, but one would suspect the overall best would be approximately $\text{Pt}_{30}\text{Ru}_{10}\text{WC}_{60}$. The onset potentials and current densities from the Pt-Ru-WC alloys were better than the pure Pt standard but were worse than the results from similar Pt-Ru-W libraries. The presence of carbon appeared to improve tungsten’s poor corrosion resistance, but simultaneously reduced its overall MOR catalytic activity.

5.3.2 Pt-Ru-WC: Oxygen Reduction Reaction

The Pt-Ru-WC system was not tested for catalytic activity in the oxygen reduction reaction.
5.4 Platinum – Ruthenium – Tantalum/Tungsten Carbide

5.4.1 Pt-Ru-WC/Ta: Methanol Oxidation Reaction

Tungsten carbide was initially examined as a corrosion resistant form of tungsten. The addition of carbon only marginally improved the corrosion resistance and failed to significantly increase the methanol oxidation performance (at 20 °C Pt75Ru0W25 = 1.1 x 10⁻³ Acm⁻² and Pt75Ru0WC25 = 7.6 x 10⁻⁴ Acm⁻²). Reports that Ta could enhance WC [263] were followed up to see if an alloy of WC/Ta and Ru with Pt could improve the catalysts properties even further. The WC/Ta alloy was made by depositing from separate WC and Ta guns, with the ratio of Ta to WC consistently kept at 2:1.

The addition of tantalum to tungsten carbide did improve the corrosion resistance. There were still a few compositions that completely corroded, with nothing but bare TiN visible after testing. Otherwise only compositions with little to no Pt showed partial corrosion, with the edges of the hexagonal catalyst pads receding 10-20%. This is in stark contrast to the undoped tungsten carbide catalyst, where all of the WC-Ru binary compositions were completely corroded after testing.

The presence of tantalum did not improve the methanol oxidation peak current density. Initially the best composition was Pt₄₃Ru₅₇ with a current density of 4.2 × 10⁻⁵ Acm⁻² and an onset potential of 0.29 V-SCE as shown in figure 5.4.1 (a). It should be noted that the performance of this catalyst and the other compositions in the library was quite poor in comparison to other libraries. Usually unconditioned Pt would achieve a current density of ~1 × 10⁻⁴ Acm⁻² but on this occasion none of the Pt standards even gave that response. After testing at higher temperatures conditioned the library, the Pt-WC/Ta compositions became more active. The best conditioned composition was
Figure 5.4.1, Peak methanol oxidation current densities of Pt-Ru-WC/Ta system (a) before and (b) after conditioning with nitrogen in the electrolyte and (c) with oxygen in the electrolyte. Measured during the 10th forward scan at 10 mV/s in 0.5 M H₂SO₄, 0.5 M methanol at 20 °C.

Pt⁵₀(WCTa)₅₀ with a current density of 3.3 x 10⁻⁴ Acm⁻² at the peak of the methanol oxidation reaction as shown in figure 5.4.1 (b), but this was still not better than the 7.6 x 10⁻⁴ Acm⁻² achieved by Pt⁷₅WC₂₅.

Testing of the methanol oxidation activity in the presence of oxygen did not show much change. Surprisingly, the best composition was Pt⁵₇(WCTa)₄₃ which had a better current density when oxygen was present (Iₚk₋O₂ = 3.8 x 10⁻⁴ Acm⁻², Iₚk₋N₂ = 2.6 x 10⁻⁴ Acm⁻²) which was unusual considering most compositions perform worse in the presence of oxygen. The onset potential for Pt⁵₇(WCTa)₄₃ was 0.40 V-SCE regardless of whether there was oxygen present or not. While interesting, this behavior is still not exceptional with the better compositions from the Pt-Ru-W system having MOR onset potentials 230 mV lower and generating ten times the peak current density. Tantalum may have improved the corrosion resistance but failed to enhance the methanol oxidation properties of the Pt-WC alloy.
5.4.2 Pt-Ru-WC/Ta: Oxygen Reduction Reaction

There were no strong oxygen reduction Pt-Ru-WCTa catalyst compositions. The most promising methanol oxidizing catalysts, ~Pt50(WCTa)50, were also the best oxygen reduction catalysts. Both Pt43(WCTa)57 and Pt57(WCTa)43 had ORR onset potentials of 0.57 V-SCE in clean electrolyte as shown in figure 5.4.2 (a). This was 43 mV better than the average Pt response. But, as mentioned in the methanol oxidation section, the average Pt performance of this library was below average. The performance of the best Pt-Ru-WCTa compositions was still worse than the best Pt-Ru-W composition which recorded an onset potential 23 mV higher than Pt43(WCTa)57. In the presence of methanol as shown in figure 5.4.2 (b), the compositions about Pt50(WCTa)50 failed to reduce oxygen, anodically oxidizing methanol instead. There were no good Pt-Ru-WC/Ta oxygen reducing catalysts in the presence of methanol; just a wide spread of mediocre compositions. The best poison resistant oxygen reducing compositions were Pt43Ru14(WCTa)43 and Pt20Ru60(WCTa)20 with unimpressive 0.54 V-SCE onset

![Diagram](image.png)

Figure 5.4.2, Onset potential of oxygen reduction for the Pt-Ru-WC/Ta system. Measurements taken during the 10th backward scan at 10 mV/s in oxygen saturated 0.5 M H2SO4 that was (a) initially clean and then with (b) 0.5 M methanol at 20 °C.
potentials. The wide disparity between the two optimum catalysts and the lack of any
trend across figure 5.4.2 (b) is an indication that there was no good methanol resistant
oxxygen reducing catalyst in the Pt-Ru-WCTa system.

5.5 Platinum – Tantalum – Tungsten Carbide

5.5.1 Pt-Ta-WC: Methanol Oxidation Reaction

Tantalum is recognized as a material that can stabilize and improve the corrosion
resistance of tungsten carbide as well as enhance catalytic activity [262]. Libraries that
covered the Pt-Ta-WC phase field were constructed and tested in the hope that the Ta
would further stabilize the more active Pt-WC compositions. The initial results from the
un-conditioned catalysts at 20 °C were promising with weak responses from binary Pt-Ta
and Pt-WC compositions but no real response from ternary Pt-Ta-WC compositions as
shown in figure 5.5.1 (a). The best performing catalyst was Pt50Ta50 with an onset
potential of 0.35 V-SCE and a peak current density of $8.9 \times 10^{-5}$ Acm$^{-2}$. This was more

Figure 5.5.1, Peak current densities of methanol oxidation for the Pt-Ta-WC system (a)
before and (b) after conditioning by testing at 40 °C. Current densities measured during
the 10$^{{th}$ forward scan at 10 mV/s in 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 °C.
than 10 times the response from the unconditioned Pt. After testing at higher temperatures conditioned the library; the performance of Pt-Ta compositions degraded and Pt-WC compositions improved as shown in figure 5.5.1 (b). The best conditioned composition was Pt$_{43}$WC$_{57}$, with a current density of $3.6 \times 10^{-3}$ Acm$^{-2}$ more than 10 times more than the average Pt response of $3.3 \times 10^{-4}$ Acm$^{-2}$. The performance of conditioned tantalum compositions was disappointing with no strong response from the majority of the library. Tantalum rich compositions appear to be of no benefit to the methanol oxidation reaction.

The results from the unconditioned library corroborate the results of Ueda et al. [263] who reported an increase in the oxidation of CO for Pt$_{66}$(TaOx)$_{33}$. Though a good CO oxidation catalyst is not necessarily a good methanol oxidation catalyst, on this occasion unconditioned Pt$_{80}$Ta$_{20}$, Pt$_{75}$Ta$_{25}$, Pt$_{50}$Ta$_{50}$ performance does confirm some enhanced catalytic properties from Pt-Ta alloys. It should be noted that the unconditioned performance of the Pt-Ta alloys was poor in comparison to other systems like Pt-Ru-W or Pt-Ru-Co.

5.5.2 Pt-Ta-WC: Oxygen Reduction Reaction

The Pt-Ta-WC system was not tested for oxygen reduction activity.

5.6 Platinum – Ruthenium – Carbon

5.6.1 Pt-Ru-C: Methanol Oxidation Reaction

Early work on the sputtering of carbon was not promising. The sputter system was capable of depositing carbon films at $1/10^{th}$ the rate of any metallic material. The
deposited films were non conductive, that is completely electrically insulating even after annealing. It was considered that deposited carbon films would be completely detrimental to the catalyst surface. To confirm these suspicions a sample Pt-Ru-C library was constructed.

The carbon rich samples for this library behaved slightly differently to the carbon rich samples from the Pt-Fe-C (section 5.19), in that the Pt-Ru-C samples spalled slightly, losing some of their surface area and exposing some TiN. X-ray diffraction did not reveal anything different, with the only indication of carbon coming from a broad hump at low 2-theta. Regardless, the carbon rich samples were catalytically inactive, failing to oxidize methanol as shown in figure 5.6.1. In fact, initially the majority of the phase diagram was inactive with the exception of the Pt rich Pt-Ru compositions that recorded weak responses \(2 - 5 \times 10^{-4} \text{ Acm}^{-2}\). Unlike the Pt-Ru-W or Pt-Ru-Co systems, there were no compositions that had a strong response before the library was conditioned.

Figure 5.6.1, (a) Peak current densities and (b) onset potentials of methanol oxidation for the Pt-Ru-C system. Current densities measured during the 10\textsuperscript{th} forward scan at 10 mV/s in 0.5 M H\textsubscript{2}SO\textsubscript{4}, 0.5 M methanol at 20 °C.
The most interesting result can be seen with the initial onset potentials as shown in figure 5.6.1 (b), where a low onset (~0.30 V-SCE) is apparent for compositions about Pt$_{80}$Ru$_{20}$ and Pt$_{37}$Ru$_{50}$C$_{13}$ but not for carbon free compositions around Pt$_{50}$Ru$_{50}$. This was of interest because it seems to shed light upon a fundamental discrepancy that has plagued Pt-Ru catalysis research. There is extensive literature [23, 122, 163, 164] on flat metallic Pt-Ru surfaces stating that ~Pt$_{80}$Ru$_{20}$ is the optimum methanol oxidation composition. These flat surface studies usually show a sub-standard performance from compositions about Pt$_{50}$Ru$_{50}$. In contrast there is extensive literature [161, 162] on Pt-Ru high surface area nanoparticles that tend to report an optimum Pt$_{50}$Ru$_{50}$ composition and sub-standard results from compositions about Pt$_{80}$Ru$_{20}$. The difference has usually been written off as a quirk of nanoparticle structure that caused the difference. Something that has never before been considered is that the nanoparticle’s carbon support plays a role.

Presented in figure 5.6.1 is the first evidence that carbon can alter the properties of a Pt-Ru catalyst. Clearly the optimum carbon free composition is ~Pt$_{80}$Ru$_{20}$ and the optimum composition with carbon is ~Pt$_{44}$C$_{12}$Ru$_{44}$. Unfortunately, this study cannot determine whether the positive affect is from carbon in the bulk or carbon on the surface. Surface carbon is more likely to be present on carbon supported nanoparticles than inter-diffused into the bulk of the nanoparticles. Assuming that a nanoparticle has carbon located on 10% of its surface sites then we have a simple explanation for the disparity between surface studies and carbon supported nanoparticle studies. Unfortunately this was not the end of the story as there were some quirks that don’t quite fit the pattern. When trying to reproduce the result with a special library that focused on
compositions in this area there were some disparities as shown in figure 5.6.2. Again Pt$_{50}$Ru$_{20}$ had the strongest current density but now the compositions about Pt$_{43}$Ru$_{43}$C$_{14}$ have current densities even worse than the previous mediocre performance. The onset potentials also don’t immediately corroborate the previous library’s data. The best onset potentials were shown by the compositions around Pt$_{70}$Ru$_{20}$C$_{10}$. Although Pt$_{43}$Ru$_{43}$C$_{14}$ has an onset potential 50 mV better than Pt$_{50}$Ru$_{50}$, the difference was not as dramatic as seen in the previous library. In this second library the optimum composition was Pt$_{50}$Ru$_{20}$ and carbon does not appear to have a strong influence on methanol oxidation catalysis.

Figure 5.6.2, (a) Peak current densities and (b) onset potentials of methanol oxidation for the second Pt-Ru-C library. Current densities measured during the 10th forward scan at 10 mV/s in 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 ºC.

Further testing after the library was conditioned didn’t truly resolve this issue as shown in figure 5.6.3. Now the optimum composition in both current density and onset potential had shifted to compositions with less Pt; Pt$_{33}$Ru$_{50}$C$_{17}$ and Pt$_{37}$Ru$_{27}$C$_{36}$. But now neither library showed a comparable performance from the Pt rich, carbon free Pt-Ru alloys. This result still agrees with the nanoparticle studies and implies that the
optimum Pt-Ru have a surface decorated with more than just 10% carbon. Unfortunately these results contradict the previous flat surface studies, including our own previous work, where it would be expected to see a strong performance from Pt – Pt_{75}Ru_{25} and a poor performance from compositions with more Ru than Pt_{50}Ru_{50}. Further work to resolve this issue is part of a manuscript in preparation.

Figure 5.6.3, (a, c) Peak current densities and (b, d) onset potentials of methanol oxidation for the (c, d) first and (a, b) second Pt-Ru-C libraries after conditioning. Current densities measured during the 10th forward scan at 10 mV/s in 0.5 M H_{2}SO_{4}, 0.5 M methanol at 20 °C.

5.6.2 Pt-Ru-C: Oxygen Reduction Reaction

The oxygen reduction was fairly consistent across the Pt-Ru-C system; figure 5.6.4, with the same consistent performance from both libraries. The best performing composition in clean electrolyte as shown in figure 5.6.4 (a) was Pt_{50}C_{50} with an onset potential of 0.54 V-SCE, but this was only 22 mV better than the average Pt performance.
The only compositions that did not perform well were the Ru-C compositions, with the exception of Ru\textsubscript{50}C\textsubscript{50}, but its response (current density) was very weak. The similar performances of the active catalysts imply that they have developed an enriched Pt skin. This is not uncommon and has been reported to occur from annealing [163] or electrochemical testing [195]. Other elements below a Pt skin have been reported to alter platinum’s structure and change its catalytic properties. Ru and C below a layer of Pt seem to have very little effect on Pt’s oxygen reduction properties. For these catalysts the oxygen reduction reaction seems only affected by the number of vacant Pt sites and not the state they are in.

![Figure 5.6.4](image)

Figure 5.6.4, Onset potential of oxygen reduction for the Pt-Ru-C system measured during the 10\textsuperscript{th} backward scan at 10 mV/s and 20 °C in (a) initially clean oxygen saturated 0.5 M H\textsubscript{2}SO\textsubscript{4} and (b) then with 0.5 M methanol.

The introduction of 0.5 M methanol as shown in figure 5.6.4 (b) increased the ORR overpotential for all of the compositions. The best composition was Pt\textsubscript{60}Ru\textsubscript{20}C\textsubscript{20} with an onset potential of 0.52 V-SCE, which was only 24 mV better than the average Pt response. Pt\textsubscript{50}C\textsubscript{50} and the compositions around Pt\textsubscript{44}Ru\textsubscript{12}C\textsubscript{44} had what seems like a poor response. These compositions were ignoring the oxygen and continuing to oxidize the
methanol like an anode. This is further evidence that carbon can have a strong effect on a Pt-Ru catalyst’s interaction with methanol.

5.7 Platinum – Ruthenium – Chromium

5.7.1 Pt-Ru-Cr: Methanol Oxidation Reaction

Libraries from the Pt-Ru-Cr system were tested in the usual manner with no compositions exhibiting an outstanding performance. The initial test of the “unconditioned” library saw fairly limited performance from all of the compositions with Pt_{60}Ru_{20}Cr_{20} generating the highest MOR peak current density of $6.41 \times 10^{-4}$ Acm$^{-2}$ as shown in figure 5.7.1 (a). This was twice the current density of the best Pt-Ru binary alloy, but the standard compositions were expected to do poorly at this initial stage. After activation the optimum composition remained Pt_{60}Ru_{20}Cr_{20}, but with a stronger current density of $1.3 \times 10^{-3}$ Acm$^{-2}$ as shown in figure 5.7.1 (b). The best Pt-Ru composition, pure Pt in this case, also improved with a current density that was approximately half that of Pt_{60}Ru_{20}Cr_{20}. The onset potential for Pt_{60}Ru_{20}Cr_{20} was $\sim 0.35$ V-SCE in both the unconditioned and conditioned tests, the same onset potential as the pure Pt samples.

Pt_{60}Ru_{20}Cr_{20} had the same onset potential as Pt, but had a higher current density. This could have been from Cr being preferentially leached and leaving a rougher pure Pt surface. But if that was the only effect then a better performance would have been expected from Pt_{75}Cr_{25}. This would imply that Cr was improving the kinetics of the rate determining step. The RDS in this potential regime is believed to principally be the oxidation of the CO$_{ads}$, usually via a non-Pt group adsorbing and dissociating water. There are many possible ways that Cr could have increased the reaction rate of such a
Figure 5.7.1, Peak current densities of methanol oxidation for the Pt-Ru-Cr system (a) before and (b) after conditioning by testing at 60 °C. Current densities measured during the 10th forward scan at 10 mV/s in 0.5 M H₂SO₄, 0.5 M methanol at 20 °C. (c) Visually assessed corrosion scores for the Pt-Ru-Cr system.

broad RDS. It could have electronically altered and improved the H₂O dissociation reaction on Ru sites. Secondly, it could have been providing a different site that opened up a new reaction pathway in the H₂O dissociation reaction. Or it may have merely improved the surface diffusion of CO_ads or O_ads groups such that separated Pt and Ru sites could be more effective. Either way the change that Cr caused on the Pt-Ru catalyst surface did not dramatically improve its efficiency.

These results agree with the few studies that have examined methanol oxidation on Pt-Cr surfaces. Choi et al. [190] reported that Pt₅₀Cr₅₀/C performed better than an equivalent pure Pt/C catalyst. Figure 5.7.1 (a) confirms that Pt₅₀Cr₅₀ can perform better than Pt. Unfortunately the activity was not maintained after conditioning. The performance after the library was conditioned agrees with Yang et al. [221], who reported that Pt₇₅Cr₂₅, Pt₆₆Cr₃₃ and Pt₅₀Cr₅₀ had a worse methanol oxidation performance than pure Pt.

The Pt-Ru samples that contained Cr were more corrosion resistant than libraries that contained Co or W as shown in figure 5.7.1 (c). Cr has potential as a stabilizer additive. For example if an active unstable ternary composition were found in another
system, then possibly with the addition of Cr the corrosion resistance could be improved without compromising the catalytic performance.

5.7.2 Pt-Ru-Cr: Oxygen Reduction Reaction

The testing of the Pt-Ru-Cr samples under cathode conditions, i.e. in the presence of oxygen, showed some interesting results. The best anode catalyst Pt$_{60}$Ru$_{20}$Cr$_{20}$ was also the best cathode catalyst with an onset potential of 0.57 V-SCE as shown in figure 5.7.2 (a). This was only 6 mV better than the average Pt performance and thus not a real standout catalyst. When the library was retested in the presence of methanol all of the compositions dropped to lower onset potentials as shown in figure 5.7.2 (b). In the presence of methanol the best oxygen reduction catalyst was Pt$_{50}$Cr$_{50}$ with an onset potential 8 mV higher than Pt. This performance was not unique to Pt$_{50}$Cr$_{50}$; 19 other compositions across the library recorded an onset potential within 6 mV of the 0.52 V-SCE maximum.

Figure 5.7.2, Oxygen reduction reaction onset potential for the Pt-Ru-Cr system measured during the 10$^{th}$ downward sweep at 10 mV/s and 20 °C in (a) clean oxygen saturated 0.5 M H$_2$SO$_4$ and then with (b) 0.5 M methanol.
The literature on Pt-Cr oxygen reducing catalysts is divided into two groups. The first group (the “Cr-Acts”) believe that Cr takes an active role and improves the kinetics of the oxygen reduction reaction on Pt [77, 213, 222, 223, 225]. The second group (the “Leachers”) believes that Cr is preferentially leached leaving a high surface area “porous sponge” of Pt that can achieve higher current densities but does not alter the reaction mechanism [79, 224, 293]. Figure 5.7.2 (a) shows that Pt and all of the Pt-Cr alloys have the same oxygen reduction onset potential, in agreement with the Leachers. However figure 5.7.2 (b) shows that Cr is of a benefit to the ORR when there is a poison present. If methanol crossover or another type of contamination was an issue in the experiments of the Cr-Acts then they would observe an enhancement from Pt-Cr alloys. Thus the results from this study cannot rule out either of the conflicting mechanisms offered in the literature on the Pt-Cr system.

Two groups [221, 294] have considered the oxygen reduction reaction for Pt-Cr catalysts in the presence and absence of methanol. Koffi et al. [294] examined the powder forms of Pt rich, Pt-Cr alloys with a rotating disk electrode rig. They found that Pt and Pt$_{90}$Cr$_{10}$ oxidized methanol instead of reducing oxygen but Pt$_{80}$Cr$_{20}$ and Pt$_{70}$Cr$_{30}$ reduced oxygen and ignored the methanol. Methanol tolerant oxygen reduction activity was also observed by Yang et al. [221] for alloys with an even higher Cr content. In the absence of methanol Pt$_{75}$Cr$_{25}$, Pt$_{66}$Cr$_{33}$ and Pt$_{50}$Cr$_{50}$ performed the same as Pt, but with methanol present the alloys had an onset potential 200 mV higher than Pt. This was much higher than the 10 mV observed in our study, but it should be noted that the Pt standard that Yang et al. [221] used for comparison, had an anodic methanol oxidation peak that severely stunted the oxygen onset potential.
5.8 Platinum – Ruthenium - Nickel

5.8.1 Pt-Ru-Ni: Methanol Oxidation Reaction

The Pt-Ru-Ni system oxidized methanol favorably with the low Pt compositions Pt_{12}Ru_{44}Ni_{44}, Pt_{14}Ru_{43}Ni_{43}, Pt_{17}Ru_{17}Ni_{66} and Pt_{20}Ni_{80} consistently performing well before and after conditioning as shown in figure 5.8.1 (a) and (b). These active compositions generated a higher current density than the maximum measurable current density (3.8 \times 10^{-3} \text{Acm}^{-2}). After activation pure Pt recorded a similarly high current density but its onset potential (0.33 V-SCE) was 120 mV higher than the ~0.21 V-SCE onset potential recorded by the active alloys. The best alloy Pt_{13}Ru_{50}Ni_{37} had an onset potential of 0.19 V-SCE a full 160 mV lower than Pt.

Figure 5.8.1, Peak current densities of methanol oxidation for the Pt-Ru-Ni system (a) before and (b) after conditioning by testing at 60 °C. Current densities measured during the 10^{th} forward scan at 10 mV/s in 0.5 M H_2SO_4, 0.5 M methanol at 20 °C. The green star represents the composition reported by [234]. (c) Visually assessed corrosion scores for the Pt-Ru-Ni system.

Unfortunately these results contradict other studies that have been reported in literature. Several binary Pt-Ni compositions have been reported with properties that exceeded pure Pt, but they were Pt_{50}Ni_{50} [176] or Pt_{75}Ni_{25} [36, 77, 213] which did not outperform Pt in our study. Park et al. [234] examined some Pt-Ru-Ni catalysts and reported Pt_{50}Ru_{40}Ni_{10} (marked with a green star in figure 5.8.1 (b)) as the optimum
composition with an onset 261 mV lower than pure Pt. This was far removed the best composition determined from this study (Pt$_{13}$Ru$_{50}$Ni$_{37}$), but Park et al. did not examine many ternary compositions. The compositions from this study that were similar to Pt$_{50}$Ru$_{40}$Ni$_{10}$ had the same onset potential as pure Pt but a much weaker methanol oxidation current density.

The corrosion resistance shown in figure 5.8.1 (c) of the system was not promising. The majority of compositions were inert to the acid attack with the exception being the active Ni rich compositions. These compositions had a corrosion score of 2, as their perimeters had receded during the electrochemical testing. This was unfortunate but, as has been stressed by He et al. [156], the most active compositions are frequently the most unstable.

When the methanol oxidation reaction was examined in saturated oxygen most compositions failed to respond as shown in figure 5.8.2. The exception was Pt$_{25}$Ni$_{75}$ with a very strong performance. After the oxygen was introduced the current density of

![Figure 5.8.2](image)

Figure 5.8.2, (a) Peak current density and (b) onset potential of methanol oxidation for the Pt-Ru-Ni system. Current densities measured during the 10$^{th}$ forward scan at 10 mV/s in oxygen saturated 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 °C.
Pt$_{75}$Ni$_{25}$ counter-intuitively remained at a very high current density, $2.1 \times 10^{-3}$ Acm$^{-2}$ as shown in figure 5.8.2 (a). The onset potential worsened with a 77 mV higher overpotential, a much more severe response than pure Pt which lost 33 mV with the introduction of oxygen as shown in figure 5.8.2 (b). The worse onset potential but consistent current density is unusual, but may be because the platinum promoter was NiO and not metallic Ni. Shen et al [233] examined Pt-NiO surfaces and did see an improvement. Unfortunately the optimum composition from their study, Pt$_{60}$(NiO)$_{40}$, conflicts with this work.

5.8.2 Pt-Ru-Ni: Oxygen Reduction Reaction

ORR testing revealed that the best composition was Pt$_{25}$Ni$_{75}$ with an onset potential of 0.58 V-SCE which was 23 mV higher than the average Pt response as shown in figure 5.8.3 (a). Not surprisingly, Ru ternary alloys were again of no benefit to the ORR. The best oxygen reducing composition in the presence of methanol was pure Pt,
with an onset potential of 0.52 V-SCE. This was mirrored by nine other compositions spread across the phase field, all with an onset potential within 5 mV of platinum’s response. There are many reports [36, 74, 77, 195, 213, 214] of \textit{Pt}_{75}\textit{Ni}_{25} being superior to pure Pt, which conflicts with this study. We found the ORR performance of \textit{Pt}_{75}\textit{Ni}_{25} to be neither better nor worse than pure Pt. This Pt-Ru-Ni system has excellent corrosion resistance but seems unsuitable for oxygen reduction with no composition truly outperforming pure Pt.

In the presence of methanol the ORR activity of the Pt-Ru-Ni system diminished as expected as shown in figure 5.8.3 (b). With the exception of \textit{Pt}_{25}\textit{Ni}_{75} (which anodically oxidized methanol), most compositions had the same mediocre ORR response. A pure Pt sample recorded the best onset potential of 0.5218 V-SCE, but even \textit{Pt}_{14}\textit{Ru}_{43}\textit{Ni}_{43} recorded an onset potential of 0.5212 V-SCE, which was not significantly different from pure Pt. There was no exceptional methanol resistant oxygen reducing composition in the Pt-Ru-Ni system.

5.9 Platinum – Nickel – Chromium

5.9.1 Pt-Ni-Cr: Methanol Oxidation Reaction

The methanol oxidation behavior of the Pt-Ni-Cr system was similar to the Pt-Ru-Ni system. Initially the best unconditioned composition was \textit{Pt}_{20}\textit{Ni}_{80} with a current density of $2.5 \times 10^{-3}$ Acm$^{-2}$ as shown in figure 5.9.1 (a). The pure Pt, being unconditioned only responded with a current density of $1.2 \times 10^{-4}$ Acm$^{-2}$. Pt-Cr and Pt-Ni-Cr compositions were completely unresponsive with barely any indication of methanol oxidation occurring on their surfaces. Despite the high current density,
Figure 5.9.1, Peak current densities of methanol oxidation for Pt-Ni-Cr system (a) before and (b) after conditioning. Measured during the 10th forward scan at 10 mV/s in 0.5 M H₂SO₄, 0.5 M methanol at 20 °C.

Pt₂₀Ni₈₀ had a relatively mediocre onset potential of 0.37 V-SCE as shown in figure 5.9.1 (b). This was 50 mV better than the average Pt response, but was not very impressive compared to the unconditioned compositions from the Pt-Ru-Co system. The high onset potential of Pt₂₀Ni₈₀ could be an indication that it experienced very early corrosion and the Ni was preferentially leaching from the surface.

After the library was conditioned by testing at 40 °C and 60 °C it showed a very different performance as shown in figure 5.9.1(b). The optimum composition was now Pt₂₆Ni₃₇Cr₃₇ with a MOR peak current density that just exceeded the system’s measurement capabilities at 3.7 × 10⁻⁴ Acm⁻². Pt₂₈Ni₃₆Cr₃₆ also had a methanol oxidation onset potential that was 0.26 V-SCE. Though faint in comparison to Pt₂₈Ni₃₆Cr₃₆, pure Pt and Pt-Cr compositions also improved with conditioning with an average current density of ~2 × 10⁻⁴ Acm⁻² and an onset potential of 0.43 V-SCE. The improved current density of Pt₂₈Ni₃₆Cr₃₆ was not just a side effect of preferential leaching because the onset potential of Pt₂₈Ni₃₆Cr₃₆ was 162 mV lower than the average onset potential of pure Pt. Interestingly, the steep decline in the peak current density of the
neighboring compositions Pt\textsubscript{30}Ni\textsubscript{40}Cr\textsubscript{30} and Pt\textsubscript{30}Ni\textsubscript{30}Cr\textsubscript{40} implies that the active composition does not stretch very far from Pt\textsubscript{28}Ni\textsubscript{36}Cr\textsubscript{36}. This composition would have been easily missed in a more traditional non-combinatorial investigation.

The corrosion resistance of the Pt-Ni-Cr system as shown in figure 5.9.2 (a), was worse than the corrosion resistance of the Pt-Ru-Ni system. This does not necessarily mean that Ru was more stable than Cr. It should be noted that in order to ensure consistent electrochemical results a few extra tests were performed on the Pt-Ni-Cr library at 20 °C. Figure 5.9.2 (a) also explains why Pt\textsubscript{20}Ni\textsubscript{80} was active initially and then inactive later. Its corrosion score of 0 means it had completely corroded from the system, probably dissolving during the high temperature testing.

![Figure 5.9.2, (a) Corrosion score of the Pt-Ni-Cr system. (b) Peak current densities of methanol oxidation for Pt-Ni-Cr system measured during the 10th forward scan at 10 mV/s in oxygen saturated 0.5 M H\textsubscript{2}SO\textsubscript{4}, 0.5 M methanol at 20 °C.](image)

The oxidation of methanol in the presence of oxygen saw a different trend across the Pt-Ni-Cr phase field as shown in figure 5.9.2, (b). Pt\textsubscript{26}Ni\textsubscript{37}Cr\textsubscript{37} remained the best catalyst composition but its activity dived to 1.3 × 10\textsuperscript{-4} Acm\textsuperscript{-2}. In comparison Pt\textsubscript{80}Cr\textsubscript{20} and Pt\textsubscript{75}Ni\textsubscript{25} did not really improve; their methanol oxidation performance just didn’t
change with the introduction of oxygen. The onset potential of Pt\textsubscript{26}Ni\textsubscript{37}Cr\textsubscript{37} shifted upward to 0.47 V-SCE but this measurement was inaccurate under these conditions. At potentials below 0.5 V-SCE Pt\textsubscript{26}Ni\textsubscript{37}Cr\textsubscript{37} recorded a steady cathodic oxygen reduction current signal, but at \(~0.47\) V-SCE this would change to an anodic methanol oxidation signal. The method that defines the methanol oxidation onset potential relies on the current density being near zero up to the methanol oxidation peak. When a current generated by another reaction distorts the baseline leading up to the methanol peak the measurement becomes more inaccurate. As the intention of this test was to find compositions that oxidize methanol but remain inert to oxygen, a condition that Pt\textsubscript{26}Ni\textsubscript{37}Cr\textsubscript{37} fails, the inaccuracy is a moot point.

There has been no report of ternary Pt-Ni-Cr compositions being used to oxidize methanol with which to compare this work. Discussion of the performance of the binary Pt-Cr and Pt-Ni compositions is contained in sections 5.7 and 5.8 respectively. There has been one report [235] of a Ni-Cr catalyst of an unspecified composition being used to oxidize methanol. Our work conflicts with this with no activity seen from any of the binary Ni-Cr compositions.

5.9.2 Pt-Ni-Cr: Oxygen Reduction Reaction

The best conditioned methanol oxidation catalyst composition was also the best oxygen reduction catalyst composition. Pt\textsubscript{26}Ni\textsubscript{37}Cr\textsubscript{37} had an onset potential of 0.54 V-SCE, 53 mV better than the average onset potential of Pt as shown in figure 5.9.3 (a). This was mirrored by reasonable performances from Pt\textsubscript{30}Ni\textsubscript{30}Cr\textsubscript{40} and Pt\textsubscript{37}Ni\textsubscript{26}Cr\textsubscript{37}, implying that compositions with 10-20 At% more Cr may also be active.
Figure 5.9.3, Onset potential of oxygen reduction for the Pt-Ni-Cr system. Measurements taken during the 10th backward scan at 10 mV/s in oxygen saturated 0.5 M H₂SO₄ that was (a) initially clean and then with (b) 0.5 M methanol at 20 °C.

The oxygen reduction activity across the Pt-Ni-Cr system changed dramatically with the introduction of 0.5 M methanol. The best composition was now Pt₄₃Ni₁₄Cr₄₃ with an onset potential of 0.53 V-SCE, which was just 22 mV better than the average onset potential of Pt. This result is quite unusual, as catalysts that showed little activity in clean electrolyte came alive in the presence of the ORR poison methanol. Unfortunately, there is no literature to compare with this counter-intuitive behavior with. The additional fact that Pt₄₃Ni₁₄Cr₄₃ was nearly inert with regard to the methanol oxidation reaction makes it an interesting possibility for a MRFC cathode catalyst.

5.10 Platinum - Ruthenium - Cobalt

5.10.1 Pt-Ru-Co: Methanol Oxidation Reaction

As seen in other systems, examination of the Pt-Ru-Co system showed that the optimum composition also changed as testing proceeded. The first room temperature test, while the library was in an unconditioned state, showed little to no response from
every composition except Pt$_{17}$Ru$_{17}$Co$_{66}$ as shown in figure 5.10.1. That composition responded so strongly it exceeded the system’s current measurement limits. Extrapolation of its cyclic voltammetry curve implies it would have a peak methanol oxidation current density of 3.96 x 10$^{-3}$ Acm$^{-2}$. This was 20x more than the unconditioned platinum on the same library. This composition also had an onset potential that was 0.2 V lower than the best Pt-Ru composition. However the promising performance of Pt$_{17}$Ru$_{17}$Co$_{66}$ diminished with subsequent tests at higher temperatures. High activity combined with unstable corrosion behavior has also been reported by Strasser et al. for the very similar Pt$_{14}$Ru$_{23}$Co$_{63}$ and Pt$_{18}$Ru$_{20}$Co$_{62}$ compositions [219].

![Figure 5.10.1](image)

Figure 5.10.1, Peak current densities of methanol oxidation for the Pt-Ru-Co system that has not been previously tested and is not conditioned. Current densities measured during the 10$^{th}$ forward scan at 10 mV/s in 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 °C.

As expected from prior experiments, 60 °C testing conditioned the library and the Pt rich, Pt-Ru alloys responded more favorably than they had at room temperature as shown in figure 5.10.2. Interestingly the compositions around Pt$_{12}$Ru$_{44}$Co$_{44}$ were also activated by this conditioning, generating current densities so strong that extrapolation
was again required to estimate their true values. Pt$_{13}$Ru$_{50}$Co$_{37}$ was the best composition, generating a peak methanol oxidation current density of $5.6 \times 10^{-3}$ Acm$^{-2}$ that was 2.5 × more than the average Pt current density as shown in figure 5.10.2 (a). This and the neighboring compositions also showed a favorable onset potential of 0.22 V-SCE as shown in figure 5.10.2 (b). This was 0.15 V lower than the 0.37 V-SCE onset potential of pure Pt. These catalyst compositions exhibiting an ability to generate a stronger methanol oxidation current density at a lower potential than Pt-Ru, are exciting possibilities as catalysts for the next generation of fuel cells.

![Figure 5.10.2](image.png)

Figure 5.10.2, (a) Peak current densities and (b) onset potentials of methanol oxidation for the Pt-Ru-Co system that has been conditioned by a previous test at 60 °C. Current densities measured during the 10$^{th}$ forward scan at 10 mV/s in 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 °C.

As mentioned in the literature survey, there have been some studies of methanol oxidation in the Pt-Ru-Co system. Most researchers [176, 206-209, 211] have examined Pt-Co binary compositions, reporting an optimum around Pt$_{50}$Co$_{50}$. Our work found that unconditioned Pt$_{25}$Co$_{75}$ outperformed Pt, but Pt$_{50}$Co$_{50}$ was about the same. Lima et al. [194] examined Pt-Ru-Co catalysts but were vague about the actual compositions
examined. Strasser et al. reported Pt_{20}Ru_{20}Co_{60} as being superior to the widely used Pt_{60}Ru_{40} or Pt_{50}Ru_{50} compositions [90]. This composition is very similar to the initially unconditioned Pt_{17}Ru_{17}Co_{66} that showed superior properties in our study. Our study and the work of Strasser et al. both used multiarray microelectrode systems to test thin film samples, except Strasser et al. did not report any testing at temperatures at higher than ambient. In a patent [220] of the Pt-Ru-Co system, they performed further testing with nanoparticle Pt-Ru-Co compositions in single cells at higher temperatures. The optimum powder composition (Pt_{27}Ru_{10}Co_{63}) they reported in the patent was even further away from the optimum conditioned composition (Pt_{12}Ru_{50}Co_{38}) of this study. The initially unconditioned Pt_{17}Ru_{17}Co_{66} of this study does agree with the studies of Strasser et al., but its later degradation and poor performance appears to be something that Strasser et al. did not observe. A summary figure of the optimum Pt-Co and Pt-Ru-Co compositions reported by other groups compared to the optimum conditioned composition determined by this study is shown in figure 5.10.3.

Figure 5.10.3, Comparison of the optimum Pt-Ru-Co fuel cell anode composition determined in this study and reported in literature.
The methanol oxidation performance of the Pt-Ru-Co system was also considered in the presence of oxygen as shown in figure 5.10.4 (a, b). Once again the presence of oxygen reduced the peak methanol current density by a factor of 10 and set the average onset potential back 0.2 V, demonstrating that its presence is detrimental to a normal fuel cell anode. The compositions around Pt12Ru44Co44 were still the most active. Curiously, the optimum composition was no longer Pt12Ru50Co38 (the best in the absence of oxygen) but Pt12Ru38Co50. The ruthenium rich Pt-Ru-Co alloy was greatly affected by the presence of oxygen, more so than the cobalt rich alloy. There are no reports Pt-Ru-Cu oxidizing methanol in the presence of oxygen to compare these results against.

![Figure 5.10.4](image)

Figure 5.10.4, (a) Peak current densities and (b) onset potentials of methanol oxidation for the conditioned Pt-Ru-Co System. Measurements made during the 10th forward scan at 10 mV/s in oxygen saturated 0.5 M H2SO4, 0.5 M methanol at 20 °C.

5.10.2 Pt-Ru-Co: Oxygen Reduction Reaction

There were no standout oxygen reduction catalyst compositions from the Pt-Ru-Co system. Figure 5.10.5 (a) shows that the same alloy group around Pt12Ru44Co44 was again the best performing ternary catalysts, but their ORR onset potential of 0.56 V-SCE
was the same as the average Pt response. The introduction of 0.5 M methanol poison reduced the efficiency of all of the catalyst compositions as shown in figure 5.10.5 (b) with the best ORR onset potential set back to 0.53 V-SCE. The best compositions were still pure Pt and the alloy group around Pt$_{12}$Ru$_{44}$Co$_{44}$ even in the presence of methanol. This screening test has established that there are no oxygen reduction catalysts from the Pt-Ru-Co system that outperform Pt. If the price of Pt was to continue to climb higher and the price of cobalt became lower then a composition around Pt$_{12}$Ru$_{44}$Co$_{44}$ may be considered in the future to replace pure Pt fuel cell catalysts.

![Figure 5.10.5](image-url)

Figure 5.10.5, Onset potential of oxygen reduction for the Pt-Ru-Co system. Measurements taken during the 10th backward scan at 10 mV/s in oxygen saturated 0.5 M H$_2$SO$_4$ that was (a) initially clean and then with (b) 0.5 M methanol at 20 °C.

Many groups [36, 74, 77, 80, 156, 197, 213, 214] examined the oxygen reducing properties of ~Pt$_{75}$Co$_{25}$ composition and reported superior performance to pure Pt. These studies tended to assess activity by examining the current density at a fixed potential. As mentioned in the literature review this can exaggerate the true performance. Examining papers that presented their raw data shows that Pt$_{75}$Co$_{25}$
usually had an onset ~25 mV higher than pure Pt [74, 80, 213, 214]. Our work conflicts with this, with there being no significant difference between oxygen reducing properties of pure Pt and Pt\textsubscript{80}Co\textsubscript{20} or Pt\textsubscript{75}Co\textsubscript{25}. Our work was in agreement with two other groups [210, 215, 228] who also failed to elicit a strong response from Pt-Co alloys. There have been no reports of a Pt-Ru-Co alloy being used to reduce oxygen.

5.11 Platinum – Titanium - Cobalt

5.11.1 Pt-Ti-Co: Methanol Oxidation Reaction

The Pt-Ti-Co system gave some initially exciting results with the strongest response to methanol oxidation ever seen from a library. 14 compositions from the Co rich region of phase field exceeded the systems measuring capabilities as shown in figure 5.11.1 (a). The best compositions from this group were Pt\textsubscript{28}Co\textsubscript{36}Ti\textsubscript{36} and Pt\textsubscript{36}Ti\textsubscript{28}Co\textsubscript{36}, with onset potentials of 0.20 V-SCE. Pt\textsubscript{14}Co\textsubscript{43}Ti\textsubscript{43} also exceeded the system’s measuring capabilities, but did so at a much later onset potential (0.40 V-SCE) than any of the other compositions. This was a similar onset potential to the pure Pt (0.43 V-SCE), but the unconditioned Pt failed to achieve the same high peak methanol

![Figure 5.11.1](image)

Figure 5.11.1, Pt-Ti-Co system with onset potentials of methanol oxidation (a) before and (b) after activation. Measured during the 10\textsuperscript{th} forward scan at 10 mV/s in 0.5 M H\textsubscript{2}SO\textsubscript{4}, 0.5 M methanol at 20 °C. (c) Visually assessed corrosion scores for Pt-Ti-Co system.
oxidation current density, reaching only $1.9 \times 10^{-3}$ Acm$^{-2}$ instead. The Pt-Ti binary compositions up to Pt$_{25}$Ti$_{75}$ behaved the same as Pt both before and after conditioning in fair agreement with literature reports [239, 240]. The good corrosion scores of binary Pt-Ti compositions (not the ternary Pt-Ti-Co compositions) show they are stable in an acid environment [218] as shown in figure 5.11.1 (c). There are no reports of MOR or corrosion testing for any ternary Pt-Ti-Co compositions.

Unfortunately the strong performance of the Pt-Ti-Co ternary compositions did not continue with later tests as shown in figure 5.11.1 (b). The 14 compositions with initially high activity completely failed and were corroded after the 60 °C test as shown in figure 5.11.1 (c). The conditioning improved the performance of pure Pt and some of the other compositions. The best conditioned catalyst composition was Pt$_{50}$Ti$_{13}$Co$_{37}$ with a current density that again exceeded the measurable limits. The MOR peak current density was determined by extrapolation to be $\sim 5.3 \times 10^{-3}$ Acm$^{-2}$ and had the promising onset potential of 0.28 V-SCE. This was $3 \times$ the current density of the pure Pt standard ($I_{pk} = 1.8 \times 10^{-3}$ Acm$^{-2}$, $V_{on} = 0.36$ V-SCE) and 180 mV lower onset potential. Unfortunately Pt$_{50}$Ti$_{13}$Co$_{37}$ was not stable, with the edges of the hexagonal pad receding (score of 2 in figure 5.11.1 (c)). This implies that in a longer test it would probably fail. Overall, the presence of Ti did not have the desired effect of stabilizing the interestingly reactive Pt-Co combination.

The lack of corrosion resistance is observable in the cyclic voltammetry curves. A reversible reaction, probably of the form

$$M \leftrightarrow M^+ + e^-$$

(18)
occurred in the forward and reverse scans at ~0.6 V-SCE as shown in figure 5.11.2 (b). This reaction occurred in the cyclic voltammetry scans of the compositions that initially showed great methanol oxidation activity and then completely corroded as shown in figure 5.11.2 (a). The identity of the dissolving species M was unknown. This reversible reaction was not seen in previously tested libraries that contained Co, which implied that the unknown species was Ti. But two samples (Pt_{20}Co_{80} and Pt_{25}Co_{75}) that contained no Ti had the same CV profile, which implied that Co could be the unknown species. This could not be confirmed by the pure Co or pure Ti samples. Unfortunately the pure samples and all the binary combinations of Ti and Co had very weak responses similar to inert TiN and did not display any sign of this reversible reaction.

Figure 5.11.2 (a) The negative current density at 0.5 V-SCE indicates compositions that were dissolving via the reversible reaction and (b) sample CV from Pt_{33}Ti_{33}Co_{33}, 0.5 M H_2SO_4, no methanol, 10 mV/s, 20 °C and 10^{th} cycle that shows the reaction.

There was no simple explanation for the system’s poor corrosion resistance. It is sufficient to state that Ti did not improve the Pt-Co system, but instead it accelerated its
deterioration. Further work, like ICP-MS of the electrolyte after initial tests, may reveal the corrosion mechanism, but as far as methanol screening is concerned the Pt-Ti-Co system failed.

The methanol oxidation reaction was also tested in the presence of oxygen. The best performing composition was Pt\textsubscript{44}Ti\textsubscript{12}Co\textsubscript{44} with a current density that just exceeded the measuring capabilities of the MMA system as shown in figure 5.11.3 (a). Pt\textsubscript{44}Ti\textsubscript{12}Co\textsubscript{44} also had the lowest onset potential of 0.32 V-SCE as shown in figure 5.11.3 (b). This behavior was unusual, with the binary composition Pt\textsubscript{44}Co\textsubscript{56} also recording a strong response. When Pt-Co binary compositions from other libraries (Pt-Ru-Co or Pt-Co-Cr for example) have been tested for methanol oxidation in the presence oxygen they have shown a negligible response. This can be taken as evidence that free Ti\textsuperscript{2+} ions deposited and altered the surface of the Pt-Co binary compositions. Though beneficial in these tests, the disturbing lack of corrosion resistance implies that a Pt-Ti-Co composition probably should not be used in a fuel cell.

Figure 5.11.3, (a) Peak current density and (b) Onset potential for compositions in Pt-Ti-Co system measured during the 10\textsuperscript{th} forward scan at 10 mV/s in oxygen saturated 0.5 M H\textsubscript{2}SO\textsubscript{4}, 0.5 M methanol at 20 °C.
5.11.2 Pt-Ti-Co: Oxygen Reduction Reaction

After the extensive corrosion only half of the compositions remained for oxygen reduction testing. One of the best ORR catalyst compositions was Pt$_{43}$Co$_{57}$, with an onset potential of 0.58 V-SCE, 72 mV better than the average Pt onset potential as shown in figure 5.11.4 (a). This is unusual because Pt-Co binary combinations tested previously in section 5.10 (Pt-Ru-Co) never responded like this. No Pt-Co composition outperformed the average Pt response in the Pt-Ru-Co system. Again the most likely scenario was that free ions in the solution deposited and altered the surface properties of the Pt-Co catalysts. The literature regarding Pt-Ti ORR catalysts mainly implies that alloys will be neither better nor worse. Our results confirm that Pt$_{75}$Ti$_{25}$ has a similar performance to Pt [74, 244] but cannot confirm the findings of groups with dramatically different experimental conditions [245-247]. There are no reports of ternary Pt-Ti-Co compositions being used for oxygen reduction.

Figure 5.11.4, Onset potential of oxygen reduction for the Pt-Co-Ti system. Measurements taken during the 10$^{th}$ backward scan at 10 mV/s in oxygen saturated 0.5 M H$_2$SO$_4$ that was (a) initially clean and then with (b) 0.5 M methanol at 20 °C.
The addition of methanol diminished the oxygen reduction performance of all the active catalysts. It can be seen that in the previous figure (figure 5.11.3) that the compositions Pt$_{43}$Co$_{57}$, Pt$_{44}$Co$_{44}$Ti$_{12}$ and Pt$_{50}$Co$_{37}$Ti$_{13}$ were oxidizing methanol quite strongly and thus not able to register a cathodic oxygen reduction potential. The best oxygen reducing composition in the presence of methanol was Pt$_{57}$Co$_{43}$, with an onset potential 26 mV higher than the average Pt response as shown in figure 5.11.4 (b). As mentioned in the preceding paragraphs, this was an abnormal response for a Pt-Co composition and is believed to have been influenced by some surface-modifying Ti$^{2+}$ ions. Catalysts modified with a partial monolayer of another element are not new, with Cu on Pt being a classic example [70, 238], but the poor corrosion resistance of the Pt-Ti-Co system does make it doubtful that it would last in a true fuel cell environment.

5.12 Platinum – Cobalt – Chromium

5.12.1 Pt-Co-Cr: Methanol Oxidation Reaction

Libraries examining the Pt-Co-Cr systems were constructed and evaluated. This system was studied with the hope of finding a catalyst that had the strong catalytic performance of a Pt-Co composition and the corrosion resistance of a Pt-Cr composition. An early ORR test was performed before the standard cycle of MOR tests at 20, 40, 20, 60 and 20 °C. Figure 5.12.1 (a) shows the initial current density for the Pt-Cr-Co system before the pure Pt samples have been conditioned. It can be seen that two samples near Pt$_{18}$Cr$_{18}$Co$_{64}$ were very active, exceeding the measurable current capacity. These samples also showed a favorable onset potential of 0.23 V-SCE. This strong performance didn’t last with the performance diminishing after the higher temperature
tests. This loss of performance was because these samples were not stable as can be seen by their corrosion score of 0 in figure 5.12.1 (c).

Figure 5.12.1, Peak current densities of methanol oxidation for the Pt-Co-Cr system (a) before and (b) after conditioning by testing at 60 °C. Current densities measured during the 10th forward scan at 10 mV/s in 0.5 M H₂SO₄, 0.5 M methanol at 20 °C. (c) Visually assessed corrosion scores for the Pt-Co-Cr system.

Figure 5.12.1 (b) shows the current densities after the library was conditioned by higher temperature testing. Conditioning activated the pure Pt samples with these pads, generating a reasonable current density during methanol oxidation of 2.5 x 10⁻⁴ Acm⁻². This was outperformed by a cluster of compositions around Pt₃₃Cr₃₃Co₃₃, with the best registering a MOR peak current density of 2.9 x 10⁻³ Acm⁻². This was almost an order of magnitude better than the conditioned Pt samples. These samples also have the advantage of better corrosion resistance, with perfect scores implying that they remained unaffected by the testing. The bulk of Pt-Cr literature focuses on its oxygen reduction properties. So it wasn’t surprising when this cluster of compositions also showed very interesting results during the oxygen reduction tests. Due to its relevance to the discussion, the oxidation of methanol in the presence of oxygen is included in the following section.
5.12.2 Pt-Co-Cr: Oxygen Reduction Reaction

Pt-Cr alloys have shown a lot of promise for improved oxygen reduction in fuel cells [221, 223, 229, 295]. Our tests of the Pt-Co-Cr system for activity in the oxygen reduction reaction were also promising. Initially as shown in figure 5.12.2 (a), Pt$_{20}$Co$_{60}$Cr$_{20}$ was the most active composition with an onset potential of 0.61 V-SCE that was 1.1 V higher than the average Pt response at the relatively poor 0.51 V-SCE. Unfortunately this performance was not maintained, with the active sample and others with a similar composition corroding away, as shown in figure 5.12.1 (c). Although these samples had deteriorated, other samples had responded more favorably to the conditioning. Figure 5.12.2 (b) shows Pt$_{28}$Co$_{36}$Cr$_{36}$ had become more active achieving the unsurpassed onset potential of 0.67 V-SCE, 110mV higher than the average Pt onset potential. This composition was stable with no visible signs of failure and the strong performance was mirrored with the nearby compositions around Pt$_{33}$Co$_{33}$Cr$_{33}$ all outperforming Pt.

![Figure 5.12.2](image1.png)

Figure 5.12.2, Oxygen reduction reaction onset potential for the Pt-Co-Cr system (a) before and (b) after conditioning. Measured at 10 mV/s in oxygen saturated 0.5 M H$_2$SO$_4$ at 20 °C. Green stars indicate the compositions reported by Seo et al. [230].
A discussion on the responses of Pt-Cr and Pt-Co binary compositions is contained in sections 5.7 and 5.10 respectively. There exists some literature regarding the ORR performance of Pt-Cr-Co ternary compositions. Shukla et al. [228] performed single cell tests, with the best alloys Pt_{52}Co_{48}, Pt_{60}Cr_{40} and Pt_{51}Co_{22}Cr_{27} achieving potentials 80, 55 and 40 mV respectively higher than pure Pt at low current densities. These results are consistent with the initial performances shown in figure 5.12.2 (a). In the other work to examine a Pt-Co-Cr catalyst under PEMFC cathode conditions, Seo et al. [230] found Pt_{76}Co_{11}Cr_{13} had an open circuit potential 54.3 mV higher than Pt. Other compositions in their work also outperformed Pt (Pt_{54}Co_{22}Cr_{24}, ΔV = 28.5 mV, Pt_{70}Co_{13}Cr_{17}, ΔV = 29.7 mV, Pt_{84}Co_{8}Cr_{8}, ΔV = 40.7 mV) but nothing exceeded Pt_{76}Co_{11}Cr_{13}. These compositions are marked with green stars in figure 5.12.2 (b). In comparison, similar compositions that we tested did not outperform Pt. Again the differences in the testing procedure and catalyst structure (Seo et al. [230] performed single cell tests on carbon supported nanoparticles) are the probable cause of the discrepancy [158].

The Pt-Co-Cr system was further tested by examining its oxygen reduction capabilities in the presence of 0.5 M methanol. As opposed to oxygen reduction, methanol oxidation is an anodic process and an improved catalyst would have a lower onset potential. Figure 5.12.3 (a) shows the onset potential of methanol oxidation, note the shading has been reversed from other ORR figures, light shading indicates a low onset potential which is preferential for methanol oxidation. This gave a very interesting result when compared with figure 5.12.3 (b). The compositions around Pt_{33}Co_{33}Cr_{33} were simultaneously the best at both oxidizing methanol and reducing
oxygen. This had never been observed on any other library tested in this system. Sometimes a catalyst would have a strong response to the ORR or the MOR but would always be weak in regards to the opposing reaction.

Figure 5.12.3, Onset potentials from the Pt-Cr-Co system (a) oxidizing methanol in saturated oxygen and (b) reducing oxygen in the presence of methanol. (c) Sample cyclic voltammetry scan that shows the oxidation of methanol during the upward sweep and the reduction of oxygen during the downward sweep.

The simultaneous anodic and cathodic reactions were not an error, as figure 5.12.3 (c) shows. The anodic methanol oxidation occurred during the upward sweep and the cathodic oxygen reduction occurred during the downward sweep. Usually under these circumstances the catalyst would behave solely as a cathode, reducing oxygen at a lower potential that would be consistent with a poisoned surface. Even if methanol was being consumed in a reaction on the surface the most likely reaction would be eqn. (19).
This reaction path doesn’t liberate or consume any electrons and thus would be undetectable by cyclic voltammetry. An anodic current from methanol oxidation is only possible if there is an oxygen deficiency eqn (20) or if water is preferentially dissociated eqn (21).

\begin{align*}
2\text{CH}_3\text{OH} + 3\text{O}_2 & \rightarrow 2\text{CO}_2 + 4\text{H}_2\text{O} \quad \text{(19)} \\
\text{CH}_3\text{OH} + \text{O}_2 & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \quad \text{(20)} \\
\text{CH}_3\text{OH} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad \text{(21)}
\end{align*}

Eqn (20) seems unlikely as it implies that the methanol dissociates hydrogen groups faster than oxygen can diffuse to the active site. However it cannot be discounted, as there was some evidence that both reactions occurred simultaneously. Methanol oxidation with a nitrogen atmosphere generated higher anodic current densities than methanol oxidation in the presence of oxygen. This implies that with the nitrogen atmosphere the reaction went via the 6 electron path (21) and with oxygen present via a combination of the 2 and 6 electron paths (20) and (21).

Unfortunately the curious behavior of the samples around Pt$_{33}$Co$_{33}$Cr$_{33}$ was transient. The oxygen reduction activity in the presence of methanol diminished slightly with each cycle of the potential. Further testing over a longer time frame saw strictly methanol oxidation with no indication of oxygen reduction. The Pt-Co-Cr system holds great possibility of being a more efficient methanol tolerant cathode in a DMFC. It may
even be suitable as a more efficient MRFC anode, and its unusual behavior raises the possibility for a MRFC that can switch anode/cathode during operation.

5.13 Palladium – Chromium – Cobalt

5.13.1 Pd-Cr-Co: Methanol Oxidation Reaction

No compositions from the Pd-Cr-Co system showed any sign of methanol oxidation activity. All of the compositions had cyclic voltammetry curves similar to the curve for pure Pd shown in 5.13.1 (a). The complete lack of activity was apparent, especially when compared to an active catalyst’s cyclic voltammetry curve, like the example of Pt in figure 5.13.1 (b) from another library. There are no reports of a Pd methanol oxidation catalyst to compare this work to, and based on the lack of response there never will be.

![Figure 5.13.1](image.png)

Figure 5.13.1, Cyclic voltammetry curve for (a) pure Pd from Pd-Cr-Co library and (b) comparative pure Pt from Pt-Fe-Ru library.

5.13.2 Pd-Cr-Co: Oxygen Reduction Reaction

The oxygen reduction cyclic voltammetry curve for all of the Pd-Cr-Co compositions was identical to their methanol oxidation curve as shown in figure 5.13.1.
There were no active oxygen reduction Pd-Cr-Co compositions, which contradicts the majority of reports on Pd and Pd-Co catalysts [52, 160, 265]. Markovic et al. [36] was the only group that did not praise Pd as the ultimate non-platinum alloy. They reported an improved performance of Pd in alkaline electrolyte but it failed to perform in acid electrolyte possibly due to anion poisoning. Our system used an acid electrolyte and so may have been blocked by the same poisoning, but positive results have been achieved with 0.5 M HClO₄ [160, 265] and 0.5 M H₂SO₄ [52].

5.14 Platinum – Cobalt – Copper

5.14.1 Pt-Co-Cu: Methanol Oxidation Reaction

The Pt-Co-Cu system had a promising oxygen reduction response. The best compositions before the library was conditioned were Pt₃₀Co₄₀Cu₃₀ and Pt₂₆Co₃₇Cu₃₇, with peak methanol oxidation current densities that exceeded the systems measuring capabilities as shown in figure 5.14.1 (a). Other low Pt compositions like Pt₂₀Co₂₀Cu₆₀ and Pt₁₆Co₁₆Cu₆₈ also responded favorably with strong current densities that easily outperformed the unconditioned Pt. Testing at higher temperatures conditioned the library and improved the performance of pure Pt as expected, but the activity of the alloys with a low Pt content diminished as shown in figure 5.14.1 (b). Due to a MMA system glitch the performance of Pt₃₀Co₄₀Cu₃₀ was not recorded, but testing of the other unconditioned active composition Pt₂₆Co₃₇Cu₃₇ was fine and its methanol oxidation response again exceeded the capabilities of the machine. The neighboring composition Pt₃₀Co₃₀Cu₄₀ also responded with a MOR peak current density so high it exceeded the measuring capabilities of the MMA.
Figure 5.14.1, Peak methanol oxidation current densities for the Pt-Co-Cu system (a) before and (b) after conditioning by testing at 60 °C. Current densities measured during the 10th forward scan at 10 mV/s in 0.5 M H2SO4, 0.5 M methanol at 20 °C.

The onset potentials for these active alloy compositions was initially 0.17 V-SCE before conditioning and then 0.30 V-SCE after conditioning. The change in onset potential implies that the Co-Cu initially had a promotional effect to the Pt, but was simultaneously being leached from the surface. After conditioning the leached surface would consist of high surface area Pt structures. This new surface would generate higher current densities but at the same onset potential as the smooth pure Pt electrodes. This would support the literature [79, 176] that preferential leaching of Pt-Co and Pt-Cu alloys leaves a rougher Pt enriched surface. The only Pt-Cu methanol oxidation study to compare these results to was the work of Page et al. [176], who found that carbon supported Pt50Cu50 was better than a Pt equivalent with an onset potential of 0.345 V-SCE. This study is contrary to the work of Page et al. as there were no Pt-Cu compositions that outperformed Pt or had an onset potential lower than Pt’s 0.39 V-SCE.
There were conditioned and unconditioned Pt-Co-Cu compositions that outperformed Pt and some even had onset potentials as low as 0.17 V-SCE before conditioning.

5.14.2 Pt-Co-Cu: Oxygen Reduction Reaction

The most active unconditioned methanol oxidation Pt-Co-Cu compositions were also the most active unconditioned oxygen reduction compositions. Pt$_{30}$Co$_{40}$Cu$_{30}$ and Pt$_{28}$Co$_{36}$Cu$_{36}$ had onset potentials of 0.63 V-SCE as shown in figure 5.14.2 (a), a very good performance that was 77 mV higher than the average Pt response. Again similar to the methanol oxidation results the low Pt compositions Pt$_{26}$Co$_{20}$Cu$_{60}$ and Pt$_{17}$Co$_{17}$Cu$_{66}$ also responded favorably with onset potentials that were higher than Pt. Figure 5.14.2 (b) shows the drastic changes that occurred after conditioning. The ORR onset potential of the initially promising compositions, Pt$_{30}$Co$_{40}$Cu$_{30}$ and Pt$_{26}$Co$_{37}$Cu$_{37}$, dropped after conditioning and the pure Pt improved. No Pt-Co-Cu composition outperformed the average Pt onset potential of 0.56 V-SCE. This agrees with Stonehart’s dim assessment that a Pt-Co-Cu catalyst would be unfeasible because of its lack of stability [79]. For

![Figure 5.14.2](image)

Figure 5.14.2, Onset potential of oxygen reduction for the Pt-Co-Cu system (a) before and (b) after conditioning. Measured during the 10th downward sweep at 10 mV/s in oxygen saturated 0.5 M H$_2$SO$_4$ at 20 °C.
the record, Stonehart went on to note that a Pt-Cu fuel cell cathode catalyst would be doubly foolish because leached Cu would poison the fuel cell’s anode [79].

This work contradicts other literature regarding the ORR activity of Pt-Cu binary compositions. Xiong et al. [201], found that Pt$_{17}$Cu$_{83}$ had an ORR onset potential 20mV higher than Pt, but a current density $\sim 100 \times$ weaker. Similar to the findings of Xiong et al., Pt$_{25}$Cu$_{75}$ had an ORR onset potential just 6 mV lower than the average Pt onset potential. Contrary to Xiong et al., the current density of Pt$_{25}$Cu$_{75}$ at the diffusion limited maximum was approximately the same as Pt. This study does agree with Xiong and Manthiram [197] that the ORR activity of Pt$_{80}$Cu$_{20}$ was approximately the same as pure Pt. In summary, there were no Pt-Co-Cu compositions that had an ORR activity exceptionally better than Pt.

5.15 Cobalt – Chromium – Copper

5.15.1 Co-Cr-Cu: Methanol Oxidation Reaction

The Co-Cr-Cu system was examined, but no composition gave any conclusive sign that it catalyzed the methanol oxidation reaction. Figure 5.15.1 (a) shows the peak current density on the Co-Cr-Cu ternary diagram where everything was poor. The best performer was Cr$_{20}$Co$_{80}$ with a current density of $1.4 \times 10^{-6}$ Acm$^{-2}$ ($\sim 100$ times worse than the usual response of pure Pt). Unfortunately the CV for Cr$_{20}$Co$_{80}$ as shown in figure 5.15.1 (b), shows that even this weak current was barely discernible from double layer charging and signal noise. Co, Cu and Cr may improve the methanol oxidation activity of Pt but they do not have any activity away from Pt.
Figure 5.15.1, (a) Peak methanol oxidation currents from a Co-Cr-Cu library where the current density measured during 5th forward sweep of cyclic voltammogram at 10 mVs\(^{-1}\) in 0.5 M H\(_2\)SO\(_4\) and 0.5 M methanol at 20 °C. (b) The standardized CV of the optimum composition Cr\(_{20}\)Co\(_{80}\) showing the poor performance.

The corrosion inspection shown in figure 5.12.2 was more interesting than the electrochemical test. As can be clearly seen, Cu-Co compositions are unstable in the acidic testing environment. But on a promising note, compositions with more than 20 At% Cr are stable. This implies that small amounts of Cr could be used in the future with a non-noble catalyst that would not have otherwise been corrosion resistant.

Figure 5.15.2, Corrosion resistance of the Cr-Co-Cu system, visually determined after electrochemical testing was completed.
There was an unusual phenomenon that occurred with this library. Usually a library will finish the annealing process looking metallic. For the Co-Cr-Cu library this was not the case. After annealing many of the test pads were a hazy blue or brown, which was assumed to be from an oxide as shown in figure 5.15.3 (a). After MMA testing most libraries will have their metallic catalyst pads discolored into a dark hazy oxide, but the opposite occurred for the Co-Cr-Cu library. Many initially hazy catalysts came out a shiny and metallic white as shown in figure 5.15.3 (b). This is mentioned because these compositions scored a “4” as they did not finish the same color that they started. So although they were judged discolored, they finished in a state that would have been considered perfect for another library.

Figure 5.15.3, Co-Cr-Cu test pads (a) before and (b) after electrochemical testing.

5.15.2 Co-Cr-Cu: Oxygen Reduction Reaction

The oxygen reduction activity of the Co-Cr-Cu system was poorer than its methanol oxidation activity. Co$_{50}$Cr$_{38}$Cu$_{12}$ was the first composition to record a
cathodic current at 0.143 V-SCE, more than 400 mV lower than what would be expected from Pt. The onset of this current was so low that it cannot even be confidently considered related to the oxygen reduction.

5.16 Platinum – Ruthenium - Copper

5.16.1 Pt-Ru-Cu: Methanol Oxidation Reaction

Pt-Cu alloys have been principally investigated as oxygen reduction catalysts, with less attention given to their possible methanol oxidation properties. As the oxygen reduction properties were of greater interest, the testing schedule was altered slightly. The first test done on the Pt-Ru-Cu system was an oxygen reduction test at 20 °C, then methanol oxidation at 20 °C, ORR at 20 °C, MOR at 60 °C, MOR at 20 °C and finally ORR at 20 °C again. This different schedule gives the same methanol oxidation information showing performance before and after conditioning, but also gave more information regarding the oxygen reduction reaction.

The unconditioned Pt-Ru-Cu system gave a promising methanol oxidation response. The best composition was Pt₁₇Ru₁₇Cu₆₆, with a peak MOR current density of $2.7 \times 10^{-3} \text{ Acm}^{-2}$ and an onset potential of 0.3 V-SCE as shown in figure 5.16.1 (a). The peak current density was ~30 times higher than the average response from the unconditioned pure Pt. Surprisingly Pt₁₇Ru₁₇Cu₆₆ did not have the best onset potential, that honor was achieved by Pt₁₂Ru₄₄Cu₄₄ with an onset of 0.25 V-SCE. In fact all of the low Pt compositions between Pt₁₇Ru₁₇Cu₆₆ and Pt₁₂Ru₄₄Cu₄₄ had low onset potentials ($0.25 – 0.3$ V-SCE) implying that there was a broad composition area that was quite active for methanol oxidation.
Figure 5.16.1, Peak current densities of methanol oxidation for the Pt-Ru-Cu system (a) before and (b) after conditioning by testing at 60 °C. Current densities measured during the 10th forward scan at 10 mV/s in 0.5 M H₂SO₄, 0.5 M methanol at 20 °C.

The promising behavior of the low Pt compositions did not continue after the library was conditioned as shown in figure 5.16.1 (b). Pt₇₄Ru₁₃Cu₁₃ was the best conditioned methanol oxidation composition of the system with a current density of 2.7 x 10⁻³ Acm⁻². The low Pt alloy was Pt₂₀Ru₂₀Cu₆₀ performed quite well, outperforming Pt with a peak current density of 2.3 x 10⁻³ Acm⁻², but the earlier active compositions were dead in comparison.

A curious side note of this system was the response of Pt₈₀Ru₂₀ with an irregularly shaped CV curve. The methanol oxidation peak of Pt₈₀Ru₂₀ occurred at 0.75 V-SCE instead of the usual 0.6 V-SCE as shown in figure 5.16.2 (a). This type of cyclic voltammetry curve has never been seen for a Pt-Ru binary composition before, with the majority of curves having a more symmetric methanol oxidation peak, like the pure Pt example in figure 5.16.2 (a). There are two possible reasons for this irregular shape. Firstly there could have been Cu⁺ ions in the electrolyte that were electrochemically
deposited on the Pt-Ru surface and modified its behavior. There was evidence that Cu ions were free in the electrolytes, as all of the compositions recorded a weak reversible reaction during their baseline scans. Figure 5.16.2 (b) shows the baseline scan of Pt$_{80}$Ru$_{20}$. Normally in other libraries that did not contain Cu the curve would be flat from 0.2 – 0.8 V-SCE. Unfortunately it is not conclusive that the weak peaks are related to the copper ions, nor that they were responsible for distorting the curve of Pt$_{80}$Ru$_{20}$. It should be noted that pure Pt and the majority of other compositions also recorded the weak peaks in their baseline scans, but did not have unusual methanol oxidation curves. The other possible reason for the distorted curve would be from a physical testing discrepancy, like an abnormally increased resistance from the TiN lead due to a photolithographic error. This would have reduced the current signal from the catalyst pad and could account for the non-symmetrical peak shape. Either way the onset of the reaction was unaffected, reiterating the importance of using two parameters to characterize these libraries.

Figure 5.16.2, (a) Methanol oxidation peaks of pure Pt and Pt$_{80}$Ru$_{20}$ showing the unusual offset peak potential of Pt$_{80}$Ru$_{20}$. (b) Cyclic voltammetry curve of Pt$_{80}$Ru$_{20}$ in clean (methanol free) electrolyte showing a reversible redox reaction around 0.50 V-SCE.
5.16.2 Pt-Ru-Cu: Oxygen Reduction Reaction

The oxygen reduction activity seemed to follow the same trend as the methanol oxidation activity. Initially the compositions between Pt$_{17}$Ru$_{17}$Cu$_{66}$ and Pt$_{12}$Ru$_{44}$Cu$_{44}$ easily outperformed Pt as shown in figure 5.16.3 (a). The best composition was Pt$_{17}$Ru$_{17}$Cu$_{66}$ with an onset potential of 0.63 V-SCE, 109 mV better than the average Pt response. Unfortunately conditioning of the library also diminished the performance of these low Pt compositions as shown in figure 5.16.3 (b). The six Pt rich compositions around Pt$_{75}$Ru$_{15}$Cu$_{15}$ all outperformed pure Pt, with the best being Pt$_{80}$Ru$_{20}$ with an onset potential of 0.53 V-SCE.

![Figure 5.16.3, Oxygen reduction reaction onset potential for the Pt-Ru-Cu system (a) before and (b) after conditioning. Measured during the 10th downward sweep at 10 mV/s in oxygen saturated 0.5 M H$_2$SO$_4$ at 20 °C.](image)

These results support the hypothesis that some free Cu$^{2+}$ ions were redeposited on Pt-Ru compositions. It also agrees with the early studies that a partial monolayer of Cu on a Pt surface could enhance the ORR activity [70, 238]. Pt$_{80}$Ru$_{20}$ would normally have a poorer ORR onset potential than pure Pt (see section 5.1.2), but assuming the weak peak in figure 5.16.2 (b) indicated the electrodeposition of a small amount of Cu
onto the Pt$_{80}$Ru$_{20}$ sample, then the improved performance can be ascribed to a bifunctional effect from Cu on the surface. Why the optimum amount of Cu was deposited on the Pt$_{80}$Ru$_{20}$ sample can only be explained by a preferential Ru adsorption. Of course this explanation is purely speculation and does contradict the RRDE work that refutes any benefit gained from a partial monolayer Cu on Pt [36]. Indeed, within the limits of experimental error Pt$_{80}$Ru$_{20}$ could outperform pure Pt without any Cu being necessarily present.

5.17 Platinum - Ruthenium - Magnesium Titanium

5.17.1 Pt-Ru-Mg$_4$Ti: Methanol Oxidation Reaction

As part of a separate work on hydrogen storage there was an interesting Mg$_4$Ti (abbreviated MT in the following discussion) target in the sputterer, that led to an unscheduled Pt-Ru-MT library being deposited for electrochemical testing. Initially the library performed surprisingly well, with a strong response from compositions about Pt$_{50}$MT$_{50}$ generating more than 5 x the current density of pure Pt. After the 40 °C test the library was partially conditioned as shown in figure 5.17.1 (a), and there was a strong response from Pt$_{43}$Ru$_{14}$MT$_{43}$, reaching 3.8 x 10$^{-4}$ Acm$^{-2}$. Though good, this is still only a tenth of the current density achieved by other very reactive compositions that exceeded the measuring capabilities of the MMA. The high current density of Pt$_{43}$Ru$_{14}$MT$_{43}$ was concurrent with a lower onset potential, 0.26 V-SCE, implying that the improved result was not merely a dissolution roughening effect.
Figure 5.17.1, (a) Peak current densities of methanol oxidation for the Pt-Ru-Mg4Ti system after partial conditioning measured on the 10th forward scan at 10 mV/s in 0.5 M H2SO4, 0.5 M methanol at 20 °C. (b) Visually assessed corrosion scores for Pt-Ru-Mg4Ti system.

However the excellent performance was not maintained. After testing at 60 °C nearly all compositions with more than 50% MT failed to respond. The post testing microscopy revealed that severe corrosion and spalling had occurred to the majority of samples as shown in figure 5.17.1 (b). Thus the improvement gained from the presence of Mg was fleeting, with its poor corrosion resistance implying that the catalyst would fail to survive in a fuel cell environment.

5.17.2 Pt-Ru-Mg4Ti: Oxygen Reduction Reaction

There weren’t many pads responding to the ORR test, with the majority of pads believed to have corroded before this final test was performed. Nonetheless, the remaining members of the Pt-Ru-Mg4Ti library were examined for oxygen reduction activity. As can be seen in figure 5.17.2 (a) there were no compositions that gave a truly outstanding oxygen reduction performance. The best composition in methanol free clean electrolyte was Pt75MT25 with an onset potential of 0.54 V-SCE, only 5 mV better.
than the average Pt response as shown in figure 5.17.2 (a). With the introduction of methanol as shown in figure 5.17.2 (b), the onset potential of all the compositions dropped. There was a greater drop for Pt$_{75}$MT$_{25}$ than for pure Pt, such that now the best performing composition was pure Pt. No ternary compositions of Pt-Ru-MT outperformed Pt under any conditions.

There is no literature regarding the oxygen reduction properties of Pt-Mg, Pt-Mg-Ti or Pt-Ru-Mg-Ti alloys. The lack of performance seen in this study suggests that if there was a report it would probably be negative.

5.18 Platinum – Iron - Ruthenium

5.18.1 Pt-Fe-Ru: Methanol Oxidation Reaction

The Pt-Fe-Ru system was one of the few systems that had the same trend of current densities before and after conditioning as shown in figure 5.18.1 (a) and (c).
The composition with the highest activity was Pt$_{43}$Fe$_{57}$ with a peak methanol oxidation current density $2.5 \times$ more than pure Pt. The onset potential of this composition was the same before (figure 5.18.1 (b)) and after activation (figure 5.18.1 (d)) but was not very impressive in comparison to previously tested libraries. The onset potential of Pt$_{43}$Fe$_{57}$ was only 0.35 V-SCE, a mere 20 mV lower than the average Pt onset potential (0.37 V-SCE). The composition with the lowest onset potential was Pt$_{13}$Fe$_{50}$Ru$_{37}$ with 0.30 V-SCE before conditioning and 0.26 V-SCE after conditioning. But at the same time the current density of Pt$_{13}$Fe$_{50}$Ru$_{37}$ was $7.5 \times 10^{-4}$ Acm$^{-2}$, 4 times less than Pt$_{43}$Fe$_{53}$. It is unusual for the composition with the lowest onset potential to not correlate with the composition with the highest peak methanol oxidation current density.

Figure 5.18.1, Peak current densities and onset potentials of methanol oxidation for the Pt-Fe-Ru system (a, b) before and (c, d) after conditioning. Measurements taken during the 10$^{th}$ forward scan at 10 mV/s in 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 °C.
Xu et al. [193] examined Pt-Fe nanoparticles on multi-walled carbon nanotubes and reported that the Fe improved the Pt active area without directly affecting the reaction. Page et al. [176] tested a commercially available carbon membrane electrode with Pt_{50}Fe_{50} and reported a similar onset potential to pure Pt. These two reports agree with our work in that Pt_{43}Fe_{57} had a similar onset potential to Pt, but its current density was significantly higher implying it was merely increasing the active area without directly affecting the reaction. The most likely way Pt_{43}Fe_{57} was increasing its active area in our study was by preferential leaching leaving a rougher surface. The improvement to the current density seen in our study wasn’t as high as the 20 × seen by Lyons et al. for Pt doped FeOX [202] but it was still significant. Shukla and Raman [15] reported that a unspecified carbon supported Pt-Fe catalyst had a similar onset potential but a weaker current density then Pt. This matches the performance of the compositions between Pt_{75}Fe_{25} and Pt_{50}Fe_{50} in our study, implying they were probably examining Pt_{50}Fe_{50}.

There is some literature of Pt-Fe-Ru compositions to compare the performance of Pt_{13}Fe_{50}Ru_{37} with. McElwee-White and Serra [296] mention an improved performance from some heterobimetallic complexes that contained Fe and Ru, but the structure of these complexes is so vastly different to a metallic surface that comparison to this study is impossible. Lima et al. [194] reported a Pt-Ru-Fe catalyst had a better methanol oxidation performance than Pt but were vague as to the actual composition.

The shape of the Pt_{13}Fe_{50}Ru_{37} and Pt_{43}Fe_{57} cyclic voltammetry curves was quite different. The final voltammetry sweeps that show the methanol oxidation peaks of Pt_{13}Fe_{50}Ru_{37} and Pt_{43}Fe_{57} are shown in figure 5.18.2. The current density of
Pt$_{13}$Fe$_{50}$Ru$_{37}$ slowly built to a mediocre peak, but in contrast the current density of Pt$_{43}$Fe$_{57}$, suddenly jumped from its late onset to a strong peak current density. In addition the Pt$_{13}$Fe$_{50}$Ru$_{37}$ curve was not symmetrical about its peak. This could have been because there were two reaction peaks superimposed on each other. Indeed when two Gaussian peaks are fitted to the curve of Pt$_{13}$Fe$_{50}$Ru$_{37}$ they have a significantly higher $R^2$ than if a single Gaussian peak was fitted to the curve. From the fitting of the two Gaussian peaks, the first peak had a low 0.26 V-SCE onset potential and the second was 0.37 V-SCE, the same as pure Pt. Based on this, Fe-Ru structures on the catalyst surface possibly oxidized methanol by another reaction pathway. The three other compositions similar to Pt$_{13}$Fe$_{50}$Ru$_{37}$ had curves that were also non-symmetrical, but there were no binary Fe-Ru compositions that oxidized methanol. So even though Fe-Ru rich compositions seemed to oxidize methanol by a different pathway, a small concentration of Pt was still necessary.

Figure 5.18.2, Portions of Pt$_{13}$Fe$_{50}$Ru$_{37}$ and Pt$_{43}$Fe$_{57}$ cyclic voltammetry curves that highlight the differing methanol oxidation reaction peaks.
This different reaction pathway had a lower activation energy equating to a lower onset potential. Simultaneously the reaction kinetics on these catalysts was slow which equated to the poor current density. Slow kinetics could have been from two sources. Firstly there may be very few sites that methanol oxidation occurred on. When only a small portion of the catalyst surface was doing all the work then obviously the conversion rate would be poor. This is equivalent to saying the catalyst had a low active area for this reaction path. Secondly the reaction may have had a slow rate determining step. The slow reaction step may have required a specific juxtaposition of molecules that occurred infrequently. For example carbon monoxide will remain poisoning a Pt site until a water group is adsorbed and dehydrogenated nearby. The whole reaction process is paused until the correct reaction molecules are brought together. If Fe-Ru was oxidizing methanol by a reaction pathway that was different from pure Pt or Pt-Ru, then it is quite likely that although the activation energy was low the rate determining step was slow. Fe-Ru alloys are promising candidates that may be suitable with the addition of a third element that improves the kinetics.

5.18.2 Pt-Fe-Ru: Oxygen Reduction Reaction

The Pt-Fe-Ru system displayed fairly mediocre oxygen reduction activity. The best composition was again Pt_{57}Fe_{50}Ru_{13} with an onset potential of 0.54 V-SCE, just 1 mV better than Pt_{43}Fe_{57} and 14 mV better than the average Pt response as shown in figure 5.18.3 (a). This result conflicted slightly with the similar work of Toda et al. [73, 195] who reported that sputter deposited Pt_{51}Fe_{49} had 150 mV higher onset potential than pure Pt. The remarkably better performance seen by Toda et al. probably occurred because their experiments used 0.1 M HClO₄, which tends inflate a catalysts performance. Other
groups [77, 197, 198] that weren’t seeking an optimum composition reported that
\( \sim \text{Pt}_{80}\text{Fe}_{20} \) was better than pure Pt. The results of this study contradict this with no real
difference between pure Pt and the alloys Pt\textsubscript{80}Fe\textsubscript{20} or Pt\textsubscript{75}Fe\textsubscript{25}. The success seen by Liu et al. [131] with Ru\textsubscript{56}Fe\textsubscript{44} performing better than pure Pt was also not reproduced by our
study.

When testing with a combination of methanol and oxygen, most of the
compositions around Pt\textsubscript{50}Fe\textsubscript{50} oxidized methanol instead of reducing oxygen as shown in
figure 5.18.3 (b). The best oxygen reduction response in the methanol/oxygen test came
from a pure Pt catalyst with an onset potential of 0.51 V-SCE. This was dampened by
the other Pt catalysts lowering the average Pt response to 0.48 V-SCE. The special
methanol oxidation behavior of the compositions around Pt\textsubscript{14}Fe\textsubscript{43}Ru\textsubscript{43} did not make any
difference to their oxygen reduction performances. Note that the low Pt catalyst
Pt\textsubscript{20}Fe\textsubscript{60}Ru\textsubscript{20} had an ORR onset potential 20 mV higher than the average Pt response but
was still quite mediocre in comparison to other systems.
5.19 Platinum – Iron – Carbon

5.19.1 Pt-Fe-C: Methanol Oxidation Reaction

Initial results weren’t very surprising, with the carbon rich compositions behaving like perfect insulators and failing show any signs of charge transfer, as indicated by the white circles in figure 5.19.1 (a). In contrast, an inert (non catalytic) conductive surface like titanium nitride would at least generate $5 \times 10^{-6}$ Acm$^{-2}$ current at the potential extremes. This would indicate that some charged species were adsorbing to the titanium nitride surface. The carbon rich compositions did not register any current; the surface was not charging and was completely insulated from the electrolyte. Carbon that is amorphous and insulating has been reported by other groups [297, 298]. However, this insulating behavior was contrary to the carbon rich compositions from the Pt-Ru-C library that registered a minimally conductive signal. The reason for this was because there was some mild spalling in the Ru-C rich samples after annealing, so even if the C layers did not conduct there were breaches and bypasses that allowed conduction. In

![Pt-Fe-C phase system displaying onset potentials of methanol oxidation (a) before and (b) after activation. Measured during the 10th forward scan at 10 mV/s in 0.5 M H$_2$SO$_4$, 0.5 M methanol at 20 °C.](image)

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contrast the Pt-Fe-C films that had no faults going into testing, there were no breaches in
the insulating barrier of the carbon rich Pt-Fe-C samples and no conductivity was
possible. There was insufficient data to shade the background of the carbon rich region
of figure 5.19.1 (a) so it is white.

As for methanol oxidation on the conductive compositions there were no strong
responses, the peak methanol oxidation current densities were 1/10th what was regularly
seen from previous libraries. Only Pt-Fe binary compositions responded to the
methanol oxidation test. The best composition in the unconditioned library was Pt80Fe20
recording a peak methanol oxidation current density of $5.8 \times 10^{-4}$ Acm$^{-2}$ and an onset
potential of 0.37 V-SCE.

There were some surprising results after cyclic voltammetry at elevated
temperatures conditioned the library as shown in figure 5.19.1 (b). Firstly a few
previously inert carbon rich compositions started responding to the tests, implying that
the carbon layer could be altered electrochemically. Note that only Pt75C25, Pt80C20,
Pt13C64Fe13 and Pt12C50Fe38 responded, while compounds with less platinum or more
carbon continued to be non-responsive. Further x-ray analysis did not reveal any
clarifying structural characteristics of these compositions. As expected, temperature
testing conditioned pure Pt; its peak methanol oxidation current density was 5 times more
than its initial value ($i_{\text{init}} = 4.0 \times 10^{-4}$ Acm$^{-2}$, $i_{\text{final}} = 1.9 \times 10^{-3}$ Acm$^{-2}$). The optimum
compositions after conditioning were Pt37Fe26C37 and Pt44Fe12C44, which recorded peak
methanol oxidation current densities of $3.8 \times 10^{-3}$ Acm$^{-2}$ and an onset potential of 0.26
V-SCE. This was twice the current density and 80 mV lower than the pure platinum
standard. The intriguing point was the high concentration of carbon in the optimum
compositions. This shows that carbon is more than a convenient support for nanoparticles and does play a role in methanol oxidation.

Comparing our result to reports from other groups is difficult. Many studies [7, 78, 189, 190] have examined Pt and Pt-Ru catalysts on different carbon supports, but no one has considered or discussed the carbon concentration as a possible variable that would affect the catalyst performance. To add to the difficulty there is no experimental technique that could accurately measure the concentration of carbon on the surface of carbon supported carbon nanoparticles. This work has shown that the concentration of carbon is a variable that should be considered if a fair comparison between catalysts is to be made.

5.19.2 Pt-Fe-C: Oxygen Reduction Reaction

The best methanol oxidation catalyst, $\text{Pt}_{44}\text{Fe}_{12}\text{C}_{44}$, was also the best oxygen reduction catalyst as shown in figure 5.19.2 (a). The oxygen reduction onset potential of $\text{Pt}_{44}\text{Fe}_{12}\text{C}_{44}$ was 0.54 V-SCE, only 20 mV better than the pure platinum standard.

![Figure 5.19.2](image)

Figure 5.19.2, (a) Onset potential of oxygen reduction for the Pt-Fe-C system measured during the 10th backward scan at 10 mV/s in oxygen saturated 0.5 M H$_2$SO$_4$. (b) Corrosion resistance of the Pt-Fe-C system based on optical microscopy assessment.
These results show that doping Fe and C into Pt provided no real catalytic enhancement to the oxygen reduction reaction. In the presence of methanol and oxygen nearly all of the catalysts ignored the oxygen and oxidized the methanol. Similar to the Pt-Ru-C system carbon seems to play no role in the oxygen reduction reaction.

The corrosion resistance of the Pt-Fe-C system was very good as shown in figure 5.19.2 (b). It seems that the deposited carbon was naturally durable and inert to electrochemical dissolution or oxidation. The only composition that showed signs of corrosion was the pure iron. This should be taken with a grain of salt as the majority of Fe-C compositions were non-conductive and incapable of any electrochemical interaction including a corrosion reaction.

5.20 Platinum – Iron – Chromium

5.20.1 Pt-Fe-Cr: Methanol Oxidation Reaction

The Pt–Fe-Cr system was disappointing with no composition showing a substantial improvement over pure platinum. During the first test at room temperature as shown in figure 5.20.1 (a), the Pt-Fe binary alloys (Pt_{80}Fe_{20} to Pt_{50}Fe_{50}) were more active than the pure Pt alloys. The best composition Pt_{57}Fe_{43} had an onset potential of 0.39 V-SCE and a peak current density of $2.7 \times 10^{-4}$ Acm$^{-2}$. Unfortunately there was no response from any composition that contained Cr at this initial unconditioned stage.

After higher temperature testing the expected stronger response from the conditioned pure Pt was recorded as shown in figure 5.20.1 (b). Pt_{64}Fe_{13}Cr_{13} also improved with conditioning with the lowest onset potential of 0.3 V-SCE which was 30 mV lower than the next two best compositions Pt_{43}Fe_{57} and pure Pt. But Pt_{64}Fe_{13}Cr_{13} did not have the
strongest peak methanol oxidation current density, instead it was just lower than the $2.1 \times 10^{-3} \text{ Acm}^{-2}$ recorded by pure platinum. Overall there was no conditioned catalyst that dramatically out performed pure platinum at methanol oxidation in the Pt-Fe-Cr system.

This was different than the performance of the Pt-Ni-Cr and the Pt-Co-Cr libraries. The other systems had compositions that responded favorably before and after conditioning. It seems that Fe was of no positive advantage to the methanol oxidation reaction. The previous results of the Pt-Fe-Ru library also implied that the Fe made no difference to the reaction, but was merely leaching out and leaving a rougher surface. The Cr appears to have stabilized and reduced Fe leaching from the Pt-Fe-Cr samples leaving no benefit or enhancement.

5.20.2 Pt-Fe-Cr: Oxygen Reduction Reaction

The oxygen reduction performance of the catalysts in this system was also disappointing. Some activity was seen from the Cr rich compositions $\text{Pt}_{25}\text{Cr}_{75}$, $\text{Pt}_{20}\text{Cr}_{80}$
and Pt₁₅Fe₂₃Cr₆₂ but they were only marginally better than pure Pt. The best composition Pt₂₅Cr₇₅ had an onset potential 60 mV higher than pure Pt but its $8 \times 10^{-5}$ Acm⁻² current density at 0.5 V-SCE was ~5 x weaker than the usual current density generated by Pt. There were no standout oxygen reduction catalyst compositions from this system.
6.1 Conclusions: Combinatorial Process

A combinatorial system that can screen different compositions for low temperature fuel cell catalysis properties has been successfully developed. The system was used to fabricate libraries of ternary compositions from binary systems that have been established as good fuel cell catalysts, or have been reported as exhibiting interesting properties. The developed synthesis and characterization systems were also used to examine systems that are less well known. The libraries were deposited on a 2” Si wafer and could contain combinations of up to five elements in 76 different samples. That complexity was unnecessary; libraries were usually fabricated with combinations of three elements in permutations that generated 49 different compositions (and 27 repeated compositions to assure reproducibility). Overall ~50 libraries have been fabricated and tested and from this over 10 000 relevant sets of data have been analyzed.

The testing successfully determined the short term activity of the different compositions in a manner that facilitated reasonable comparison. The combinatorial libraries avoided many problematic variables like particle size and catalyst loading which can distort a true fuel cell test. This testing constituted a preliminary screen that recognized compositions that have a naturally high activity. Catalysts that were inactive in the short timeframe of these tests will also be inactive over longer times. These poor
performing compositions have been eliminated from further consideration and will not be unnecessarily examined in an expensive fuel cell test. Future work will be to fabricate the best compositions as high surface area powders on a conductive support for testing in a true fuel cell environment.

This combinatorial screening process was not perfect; to remain feasible some sacrifices were made. The samples were made by sputter deposition which gave precise control of the composition. But sputter deposition would be difficult to apply to real fuel cell catalyst fabrication. Though deposition can achieve extremely light loadings, there is no reliable deposition method that can penetrate into the tortuous three dimensional structure of a fuel cell’s membrane electrode assembly. A superior composition that was discovered on a sputter deposited library may not be immediately replicated in a fuel cell test. Many issues are involved with powder versions of catalysts that may exist to varying degrees in thin films including the formation of enriched skins or the preferential leaching of an element. These complex issues raise uncertainty around the exact composition or whether the same surface could be reproduced on a nanoparticle.

Further and more intricate testing could always be applied to the thin film libraries to resolve some issues of doubt. For example if AES was indefinitely available then the exact surface composition could be determined before and after every test. But these combinatorial library samples are not actual fuel cell catalysts. The responses from these thin film samples during testing gives a simplified indication of how a nanoparticle catalyst, with a similar composition, may behave in a fuel cell environment. But the behavior is not guaranteed to be replicated. With this in mind further testing
and analysis of these combinatorial samples seems of little value. Further testing may elucidate some of the quirky behavior of the thin film samples but unless the same behavior is also observed in a fuel cell nanoparticle then it would not be worth pursuing.

The simplifications made to keep the testing feasible were balanced against maintaining accuracy in the results. Some very interesting trends were seen across systems and some insights gained. Some systems, Pt-Ni-Cr in particular, had active compositions that were isolated; there was no trend of positive activity leading to the optimum composition region. This composition would have been missed in a more traditional non-combinatorial investigation. Other exciting results came from the testing of the Pt-Ru-C system. These results provided an eloquent explanation as to why the optimum flat surface catalyst composition never matched the optimum carbon supported nanoparticle composition. This is an exciting result that would never have been found with a regular fuel cell catalyst investigation. It is also doubtful whether any flat surface study would have bothered considering carbon as a composition variable. This result was only discovered by performing an exhaustive combinatorial investigation.

6.2 Conclusions: DMFC Anode, Methanol Oxidation Catalysts

The screening system was first used to characterize the Pt-Ru system, achieving results that compared favorably with similar studies reported in the literature. It was found that cycling the potential at 60 °C conditioned the library and made some previously inert compositions very active. The optimum conditioned Pt-Ru composition was $\text{Pt}_90\text{Ru}_{10} \pm 5 \text{ At\%}$, achieving a methanol oxidation onset potential of $0.29 \text{ V-SCE} \pm 0.02 \text{ V}$ and a peak current density of $3.5 \text{ Acm}^{-2} \pm 0.2 \text{ Acm}^{-2}$. The composition and
strong current density of this composition compared well with literature reports, but the onset potential was poorer than the best Pt-Ru catalysts reported in literature. These parameters were the criteria used to judge the performance of all other combinatorial libraries.

Many ternary systems were examined for improved methanol oxidation with the best unconditioned compositions summarized in table 6.2.1. Listed are the compositions with the highest current density at the peak of the methanol oxidation reaction (i_Pk) and the compositions with the lowest MOR onset potential (E_ONSET). There are also two other metrics that are helpful when comparing results between libraries; firstly is the ratio of the peak current densities of the best composition and the pure Pt standard from the same library (i/i_Pt). Secondly is the offset between the onset potentials of the best composition and the pure Pt standard on the same library (ΔE_Pt). Though helpful these parameters should be considered carefully, as sometimes they merely indicate that the Pt standard performed poorly rather than the best composition did remarkably well.

The typically poor performance of unconditioned Pt makes it hard to judge the relative merit of other unconditioned compositions. For example there were six systems (highlighted in blue in table 6.2.1) that exceeded the measurable limits of the MMA system (0.1 mA or 3.8 × 10^{-3} Acm^{-2}). During these same tests the Pt standards achieved peak current densities between 2 × 10^{-5} Acm^{-2} and 4 × 10^{-4} Acm^{-2}. Thus based solely on i/i_Pt, Pt_{43}Ru_{14}MT_{43} was the best unconditioned composition and 10 times more active than Pt_{17}Ru_{17}Co_{66}. This was not true in reality, as Pt_{43}Ru_{14}MT_{43} performed 200 times better than a very poor performing Pt standard. The surface of that Pt standard was probably
TABLE 6.2.1
BEST UNCONDITIONED METHANOL OXIDATION CATALYST COMPOSITIONS

<table>
<thead>
<tr>
<th>System</th>
<th>Composition with best $i_{pk}$</th>
<th>$i_{pk}$ (Acm$^{-2}$)</th>
<th>$i/i_{pt}$</th>
<th>Composition With best $E_{onset}$</th>
<th>$E_{onset}$ V-SCE</th>
<th>$\Delta E_{pt}$ mV</th>
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<tbody>
<tr>
<td>Pt-Ru-W</td>
<td>Pt$<em>{25}$W$</em>{75}$</td>
<td>1.06 × 10$^{-3}$</td>
<td>7</td>
<td>Pt$<em>{66}$Ru$</em>{17}$W$_{17}$</td>
<td>0.165</td>
<td>200</td>
</tr>
<tr>
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<td>7.59 × 10$^{-4}$</td>
<td>8</td>
<td>Pt$<em>{13}$Ru$</em>{51}$WC$_{36}$</td>
<td>0.355</td>
<td>128</td>
</tr>
<tr>
<td>Pt-Ru-WC/Ta</td>
<td>Pt$<em>{43}$Ru$</em>{57}$</td>
<td>4.18 × 10$^{-5}$</td>
<td>2</td>
<td>Pt$<em>{37}$Ru$</em>{50}$W$<em>{10}$(WCTa)$</em>{13}$</td>
<td>0.295</td>
<td>178</td>
</tr>
<tr>
<td>Pt-Ta-WC</td>
<td>Pt$<em>{60}$Ta$</em>{50}$</td>
<td>8.90 × 10$^{-5}$</td>
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<td>Pt$<em>{60}$Ta$</em>{50}$</td>
<td>0.355</td>
<td>0</td>
</tr>
<tr>
<td>Pt-Ru-C</td>
<td>Pt$<em>{75}$Ru$</em>{25}$</td>
<td>5.48 × 10$^{-4}$</td>
<td>1</td>
<td>Pt$<em>{44}$Ru$</em>{44}$C$_{12}$</td>
<td>0.290</td>
<td>55</td>
</tr>
<tr>
<td>Pt-Ru-Cr</td>
<td>Pt$<em>{50}$Ru$</em>{20}$Cr$_{50}$</td>
<td>6.41 × 10$^{-4}$</td>
<td>2</td>
<td>Pt$<em>{12}$Ru$</em>{44}$Cr$_{44}$</td>
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<td>140</td>
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<td>227</td>
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<tr>
<td>Pt-Ni-Cr</td>
<td>Pt$<em>{50}$Ni$</em>{80}$</td>
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<td>21</td>
<td>Pt$<em>{50}$Ni$</em>{80}$</td>
<td>0.370</td>
<td>50</td>
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<tr>
<td>Pt-Ru-Co</td>
<td>Pt$<em>{17}$Ru$</em>{17}$Co$_{66}$</td>
<td>3.96 × 10$^{-3}$</td>
<td>21</td>
<td>Pt$<em>{17}$Ru$</em>{17}$Co$_{66}$</td>
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<td>242</td>
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<tr>
<td>Pt-Ti-Co</td>
<td>Pt$<em>{28}$Ti$</em>{26}$Co$_{48}$</td>
<td>3.80 × 10$^{-3}$</td>
<td>10</td>
<td>Pt$<em>{28}$Ti$</em>{30}$Co$_{36}$</td>
<td>0.200</td>
<td>175</td>
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<td>Pt$<em>{50}$Co$</em>{50}$Cr$_{20}$</td>
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<td>Pt$<em>{50}$Co$</em>{60}$Cr$_{10}$</td>
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<td>105</td>
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<td>Pt$<em>{28}$Co$</em>{36}$Cu$_{36}$</td>
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<td>Pt$<em>{12}$Ru$</em>{44}$Cu$_{44}$</td>
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<td>222</td>
</tr>
<tr>
<td>Pt-Ru-Mg$_{4}$Ti</td>
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<td>3.80 × 10$^{-3}$</td>
<td>208</td>
<td>Pt$<em>{43}$Ru$</em>{44}$MT$_{43}$</td>
<td>0.255</td>
<td>0</td>
</tr>
<tr>
<td>Pt-Fe-Ru</td>
<td>Pt$<em>{43}$Ru$</em>{50}$Fe$_{57}$</td>
<td>2.52 × 10$^{-3}$</td>
<td>2</td>
<td>Pt$<em>{13}$Ru$</em>{57}$Fe$_{50}$</td>
<td>0.305</td>
<td>53</td>
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<tr>
<td>Pt-Fe-C</td>
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<td>1</td>
<td>Pt$<em>{30}$Fe$</em>{20}$</td>
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<td>Pt$<em>{57}$Fe$</em>{43}$</td>
<td>0.395</td>
<td>60</td>
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</tbody>
</table>

The table shows the best unconditioned methanol oxidation catalyst compositions, including the system, composition with the best $i_{pk}$, $i_{pk}$ value, $i/i_{pt}$ ratio, composition with the best $E_{onset}$, $E_{onset}$ value relative to the standard calomel electrode (V-SCE), and the change in $E_{pt}$ value. The compositions range from Pt-Ru-W to Pt-Fe-Cr, with varying combinations of metals like Pt, Ru, W, WC, Ta, Pt, Ru, Ni, Cu, Mg, Ti, Cr, Fe, and Mg$_{4}$Ti. The table also highlights the importance of using other non-electrochemical techniques to gather more information and interpret unusual behavior.

Choked with Mg from the many corroding samples in the Pt-Ru-Mg$_{4}$Ti system. The downside of testing many compositions in parallel in the same electrolyte was that corroding specimens could alter the performance of their neighbors. This highlights the importance of using another non-electrochemical technique, like the microscopy inspection, to gather more information and aid in interpreting unusual behavior.

To better assess the relative performance of the different libraries, the onset potential should be considered as well. The compositions from the Pt-Ru-MT and Pt-Co-Cr had MOR onset potentials that were close to pure Pt, implying that they were not lowering the energetics of the reaction, but were probably just preferentially leaching and increasing the active area. There were four systems that achieved a high current...
density (> $3.8 \times 10^{-3} \text{ Acm}^{-2}$) and a low onset potential (< 0.2 V-SCE). The best compositions from those systems were; Pt$_{20}$Ni$_{80}$, Pt$_{17}$Ru$_{17}$Co$_{66}$, Pt$_{26}$Ti$_{26}$Co$_{48}$ and Pt$_{28}$Co$_{36}$Cu$_{36}$. Unfortunately the performance of the four good catalysts diminished with further testing.

None of the unconditioned catalysts that outshone Pt initially were still active at the conclusion of the testing but some other compositions did become more active, as shown in table 6.2.2. Conditioned Pt behaved more reproducibly achieving at least $1 \times 10^{-3} \text{ Acm}^{-2}$ peak methanol oxidation current density on most libraries (the exceptions being Pt-Ta-WC and Pt-Ni-Cr). There were four systems that achieved strong peak

<table>
<thead>
<tr>
<th>System</th>
<th>Composition with best $i_{pk}$</th>
<th>$i_{pk}$ (Acm$^{-2}$)</th>
<th>$i/i_{Pt}$</th>
<th>Composition with best $E_{onset}$</th>
<th>$E_{onset}$ V-SCE</th>
<th>$\Delta E_{Pt}$ mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru-W</td>
<td>Pt$<em>{44}$Ru$</em>{12}$W$_{44}$</td>
<td>$1.90 \times 10^{-3}$</td>
<td>2</td>
<td>Pt$<em>{44}$Ru$</em>{12}$W$_{44}$</td>
<td>0.165</td>
<td>225</td>
</tr>
<tr>
<td>Pt-Ru-WC</td>
<td>Pt$<em>{12}$WC$</em>{76}$</td>
<td>$1.39 \times 10^{-3}$</td>
<td>2</td>
<td>Pt$<em>{12}$Ru$</em>{44}$WC$_{44}$</td>
<td>0.310</td>
<td>165</td>
</tr>
<tr>
<td>Pt-Ru-WC/Ta</td>
<td>Pt$<em>{50}$ (WCTa)$</em>{50}$</td>
<td>$3.32 \times 10^{-4}$</td>
<td>3</td>
<td>Pt$<em>{50}$ (WCTa)$</em>{50}$</td>
<td>0.330</td>
<td>132</td>
</tr>
<tr>
<td>Pt-Ta-WC</td>
<td>Pt$<em>{43}$WC$</em>{57}$</td>
<td>$3.62 \times 10^{-4}$</td>
<td>3</td>
<td>Pt$<em>{43}$WC$</em>{57}$</td>
<td>0.225</td>
<td>105</td>
</tr>
<tr>
<td>Pt-Ru-C</td>
<td>Pt$<em>{38}$Ru$</em>{28}$C$_{36}$</td>
<td>$3.12 \times 10^{-3}$</td>
<td>3</td>
<td>Pt$<em>{38}$Ru$</em>{28}$C$_{36}$</td>
<td>0.175</td>
<td>185</td>
</tr>
<tr>
<td>Pt-Ru-Cr</td>
<td>Pt$<em>{60}$Ru$</em>{20}$Cr$_{20}$</td>
<td>$1.33 \times 10^{-3}$</td>
<td>2</td>
<td>Pt$<em>{43}$Ru$</em>{43}$Cr$_{14}$</td>
<td>0.315</td>
<td>62</td>
</tr>
<tr>
<td>Pt-Ru-Ni</td>
<td>Pt$<em>{28}$Ni$</em>{75}$</td>
<td>$3.81 \times 10^{-3}$</td>
<td>1</td>
<td>Pt$<em>{43}$Ni$</em>{50}$Ni$_{37}$</td>
<td>0.190</td>
<td>137</td>
</tr>
<tr>
<td>Pt-Ni-Cr</td>
<td>Pt$<em>{28}$Cr$</em>{36}$Ni$_{36}$</td>
<td>$3.77 \times 10^{-3}$</td>
<td>16</td>
<td>Pt$<em>{28}$Cr$</em>{36}$Ni$_{36}$</td>
<td>0.265</td>
<td>162</td>
</tr>
<tr>
<td>Pt-Ru-Co</td>
<td>Pt$<em>{12}$Ru$</em>{50}$Co$_{37}$</td>
<td>$3.80 \times 10^{-3}$</td>
<td>2</td>
<td>Pt$<em>{12}$Ru$</em>{44}$Co$_{44}$</td>
<td>0.220</td>
<td>142</td>
</tr>
<tr>
<td>Pt-Ti-Co</td>
<td>Pt$<em>{50}$Ti$</em>{13}$Co$_{37}$</td>
<td>$3.80 \times 10^{-3}$</td>
<td>2</td>
<td>Pt$<em>{50}$Ti$</em>{13}$Co$_{37}$</td>
<td>0.285</td>
<td>77</td>
</tr>
<tr>
<td>Pt-Co-Cr</td>
<td>Pt$<em>{32}$Co$</em>{30}$Cr$_{40}$</td>
<td>$2.98 \times 10^{-3}$</td>
<td>7</td>
<td>Pt$<em>{32}$Co$</em>{30}$Cr$_{40}$</td>
<td>0.360</td>
<td>20</td>
</tr>
<tr>
<td>Pt-Co-Cu</td>
<td>Pt$<em>{32}$Co$</em>{30}$Cu$_{40}$</td>
<td>$3.77 \times 10^{-3}$</td>
<td>2</td>
<td>Pt$<em>{32}$Co$</em>{30}$Cu$_{40}$</td>
<td>0.300</td>
<td>-10</td>
</tr>
<tr>
<td>Pt-Ru-Cu</td>
<td>Pt$<em>{68}$Ru$</em>{17}$Cu$_{17}$</td>
<td>$2.68 \times 10^{-3}$</td>
<td>1</td>
<td>Pt$<em>{28}$Ru$</em>{36}$Cu$_{36}$</td>
<td>0.295</td>
<td>75</td>
</tr>
<tr>
<td>Pt-Ru-Mg$_4$Ti</td>
<td>Pt$_{100}$</td>
<td>$8.95 \times 10^{-3}$</td>
<td>1</td>
<td>Pt$<em>{33}$Ru$</em>{33}$MT$_{33}$</td>
<td>0.440</td>
<td>55</td>
</tr>
<tr>
<td>Pt-Fe-Ru</td>
<td>Pt$<em>{43}$Fe$</em>{57}$</td>
<td>$2.99 \times 10^{-3}$</td>
<td>2</td>
<td>Pt$<em>{13}$Ru$</em>{37}$Fe$_{50}$</td>
<td>0.265</td>
<td>100</td>
</tr>
<tr>
<td>Pt-Fe-C</td>
<td>Pt$<em>{44}$Fe$</em>{17}$C$_{44}$</td>
<td>$3.80 \times 10^{-3}$</td>
<td>2</td>
<td>Pt$<em>{44}$Fe$</em>{17}$C$_{44}$</td>
<td>0.265</td>
<td>80</td>
</tr>
<tr>
<td>Pt-Fe-Cr</td>
<td>Pt$_{100}$</td>
<td>$2.12 \times 10^{-3}$</td>
<td>1</td>
<td>Pt$<em>{68}$Fe$</em>{17}$Cr$_{17}$</td>
<td>0.300</td>
<td>32</td>
</tr>
</tbody>
</table>
current densities and low onset potentials; Pt-Ru-W, Pt-Ru-C, Pt-Ru-Ni and Pt-Ru-Co. That these systems all contained Pt and Ru attests to their importance in the methanol oxidation reaction. The best catalyst that did not contain Ru was Pt$_{43}$WC$_{57}$ with a reasonable peak current density and onset potential.

There was both agreement and contradiction between the best compositions determined from this study and those reported in literature. There have been many variations in catalyst preparation and testing procedures reported by other groups that makes the possibility of a fair comparison difficult. Usually results obtained in this study would agree with flat surface studies of polycrystalline bulk alloys and conflict with work done on carbon supported nanoparticles. Not only is unusual behavior possible on the high energy facets of a nanoparticle, but this study showed that even the presence of carbon could also skew the optimum composition. When this study concurred with other reports it was usually the unconditioned compositions that agreed. This highlights the necessity of also considering a compositions corrosion resistance. A composition that was initially very active was quite often also the least stable, but there were some systems that had active and corrosion resistant compositions.

The cost of Pt is currently $1200 Oz$^{-1}$ and the cost of Ru in the last four months has risen from $160 Oz$^{-1}$ to $800 Oz$^{-1}$. The average loading of catalyst in a real fuel cell is 0.04 gcm$^{-2}$. From this, the value of precious metal included in a fuel cell is $0.19$ cm$^2$ for pure Pt and $0.16$ cm$^2$ for Pt$_{50}$Ru$_{50}$. This does not include the cost of fabricating the Pt and Ru into carbon supported high surface area nanoparticles. There were many compositions from this study that performed as well as Pt and had a much lower noble metal content; in particular, the Ni alloys Pt$_{25}$Ni$_{75}$ and Pt$_{26}$Cr$_{36}$Ni$_{36}$ have $\sim\frac{1}{4}$
the Pt content and no Ru. This does not necessarily mean that the catalysts would cost 25% less. The process required to fabricate these compositions as active, high surface area, nanoparticles is unknown. The fabrication would probably be more complex, especially for the ternary composition, and thus more costly. Even with this caution in mind, the determination of active compositions with reduced noble metal content is a positive step towards reducing the cost of fuel cell catalysts.

6.3 Conclusions: PEMFC Cathode, Oxygen Reduction Catalysts

The sluggish kinetics of the oxygen reduction reaction is responsible for 300 mV of overpotential in low temperature fuel cells. Improving catalysts to overcome this barrier is the focus of many research groups. This study successfully examined many systems for improved activity in the oxygen reduction reaction. A summary of the best catalysts from the different systems is given in table 6.3.1. Listed are the systems, the best performing composition from that system, the potential at the onset of the oxygen reduction reaction (\(E_{\text{ONSET}}\)) and the difference between the best composition and the Pt standard on the same library (\(\Delta E_{\text{Pt}}\)).

The performance of each catalyst was compared to the average performance of pure Pt standards on the library. Carbon supported pure Pt nanoparticles are the industry norm for low temperature fuel cell cathode catalysts. The onset potential of Pt determined with our system was 0.568 ± 0.008 V-SCE which agreed well with other work under similar conditions in the literature. Later tests with systems that contained carbon (Pt-Ru-C and Pt-Fe-C) showed that Pt\(_{50}\)C\(_{50}\) had a ~20 mV higher onset potential implying that carbon was influencing the reaction. This is a very interesting observation,
### TABLE 6.3.1

**BEST OXYGEN REDUCING CATALYSTS**

<table>
<thead>
<tr>
<th>System</th>
<th>Composition with lowest $E_{\text{ONSET}}$ (V-SCE)</th>
<th>$E_{\text{ONSET}}$ (V-SCE)</th>
<th>$\Delta E_{\text{Pt}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru</td>
<td>$\text{Pt}_{100}$</td>
<td>0.568</td>
<td>0</td>
</tr>
<tr>
<td>Pt-Ru-W</td>
<td>$\text{Pt}<em>{44}\text{Ru}</em>{12}\text{W}_{44}$</td>
<td>0.593</td>
<td>43</td>
</tr>
<tr>
<td>Pt-Ru-WC/Ta</td>
<td>$\text{Pt}<em>{57}(\text{WCTa})</em>{43}$</td>
<td>0.571</td>
<td>43</td>
</tr>
<tr>
<td>Pt-Ru-C</td>
<td>$\text{Pt}<em>{50}\text{C}</em>{50}$</td>
<td>0.541</td>
<td>22</td>
</tr>
<tr>
<td>Pt-Ru-Cr</td>
<td>$\text{Pt}<em>{86}\text{Ru}</em>{20}\text{Cr}_{20}$</td>
<td>0.565</td>
<td>6</td>
</tr>
<tr>
<td>Pt-Ru-Ni</td>
<td>$\text{Pt}<em>{25}\text{Ni}</em>{75}$</td>
<td>0.582</td>
<td>23</td>
</tr>
<tr>
<td>Pt-Ni-Cr</td>
<td>$\text{Pt}<em>{56}\text{Ni}</em>{37}\text{Cr}_{37}$</td>
<td>0.543</td>
<td>54</td>
</tr>
<tr>
<td>Pt-Ru-Co</td>
<td>$\text{Pt}<em>{44}\text{Ru}</em>{43}\text{Co}_{43}$</td>
<td>0.559</td>
<td>1</td>
</tr>
<tr>
<td>Pt-Ti-Co</td>
<td>$\text{Pt}<em>{43}\text{Co}</em>{57}$</td>
<td>0.577</td>
<td>72</td>
</tr>
<tr>
<td>Pt-Co-Cr</td>
<td>$\text{Pt}<em>{52}\text{Co}</em>{38}\text{Cr}_{37}$</td>
<td>0.673</td>
<td>107</td>
</tr>
<tr>
<td>Pt-Co-Cu</td>
<td>$\text{Pt}_{100}$</td>
<td>0.563</td>
<td>0</td>
</tr>
<tr>
<td>Pt-Ru-Cu</td>
<td>$\text{Pt}<em>{80}\text{Ru}</em>{20}$</td>
<td>0.53</td>
<td>18</td>
</tr>
<tr>
<td>Pt-Ru-Mg$_2$Ti</td>
<td>$\text{Pt}<em>{55}\text{Mg}</em>{25}\text{Ti}_{25}$</td>
<td>0.535</td>
<td>5</td>
</tr>
<tr>
<td>Pt-Fe-Ru</td>
<td>$\text{Pt}<em>{13}\text{Fe}</em>{87}\text{Ru}_{13}$</td>
<td>0.537</td>
<td>14</td>
</tr>
<tr>
<td>Pt-Fe-C</td>
<td>$\text{Pt}<em>{50}\text{C}</em>{50}$</td>
<td>0.541</td>
<td>22</td>
</tr>
<tr>
<td>Pt-Fe-Cr</td>
<td>$\text{Pt}<em>{50}\text{Cr}</em>{50}$</td>
<td>0.571</td>
<td>66</td>
</tr>
</tbody>
</table>

As carbon is usually assumed to be an inert support that does not directly affect the reaction. Many studies have shown different activities for different types of carbon support, but the differences were always ascribed to physical characteristics of the supports like particle size or conductivity. This study provides evidence that carbon directly interacts with Pt to improve the onset potential of oxygen reduction. Unfortunately, whether carbon plays a role in nanoparticle catalysts would be difficult to discern. There is no way to conclusively analyze carbon supported nanoparticles and distinguish between carbon in the Pt nanoparticles, on the nanoparticle’s surface or the carbon making up the support. Theoretically, a catalyst supported on a non carbon
material may answer this question, but carbon is also a common contaminant in many nanoparticle fabrication processes.

Some systems responded poorly; there were no compositions in the “Pt free” Pd-Co-Cr or Co-Cr-Cu systems that could be coaxed to reduce oxygen at all. This illustrates the importance of Pt, it can be alloyed with other components but its presence seems to be vital for an effective low temperature oxygen reduction catalyst. Though Ru was beneficial for the methanol oxidation reaction, its presence was of little benefit to the oxygen reduction reaction. Instead the four systems that contained Cr or Co (Pt-Ni-Cr, Pt-Ti-Co, Pt-Co-Cr and Pt-Fe-Cr) had compositions with favorable responses to the oxygen reduction reaction. Indeed, the best catalyst overall was Pt$_{27}$Co$_{36}$Cr$_{37}$ with an onset potential of 0.673 V-SCE, 107 mV better than the standard pure Pt. This validates the early reports and patents on Pt-Co-Cr catalysts initially for the PAFC and the more recently for the PEMFC. Pt$_{27}$Co$_{36}$Cr$_{37}$ also has the benefit of having a low Pt content and therefore, based on the precious metal value, presumably cost less to produce.

There was evidence that some elements (Cu, Ti and Fe in particular) leached from some compositions and affected the reaction kinetics of other alloys. A transition metal ion could alter the ORR reaction while in solution, or it could have diffused and during a potential cycle electrodeposited on another sample. This electrodeposition of free ions could skew the composition of a sample or clot the surface with inactive regions. Free ions were believed to be the principal reason for variation of the Pt standards between libraries. This problem is of most concern in the continuation of this work with powder synthesis and characterization. If the best oxygen reducing composition (Pt$_{27}$Co$_{36}$Cr$_{37}$)
cannot be reproduced as a carbon supported nanoparticle then further analysis needs to be applied to the thin films. Surface characterization techniques may reveal that the surface of the active composition was altered from the nominal pad composition or had a very specific configuration of atoms. A special fabrication process may be required to replicate this surface on a nanoparticle.

6.4 Conclusions: MRDMFC Anode and Cathode, Poison Resistant Catalysts

Methanol is a devastating poison that can deactivate the pure Pt catalyst on a DMFC cathode. Similarly oxygen that permeates into the anode of a PEMFC reduces the cell’s efficiency by completing the fuel cell reaction prematurely and short-circuiting some otherwise useful energy. This makes a cathode catalyst that is resistant to methanol or an anode catalyst that ignores oxygen desirable. If the selectivity of these catalysts can be tailored sufficiently then they may even make the concept of a MRDMFC feasible.

A summary of the best poison resistant catalyst compositions is presented in table 6.4.1. Listed are the systems, the composition that was the best at reducing oxygen in the presence of methanol (ORR\text{METH}), that composition’s onset potential (E_{\text{ORR-METH}}) and the difference between it and the Pt standard (\Delta E_{\text{Pt}}). Also shown are the compositions that were the best at oxidizing methanol (MOR\text{Oxygen}), their peak current densities (I_{\text{pk-Oxygen}}) and onset potentials (E_{\text{MOR-Oxygen}}), all in the presence of oxygen. The latter information should be considered with care, since the presence of oxygen substantially shifted the baseline which, when corrected, slightly inflated the current densities and
positively shifted the onset potentials. This was why the Pt-Ru-W, Pt-Co-Ti and Pt-Fe-C registered current densities higher than the measurable limit.

### TABLE 6.4.1
**BEST POISON RESISTANT CATALYST COMPOSITIONS**

<table>
<thead>
<tr>
<th>System</th>
<th>Composition</th>
<th>( \Delta E_{\text{Pt}} ) (mV)</th>
<th>( E_{\text{ORR-METH}} ) (V-SCE)</th>
<th>( I_{\text{Pt-Oxygen}} ) (Acm(^{-2}))</th>
<th>( E_{\text{MOR-Oxygen}} ) (V-SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru-W</td>
<td>Pt(_{100})</td>
<td>0</td>
<td>0.529</td>
<td>Pt(<em>{44})Ru(</em>{12})W(_{44})</td>
<td>3.94 \times 10(^{-3})</td>
</tr>
<tr>
<td>Pt-Ru-WCTa</td>
<td>Pt(<em>{43})Ru(</em>{14})(WCTa)(_{43})</td>
<td>0.546</td>
<td>29</td>
<td>Pt(<em>{57})(WCTa)(</em>{43})</td>
<td>3.82 \times 10(^{4})</td>
</tr>
<tr>
<td>Pt-Ru-C</td>
<td>Pt(<em>{60})Ru(</em>{20})C(_{20})</td>
<td>0.524</td>
<td>24</td>
<td>Pt(<em>{44})Ru(</em>{12})C(_{44})</td>
<td>2.82 \times 10(^{-3})</td>
</tr>
<tr>
<td>Pt-Ru-Cr</td>
<td>Pt(<em>{50})Cr(</em>{50})</td>
<td>0.527</td>
<td>8</td>
<td>Pt(<em>{50})Ru(</em>{50})</td>
<td>1.37 \times 10(^{-3})</td>
</tr>
<tr>
<td>Pt-Ru-Ni</td>
<td>Pt(_{100})</td>
<td>0.522</td>
<td>0</td>
<td>Pt(<em>{25})Ni(</em>{75})</td>
<td>2.14 \times 10(^{-3})</td>
</tr>
<tr>
<td>Pt-Ni:Cr</td>
<td>Pt(<em>{43})Ni(</em>{14})Cr(_{43})</td>
<td>0.534</td>
<td>22</td>
<td>Pt(<em>{57})Ni(</em>{36})Cr(_{37})</td>
<td>1.25 \times 10(^{-4})</td>
</tr>
<tr>
<td>Pt-Ru-Co</td>
<td>Pt(<em>{12})Ru(</em>{50})Co(_{38})</td>
<td>0.535</td>
<td>3</td>
<td>Pt(<em>{12})Ru(</em>{38})Co(_{50})</td>
<td>7.94 \times 10(^{-4})</td>
</tr>
<tr>
<td>Pt-Ti-Co</td>
<td>Pt(<em>{57})Co(</em>{43})</td>
<td>0.525</td>
<td>26</td>
<td>Pt(<em>{54})Co(</em>{44})Ti(_{12})</td>
<td>4.00 \times 10(^{-3})</td>
</tr>
<tr>
<td>Pt-Co-Cr</td>
<td>Pt(<em>{30})Co(</em>{40})Cr(_{30})</td>
<td>0.579</td>
<td>65</td>
<td>Pt(<em>{27})Co(</em>{36})Cr(_{37})</td>
<td>7.80 \times 10(^{-4})</td>
</tr>
<tr>
<td>Pt-Ru-Mg(_{4})Ti</td>
<td>Pt(_{100})</td>
<td>0.539</td>
<td>12</td>
<td>Pt(<em>{33})Ru(</em>{33})MT(_{33})</td>
<td>5.11 \times 10(^{-5})</td>
</tr>
<tr>
<td>Pt-Fe-Ru</td>
<td>Pt(_{100})</td>
<td>0.510</td>
<td>25</td>
<td>Pt(<em>{43})Fe(</em>{57})</td>
<td>4.80 \times 10(^{-4})</td>
</tr>
<tr>
<td>Pt-Fe-C</td>
<td>Pt(<em>{60})C(</em>{50})</td>
<td>0.486</td>
<td>45</td>
<td>Pt(<em>{54})Fe(</em>{12})C(_{44})</td>
<td>4.03 \times 10(^{-3})</td>
</tr>
<tr>
<td>Pt-Fe-Cr</td>
<td>Pt(<em>{15})Fe(</em>{20})Cr(_{62})</td>
<td>0.514</td>
<td>20</td>
<td>Pt(<em>{28})Fe(</em>{9})Cr(_{75})</td>
<td>1.46 \times 10(^{-3})</td>
</tr>
</tbody>
</table>

The presence of methanol reduced the oxygen reduction onset potential for every system with only a few exceptions. Pt\(_{43}\)Ni\(_{14}\)Cr\(_{43}\) had a better oxygen reduction performance in the presence of methanol than in clean electrolyte. Unfortunately its onset potential was still weak in comparison to other libraries. There were no compositions in the Pt-Ru-Ni, Pt-Ru-Mg\(_{4}\)Ti or Pt-Fe-Ru systems that could outperform pure Pt in the presence of methanol. The catalysts in these systems were either inert or preferentially oxidized methanol instead. The best oxygen reducing composition in the presence of methanol was Pt\(_{30}\)Co\(_{40}\)Cr\(_{30}\) with an onset potential of 0.579 V-SCE which is
similar to pure Pt in clean electrolyte. Unfortunately this strong oxygen reduction performance occurred simultaneously with a strong methanol oxidation reaction. This makes the Pt-Co-Cr catalysts unsuitable as a cathode of a mixed reactant fuel cell.

Oxygen also reduced the methanol activity of every composition. There was no composition that maintained a low methanol oxidation onset potential in the presence of oxygen. Surprisingly, some compositions showed no detrimental effects to their peak current densities. The best composition to oxidize methanol in the presence of oxygen was Pt_{44}Ru_{12}W_{44} with a peak current density beyond the measurable limit of the system and an onset potential of 0.479 V-SCE. Curiously, the methanol oxidation was very sensitive to the presence of oxygen, with onset potentials changing by ~300 mV. Oxygen reduction in the presence of methanol was much less sensitive in comparison with the onset potentials only changing ~40 mV. This contradicts the thrust of PEMFC membrane research which focuses on stopping methanol from poisoning the cathode.

6.5 Conclusions: Future Work

A combinatorial system was developed, fabricated and tested for the purpose of evaluation potential fuel cell catalysts. It has been used to successfully screen many ternary composition systems, identifying several compositions that outperformed the standard catalysts currently used in fuel cells. The next stage of this work would be to fabricate the optimum compositions in a powder form and examine them in true fuel cell conditions. The fabrication and testing of the combinatorial samples may have skewed the surface composition in a way that cannot be replicated by current powder synthesis techniques. Such surface modification during fuel cell operation is a well
known occurrence in powders, so it likely also happened in these films. Even if the compositions specified by this study are exact, powder synthesis is difficult, sometimes more of an art than a science. A composition that is inherently more active, as observed from thin film measurements may still respond poorly as a powder because another variable (like particle size) was not optimized.

Further work should be performed examining the active compositions and determining characteristics that they have in common. This kind of study has been already been performed for many structural characteristics (for example interatomic spacing or d-band shift) and related to oxygen reducing performance. Unfortunately these previous studies have mainly been DFT calculations on models that required simplifications and assumptions to remain feasible. This study gave the physical performance of actual composition samples in a simulated fuel cell environment. If this data was correlated to an atomic property of the compositions then more accurate trends may emerge. This would help to guide the selection of future compositional systems to be tested.

Mapping such intricate trends across multiple systems would require the improved data mining tools. This study developed some data mining tools while simultaneously optimizing the electrochemical testing. The tools are far from perfect, with only rough comparisons of individual properties possible, like the onset potential vs. composition for one library. More complex comparisons are not feasible with the current data mining tools. For example, a plot of the measured lattice parameter for every nickel composition that had a minimum 0.56 V-SCE onset potential and corrosion score higher than 4, would take a day to compile.
The data mining software, Spotfire, can facilitate irregular comparison queries like the above example but it has other drawbacks. It cannot cope with the vast quantities of raw data that are generated during experiments and requires other data mining programs. Firstly a program must compile the information from the different experimental tests (x-ray, MMA, microscope, etc.). Secondly another program must filter 99% of the raw data and pass on only the bare minimum of relevant information regarding a composition’s properties. Whether the preparation programs functioned properly can only be assessed once the filtered database is uploaded into Spotfire. This can lead to some painfully tedious loops with incomplete datasets in Spotfire requiring changes to the compiling and filtering programs. Ideally the data mining program should be improved so that all of the raw data is organized, and any comparison query could be facilitated within the one program.

The testing equipment could be improved, but modifications would have to be considered with caution. The libraries are built at the limits of the deposition system. For example, the titanium nitride base cannot be deposited thicker than 2000 Å or internal stresses will spall and destroy the film. Also the stoichiometry of the titanium nitride is assessed after deposition based solely on a visual interpretation of the color. Enhancements to the deposition system may relieve the constraints that currently limit the deposition. For example, some possibilities would be isolating the substrate for heating and biasing, in situ calibration of the deposition or simultaneous mass spectrometry testing. The electrochemical testing could also be improved. For example, an impellor could be included in the rig that would move the electrolyte and push back the diffusion limit of the oxygen reduction reaction. With careful calibration experiments at different
impellor speeds could possibly even be compared to the results of rotating disk electrode experiments and also establish actual rate constants. The value that these modifications bring would have to be balanced against the losses they would simultaneously incur. The most major drawback of any change would be that it would weaken the ability to compare previous work with future work. Improving the quality of the measurements made by the system would not be worth pursuing if it simultaneously made all previous data sets incomparable to any future work.
Sub DataExtract()
Dim CounterA, CounterB, CounterC, CounterD As Integer
Dim Seeker(10), Ori(8) As Variant
Dim Alpha(156) As String
' Alpha variant contains the alphabet Alpha(1) = A, Alpha(2) = B, etc.
For CounterA = 1 To 26
Alpha(CounterA) = Mid(Range("A1").Offset(0, CounterA - 1).Address, 2, 1)
Next
For CounterA = 27 To 156
Alpha(CounterA) = Mid(Range("A1").Offset(0, CounterA - 1).Address, 2, 2)
Next
' Delete unnecessary rows from "raw no meth"
Sheets("Raw No Meth").Select
Range("A1").Select
For CounterA = 1 To 1000
If Range("A1").Offset(CounterA, 0).Text = "Time" Then
If CounterA > 8 Then
Rows("1:2").Delete
Rows("3:4").Delete
Rows("6:" & CounterA - 12).Delete
Rows("8:12").Delete
CounterA = 1000
End If
End If
End If
End If
End If
Next
' Check that the right data set is pasted in sheet 1
If CounterA = 999 Then
CounterB = MsgBox("You need to paste some data", vbOKOnly, "Goose")
End
End If
End If
Next
' Delete unresponsive columns from "raw no meth" and "raw + meth"
If Left(Range("A2").Text, 3) <> "Non" Then
Range("A2").Formula = "Non-responsive Hex's: ":
For CounterA = 6 To 106
Range("A1").Offset(0, CounterA - 1).Formula = "+STDEV(" & Range("A50:A5000").Offset(0, CounterA - 1).Address & ")"
If Range("A1").Offset(0, CounterA - 1).Value < 0.000001 Then
If Range("B2").Value = 0 Then Range("A2").Formula = Range("A2").Text & Range("A1").Offset(8, CounterA - 1).Text & ", 
Range("B2").Formula = ""
Seeker(5) = 0
For CounterB = 1 To 4
If CounterA > 26 Then
End
End If
End If
End If
End If
Next
Seeker(5) = Seeker(5) + 1
CounterA = CounterA - 26
End If
Next
Columns(Alpha(Seeker(5)) & Alpha(CounterA) & ":" & Alpha(Seeker(5)) & Alpha(CounterA)).Delete
Sheets("Raw + Meth").Select
Columns(Alpha(Seeker(5)) & Alpha(CounterA) & ":" & Alpha(Seeker(5)) & Alpha(CounterA)).Delete
Sheets("Raw No Meth").Select
CounterA = 26 * Seeker(5) + CounterA - 1
End If
Range("A1").Offset(0, CounterA - 1).Formula = ""
If Range("A1").Offset(8, CounterA).Text = "" Then CounterA = 106
Next
End If
' Delete unnecessary rows from "raw + meth"
Sheets("Raw + Meth").Select
Range("A1").Select
For CounterA = 1 To 1000
If Range("A1").Offset(CounterA, 0).Text = "Time" Then
If CounterA > 8 Then
Rows("1:2").Delete
Rows("3:4").Delete
Rows("6:" & CounterA - 12).Delete
Rows("8:12").Delete
CounterA = 1000
End If
End If
End If
Next
For CounterA = 1 To 100
If Mid(Range("A1").Text, CounterA, 2) = "oC" Then Sheets("Analysis").Range("A1").Formula =
Mid(Range("A1").Text, CounterA - 3, 2)
If CounterA = 100 Then
If Sheets("Analysis").Range("A1").Formula = "" Then
CounterA = MsgBox("Can't determine the temperature from the file name", vbOKOnly, "Screw Up")
End
End If
End If
Next
For CounterA = 1 To 100
If Mid(Range("A1").Text, CounterA, 2) = "oC" Then Sheets("Analysis").Range("A1").Formula =
Mid(Range("A1").Text, CounterA - 3, 2)
If CounterA = 100 Then
If Sheets("Analysis").Range("A1").Formula = "" Then
CounterA = MsgBox("Can't determine the temperature from the file name", vbOKOnly, "Screw Up")
End
End If
End If
Next
Sheets("Analysis").Select
'Collect the deleted columns and the raw data file names on the Analysis sheet
Range("A2").Formula = "=""Raw No Meth!A2"
Range("A3").Formula = "=""Raw No Meth!A6"
Range("A4").Formula = "=""Raw + Meth!A6"
Range("A5").Formula = "=""Raw No Meth!A7"
Range("A6").Formula = "=""Raw + Meth!A7"
Range("A1:A6").Copy
Range("A1").PasteSpecial xlValues
'Pull out the library name
For CounterA = 200 To 1 Step -1
If Mid(Range("A4").Text, CounterA, 1) = "," Then
CounterB = CounterA + 1
CounterA = 1
End If
Next
For CounterA = CounterB To 200
If Mid(Range("A4").Text, CounterA, 1) = " " Then
CounterC = CounterA - CounterB
CounterA = 200
End If
Next
Sheets("analysis").Range("A7").Formula = Mid(Range("A4").Text, CounterB, CounterC)
Ori(1) = Sheets("analysis").Range("A7").Text
'Check compositions and update the Map
Sheets("Map").Select
Range("G29").Formula = "=G30&H30&I30"
Range("G28").Formula = "=len(G29)"
Ori(2) = ActiveWorkbook.Name
Workbooks.Open FileName:="D:\chug stuff\Chug at ND\Excel Files\0x Maps.xls", UpdateLinks:=0
For CounterA = 1 To 10000 Step 23
   If Range("A1").Offset(CounterA, 0).Text = " " Then
      CounterA = MsgBox("Can't find the Appropriate Map", vbOKOnly, "Horsefly")
   End If
   If Range("A1").Offset(CounterA, 0).Text = Ori(1) Then
         For CounterB = 1 To 3
            Ori(CounterB + 2) = Range("a1").Offset(CounterA + CounterB, 0).Text
         Next
         Range("C3:U23").Offset(CounterA - 1, 0).Copy
         Windows(Ori(2)).Activate
         Range("B5").PasteSpecial xlAll
         Windows("0x Maps").Activate
         ActiveWorkbook.Save
         ActiveWindow.Close
         For CounterB = 1 To 3
            Range("F30").Offset(0, CounterB).Formula = Ori(CounterB + 2)
         Next
         CounterA = 10000
   End If
Next
If CounterA = 2 Then End
'Bring the Scribner group:segment labels on to the analysis page
Sheets("Analysis").Select
For CounterA = 1 To 100
   Range("E4").Offset(0, CounterA).Formula = "='Raw No Meth!' & Alpha(CounterA + 5) & "9"
   Range("E4").Offset(0, CounterA).Formula = Range("E4").Offset(0, CounterA).Value
If Range("E4").Offset(0, CounterA).Value = 0 Then
   Range("E4").Offset(0, CounterA).Delete
   CounterA = 100
End If
Next
   Titles
   Range("E1").Formula = "Grid Position"
   Range("E2").Formula = "X-Y Co-Ord"
   Range("E3").Formula = "Corrosion"
   Range("E4").Formula = "Raw Label"
   Range("E5").Formula = "Composition 1"
   Range("E6").Formula = "Composition 2"
Range("E7").Formula = "Composition 3"
Range("E8").Formula = "X - Co Ord"
Range("E9").Formula = "Y - Co Ord"
Range("E10").Formula = "Area"
Seeker(1) = 3
For CounterA = 1 To 100
    If Range("E1").Offset(Seeker(1), CounterA).Text <> "" Then
        If Left(Right(Range("E1").Offset(Seeker(1), CounterA).Text, 2), 1) <> 0 Then
            If Mid(Range("E1").Offset(Seeker(1), CounterA).Text, 5, 1) = "," Then
                Range("E1").Offset(0, CounterA).Formula = Alpha(Left(Right(Range("E1").Offset(Seeker(1), CounterA).Text, 2), 1)) & Mid(Range("E1").Offset(Seeker(1), CounterA).Text, 4, 1)
            Else
                Range("E1").Offset(0, CounterA).Formula = Alpha(Left(Right(Range("E1").Offset(Seeker(1), CounterA).Text, 2), 1)) & Mid(Range("E1").Offset(Seeker(1), CounterA).Text, 4, 2)
            End If
        Else
            If Mid(Range("E1").Offset(Seeker(1), CounterA).Text, 5, 1) = "," Then
                Range("E1").Offset(0, CounterA).Formula = Alpha(Left(Right(Range("E1").Offset(Seeker(1), CounterA).Text, 3), 2)) & Mid(Range("E1").Offset(Seeker(1), CounterA).Text, 4, 1)
            Else
                Range("E1").Offset(0, CounterA).Formula = Alpha(Left(Right(Range("E1").Offset(Seeker(1), CounterA).Text, 3), 2)) & Mid(Range("E1").Offset(Seeker(1), CounterA).Text, 4, 2)
            End If
        End If
    Else
        CounterA = 100
    End If
Next
'Find the edge of the data and use seeker(2) to set the limit
For CounterA = 1 To 100
    If Range("F1").Offset(0, CounterA) = "" Then
        Seeker(2) = CounterA + 5
        CounterA = 100
    End If
Next
'Increase CounterB to 6 if area information is available
For CounterB = 1 To 5
    If Range("E2").Offset(0, 1).Text <> "" Then
        Range("E5").Offset(CounterB - 1, 1).Formula = _
        "=VLOOKUP(" & Range("E1").Offset(0, 1).Address(rowabsolute:=false, ColumnAbsolute:=false) & ",Map!$B$30:$T$106,4,FALSE)"
        Range("E2").Offset(1, 1).Formula = "=VLOOKUP(" & Range("E1").Offset(0, 1).Address(rowabsolute:=false, ColumnAbsolute:=false) & ",Map!$B$30:$T$106,3,FALSE)"
        Range("F2" & Alpha(Seeker(2)) & "3").FillRight
    End If
Next
100
'Data Column Labels
Range("A14").Offset(0, 0).Formula = "TimeNoM"
Range("A14").Offset(0, 0).Characters(Start:=5, Length:=3).Font.Subscript = True
Range("A14").Offset(0, 1).Formula = "TimeMeth"
Range("A14").Offset(0, 1).Characters(Start:=5, Length:=4).Font.Subscript = True
Range("A14").Offset(0, 2).Formula = "VBase NoM"
Range("A14").Offset(0, 2).Characters(Start:=2, Length:=4).Font.Subscript = True
Range("A14").Offset(0, 3).Formula = "VBase Meth"
Range("A14").Offset(0, 3).Characters(Start:=2, Length:=4).Font.Subscript = True
Range("A14").Offset(0, 4).Formula = "Diff"
Range("F14").Formula = "=F2"
Range("F14: & Alpha(Seeker(2)) & "14").FillRight
Range("F14: & Alpha(Seeker(2)) & "14").Copy
Range("F14: & Alpha(Seeker(2)) & "14").PasteSpecial Paste:=xlPasteValues
'Match the Base voltage starting point from the No Meth to the Meth data
Seeker(1) = Sheets("Raw No Meth").Range("D10").Value
Seeker(3) = Sheets("Raw + Meth").Range("D10").Value
If Abs(Seeker(1) - Seeker(3)) > 0.01 Then
If Seeker(1) > Seeker(3) Then
Sheets("Raw No Meth").Select
For CounterA = 1 To 1000
If Range("D9").Offset(CounterA, 0).Value < Seeker(3) Then
If Abs(Range("D9").Offset(CounterA, 0).Value - Seeker(3)) < Abs(Range("D9").Offset(CounterA - 1, 0).Value - Seeker(3)) Then
Rows("10:" & CounterA + 8).Select
Selection.Delete
CounterA = 1000
Else
Rows("10:" & CounterA + 7).Select
Selection.Delete
CounterA = 1000
End If
End If
Next
Else
Sheets("Raw + Meth").Select
For CounterA = 1 To 1000
If Range("D9").Offset(CounterA, 0).Value < Seeker(1) Then
If Abs(Range("D9").Offset(CounterA, 0).Value - Seeker(1)) < Abs(Range("D9").Offset(CounterA - 1, 0).Value - Seeker(1)) Then
Rows("10:" & CounterA + 8).Select
Selection.Delete
CounterA = 1000
Else
Rows("10:" & CounterA + 7).Select
Selection.Delete
CounterA = 1000
End If
End If
Next
End If
End If
'Only collect the shortest time point
Sheets("Raw No Meth").Select
For CounterA = 1 To 10000
If Range("A100").Offset(CounterA, 0).Text = "" Then
Seeker(1) = CounterA + 90 + 14
CounterA = 10000
End If
Next
Sheets("Raw + Meth").Select
For CounterA = 1 To 10000
If Range("A100").Offset(CounterA, 0).Text = "" Then
If CounterA + 90 + 14 < Seeker(1) Then
Seeker(1) = CounterA + 90 + 14
CounterA = 10000
Else:
CounterA = 10000
End If
End If
Next
Sheets("Analysis").Select
Range("A14").Offset(1, 0).Formula = "='Raw No Meth'!A10"
Range("A14").Offset(1, 1).Formula = "='Raw + Meth'!A10"
Range("A14").Offset(1, 2).Formula = "='Raw No Meth'!D10"
Range("A14").Offset(1, 3).Formula = "='Raw + Meth'!D10"
Range("A14").Offset(1, 4).Formula = "=C15 - D15"
Range("A14").Offset(1, 5).Formula = "='Raw + Meth'!F10-'Raw No Meth'!F10"
Range("F15." & Alpha(Seeker(2)) & "15").Select
Selection.FillRight
'Filldown in a series of steps - got an error message if done in one go -> "selection is too large"
For CounterA = 1 To Seeker(1) Step 100
Range("A13." & Alpha(Seeker(2)) & "114").Offset(CounterA, 0).Select
Selection.FillDown
Range("A13." & Alpha(Seeker(2)) & "114").Offset(CounterA - 1, 0).Select
Selection.Copy
Selection.PasteSpecial Paste:=xlPasteValues
Next
Range("A" & Seeker(1) + 1 & ":" & Alpha(Seeker(2)) & CounterA + 15).Select
Selection.Delete
Range("A15").Select
Seeker(2) = Seeker(2) + 1
Range(Alpha(Seeker(2)) & "14").Select
Range(Alpha(Seeker(2)) & "14").Formula = ":=D14"
Range(Alpha(Seeker(2)) & "14." & Alpha(Seeker(2)) & Seeker(1)).Select
Selection.FillDown
For CounterA = 1 To Seeker(2) - 6
Range("E10").Offset(0, CounterA).Formula = Seeker(2) - 4 - CounterA
Next
Seeker(4) = 1
For CounterC = 1 To 50
Range("E11").Offset(2 * CounterC - 2, 0).Formula = ":IPEAK " & CounterC
Range("E11").Offset(2 * CounterC - 2, 0).Characters(Start:=2, Length:=4).Font.Subscript = True
Range("E11").Offset(2 * CounterC - 1, 0).Formula = ":VPEAK " & CounterC
Range("E11").Offset(2 * CounterC - 1, 0).Characters(Start:=2, Length:=4).Font.Subscript = True
'Max
For CounterA = Seeker(4) + 1 To Seeker(4) + 1000
'Range("D14").Offset(CounterA, 0).Select
'If Range("D14").Offset(CounterA - 1, 0).Value > Range("D14").Offset(CounterA, 0).Value Then
'If Range("D14").Offset(CounterA, 0).Value < Range("D14").Offset(CounterA + 1, 0).Value Then
If Range("D14").Offset(CounterA - 1, 0).Value <= Sheets("Map").Range("A1").Value Then
If Range("D14").Offset(CounterA, 0).Value >= Sheets("Map").Range("A1").Value Then
Seeker(3) = CounterA + 14
204
End If
End If
'If Range("D14").Offset(CounterA - 1, 0).Value < Range("D14").Offset(CounterA, 0).Value Then
'If Range("D14").Offset(CounterA, 0).Value > Range("D14").Offset(CounterA + 1, 0).Value Then
If Range("D14").Offset(CounterA - 1, 0).Value <= Sheets("Map").Range("B1").Value Then
If Range("D14").Offset(CounterA, 0).Value >= Sheets("Map").Range("B1").Value Then
Seeker(4) = CounterA + 14
Range("F9").Offset(CounterC * 2, 0).Formula = "=MAX(F & Seeker(3) & ":F & Seeker(4) & ")"
Range("F9").Offset(CounterC * 2 + 1, 0).Formula = "=VLOOKUP(F & 9 + 2 * CounterC & ",F & Seeker(3) & ":$ & Alpha(Seeker(2)) & ":$ & _")
Seeker(4) = ",F10,FALSE"
Range("F9" & Alpha(Seeker(2) - 1) & ":10").Offset(CounterC * 2, 0).Select
Selection.FillRight
Rows("1:2").Offset(10 + CounterC * 2, 0).Select
Selection.Insert
Seeker(6) = CounterA
CounterA = 1000000
End If
End If
Next
Seeker(5) = CounterC
If CounterA = Seeker(4) + 1001 Then CounterC = 50
Next
Seeker(5) = Seeker(5) - 1
'
'average of the data
Range("E11").Offset(Seeker(5) * 2, 0).Formula = "IAVERAGE"
Range("E11").Offset(Seeker(5) * 2, 0).Characters(Start:=2, Length:=7).Font.Subscript = True
Range("E11").Offset(Seeker(5) * 2 + 1, 0).Formula = "VAVERAGE"
Range("E11").Offset(Seeker(5) * 2 + 1, 0).Characters(Start:=2, Length:=7).Font.Subscript = True
Seeker(6) = ":=AVERAGE(F11"
For CounterA = 1 To Seeker(5) - 1
Seeker(6) = Seeker(6) & ", F" & 2 * CounterA + 11
Next
Seeker(6) = Seeker(6) & ")"
Range("E11").Offset(Seeker(5) * 2, 1).Formula = Seeker(6)
Range("E11:E12").Offset(Seeker(5) * 2, 1).Select
Selection.FillDown
Range("E11" & Alpha(Seeker(2) - 2) & ":12").Offset(Seeker(5) * 2, 1).Select
Selection.FillRight
'______________________________________________________________ Vonset
Seeker(5) = Seeker(5) + 1
Rows("1:2").Offset(10 + Seeker(5) * 2, 0).Select
Selection.Insert
Range("E11").Offset(Seeker(5) * 2, 0).Formula = "Vonset"
Range("D11").Offset(Seeker(5) * 2, 0).Formula = 0.00005
Range("C11").Offset(Seeker(5) * 2, 0).Formula = ":=max(F & Seeker(5) * 2 + 11 & ":" & Alpha(Seeker(2) - 1) & ":& Seeker(5) * 2 + 11 & ":")"
Range("F11").Offset(Seeker(5) * 2, 0).Formula = "=OFFSET($D$" & Seeker(4) - 158 & ",101-COUNTIF(F" & Seeker(4) - 157 & ":F & Seeker(4) - 57 & ":" & Seeker(4) & ":" & Range("D11").Offset(Seeker(5) * 2, 0).Address & ":"),0)"
Range("E11").Offset(Seeker(5) * 2 + 1, 0).Formula = "Vonstand"
Range("F11").Offset(Seeker(5) * 2 + 1, 0).Formula = ":=IF(" & Range("F11").Offset(Seeker(5) * 2, 0).Address(False, False) & ":" & Range("C11").Offset(Seeker(5) * 2, 0).Address & ":" & Range("F11").Offset(Seeker(5) * 2, 0).Address(False, False) & ":")"
Range("F11:" & Alpha(Seeker(2) - 1) & "12").Offset(Seeker(5) * 2, 0).Select
Selection.FillRight
' __________________________________________ Current Density at V = 0.5 meth and no meth
Seeker(5) = Seeker(5) + 1
Rows("1:2").Offset(10 + Seeker(5) * 2, 0).Select
Selection.Insert
Range("E11").Offset(Seeker(5) * 2, 0).Formula = "IV=0.5 (no meth)"
Range("E11").Offset(Seeker(5) * 2, 0).Characters(Start:=2, Length:=5).Font.Subscript = True
Range("E11").Offset(Seeker(5) * 2 + 1, 0).Formula = "IV=0.5 (meth)"
Range("E11").Offset(Seeker(5) * 2 + 1, 0).Characters(Start:=2, Length:=5).Font.Subscript = True
For CounterA = Seeker(4) - 250 To Seeker(4) - 750 Step -1
If Sheets("Raw No Meth").Range("D14").Offset(CounterA, 0).Value >= 0.4997 Then
  Seeker(3) = CounterA + 13
  Range("F11").Offset(Seeker(5) * 2 + 0).Formula = "=";'Raw No Meth'!F" & Seeker(3)
  Range("D11").Offset(Seeker(5) * 2 + 0).Formula = "=";'Raw No Meth'!D" & Seeker(3)
  CounterA = Seeker(4) - 750
End If
Next
For CounterA = Seeker(4) - 250 To Seeker(4) - 750 Step -1
If Sheets("Raw + Meth").Range("D14").Offset(CounterA, 0).Value >= 0.4997 Then
  Seeker(3) = CounterA + 13
  Range("F11").Offset(Seeker(5) * 2 + 1, 0).Formula = "=";'Raw + Meth'!F" & Seeker(3)
  Range("D11").Offset(Seeker(5) * 2 + 1, 0).Formula = "=";'Raw + Meth'!D" & Seeker(3)
  CounterA = Seeker(4) - 750
End If
Next
Range("F9:" & Alpha(Seeker(2) - 1) & "10").Offset(Seeker(5) * 2 + 2, 0).Select
Selection.FillRight
' _____________________________________________ Vorrier
Seeker(5) = Seeker(5) + 1
Rows("1:2").Offset(10 + Seeker(5) * 2, 0).Select
Selection.Insert
Range("E11").Offset(Seeker(5) * 2, 0).Formula = "Vorr(5e-5)"
Range("D11").Offset(Seeker(5) * 2, 0).Formula = -0.00005
Range("C11").Offset(Seeker(5) * 2, 0).Formula = "=min(F" & Seeker(5) * 2 + 11 & ":" & Alpha(Seeker(2) - 1) & Seeker(5) * 2 + 11 & "")"
Range("F11").Offset(Seeker(5) * 2, 0).Formula = "=OFFSET('Raw + Meth'!$D$" & Seeker(4) - 504 & "," & (201 - COUNTIF('Raw + Meth'!F" & Seeker(4) - 503 & ":F" & Seeker(4) - 303 & "," & Range("D11").Offset(Seeker(5) * 2, 0).Address & "", ")" & ",&")", 0))"
Range("E11").Offset(Seeker(5) * 2 + 1, 0).Formula = "Vorr(1e-5)"
Range("D11").Offset(Seeker(5) * 2 + 1, 0).Formula = -0.00001
Range("F11").Offset(Seeker(5) * 2 + 1, 0).Formula = "=OFFSET('Raw + Meth'!$D$" & Seeker(4) - 504 & "," & (201 - COUNTIF('Raw + Meth'!F" & Seeker(4) - 503 & "," & Range("D11").Offset(Seeker(5) * 2 + 1, 0).Address & ")", 0))"
Range("F11" & Alpha(Seeker(2) - 1) & "12").Offset(Seeker(5) * 2, 0).Select
Selection.FillRight
'Plot as columns on the map page
Sheets("Map").Select
Range("N29").Offset(0, 0).Formula = (Seeker(5) * 2 + 9
Range("N29").Offset(0, 1).Formula = 28
Range("N29").Offset(0, 2).Formula = 29

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Sub PlotTernOnMapSheet()
Dim CounterA, CounterB, CounterC, CounterD, Col(3) As Integer
Dim Seeker(6) As Variant
Dim Label(4) As String
Dim Maax, Miin, MinBase(3), IntBase(3), MaxBase(3) As Variant
Label(1) = Sheets("Map").Range("G30").Text
Label(2) = Sheets("Map").Range("H30").Text
Label(3) = Sheets("Map").Range("I30").Text
Sheets("Analysis").Select
For CounterA = 100 To 1 Step -1
    If Mid(Range("A4").Text, CounterA, 1) = "\\" Then
        Seeker(5) = CounterA + 1
        CounterA = 1
    End If
Next
Label(4) = Mid(Range("A4").Text, Seeker(5), 100)
Sheets("Map").Select
Range("T31:X106,Y32:AA106").Select
Selection.ClearContents
Range("T31").Select
CounterB = 1
For CounterA = 1 To 100
    If Range("J30").Offset(CounterA, 0).Text <> "\\" Then '0th
        Seeker(1) = Round(Range("J30").Offset(CounterA, 0).Value, 2) & Round(Range("J30").Offset(CounterA, 1).Value, 2)
        For CounterC = 1 To 50
            If Range("T30").Offset(CounterC, 0).Text = Seeker(1) Then '1st
                CounterC = 50
            Else
                If Range("T30").Offset(CounterC, 0).Text = "\\" Then '2nd
                    If Range("J30").Offset(CounterA, 7).Value > -0.000000001 Then '3rd
                        Seeker(6) = CounterC
                    End If
                    Range("T30").Offset(CounterC, 1).Formula = "\\" & "\\" & Seeker(1) & "\\" & "\\" & Seeker(6) & "\\" & "\\" & Range("J30").Offset(CounterA, 0).Value, 2)
                    Range("T30").Offset(CounterC, 2).Formula = Round(Range("J30").Offset(CounterA, 1).Value, 2)
                    Seeker(2) = Range("J30").Offset(CounterA, 4).Address
                Else
                    If Range("T30").Offset(CounterC, 0).Text = "\\" Then '4th
                        If Range("J30").Offset(CounterA, 7).Value > -0.000000001 Then '5th
                            Seeker(6) = CounterC
                        Else
                            Range("T30").Offset(CounterC, 1).Formula = "\\" & "\\" & Seeker(1) & "\\" & "\\" & Seeker(6) & "\\" & "\\" & Range("J30").Offset(CounterA, 0).Value, 2)
                            Range("T30").Offset(CounterC, 2).Formula = Round(Range("J30").Offset(CounterA, 1).Value, 2)
                            Seeker(2) = Range("J30").Offset(CounterA, 4).Address
                        End If
                    Else
                        Seeker(6) = CounterC
                    End If
                    Range("T30").Offset(CounterC, 1).Formula = "\\" & "\\" & Seeker(1) & "\\" & "\\" & Seeker(6) & "\\" & "\\" & Range("J30").Offset(CounterA, 0).Value, 2)
                    Range("T30").Offset(CounterC, 2).Formula = Round(Range("J30").Offset(CounterA, 1).Value, 2)
                    Seeker(2) = Range("J30").Offset(CounterA, 4).Address
                End If
            End If
        Next
    End If
Next
End Sub
Seeker(3) = Range("J30").Offset(CounterA, 5).Address
Seeker(4) = Range("J30").Offset(CounterA, 7).Address
For CounterD = CounterA + 1 To 100
    If Range("J30").Offset(CounterD, 0).Text <> "" Then '4th
        If Round(Range("J30").Offset(CounterD, 0).Value, 2) & Round(Range("J30").Offset(CounterD, 1).Value, 2) = Seeker(1) Then '5th
            If Range("J30").Offset(CounterD, 7).Value > -0.000000001 Then '6th
                Seeker(2) = Seeker(2) & ", " & Range("J30").Offset(CounterD, 4).Address
                Seeker(3) = Seeker(3) & ", " & Range("J30").Offset(CounterD, 5).Address
                Seeker(4) = Seeker(4) & ", " & Range("J30").Offset(CounterD, 7).Address
            End If '6th
        End If '5th
    End If '4th
    If Range("J30").Offset(CounterD, 0).Text = "" Then CounterD = 100
Next
Range("T30").Offset(CounterC, 3).Formula = ";if(sum(" & Seeker(4) & ");0)
Range("T30").Offset(CounterC, 4).Formula = ";if(count(" & Seeker(4) & ");1;stdev(" & Seeker(4) & ");0)
CounterC = 50
Else: CounterC = 50
End If '3rd
End If '2nd
End If '1st
Next
If Range("J30").Offset(CounterA, 0).Text = "" Then CounterA = 100
End If '0th
Next
Range("Y31:AA" & Seeker(6) + 30).Select
Selection.FillDown
' Background Square
    ActiveSheet.Shapes.AddShape(msoShapePointFill, 140, 50, 320, 280).Select
' Plot the grid of triangles
For CounterA = 1 To 55
    ActiveSheet.Shapes.AddShape(msoShapeIsoscelesTriangle, 200 + 200 * Range("IP30").Offset(CounterA, 0), 100 + 200 * Range("IQ30").Offset(CounterA, 0), 20#, 17.32).Select
    Selection.ShapeRange.Flip msoFlipVertical
    Selection.ShapeRange.Fill.Visible = msoFalse
Next
' Plot the grid of colored triangles
Maax = Sheets("Background").Range("C3").Value
Miin = Sheets("Background").Range("C2").Value
For CounterA = 1 To 400
    Seeker(5) = Sheets("Background").Range("I10").Offset(CounterA, 0).Value
    If Sheets("Background").Range("CH10").Offset(CounterA, 0).Value <> 0 Then
        For CounterB = 1 To 3
            MinBase(CounterB) = Sheets("Background").Range("A5").Offset(1, CounterB).Value
            IntBase(CounterB) = Sheets("Background").Range("A5").Offset(2, CounterB).Value
            MaxBase(CounterB) = Sheets("Background").Range("A5").Offset(3, CounterB).Value
            If (Seeker(5) - Miin) / (Maax - Miin) < 0.5 Then
                Col(CounterB) = (Seeker(5) - Miin) / (Maax - Miin) / 0.5 * (IntBase(CounterB) - MinBase(CounterB)) + MinBase(CounterB)
            Else
                Col(CounterB) = 1
            End If
        Next
    End If
Next
Col(CounterB) = ((Seeker(5) - Min) / (Max - Min) - 0.5) / 0.5 * (MaxBase(CounterB) - MinBase(CounterB))
End If
Next
Else
Col(1) = 256
Col(2) = 256
Col(3) = 256
End If
ActiveSheet.Shapes.AddShape(msoShapeIsoscelesTriangle, 195 + 5 * Sheets("Background").Range("C10").Offset(CounterA, 0), 91.44 + 8.66 * Sheets("Background").Range("C10").Offset(CounterA, 1), 10#, 8.66).Select
If Sheets("Background").Range("H10").Offset(CounterA, 0).Text = "FALSE" Then
  Selection.ShapeRange.Flip msoFlipVertical
  Selection.ShapeRange.Fill.ForeColor.RGB = RGB(Col(1), Col(2), Col(3))
  Selection.ShapeRange.Line.ForeColor.RGB = RGB(Col(1), Col(2), Col(3))
Next
For CounterA = 1 To 55
  ActiveSheet.Shapes.AddShape(msoShapeIsoscelesTriangle, 200 + 200 * Range("IP30").Offset(CounterA, 0), 100 + 200 * Range("IQ30").Offset(CounterA, 0), 20#, 17.32).Select
  Selection.ShapeRange.Flip msoFlipVertical
  Selection.ShapeRange.Fill.Visible = msoFalse
Next
'Title
ActiveSheet.Shapes.AddTextbox(msoTextOrientationHorizontal, 150, 52, 300, 40).Select
  Selection.Characters.Text = Label(4) & ", " & Range("O30").Text
  With Selection.Characters.Font
    .Name = "Arial"
    .FontStyle = "Bold"
    .Size = 12
  End With
  Selection.ShapeRange.Fill.Visible = msoFalse
  Selection.ShapeRange.Line.Visible = msoFalse
  Selection.HorizontalAlignment = xlCenter
'Label the Corners
ActiveSheet.Shapes.AddTextbox(msoTextOrientationHorizontal, 181, 85, 30, 20).Select
  Selection.Characters.Text = Label(1)
  With Selection.Characters.Font
    .Name = "Arial"
    .FontStyle = "Bold"
    .Size = 12
  End With
  Selection.ShapeRange.Fill.Visible = msoFalse
  Selection.ShapeRange.Line.Visible = msoFalse
ActiveSheet.Shapes.AddTextbox(msoTextOrientationHorizontal, 400, 85, 30, 20).Select
  Selection.Characters.Text = Label(2)
  With Selection.Characters.Font
    .Name = "Arial"
    .FontStyle = "Bold"
    .Size = 12
  End With
  Selection.ShapeRange.Fill.Visible = msoFalse
  Selection.ShapeRange.Line.Visible = msoFalse
Selection.Characters.Text = Label(3)
With Selection.Characters.Font
    .Name = "Arial"
    .FontStyle = "Bold"
    .Size = 12
End With
Selection.ShapeRange.Fill.Visible = msoFalse
Selection.ShapeRange.Line.Visible = msoFalse
Selection.HorizontalAlignment = xlCenter
For CounterA = 1 To 11
    Selection.Characters.Text = Range("HX30").Offset(CounterA, 2).Value
    With Selection.Characters.Font
        .Name = "Arial"
        .Size = 12
    End With
    Selection.ShapeRange.Fill.Visible = msoFalse
    Selection.ShapeRange.Line.Visible = msoFalse
    If Range("HX30").Offset(CounterA, 4).Text = "xlcenter" Then Selection.HorizontalAlignment = xlCenter
    If Range("HX30").Offset(CounterA, 4).Text = "xright" Then Selection.HorizontalAlignment = xlRight
Next
For CounterA = 1 To 100
    If Range("J30").Offset(CounterA, 7).Value = -0.0000001 Then
        With ActiveSheet.Shapes.AddShape(msoShapeOval, _
            200 + 200 * Range("J30").Offset(CounterA, 0).Value - 3, _
            100 + 200 * Range("J30").Offset(CounterA, 1).Value - 3, 6, 6)
            .Fill.ForeColor.RGB = RGB(256, 256, 256)
            .Line.ForeColor.RGB = RGB(256, 256, 256)
            .Line.Weight = 0.25
            .Shadow.Type = msoShadow17
            .Shadow.ForeColor.RGB = RGB(256, 0, 0)
            .Shadow.Transparency = 0.6
        End With
    End If
Next
For CounterA = 1 To 100
    If Range("J30").Offset(CounterA, 7).Value = -0.0000002 Then
        With ActiveSheet.Shapes.AddShape(msoShapeOval, _
            200 + 200 * Range("J30").Offset(CounterA, 0).Value - 3, _
            100 + 200 * Range("J30").Offset(CounterA, 1).Value - 3, 6, 6)
            .Fill.ForeColor.RGB = RGB(256, 256, 256)
            .Line.ForeColor.RGB = RGB(256, 256, 256)
            .Line.Weight = 0.25
            .Shadow.Type = msoShadow17
            .Shadow.ForeColor.RGB = RGB(256, 0, 0)
        End With
    End If
Next
For CounterA = 1 To 100
    If Range("J30").Offset(CounterA, 7).Value = 0 Then
        With ActiveSheet.Shapes.AddShape(msoShapeOval, _
            200 + 200 * Range("J30").Offset(CounterA, 0).Value - 3, _
            100 + 200 * Range("J30").Offset(CounterA, 1).Value - 3, 6, 6)
            .Fill.ForeColor.RGB = RGB(256, 256, 256)
            .Line.ForeColor.RGB = RGB(256, 256, 256)
            .Line.Weight = 0.25
            .Shadow.Type = msoShadow17
            .Shadow.ForeColor.RGB = RGB(256, 0, 0)
            .Shadow.Transparency = 0.6
        End With
    End If
Next
200 + 200 * Range("J30").Offset(CounterA, 0).Value - 3, _  
100 + 200 * Range("J30").Offset(CounterA, 1).Value - 3, _
' .FillColor.ForeColor.RGB = RGB(0, 0, 0)  
' .FillColor.RGB = RGB(0, 0, 0)  
' .LineStyle.ForeColor.RGB = RGB(0, 0, 0)  
' .Line.Visible = msoFalse  
' .Shadow.Type = msoShadow17  
' .Shadow.ForeColor.RGB = RGB(0, 0, 0)  
' .Shadow.Transparency = 0.6  
End With  
End If  
Next  
For CounterA = 1 To 100  
'If Range("T30").Offset(CounterA, 3).Value >= 1 Then  
With ActiveSheet.Shapes.AddShape(msoShapeOval, _  
200 + 200 * Range("T30").Offset(CounterA, 1).Value - 3, _  
100 + 200 * Range("T30").Offset(CounterA, 2).Value - 3, _
' .FillColor.RGB = RGB(Range("T30").Offset(CounterA, 5).Value, _  
Range("T30").Offset(CounterA, 6).Value, _  
Range("T30").Offset(CounterA, 7).Value)  
' .LineStyle.RGB = RGB(256, 256, 256)  
' .Line.Weight = 0.25  
' .Shadow.Type = msoShadow17  
End With  
If Range("T30").Offset(CounterA + 1, 0).Text = "" Then CounterA = 100  
Next  
' + + + + + + + + + Scale Bar + + + + + + + + +  
For CounterA = 0 To 10  
With ActiveSheet.Shapes.AddShape(msoShapeOval, 380, _  
270 - 10 * CounterA, 10, 10)  
' .FillColor.RGB = RGB(Range("V12").Offset(CounterA, 1).Value, _  
Range("V12").Offset(CounterA, 2).Value, _  
Range("V12").Offset(CounterA, 3).Value)  
End With  
Next  
For CounterA = 0 To 5  
ActiveSheet.Shapes.AddTextbox(msoTextOrientationHorizontal, 392, 263 - 20 * CounterA, 100, 20).Select  
If Left(Range("O30").Text, 1) <> "V" Then Selection.Characters.Text = Range("AA12").Offset(CounterA * 2, 0).Text _  
Else Selection.Characters.Text = Range("AB12").Offset(CounterA * 2, 0).Text  
With Selection.Characters.Font  
' .Name = "Arial"  
' .Size = 12  
End With  
If Left(Range("O30").Text, 1) <> "V" Then Selection.Characters(Start:=9, Length:=3).Font.Superscript = True  
Selection.ShapeRange.Fill.Visible = msoFalse  
Selection.ShapeRange.Line.Visible = msoFalse  
End With  
Next  
ActiveSheet.Shapes.AddTextbox(msoTextOrientationHorizontal, 380 + 12, 150, 80, 20).Select  
If Left(Range("O30").Text, 1) <> "V" Then Selection.Characters.Text = "I(Acm-2)" _  
Else Selection.Characters.Text = "E(V-SCE)"  
With Selection.Characters.Font  
' .Name = "Arial"  

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.FontStyle = "Bold"
.Size = 12
End With
If Left(Range("O30").Text, 1) <> "V" Then Selection.Characters(Start:=6, Length:=2).Font.Superscript = True
Selection.ShapeRange.Fill.Visible = msoFalse
Selection.ShapeRange.Line.Visible = msoFalse
Range("A1").Select
For CounterA = 1 To 10
Beep
Next
End Sub


219. P. Strasser, S. Gorer, Q. Fan, K. Chondroudis, K. Cendak, D. Giaquinta, and M. Devenney, in *High Throughput Screening in Chemical Catalysis*


