PALLADIUM RUTHENIUM MEMBRANES FOR HYDROGEN SEPARATION BY ELECTROLESS CO-DEPOSITION

by

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Prior published research has claimed that the Pd95.5Ru4.5 (mass %) binary alloy has desirable properties as a high temperature hydrogen separation membrane. These properties include increased permeability and mechanical strength. The objective of this work was to develop a convenient method to fabricate composite membranes using electroless plating.

A carbonless, PdRu co-depositional electroless bath was developed to deposit thin PdRu alloy membranes onto a variety of supports; a 4.5 wt% Ru alloy was desired. These membranes were characterized using nanoindentation, electron microscopy, x-ray diffraction, and pure gas permeation testing. All supports were prepared and activated prior to deposition; deposition was performed in flowing systems when permitted.

The main conclusions of this work are:

- membranes deposited using this bath are roughly twice as hard as palladium membranes,
- membranes that exhibit high hydrogen flux (greater than one mol/m²·s) and high hydrogen selectivity (greater than 35,000) can be deposited with this bath,
- membranes deposited using this bath contain low amounts (less than 2 wt%) of ruthenium.

A membrane of thickness less than 1.5 microns was deposited onto a porous stainless steel support and was thermally cycled to temperatures up to 600°C under pure
gas feeds of hydrogen and nitrogen. This membrane was stable for three thermal cycles before failing during the fourth.

Membranes of roughly equivalent thickness (~2.2 microns) were prepared on porous ceramic substrates using two variations of the co-depositional electroless bath and a carbonless, pure Pd electroless bath. Permeation tests were conducted at 400°C under pure gas feeds of hydrogen and nitrogen. These membranes were characterized using environmental scanning electron microscopy (ESEM) and energy dispersive x-ray spectroscopy (EDX).

Three films were deposited onto dense alumina discs using the two variations of the co-depositional electroless bath and the carbonless, pure Pd electroless bath. These films were characterized using x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), and nanoindentation.

It was found that the ruthenium content of the alloy was below the detection threshold of the XPS and EDX testing but non-zero as XRD did detect distinct ruthenium peaks; the ruthenium content of the alloy was likely below the desired 4.5 wt%. The surface structure of the alloy was also grossly different than that of palladium; the alloy possessing large lobes and possible pores not present in samples of pure palladium. During performance testing, it was found that the hydrogen flux of the alloy was approximately the same as that of palladium but the alloy was more thermally stable. The alloy was almost twice as hard as palladium and single cycles of the alloy resulted in a significantly higher reduction of nitrogen leak rates compared to single cycles of palladium. Burst testing was inconclusive but revealed that the tensile strength of deposited films was greater than that expected.
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CHAPTER 1
INTRODUCTION

With recent concerns over global warming and carbon emissions leading to a greenhouse gas effect, there has been a pursuit of cleaner burning fuels. One of these fuels is hydrogen. Hydrogen can be used to fuel electrochemical reactions in fuel cells or be combusted; the product in both cases is water. While many of the common methods to produce hydrogen do lead to the formation of carbon emissions, it is much more practical to collect the carbon emissions from hydrogen production in a few industrial plants than attempting to collect the carbon emissions from fossil fuels in every single fuel burning device.

1.1 Hydrogen Production

Hydrogen is currently being industrially produced through processes such as catalytic partial oxidation (CPOX), steam reforming (SR), gasification, the water gas shift reaction (WGS), and autothermal reforming (AR). Through gasification of biomass, the production of hydrogen can be considered to be renewable.

1.1.1 Catalytic Partial Oxidation

CPOX is a process in which hydrogen is formed by partially oxidizing a hydrocarbon with oxygen in the presence of a catalyst. The general overall equation for CPOX is given below:
\[ C_x H_y + \frac{1}{2} xO_2 \xrightarrow{\text{SR}} xCO + \frac{1}{2} yH_2 \] (1.1)

Pure oxygen can be expensive and it is often air that is fed to the reaction. This results in an additional 1.88 \( x \) moles of nitrogen existing in the product stream, resulting in a product stream that is much more dilute in hydrogen. Using methane as the hydrocarbon feed and maintaining a stoichiometric feed of air, the product stream is a maximum of 50.8\% hydrogen. This reaction is exothermic and can be catalyzed by nickel. It is usually performed at temperatures above 1000°C to prevent the formation of C which can deactivate the catalyst.

### 1.1.2 Steam Reforming

SR is a process in which hydrogen is formed by reacting a hydrocarbon with steam. The general equation for SR is given as:

\[ C_x H_y + xH_2O \xrightarrow{\text{SR}} xCO + \left( \frac{1}{2} y + x \right) H_2 \] (1.2)

This reaction usually is performed at temperatures between 700 to 1000°C. This reaction is fairly endothermic and requires an energy input to remain at temperature. Energy must also be invested into vaporizing and heating the water fed into the reaction. Using methane as the hydrocarbon feed yields a product stream with a maximum hydrogen content of 75\%.

### 1.1.3 Gasification

Gasification is the heating of coal or solid biomass in the presence of steam, air, and, usually, a catalyst. The general equations for gasification are:
1.1.4 Water Gas Shift

All of the three previous techniques result in the production of a product stream containing hydrogen and carbon monoxide. Such a stream is known as synthesis gas or syngas. Syngas can be further reacted with water to produce more hydrogen by way of the WGS:

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (1.5)

WGS is slightly exothermic. WGS can reduce the CO content of syngas to 0.2 to 1.0%\(^1\) resulting in product streams that are much richer in hydrogen.

1.1.5 Autothermal Reforming

AR combines the exothermic CPOX and WGS reactions with the endothermic SR reaction to create a system of reactions that is overall isothermal. This is advantageous because it eliminates the need for heat exchangers. The trade off with AR is that the hydrogen yield is less than that could be obtained by combining SR with WGS.

1.2 Hydrogen Purification

As can be seen from each reaction, the hydrogen produced is not pure but is mixed with other species such as nitrogen, carbon dioxide, and carbon monoxide, as well as any contaminates (H\(_2\)S) that may be in the hydrocarbon feed. For applications that require pure hydrogen, the presence of these additional species is often unacceptable.
1.2.1 Pressure Swing Absorption

One method of purifying these streams is pressure swing absorption (PSA). PSA is a batch process that involves three main steps:

1) The mixed gas stream is fed through an absorbent bed. Hydrogen passes through the bed unadsorbed while higher molecular weight species adsorb into the pores of the adsorbent material.

2) After operating for some time, the bed becomes saturated and is unable to adsorb any more of the heavier species. At this point, flow to the bed is cut off.

3) The bed is depressurized and purged with hydrogen so that it regenerates.

Because PSA is a batch process, two or more beds are needed to run PSA continuously. Currently, PSA can be used to produce 99.99% (four 9's) pure hydrogen. Due to the way PSA is configured, the product stream experiences a small pressure drop in crossing over the bed but ultimately retains pressure. This means that the hydrogen produced is roughly the same pressure as that of the feed into the PSA.

1.2.2 Palladium Membranes

Another method of purifying hydrogen is using palladium membranes. Due to palladium's unique properties, 100% pure product streams are theoretically possible. This is important because some processes require over 99.99% purity. For instance, PEM fuel cells can be poisoned by less than 10 ppm of CO and therefore require very pure hydrogen feeds.
With palladium membranes, a pressurized feed is fed to the membrane module and hydrogen permeates across the membrane. The pressure of the permeate can be varied but the driving force for permeation is the partial pressure of the hydrogen so the permeate partial pressure must be less than that of the feed for permeation to occur. Additionally, because the permeance is not linearly related to the partial pressure of hydrogen but to the partial pressure of hydrogen raised to a factor between 0.5 to 1, pressuring the permeate can lead to severely decreased fluxes. Because of this, many configurations of palladium membranes have the permeate non-pressurized which means that hydrogen produced often has to be re-pressurized to be transported or stored.

1.3 Aim and Organization of This Work

This work evaluates the properties and performance of palladium ruthenium membranes deposited using an electroless, co-depositional bath, onto a variety of supports. Palladium-ruthenium alloys have reported properties of increased permeability and mechanical strength that would make them attractive for hydrogen separation applications. By simultaneously depositing palladium and ruthenium so that the composition of the alloy is homogenous, the electroless, co-depositional bath offers a way to reliably manufacture thin membranes of this alloy.

Chapter 2 presents a background on palladium and the techniques commonly used to fabricate membranes out of it and its alloys. Chapter 3 discusses a variety of characterization techniques used to determine the properties and performance of palladium membranes. Chapter 4 details the fabrication of numerous palladium ruthenium membranes and subsequent characterization. Chapter 5 is a summary of
conclusions reached in this work and Chapter 6 is a presentation of suggestions for future research.
CHAPTER 2
BACKGROUND AND LITERATURE REVIEW

The property of palladium of being permeable to hydrogen and no other gas have led to interest in the element and its possible industrial applications. Attempts to take advantage of this property have led to development of techniques of making membranes out of palladium.

2.1 Discovery of Palladium

Palladium was first identified in 1802 and accepted as an element in 1805 after being isolated from platina ore by William Wollaston. Wollaston mainly promoted palladium for use in a palladium-gold alloy that was suitable for the manufacture of corrosion resistant scientific instruments. It wasn’t until 1866 that Thomas Graham discovered that palladium would absorb over 600 times its volume in hydrogen without letting other gases penetrate it. Palladium soon received attention as a way to purify hydrogen from a feed stream. Because palladium only allows hydrogen to permeate through it, it should be possible to have one hundred percent selectivity towards hydrogen using a palladium based membrane.
2.2 Mechanism for Transport of Hydrogen through Palladium

Theoretical work into the hydrogen conducting ability of palladium has resulted in a proposed six step mechanism for the transport of hydrogen through a palladium membrane. In order to pass through palladium, hydrogen has to:

1) diffuse to the surface
2) adsorb onto the surface
3) dissociate
4) diffuse through the palladium bulk
5) recombine
6) be desorbed from surface.

Hydrogen is believed to diffuse through the bulk in atomic form. Because hydrogen and only hydrogen is carried across palladium using this mechanism, palladium membranes can theoretically be used to obtain infinite selectivity towards hydrogen. A graphical representation of these six steps can be seen in Figure 2.1.
Figure 2.1 Cartoon illustrating the six step mechanism proposed for the diffusion of hydrogen through a palladium membrane.

The overall, steady-state flux of hydrogen can be described by combining Fick's first law with Sievert's law (assuming that diffusivity is constant throughout the membrane):\(^8\):

\[
J = \frac{P}{l} \left( p_1 - p_2 \right)
\]  

(2.1)

In the mechanism, step 4) is usually considered to be the rate limiting step and Sievert's law was created to describe hydrogen flux across such diffusion-limited palladium media. In the equation, \(J\) represents the hydrogen flux through the membrane.
(mol/m²·s). \( l \) is the thickness of the membrane (m). \( P \) is the permeability of the membrane (mol·m²·s⁻¹·Pa⁻¹). \( p_1 \) and \( p_2 \) correspond to the partial pressures of hydrogen on either side of the membrane (Pa). \( n \) is an exponential factor that can be obtained through nonlinear regression of flux data at different conditions.

As a first approximation, \( n \) can be set as equal to 0.5 because the hydrogen molecule splits into two separate entities as it is absorbed onto the surface. However, as palladium membranes become thinner, deviations from Sievert's law arise; Criscuoli et al.⁹ found that there was a 45% error in flux calculated for a five micron thick Pd membrane (85% error in that of a membrane one micron thick) when using Sievert's law. It is believed that as a membrane becomes thinner, the surface effects become rate limiting¹⁰,¹¹. For supported palladium membranes (asymmetrical membranes), resistance to flow introduced by the support can be very significant for thinner membranes. For this reason, much research has been done into improving supports used for hydrogen gas separation.

2.3 Difficulties with Palladium

Although palladium has a theoretical infinite selectivity to hydrogen, this is not always the case in practice. If there are defects in the membrane, selectivity will drop.

There is evidence from literature that the palladium can be poisoned by carbon monoxide and hydrogen sulfide¹²,¹³. These chemicals, often found in industrial streams, will strongly bind to palladium surface sites. Because these molecules cannot diffuse through the palladium bulk, they end up residing on the surface with the net result of deactivating the membrane, preventing regions from absorbing and dissociating
hydrogen. In the case of carbon monoxide, if solid carbon forms on the surface, it can
dissolve into bulk; solid carbon is soluble in palladium\textsuperscript{14}. This drives down flux and
performance of a membrane. While poisoning should not affect the selectivity of a
perfect membrane, it will severely impact the selectivity of a membrane with defects; by
decreasing hydrogen flux while keeping the leak gas flux essentially constant, the ratio of
the two will naturally decrease.

Another potential issue with a palladium membrane is that hydrogen is almost too
soluble in palladium. It is soluble to the point where early researchers considered it to be
a new alloy, hydrogenium, after it had taken in large values of hydrogen\textsuperscript{4}. The lattice
constant of palladium metal in the absence of hydrogen is 3.890 Å\textsuperscript{15}. The lattice constant
of palladium in the α-hydride phase is 3.894 Å\textsuperscript{15}. In most cases, palladium can transfer
between its ground phase and α-hydride without compromising the mechanical integrity
of a membrane due to the 0.1% differences in the lattice constants. As more hydrogen is
taken into the palladium bulk, the β-hydride phase becomes prevalent. With a lattice
constant of 4.025 Å\textsuperscript{15}, 3.7% increase of the lattice constant of palladium in the absence of
hydrogen, transition to the β-hydride can cause a membrane to swell, embrittle and
rupture. One method to avoid the phase transition is to only introduce hydrogen to
membranes above 295°C, the critical temperature of the phase transition. The hydride
phase transition diagram can be seen in Figure 2.2.

Running at high temperature operations is not feasible at all times and membranes
may be cycled to room temperatures for reasons of maintenance or process modification.
It is nearly impossible to completely purge all the hydrogen from a saturated membrane
so the membrane will likely still be at risk of embrittlement if it is thermally cycled back down to room temperature.

Figure 2.2 Phase transition diagram of palladium in the presence of hydrogen\textsuperscript{16}.

2.4 Palladium Alloys

One way of compensating for the weaknesses of palladium membranes is by introducing an alloying metal into the bulk palladium. Palladium alloys have been noted to have a multitude of properties that are higher than that of pure palladium.

Binary palladium alloys will be commonly referred to in this paper in the form PdM\textsubscript{x}, where “M” is the alloying metal and “x” is the weight percentage of “M” in the bulk unless explicitly stated otherwise. Ternary alloys will be commonly referred to in the form PdM\textsubscript{x}N\textsubscript{y} where “M” and “N” refer to alloying metals and “x” and “y” refer to
the weight percentage (unless explicitly stated otherwise) of “M” and “N” in the bulk, respectively.

Palladium silver shows a marked increase with flux at silver mass concentration ranging from 20 to 30 wt% with a maximum around 23%\textsuperscript{16}. The alloy is much softer than pure palladium and is therefore much easier to work with mechanically\textsuperscript{17}. This lends the alloy to manufacture by cold rolling. The presence of silver in the above concentrations also leads to the depression of the critical temperature of the two phase region to below room temperature\textsuperscript{17}. Because of the increased permeance, relative low price of silver (compared to that of palladium), suitability for synthesis of the material through cold rolling, and depression of the two phase region, palladium silver was one of the originally industrially pursued palladium alloys and is still commonly used today.

Palladium copper is noted for possessing resistances to hydrogen sulfide, common in some industrial product streams, as well as increased permeance to hydrogen at compositions extremely close to 40 wt% Cu; a few wt% above or below 40 wt% results in drastically reduced permeability\textsuperscript{16}. Because of the slim margin of error provided by palladium copper in reaching the 40 wt%, this alloy lends itself to fabrication by cold rolling and physical vapor deposition but experiences difficulty with techniques like electroless plating which have less control over alloy composition.

Other studied alloys include palladium gold alloys that exhibit high permeabilities at gold concentrations under 20 wt% as well as noted resistance to sulfur poisoning\textsuperscript{16}. 
2.4.1 Palladium Ruthenium

Palladium ruthenium (PdRu) alloys have been known since 1966 when the Engelhard Corporation filed a US Patent. The patent stated that the desired ruthenium content was between 2 to 5 wt% with the optimal atomic concentration being 4.5 wt%. The patent claimed that the alloy had permeability 74% higher than that of pure palladium at 350°C (28% higher than that of a PdAg$_{27}$ membrane at the same conditions), the alloy had a 94% higher ultimate tensile strength than that of pure Pd after being annealed at 900°C, a 224% higher yield strength and an ultimate hoop strength that is at least 58% higher (limitations in the test set-up prevented the ultimate hoop strength of the alloy being recorded).

Although there is evidence which suggests that the permeability of the PdRu alloy is much lower than reported, being either far below that of pure Pd or roughly equivalent, the claim of higher tensile strength was supported – specifically the unannealed tensile strength of the alloy was 145% higher than that of the unannealed palladium while the tensile strength of the annealed alloy was 358% higher than that of the annealed palladium (in both cases the tensile strength of the annealed material was less than that of the unannealed). The maximum permeability has been confirmed to be around 4.5 at% and additional claims have been made that the alloy is thermally stable at temperatures up to 823K.

Recent work with the PdRu alloy includes testing of a membrane reactor using a 100 micron thick PdRu$_{5.5}$ tube in a methane steam reforming reaction. The PdRu tube was used as a means of both catalyzing the WGS reaction and simultaneously separating out hydrogen from the product stream. The membrane reactor had a much higher
methane conversion than that of a SiO₂ membrane reactor that used similar amounts of
catalyst. The authors concluded that their configuration of a membrane reactor would be
economically feasible if a palladium ruthenium membrane less than 10 microns in
thickness could be provided.

2.5 Synthesis of Palladium Membranes

Early palladium membranes were comprised of thick walled palladium tubes (in
this paper, “thick” will be used to describe membranes of thickness greater than 10
microns and “thin” those of thickness of 10 microns or less). These thick tubes, although
capable of producing pure hydrogen, were economically limited under most
circumstances for two main reasons. The first is that palladium is rare and
relatively expensive. A thick-walled membrane is made of a lot of palladium and is
therefore expensive. The second is that hydrogen flux, related by equation 2.1, through
palladium is inversely related to membrane thickness. This means that a thick-walled
membrane will have relatively low hydrogen flux. Both of these issues can be resolved
by making the palladium membrane thinner; however, a few issues arise in making the
membranes thinner.

One issue in making thin palladium membranes is as the membranes become
thinner, they are likely to display defects in their structure. These defects are holes in the
membrane, discontinuities in the surface where there is no preferential selectivity to
hydrogen (any gas can permeate through). This lack of selectivity is not desirable.
While the hydrogen flux through a palladium membrane will increase with decreased
thickness, the probability that the membrane will have defects also increases. There are
steps that can be taken to minimize the probability of defects forming in the membrane. The biggest issue in making thinner membranes, however, is physically making the thinner membranes.

2.5.1 Cold Rolling

Cold rolling is a technique used to manufacture palladium and palladium alloy membranes. By repeatedly passing bulk metal through rollers while the metal is below its recrystallization temperature, the thickness of the metal is decreased and the strength and hardness of the metal increase. Cold rolling provides excellent control over membrane composition but requires expensive equipment to produce films thinner than 25 microns\(^1\). Additionally, while cold rolling is good for palladium and “soft” palladium alloys, “harder” alloys, such as palladium-yttrium, are difficult to work with. Hardness is a measure of a material’s resistance to deformation; a harder material requires much greater force to roll into thin sheets than a softer material does. Although cold rolling continues to advance, the cost of producing the film greatly eclipses the cost of the materials in the film itself.

2.5.2 Plasma Sputtering

Plasma sputtering is a physical vapor deposition technology. It involves heating an inert gas and firing it in a vacuum into a metal bulk consisting of the material that is desired for the membrane. This excites atoms in the bulk, causing them to be ejected from the bulk and deposited onto the sputtering target located opposite of the bulk. While there is some random dispersion caused by this method, the membrane deposited
by this method usually has similar composition to that of the bulk, resulting in homogenous alloys being fabricated from a homogeneous alloy bulk (alloys can also be fabricated by alternative sputterings with different metal bulks onto the target).

After a desired thickness has been deposited onto the target, the sputtering can be turned off and the membrane can be separated from the target. Plasma sputtering has been successfully used to create defect-free, free-standing, palladium alloy membranes of 1.6 microns\textsuperscript{20}. The advantages of plasma sputtering are that it can create very thin films and that excellent control is possible over both the thickness and composition of a membrane. The disadvantages to plasma sputtering includes that it requires expensive equipment, dedicated laboratory space, and that it is limited in the size of membranes it can produce. Additionally, supports must be planar; sputtering can not be easily used to synthesize membranes onto complex geometries.

\textbf{2.6 Electroless Deposition of Palladium}

Another technique used to create thin palladium membranes is electroless deposition (also referred to as electroless plating). With electroless plating, a support is exposed to an aqueous solution containing palladium precursor salts, solvating agents, complexing agents, reducing agents and, optionally, stabilizing agents. In the presence of the support, the palladium in solution reacts with the reducing agent and is deposited as metallic palladium. The basic reaction for palladium deposition is described below:

\begin{equation}
2Pd^{2+} + N_2H_4 + 4OH^- \rightarrow 2Pd^0 + N_2 + 4H_2O
\end{equation} (2.2)
This reaction can be considered irreversible because the nitrogen produced evolves as a gas and leaves solution.

Reaction 2.2 is self-catalyzing; palladium metal on the surface of the support promotes palladium deposition. To take advantage of this, supports are often seeded with palladium nucleation sites (activated) prior to electroless plating. Reaction 2.2 can also take place between two palladium atoms in solution. This is undesirable because it results in a loss of palladium in solution and can lead to the formation of particles. These particles generally precipitate out of solution and can be carried around by currents in the fluid, occasionally adhering to the surface of the support. This is undesirable because the particles can be latter dislodged from the surface resulting in bare patches and defects.

Under normal conditions, the aqueous reaction is much slower than the surface reaction and is insignificant. However, if conditions in the bath are such that the kinetics of the plating reaction are fast enough that the aqueous reaction becomes relevant, then the bath can become unstable and “crash” out of solution. A crashed bath looks smoky or cloudy due to large number of palladium particles formed.

Electroless plating has several advantages over cold rolling and plasma deposition. The primary is cost and ease of setting up an electroless plating system. Unlike cold rolling and plasma deposition, no special equipment is needed to electroless deposit a membrane onto a support. Basic deposition can be done in a batch configuration with a graduated cylinder and a hot plate. More complex set-ups involve use of peristaltic pumps so that the plating solution is constantly cycled. This set-up is usually preferred because it helps dislodge nitrogen bubbles formed during the plating
reaction that become lodged on the surface of the plating support. Pictures of electroless plating equipment can be seen in Figures 2.3 and 2.4.

Figure 2.3 Clear PVC shell set-up used for electroless deposition.

Figure 2.4 Electroless deposition set-up for tubular membranes
The disadvantages of electroless plating are mostly involved with the limited control over the membranes given by the technique. With electroless plating, there is variation in the amount of palladium deposited in a cycle. This makes the synthesis of a membrane of an exact thickness very difficult. Large pores in the support or other factors can lead to defects in the plated film. Additionally, it is very difficult to create alloys of exact composition using sequential deposition cycles due to the variations in thicknesses deposited in each cycle.

2.6.1 Electroless Co-Deposition

One way of circumventing the issue of difficulty in controlling alloy composition is co-deposition. By using a bath that contains both metal precursors, the desired metals can be deposited simultaneously. In theory, this could lead to a plated membrane that is homogenous without need for annealing; the only alternate way to form a homogenous alloy through electroless plating is to sequentially plate the metals and then to anneal the result. It is debatable, however, if the deposited membranes are homogenous; the individual plating rates of palladium and silver in a co-depositional bath were shown to vary with plating time, concentration of reducing agent, metal ion concentration and temperature\textsuperscript{21}. If the plating kinetics are not constant during plating, then the rates of metal deposition, and amount of each metal present, will vary with time leading to varying composition with temperature.
2.7 Activation of Supports

Because there are two competing reactions during electroless plating and because the reaction is autocatalytic, it is important to have nucleation sites present on the surface intended for plating before the plating begins. These sites will not only provide catalyst for the surface plating reaction and encourage preferential formation of a membrane, they also may provide an anchoring effect that binds the membrane more strongly to the support – activation can result in the deposition of palladium particles inside of pores leading to the membrane being deposited partially inside the support rather than on top of it.

There are two major methods of activating a support available in the art. The first involves alternate dippings of the support into baths of tin chloride to sensitize the support and then palladium chloride to activate it. In this process, tin binds to the surface of the support and the palladium, which does not bind strongly to the support, binds to the tin. This method has the unfortunate effect of introducing tin to the support and membrane and may lead to small amounts of tin present in the membrane. The presence of this tin can leads to the increased formation of defects in membranes\textsuperscript{22}. Even if defects do not form, the tin may not be desireable; at a tin compositions higher than 0.9 at\%, the permeability of the alloy is drastically lower than that of pure palladium\textsuperscript{15}.

An alternative method involves exposure of the support to a palladium acetate and chloroform solution and then exposing the support to high temperatures to pyrolyze any remaining carbon. Treatment can involve multiple dippings of the support into the solution or spraying it on using an airbrush. The airbrush method is currently favored because all the palladium sprayed onto the support ends up on the support whereas the
dipping method can lead to smears, streaking and counterproductive progress as each
dipping can and will remove some palladium put down by previous dippings.
Basic procedure used to deposit membranes onto supports will be detailed in this chapter. Additionally, there are numerous techniques used to characterize the membranes deposited onto the supports. This chapter briefly discusses each method.

3.1 Electroless Deposition of Palladium and Palladium Alloys

The electroless deposition of palladium and palladium alloy films is a detailed procedure involving many steps.

3.1.1 Composition of Electroless Baths

The standard Pd electroless plating bath referred to in this paper is summarized in Table 3-1.

<table>
<thead>
<tr>
<th>Table 3-1 Composition of 80 mL of pure Pd electroless deposition bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium Precursor</td>
</tr>
<tr>
<td>Complexing Agent</td>
</tr>
<tr>
<td>Reducing Agent</td>
</tr>
<tr>
<td>Solvating Agent</td>
</tr>
</tbody>
</table>
In this bath, PdCl2 is used as the palladium precursor. HCl is the solvating agent and is used to help the palladium salt dissolve in solution. NH4OH is the complexing agent used and provides the hydroxide ions needed for the plating reaction. Hydrazine serves as the reducing agent. The balance of the bath is deionized water.

It should be noted that Na2EDTA is common in many electroless Pd plating baths but is not included in this one. While Na2EDTA is a stabilizing agent and helps prevent the bath from crashing out of solution, it also introduces a carbon containing compound into the otherwise inorganic solution. The presence of carbon in the electroless bath can lead to the presence of carbon in the membrane\cite{23,24}. Low concentrations of hydrazine and careful regulation of bath temperature are used in place of Na2EDTA to maintain bath stability in our fabrication method.

The plating bath is prepared by adding the HCl to the distilled water, then the metal precursor then the ammonium hydroxide. It usually takes several hours for the salt to completely dissolve. The reducing agent is added directly prior to plating.

Two variants of a PdRu co-depositional bath were created in order to manufacture PdRu membranes from one bath, a high Ru and a low Ru bath. The composition of the high Ru bath is summarized in Table 3-2 and the composition of the low Ru bath in Table 3-3. The only significant difference between these two baths is the amount of ruthenium precursor present.

Again, the balance is deionized water. Preparation of the bath is slightly different than that of the pure Pd bath. 80 mL of the pure Pd bath without hydrazine are mixed up and then added to the ruthenium salt dissolved in 20 mL of deionized water. The
resulting solution is manually shaken and then sonicated to ensure uniformity. Hydrazine is added immediately prior to plating.

3.1.2 Preparation of Supports for Activation

One large requirement of electroless plating is that there must be a support for the membrane to be deposited on. While just about any material is acceptable for actual

Table 3-2 Composition of 100 mL of the high Ru co-deposition bath

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium Precursor</td>
<td>0.4360 g PdCl₂</td>
</tr>
<tr>
<td>Ruthenium Precursor</td>
<td>0.0402 g RuCl₃</td>
</tr>
<tr>
<td>Complexing Agent</td>
<td>31.2 mL 30% NH₄OH</td>
</tr>
<tr>
<td>Reducing Agent</td>
<td>0.8 mL N₂H₄ (1.63 M)</td>
</tr>
<tr>
<td>Solvating Agent</td>
<td>1.1 mL HCl</td>
</tr>
</tbody>
</table>

Table 3-3 Composition of 100 mL of the low Ru co-deposition bath

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palladium Precursor</td>
<td>0.4360 g PdCl₂</td>
</tr>
<tr>
<td>Ruthenium Precursor</td>
<td>0.0268 g RuCl₃</td>
</tr>
<tr>
<td>Complexing Agent</td>
<td>31.2 mL 30% NH₄OH</td>
</tr>
<tr>
<td>Reducing Agent</td>
<td>0.8 mL N₂H₄ (1.63 M)</td>
</tr>
<tr>
<td>Solvating Agent</td>
<td>1.1 mL HCl</td>
</tr>
</tbody>
</table>
deposition, the support should lend itself to characterization tests. In the scope of this paper, GTC tubular porous alumina (GTC-998), planar porous stainless steel plates (Mott Corporation), tubular porous stainless steel (Pall Corporation AccuSep) supports and dense Alfa Aesar Al-23 alumina discs were used as supports for Pd-Ru and pure Pd membranes. It should be noted that not all electrolessly deposited membranes have to be supported; there is current work in our group on fabricating unsupported palladium alloy membranes using electroless plating\textsuperscript{19}.

3.1.2.1 Preparation of Tubular Ceramic Supports

Before activating the GTC ceramic supports, the supports were prepared by sanding. Sanding ensures that the surface of the support is free of large artifacts that may lead to defects in membranes. To evenly sand the supports, a section of heat shrink tubing was placed over both ends of the support and shrunk tightly into place by heating with a heat gun. This serves to both prevent the support from being crushed by the drill and to prevent the ends from being sanded down so that they would fit in stainless steel compression fittings. With the tubing protecting the ends of the support, the support was snugly installed into the power drill (similar to how a drill bit would be installed) with care being made not to over tighten or damage the support.

With the drill spinning, sandpaper was run up and down the length of the support. The first type of sandpaper used was 120 grit sandpaper. This grit paper was used to break the existing outer surface of the support and to reduce the thickness of the support. It was found that there was significant support resistance provided by the GTC ceramic supports and that by reducing the wall thickness, this resistance would decrease at the
cost of mechanical strength. Occasionally, dense chunks of silica glass were encountered in the supports during this step. If the glass could not be sanded through, the support was discarded.

After sanding, the support was polished using the same heat shrink tubing and power drill configuration with increasing grit sizes of sand paper of 220, 320, 400, 600, and 1500. After using the 1500 grit sandpaper, the support should be smooth enough to reflect light. After polishing, the support was placed in a deionized water bath and sonicated for two minutes. The water bath was replaced when it became cloudy in appearance. After sonication it was usual for the support to have the appearance of deep gouges and scratches, possibly due to loose ceramic powder being removed from the surface. These gouges and scratches did not appear to have an adverse effect on membrane performance. After sonication, the support was dried in a furnace at 130°C overnight to ensure that it was dry.

After drying, sanded parts were covered with Teflon tape and the unsanded ends of the ceramic support were glazed three times with GL 612 Diamond Clear Gloss Glaze (Duncan) with time given for the glaze to dry between applications. The Teflon tape was then removed and the support was fired at 880°C for five hours under standing air. The ends of the support are glazed to create an impermeable seal; important because the testing fittings would damage a membrane so the ends cannot be plated and remain leak free with testing. Application of the glaze can be done before or after activation.
3.1.2.2 Preparation of Metallic Supports

There are two primary challenges in preparing Pd alloy composite membranes on stainless steel supports. First, while the average pore size of the porous stainless steel sheet was found to be approximately one micron in diameter, pore size was found to vary wildly with some pores being greater than two microns wide. Large pores require very thick Pd films to bridge. Second, at the high temperatures required for operation of most palladium based membranes, the palladium can diffuse into the metal bulk of the support leading to membrane failure. The presence of these metals in the membrane can lead to membrane failure due to defects being formed by migration of palladium away from pores.

One way to address these challenges is to deposit an oxide coating on the stainless steel sheet. The presence of an oxide coating creates a diffusion barrier and reduces the surface roughness of the substrate. However, the oxide coating does reduce the flow of all gases through the support. Care must taken so that the oxide coating is as thin as possible to minimize the pressure drop through the stainless steel support. This barrier usually consists of a metal oxide layer that is traditionally formed in the art by oxidizing the support or by coating the support with a slip of ceramic particles and firing it.

Because the Mott plates did not possess diffusion barriers, diffusion barriers were created using both oxidation and via a slip for different embodiments. To make the diffusion barrier, a slip was made by suspending 8 mol% yttria stabilized zirconia (YSZ, Tosoh product 8YSB) in ethanol. The slip was roughly 10:1 ethanol to YSZ. Some palladium acetate (~0.1%) was added to the slip to help with activation and adhesion of the Pd film to the diffusion barrier, although the realized benefits of doing this are
debatable. Before use, the slip was well mixed to ensure uniformity of suspension. This was accomplished by using a stir bar and a magnetic stir plate. The longer the slip is mixed for, the more uniform the suspension so longer times are better. The slips used had been mixed continuously for several months. The mixing vessels were kept air tight to prevent ethanol evaporation. Additional ethanol was added to the solution if it appeared to be thicker than desired.

Prior to dipping, one side of the platelet is masked off because having a diffusion barrier on both sides would result in an unnecessary flow resistance. Masking was done using thick, yellow, electrical tape. The edges of the front of the platelet can be masked with tape or they can be carefully wiped off using ethanol after the barrier is applied and before the platelet is fired. When the platelet is properly masked, it should be heated to 70°C in an oven. By preheating the platelet, the ethanol in the slip solution will flash off faster, resulting in a lowered chance that the slip will streak and create non-uniformities in the barrier.

The slip should be poured into a container that the platelet can fit inside. If there are large clumps of YSZ present in the slip, then the suspension process maybe inadequate. The slip can be filtered by pouring it through a sieve prior to dipping. Additionally, the area worked in should be as dust free as possible – dust on the surface of the support can be burnt away and result in large defects that the Pd membrane cannot bridge. The membrane should be vertically submerged and slowly withdrawn from the slip. Once withdrawn, it should be held horizontally until most of the ethanol has flashed off. If the edges were not masked, they should be carefully cleaned with ethanol at this time (take special care not to remove the barrier from the porous region). It is better to
have some of the barrier left on a dense region than to remove the barrier from the porous. After dipping, the platelet should be reheated to 70°C. The dipping should be performed eight times with alternation between which half of the membrane is higher when it is dipped. The container used for these dippings can be seen in Figure 3.1.

Once the dipping is complete, the masking tape should be removed from the support. Any unused slip can be poured back into the stirring vessel – more ethanol can be added if the slip looks viscous or thick. If any zirconia slip ended up on the masked part of the platelet, it should be removed with ethanol. The platelet should be suspended on small ceramic blocks (evenly distributed along the densified part of the platelet) and placed into a vessel. This vessel, known as a boat, is a ceramic tub with a lid. The lid

Figure 3.1 Container used for dip-coating planar metal supports
has a hole that can be connected to a gas line. The boat was heated from room
temperature to 300°C at a rate of 20°C/hr with 300 mL/min of air fed to it. It was held at
300°C for four hours. During these four hours, the gas was switched to a 400 mL/min
feed of nitrogen. Under nitrogen, it was heated to 800°C at a rate of 100°C/hr where it
dwelled for 1 hour. Still under nitrogen, it was then cooled to 25°C at the rate of
100°C/hr. After being thermally cycled, the slip is dark grey in color and likely heavily
oxidized.

This process should be done two to three times per platelet depending on average
pore size of the support until an acceptable pore size distribution is obtained.

All of the Pall AccuSep supports were received with a diffusion barrier already
applied and no additional support preparation was required.

3.1.2.3 Preparation of Dense Alumina Supports

For the Alfa Aesar Al-23 dense alumina discs, no special preparation was
performed. It should be noted that due to the non-porous nature of these supports, no
permeation data are available for samples deposited on these discs.

3.1.3 Characterization of Porous Supports

Porous supports can be characterized by obtaining dry flow rates and pore size
distribution after being prepared to give an idea of the maximum performance possible of
a membrane deposited onto the support.

A weight would be obtained for the support at this time. Dry flow rates are
obtained by installing the support into a leak test housing (as seen in Figure 3.7),
pressuring it, and recording the nitrogen leak rate. This recorded rate serves as an upper limit for hydrogen flow through any membrane; the flux of hydrogen through a bare support at 400°C was found to be approximately 50\% greater than the flux of nitrogen at room temperature. This means that the dry nitrogen flow rates can be used to estimate theoretical maximum hydrogen flow rates. The support should then be left submerged in a 2:1 water to ethanol mixture overnight (12 hours). This gives the solution adequate time to completely fill the pores of the support.

After soaking, the support is installed into test housing; it is recommended to do this as quickly as possible to prevent the support from drying out. For platelets, one side of the platelet is slowly pressurized until a nitrogen flow rate can be observed. For tubular supports, a leak test housing was used and the support was pressurized from the shell-side. Usually, this flow rate is around 0.1 mL/min. The pressure at which nitrogen flow was first detected is referred to as the bubble point. The pressure is then increased in small steps (~15 kPa) and the flow rate is recorded at each pressure. These rates are known as the wet flow rates.

With dry and wet flow rates, the pore size distribution of the support can be determined using known pore sizes and percent differential flow (PDF). The pore size that corresponds to a wet flow pressure difference can be calculated from the Young-Laplace equation:

\[
r_p = \frac{2\gamma \cos \theta}{\Delta P}
\]  

(3.1)
“r_p” is the pore radius and ΔP is the wet flow pressure. The surface tension of the ethanol-water solution, γ, is roughly 30.5 dyn/cm at room temperature\(^{25}\). The contact angle, θ, is usually assumed to be 0°. The equation can be then simplified to:

\[
 r_p = \frac{8.24 \mu \text{m}}{\Delta P \text{ psi}}
\]  

(3.2)

Percent differential flow (PDF), Q_p,n, can be calculated by using the dry and wet flow rates:

\[
 Q_{p,n} = 50 \left( \frac{Q_{d,n+1}}{Q_{w,n+1}} - \frac{Q_{d,n-1}}{Q_{w,n-1}} \right) \%
\]  

(3.3)

Q_{d,n+1} is the dry flow rate at the next highest recorded pressure and Q_{d,n-1} is the flowrate at the next lowest pressure. Q_w refers to wet flow rates. Q_d can usually be obtained through linear interpolation of a few data points. Q_{p,n} cannot be calculated for the first and last wet flow measurement.

With r_p and Q_p known, average pore size can be calculated with:

\[
 r_p = \frac{\sum_{n=1}^{\infty} r_{p,n} Q_{p,n}}{\sum_{n=1}^{\infty} Q_{p,n}}
\]  

(3.4)

Multiplying the average pore size by two gives the average pore diameter and a good feel for the size of gaps that the membrane has to bridge across. If there are a few large pores or if the average pore size for a planar metal support is comparable towards the ideal thickness of the membrane, it may be advisable to apply another diffusion barrier coating. Deciding to do this can be delicate; a thicker diffusion barrier is a larger
resistance to flow but a thick palladium membrane that bridges gaps in the support is also a larger resistance to flow. Average pore size can be visualized by plotting PDF versus pore size. Examples of these plots for GTC ceramic and Mott stainless steel supports can be seen in Figures 3.2 to 3.4.

![Figure 3.2](image1.png) **Figure 3.2** PDF versus pore radius for a GTC ceramic support. Average pore radius is 0.07 microns.

![Figure 3.3](image2.png) **Figure 3.3** PDF versus pore radius for a Mott stainless steel support (no diffusion barrier). Average pore radius is 0.51 microns. 27% of PDF for pores above one micron in diameter. Incomplete curve due to flow measurement limitations.
Figure 3.4 PDF versus pore radius for a Mott stainless steel support with one coating of YSZ diffusion barrier. Average pore radius is 0.16 microns. 0.1% of PDF for pores above one micron in diameter. Incomplete curve due to flow measurement limitations.

Dry nitrogen leak rates are often recorded for plated membranes to see if they have a suitably low leak rate and that they have properly been installed into the test housing prior to ideal gas testing.

3.1.4 Activation of Supports

For our activations, an H #3 Airbrush Complete Set (Paasche) was used to spray activation solution onto supports. A detailed summary of the activation procedure used in this work follows:

1) Support was cleaned and dried. A weight was recorded for the support.

2) Support was exposed to a solution of 3.5g palladium acetate dissolved in 100 mL chloroform. The method of exposure was dispersion via airbrush using air fed to the nozzle at 140 kPa. During this exposure, tubular supports were slowly rotated
so that the chloroform was given adequate time to flash off so that pooling of solution did not occur. Support was exposed until it was uniformly a dark orange color. As long as the color after activation was uniform, the activation was assumed to be uniform as well.

3) Carbon deposited on the surface of the support was pyrolyzed by placing the support in an oven in standing air and running an activation cycle. The cycle consists of heating to 350 °C at a rate of 60 °C/hr, dwelling for 5 hours and then cooling to room temperature at a rate of 60 °C/hr.

4) Support is cleaned of loose Pd using a lint free cloth. A weight was recorded for the support.

If the support is of a uniform black color, activation is considered complete. If the support is not of a uniform black color, it is re-exposed to activation solution until it is black in color and steps 3 to 5 are repeated.

3.1.5 Electroless Deposition of Palladium

Electroless deposition of palladium membranes onto supports is a two step process involving reduction and plating.

3.1.5.1 Reduction

Before each plating cycle, the support should be reduced to reduce the palladium oxide present on the activated support. Reduction was performed by soaking the activated support in the reduction solution detailed in Table 3-4 for at least twenty minutes at ~50°C.
Table 3-4 Composition of 100 mL of the reducing solution

<table>
<thead>
<tr>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>34mL 31% NH₄OH</td>
</tr>
<tr>
<td>0.5 mL N₂H₄ Solution</td>
</tr>
<tr>
<td>65.5 mL H₂O</td>
</tr>
</tbody>
</table>

N₂H₄ solution is made from 6.5 grams of 60% N₂H₄ in 100 mL H₂O. After reducing, the front of the support should be lightly rinsed in distilled water.

3.1.5.2 Plating

After reducing the activated support, it is installed into a plating housing.

For planar supports, the plating housing used was made of clear PVC plastic and can be seen in Figure 3.5. Two large holes were drilled in the center of both sheets and twelve small holes were drilled around the perimeter of the sheets, evenly spaced. The large tubes were connected to fittings that connected to flow tubing. The small holes were used with bolts and nuts to fasten the housing shut and make it leak tight. The support was placed between two thick Buna-nitrile (Buna-N) rubber gaskets and then bolted between the PVC sheets. A 50°C water flow was run on the backside of the platelet.
Figure 3.5 Plating housing used for electroless plating of planar metal supports

For tubular supports, the housing shown in Figure 2.1 was used. One pump was used to flow plating solution on the shell-side of the support. A second pump was used to flow 50°C water through the lumen of the support.

The dense, ceramic Al-23 discs were plated in a 50 mL beaker suspended in a hot bath maintained at 50°C.

For all supports, each plating cycle lasted 25 minutes. Plating solution was kept in a hot bath maintained at 50°C. For set-ups that could be installed into plating housings, the solution was pumped through the test housing. For one cycle of palladium, 40 mL of palladium plating solution was used for the ceramic discs, 80 mL of the solution for tubular supports, and 120 mL of the solution for the planar stainless steel supports. Commonly, multiple cycles were deposited at once. If the support hasn’t been allowed to dry, there is no need to reduce between cycles.
After plating is complete, membranes on porous supports should be slowly dried. A recommended drying cycle would be heating to 130°C at 20°C/hr, dwelling for an hour and then cooling back to room temperature. This slow drying is to prevent the formation of steam in the pores of the support which may damage the membrane. Membranes on dense supports can be heated directly to 130°C for drying because there are no pores for water to be trapped in, in a dense support.

### 3.1.6 Electroless Deposition of Palladium Ruthenium

For a cycle of palladium ruthenium, the same overall procedure used to deposit cycles of palladium should be used. Because of the additional volume of water needed to dissolve the ruthenium salt, larger volumes of solution are used. For one cycle of palladium, 50 mL of palladium plating solution was used for the ceramic discs, 100 mL of the solution for tubular supports, and 150 mL of the solution for the planar stainless steel supports.

Unlike the pure Pd bath which is clear and colorless, both PdRu baths are initially a dark brown. As the the bath is deposited, has been observed to turn from the dark brown to a bright red or light pink color. Holding the solution up to light reveals several small particles in the initial solution. This may be due to a solubility limitation of Ru salt into solution. After plating, the particles are no longer visible implying that these particles have dissolved into solution or have been deposited onto the surface of the membrane.
3.1.7 Maintenance of Plating Equipment

After every plating, the equipment used was examined. If any of it looked like it had palladium on it, it was cleaned because the deposition reaction is auto-catalyzed by Pd. Cleaning involved soaking housing and container that held the plating solution in concentrated nitric acid overnight. Plating tubing (Tygon) was replaced if it looked like it had metal deposited on it.

3.2 Characterization of Membranes

After a membrane is deposited onto a support, it can be characterized using a variety of methods.

3.2.1 Membrane Thickness

Thickness of a membrane is important because the hydrogen flux through a membrane is related to thickness. There are numerous techniques to calculate membrane thickness available in the art, the most basic using mass gain and density. The equation is as follows:

\[
l = \frac{\Delta m}{\rho A}
\]  

(3.5)

\(\Delta m\) is the recorded mass gain before and after plating (g), \(\rho\) is the density of the metal (g/cm\(^3\)), \(A\) is the plated area (cm\(^2\)). Area is obtained by using calipers to determine the diameter and length of the plated region. This equation gives the average thickness of the membrane; the actual thickness could vary significantly along different parts of the membrane.
3.2.2 Thickness of Palladium Films

With the density of palladium known to be 12.023 g/cm³, 3.1 simplifies to:

\[ l = 831.739 \frac{\Delta m}{A} \left[ \frac{\mu m \cdot cm^2}{g} \right] \]  

(3.6)

The mass gain used for this calculation is typically based off of the weight after the final activation of the support. The palladium deposited during the activation process is considered to not affect the performance of the membranes (beyond creating a series of nucleation sites that lead to better films) and is therefore not usually included in the thickness of the membrane. A typical cycle of palladium should add between 0.6 to 1.2 microns of palladium to a membrane. Because hydrogen flux is inversely related to membrane thickness, it is desirable for membranes to be as thin as possible without having defects.

3.2.2.1 Thickness of Palladium Ruthenium Films

To calculate a thickness gain for a PdRu cycle, equation 3.2 can be used for a first approximation. The density of ruthenium is very similar to that of palladium and any error introduced by assuming that they’re the same is negligible. A typical cycle of 25 minutes of PdRu usually adds 0.6 microns to a membrane.

3.2.3 Visual Leak Testing

If a membrane has a measurable nitrogen leak (N₂ leak rate greater than 1·10⁴ mol/m²·s at 137 kPa), the location of the leak can be determined by using visual leak testing. To perform a visual leak test, visual leak housing is used. The visual leak
housing uses the bottom half of the test housing and an open PVC frame with bolt holes for the top for platelets, as seen in Figure 3.6, or the leak test housing sans stainless steel outer shell, seen in Figure 3.7, for tubular supports (the support is pressurized from the tube-side).

Figure 3.6 Visual leak test housing for use with the planar metal supports
When the membrane is properly installed into the test housing, the membrane may be pressurized from the backside. Care should be taken to do this slowly and to not let the internal pressure exceed 40 kPa or damage to the membrane may occur. Once pressurized, ethanol-water solution (the same solution used in the wet flow testing) is poured into the open cavity of the test housing for planar supports. The solution is poured into a graduated cylinder and the membrane submerged in it for tubular supports. A record of where the stream of bubbles is coming from is made. Occasionally, no leak will be visible. In this case, pressure can be increased or dry nitrogen leak rates can be re-obtained, the latter performed on the assumption that the membrane was not properly installed into the test housing during initial testing.

3.2.4 Ideal Gas Separation Test

The ideal gas separation test involves heating the membrane up to operational temperature under an inert gas and then operating it with alternating pure hydrogen and nitrogen feeds. Standard operational temperature is 400°C. The gas fluxes at various
pressures are calculated using the flow rates from bubble film flowmeters and the membrane area.

3.2.4.1 Test Equipment

In order to operate the membrane at temperature, it must be first installed into a device capable of being heated to those temperatures.

For tubular supports, a shell and tube configuration is used. The membrane is installed into Swagelok fittings using graphite ferrules. A membrane installed into these fittings is then installed into a leak check housing where it is confirmed that the fittings are snug and that the membrane’s leak rate is not significantly higher than what was previously measured. It is typical for the leak rate to apparently decrease due to the tighter seal provided by the graphite ferrules. Once the leak rate is confirmed to be acceptable, the membrane is installed into a test module. Stainless steel ferrules can be used in place of graphite ferrules for stainless steel supports. A picture of a membrane install into fittings can be seen in Figure 3.8. A schematic of a membrane installed into a test module can be seen in Figure 3.9. A PFD of this process can be seen in Figure 3.10. The test module has five Swagelok Quick-Connect ports that are used to afford a feed, retentate, permeate and sweep feed. Pictures of a test module installed into an oven can be seen in Figure 3.11.
Figure 3.8 Membrane plated on a GTC ceramic support installed in fittings. Membranes are installed into test modules (as seen in Figure 3.7) before testing.
Figure 3.9 Schematic of membrane installed into test module.
Figure 3.10 PFD of ideal gas separation test stand.

Figure 3.11 Test module in oven. The lines feeding into the module (from 3 'o clock, CW) are the sweep, gauge, feed, retentate and permeate.
For planar membranes, a slightly different configuration is used. Planar membranes are sandwiched between two graphite ferrules cut from a sheet of graphite paper and bolted between the two sides of the planar test module. This configuration is identical to that used for determining nitrogen leak rate at room temperature with the substitution of graphite ferrules in place of the butyl rubber ones. Like tubular supports, it should be ensured that the nitrogen leak rate at room temperature is close to that measured using the leak check housing. Like the shell and tube configuration, the planar test module possess four lines: a feed, a sweep, a retentate and a permeate. This test housing can be seen in Figure 3.12.

![Test module used with planar membranes. This module was also used to obtain nitrogen leak rates. The backside of this module is used in visual leak testing.](image)

The feed line is used to provide gas to the membrane side of a support. The sweep line is used to provide gas to the backside of a support. The permeate line collects any gas that passes through the membrane in addition to sweep gas. The retentate line
collects any gas fed to the membrane through the feed that does not pass through the membrane.

3.2.4.2 Testing Conditions

For ideal gas separation tests, feed gas was either pure hydrogen or pure nitrogen. Gases used were industrial hydrogen (99.9% purity), hydrogen grade 5 UHP (99.999% purity), industrial nitrogen (99.0% purity), and nitrogen grade 5 UHP (99.999% purity), all from General Air. While switching from hydrogen to nitrogen, a fifteen minute nitrogen sweep is run so that any residual hydrogen in the membrane is purged so that the nitrogen leak rate is not artificially inflated.

3.2.4.3 Air Purging

Because there is evidence in the literature that surface roughness leads to increased hydrogen flux through the membrane\textsuperscript{26}, air purging is often performed on membranes. It is believed that exposure to oxygen can result in the rearrangement and roughening of a palladium based membrane’s surface\textsuperscript{26}. An air purge consists of operating the membrane under nitrogen with a nitrogen sweep, switching the feed gas to air for a set amount of time, and then returning the feed to nitrogen. Air grade zero (19.5 to 23.5% O\textsubscript{2}, THC $\leq$ 1 PPM), from General Air, was used for air purging.

3.2.4.4 Error in Measurements

All flow rates were recorded using bubble film flow meters. Digital flow meters were used for flow rates of 2 to 5000 mL/min. Analog flow meters were used in
conjunction with digital stopwatches for flows of less than 2 mL/min as well as some flows between 100 and 3000 mL/min. Measurements were taken as the average of multiple trials after the flow was determined to be steady state. Generally, three measurements within 0.06 s of each other were considered valid. Care was taken so that only one bubble was being recorded at a time for the digital flow meters. Multiple bubbles can rotate as they rise up the flow meter greatly skewing results.

Due to the nature of the calculation, longer measurements tend to have less error. Analog measurements were taken so that the measuring time averaged around ten seconds and never dropped below two seconds if possible. Larger flow meters were used whenever practical.

### 3.2.5 Environmental Scanning Electron Microscopy

Environmental scanning electron microscopy, ESEM, is similar to scanning electron microscopy (SEM) except that it can be used in the absence of a strong vacuum. A strong vacuum was maintained during all uses of the ESEM however so discussion of it will be treated as discussion of SEM. The vacuum allows for better electron micrographs to be obtained; there are no air molecules present to interfere with signals.

SEM creates images by bombarding a sample with a high energy electron beam resulting in the atoms of the sample generating secondary electrons, back scatter electrons, characteristic x-rays as well as other signals. Specialized detectors measure the reflected high energy beam and generated electrons and create a map of intensity from these measurements. SEM can be used to magnify samples up to 250,000x.
3.2.6 Energy Dispersive X-ray Spectroscopy

Energy dispersive x-ray spectroscopy (EDX) takes the characteristic x-rays generated by a sample exposed to high energy electron beam used in SEM and converts them into voltages using a detector. By collecting these voltages and averaging over time, a spectra can be constructed. This spectra can be compared to that of known samples to determine elemental composition of a sample. EDX is limited in that often time characteristic peaks on the spectra often overlap with each other.

3.2.7 X-Ray Diffraction

X-ray diffraction (XRD) involves bombardment of a planar sample with a known type of x-ray radiation at a range of angles. At each angle, the scattered intensity is recorded. If an angle corresponds with a crystal phase present in the sample, the radiation will be reflected into a detector resulting in a high count per second (CPS). If there is no corresponding crystal phase, the radiation will be scattered resulting in a low CPS. By measuring the CPS at different angles, a spectra is created. Peaks from this spectra can be compared with the known peaks of a sample to identify elements present in the sample.

XRD can also be used to determine lattice constants. For a cubic crystalline system,

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

where $h$, $k$ and $l$ are the cubic plane number when given in the form $(h k l)$, $a$ is the lattice constant. $d$ is given by
\[ d = \frac{\lambda}{2 \sin \theta} \]  \hspace{1cm} (3.8)

where \( \lambda \) is the wavelength of the x-ray used in the XRD and \( \theta \) is the incident angle of the x-ray beam. Palladium has a crystalline cubic structure.

For materials with a crystalline hexagonal structure,

\[ \frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \]  \hspace{1cm} (3.9)

where \( d, h, k, \) and \( l \) are defined as above. \( a \) and \( c \) are lattice parameters of the hexagonal system.

### 3.2.8 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface analysis technique that involves the bombardment of a surface with a beam of x-rays. Unlike XRD, which finds the surface geometry, XPS is useful in determining the exact composition of a sample. The number of and kinetic energy of the electrons released by the surface is measured. By comparing the spectra obtained by a sample to that of known standards, composition of a sample can be obtained. Due to the nature of XPS, only the top 10 nm of a sample are measured.

### 3.2.9 Ultimate Tensile Strength

Ultimate tensile strength, UTS, is the amount of pressure a material can withstand before it completely and irreversibly mechanically fails. An analog for membranes would be the pressure at which a membrane ruptures. UTS is dependent not only upon the elemental composition of a material but also the method used to create the material.
Traditional UTS testing requires a prepared sample of specific dimensions. Unfortunately, preparation of a sample of the specific dimensions is not realistically feasible for micron thin, supported membranes.

An alternative way of determining the UTS of a tubular material is by relating it to the bursting pressure, as seen in the equation below:

\[
P_{burst} = \sigma_{UTS} \frac{2l}{(D_o - l)}
\]

(3.10)

By creating a tube of the material and internally pressuring it until it bursts, UTS can be obtained. \( \sigma_{UTS} \) is the UTS of the material, \( P_{burst} \) is the pressure that the tube burst at and \( D_0 \) is the outer diameter of the tube.

3.2.10 Nanoindentation Testing

Indent hardness of a material is the resistance of a material to permanent and plastic deformation due to mechanical stress on the object. Indent hardness is measured by indenting a material with a probe of known mechanical properties and a known mechanical load, and then measuring the size of the resulting indentation. The harder a material is, the smaller the indentation will be. Nanoindentation testers use very small probes and only indent a few hundred nanometers into the surface of a sample. Harder materials usually deform at higher pressures than softer materials do.
CHAPTER 4
CHARACTERIZATION OF PALLADIUM RUTHENIUM MEMBRANES
DEPOSITED USING A SINGLE CARBONLESS CO-DEPOSITIONAL ELECTROLESS PLATING BATH

This chapter details the performance and characterization of Pd and PdRu membranes deposited using the electroless deposition baths described in Chapter 3.

4.1 Abstract

The PdRu alloy is reported by published literature to have properties that are desirable in high temperature, hydrogen separation membranes. These properties include high permeability and improved mechanical strength\(^2,3\). A carbonless, PdRu co-depositional electroless bath was developed to deposit PdRu alloy membranes onto a variety of supports. Performance testing of the alloy reveals that it is similar in permeability to pure Pd while possessing increased thermal and mechanical stability, possibly due to depression of the critical temperature of the two-hydride phase of palladium and increased tensile strength. Characterization of the alloy with x-ray diffraction reveals that it exists in two distinctly separate phases; an enriched ruthenium and an enriched palladium phase.
4.2 Introduction

Composite membranes, consisting of a thin Pd alloy film supported on a porous substrate, have been investigated as a means of reducing the membrane cost and improving the flux of high temperature, hydrogen separation membranes. There is evidence in the literature that the addition of ruthenium to palladium results in enhanced stability, particularly for high temperature applications\(^3\). Specifically, there have been claims made that addition of 2-5 wt.% ruthenium to a palladium membrane increases the membrane's tensile strength, permeability to hydrogen and stability to temperature changes in the presence of hydrogen\(^2,3,15,18\).

Electroless plating is known in the art as a method for depositing thin, metallic membranes onto supports. In order to take advantage of the properties of palladium ruthenium alloys, a single, co-depositional bath was developed. By using a co-depositional bath, both palladium and ruthenium are deposited at the same time resulting in a theoretically homogenous membrane. The bath was made without any organic compounds to eliminate the possibility of carbon being deposited into membranes, preventing any potential decreased performance of membranes from carbon contamination\(^28\).

The objectives of this investigation were to use this bath to fabricate thin PdRu alloy composite membranes, characterize the PdRu membranes that were fabricated using a variety of characterization techniques, and compare the performance of the PdRu membranes to those made with pure Pd.
4.3 Experimental

Membranes were electrolessly deposited onto a variety of supports, characterized with a variety of surface and mechanical property characterization techniques and permeation tested with pure gases over a range of temperatures.

4.3.1 Preparation of Membranes

Membranes were deposited on tubular Coors Ceramics (GTC-998) and Pall Corporation AccuSep (zirconia/stainless steel) supports as well as planar porous stainless steel plates (Mott Corporation) and dense Al-23 ceramic discs (Alfa Aesar). These supports were prepared prior to plating as detailed in Chapter 2.

Membranes were plated onto these supports using the baths described in Table 2-1, Table 2-2, and Table 2-3, using the technique outlined in Chapter 2. The following reactions are proposed for deposition of palladium and ruthenium onto the activated supports:

\[ 2Pd^{2+} + N_2H_4 + 4OH^- \rightarrow 2Pd^0 + N_2 + 4H_2O \]  

\[ 4Ru^{3+} + 3N_2H_4 + 12OH^- \rightarrow 4Ru^0 + 3N_2 + 12H_2O \]

A summary of the various membranes plated for this investigation can be seen in Table 4-1. Thicknesses were calculated using equation 3.5.

While working with the porous stainless steel plates, multiple techniques were used while attempting to lower the nitrogen leak rate through the plates at room temperature including putting one cycle of pure Pd, two cycles of pure Pd and one cycle of the Pd-Ru co-depositional bath on the plate. Each plate had been previously plated
with at least two cycles of Pd prior to the attempt to lower its nitrogen leakrate. Eighteen plating cycles were conducted on nine membranes supported on Mott plates of known leak rates in order to reduce the leak rate. Seven of these plating cycles were of low Ru, four were of one cycle of pure Pd and nine were of two cycles of pure Pd. A summary of these experiments can be seen in Table 4-2. Results from Table 4-2 show that one cycle of the low Ru bath had a greater impact in leak rate reduction on average than up to two cycles of the pure Pd bath.

Table 4-1 Summary of membranes used in investigation

<table>
<thead>
<tr>
<th>Support Type</th>
<th>Reference Name</th>
<th>Bath Used</th>
<th>Thickness (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTC-Ceramic</td>
<td>CSM 169</td>
<td>high Ru</td>
<td>2.4</td>
</tr>
<tr>
<td>GTC-Ceramic</td>
<td>CSM 171</td>
<td>pure Pd</td>
<td>2.2</td>
</tr>
<tr>
<td>GTC-Ceramic</td>
<td>CSM 172</td>
<td>low Ru</td>
<td>2.3</td>
</tr>
<tr>
<td>GTC-Ceramic</td>
<td>CSM 177</td>
<td>low Ru</td>
<td>n/a</td>
</tr>
<tr>
<td>GTC-Ceramic</td>
<td>CSM 192</td>
<td>pure Pd</td>
<td>4.4</td>
</tr>
<tr>
<td>GTC-Ceramic</td>
<td>CSM 195</td>
<td>low Ru</td>
<td>2.6</td>
</tr>
<tr>
<td>AccuSep</td>
<td>CSM 146</td>
<td>low Ru</td>
<td>1.4**</td>
</tr>
<tr>
<td>Al-23 Ceramic</td>
<td>Pure Pd Disc</td>
<td>pure Pd</td>
<td>4.5</td>
</tr>
<tr>
<td>Al-23 Ceramic</td>
<td>Low Ru Disc</td>
<td>low Ru</td>
<td>6.7</td>
</tr>
<tr>
<td>Al-23 Ceramic</td>
<td>High Ru Disc</td>
<td>high Ru</td>
<td>6.2</td>
</tr>
</tbody>
</table>

*Support shattered while being removed from plating housing
** CSM 146 was re-plated after testing to a thickness of 1.9 microns
Table 4-2 Summary of leak reduction results for Mott platelets
<table>
<thead>
<tr>
<th>Reference Name</th>
<th>Repair Method</th>
<th>Percent Decrease in Leak Rate [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>Two Cycles Pd</td>
<td>36.5</td>
</tr>
<tr>
<td>#1</td>
<td>Two Cycles Pd</td>
<td>50.8</td>
</tr>
<tr>
<td>#1</td>
<td>Two Cycles Pd</td>
<td>51.6</td>
</tr>
<tr>
<td>#3</td>
<td>Two Cycles Pd</td>
<td>66.9</td>
</tr>
<tr>
<td>#3</td>
<td>Two Cycles Pd</td>
<td>86.1</td>
</tr>
<tr>
<td>#4</td>
<td>Two Cycles Pd</td>
<td>67.1</td>
</tr>
<tr>
<td>#4</td>
<td>Two Cycles Pd</td>
<td>49.6</td>
</tr>
<tr>
<td>A-3</td>
<td>Two Cycles Pd</td>
<td>52.9</td>
</tr>
<tr>
<td>B-4</td>
<td>Two Cycles Pd</td>
<td>90.6</td>
</tr>
<tr>
<td>#3</td>
<td>One Cycle Pd</td>
<td>36.3</td>
</tr>
<tr>
<td>#4</td>
<td>One Cycle Pd</td>
<td>7.0</td>
</tr>
<tr>
<td>#4</td>
<td>One Cycle Pd</td>
<td>27.8</td>
</tr>
<tr>
<td>A-1</td>
<td>One Cycle Pd</td>
<td>14.3</td>
</tr>
<tr>
<td>A-1</td>
<td>One Cycle Pd</td>
<td>55.6</td>
</tr>
<tr>
<td>#1</td>
<td>Two Cycle PdRu</td>
<td>58.2</td>
</tr>
<tr>
<td>A-4</td>
<td>Two Cycle PdRu</td>
<td>50.8</td>
</tr>
<tr>
<td>A-4</td>
<td>Two Cycle PdRu</td>
<td>74.0</td>
</tr>
<tr>
<td>A2</td>
<td>Two Cycle PdRu</td>
<td>60.2</td>
</tr>
<tr>
<td>B1</td>
<td>Two Cycle PdRu</td>
<td>95.5</td>
</tr>
<tr>
<td>B4</td>
<td>Two Cycle PdRu</td>
<td>85.5</td>
</tr>
<tr>
<td>B4</td>
<td>Two Cycle PdRu</td>
<td>94.9</td>
</tr>
</tbody>
</table>

### 4.3.2 Characterization Techniques

In order to characterize the membrane deposited by the co-depositional baths, various tests were performed. Tests included electron microscopy with ESEM and compositional analysis using EDX and XPS.

Nanoindentation using a NanoIndentor XP™ instrument with a sample depth of 500 nm (the indentation probe went 500 nm into the sample) and a sample spread of 50 nm (indentation sites were spaced 50 nm apart from each other). The machine was calibrated using silicon.
XRD was performed using Cu-Kα radiation (λ = 1.540562 Å) from θ = 30 to 90° (step size 0.05°, 4 seconds per step).

4.3.3 Performance Testing

Several membranes were installed into test housings and operated at high temperature. Temperature was maintained at 400°C for all gas permeation tests except for the thermal stability tests where temperature was increased to a maximum of 600°C. Heating and cooling of all membranes was done with a nitrogen feed and sweep of no less than 150 mL/min. Heating rate was approximately 0.5°C/min for all membranes.

Testing was done using pure gas feeds of hydrogen and nitrogen. Grade zero UHP gases (General Air) were used in the testing of CSM 146, industrial grade gases were used in all other tests (General Air). Transitions between gases and air purges were performed as described in Chapter 2.

4.4 Results and Discussion

This section is devoted to detailing the performance and characterization of the deposited membranes.

4.4.1 Permeation Testing of Membranes

Permeation testing of membranes was performed on membranes deposited on one Pall AccuSep support and three GTC ceramic supports. Leak test measurements were made for nine different Mott plates.
4.4.1.1 CSM 146

Dry flow of nitrogen through the bare Pall AccuSep support before activation and plating was recorded to be 1.72 mol/m²·s at 137.9 kPa. After plating, a leak rate of 2.5·10⁻⁵ mol/m²·s of nitrogen was recorded at 551.6 kPa. This nitrogen leak rate was extremely low in comparison to other membranes of similar thicknesses.

CSM 146 was installed into a stainless steel test housing with graphite ferrules and operated at 400°C. At the end of the test at 400°C, the hydrogen flux at 137.9 kPa driving force was 1.08 mol/m²·s (280 SCFH/ft²) and the nitrogen flux was 2.80·10⁻⁵ mol/m²·s (0.0075 SCFH/ft²) resulting in an ideal separation factor of 37,200. This performance can be seen in Figure 4.1. Comparison between the flux of CSM 146 and that of several pure Pd membranes can be seen in Figure 4.2. Figure 4.2 shows the hydrogen flux of CSM 146 to be slightly higher than what would be expected of a pure Pd membrane of equivalent thickness. Compared to membranes created using other methods in our groups, flux and selectivity for CSM 146 are both very high.

After heating the membrane to 500°C, the hydrogen flux increased to 1.10 mol/m²·s and the nitrogen flux increased to 8.8·10⁻⁵ mol/m²·s (0.023 SCFH/ft²) after 48 hours resulting in a separation factor of 12,600. After cooling to room temperature, a segment of the stainless steel tubing that fed into CSM 146's fittings into was torn off while attempting to loosen the fittings from the tubing. No visual leak was detected for CSM 146 at 137.9 kPa indicating that the membrane itself was not the source of the nitrogen leak.
CSM 146 (Pall#061907-66) 1.4 micron Pd/Ru membrane

Flux at 137.9 kPa and 400 °C

Figure 4.1 Flux of hydrogen and nitrogen through CSM 146 at 400°C, 137.9 kPa driving force (▲ corresponds to hydrogen fluxes, ▼ corresponds to nitrogen fluxes).
Figure 4.2 Hydrogen flux vs. thickness for CSM 146 and several pure Pd membranes. After replacing the tubing, CSM 146 was retested at 400°C. After stabilizing at 400°C, the hydrogen flux at 137.9 kPa driving force had decreased to 0.98 mol/m²·s and the nitrogen to 3.7·10⁻⁵ mol/m²·s resulting in an ideal separation factor of 26600. After being raised to 450°C, the membrane stabilized with a hydrogen flux at 137.9 kPa driving force of 1.07 mol/m²·s and a nitrogen flux of 3.8·10⁻⁵ mol/m²·s resulting in an ideal separation factor of 28037. The membrane was then heated to 500°C where it stabilized with a hydrogen flux at 137.9 kPa driving force of 1.11 mol/m²·s and a nitrogen flux of 9.0·10⁻⁵ mol/m²·s resulting in an ideal separation factor of 12320. After cooling, the leak was determined to be due to a two small leaks on the surface of the membrane. An additional cycle of PdRu was plated on the support. This resulted in the estimated
thickness increasing to 1.9 microns.

After replating, the membrane was thermally cycled two more times. Eventually, it was heated to 600°C where the leak rate rose drastically to $9.7 \times 10^{-3}$ mol/m$^2$·s. After cooling the membrane to room temperature, large sections of the membrane had developed into a bulging "crisscross" pattern. A visual leak test of the membrane caused one of these sections to rupture at 34.5 kPa of internal pressure with an audible popping noise.

Summaries of the performance of 146 can be seen in Figures 4.3, 4.4 and 4.5. The flux and separation factor results for 146 during the first thermal cycle are some of the best seen for membranes deposited onto the AccuSep supports and there is great interest in being able to deposit additional membranes with similar properties. Any beneficial decrease in leak rate provided by the additional plating cycle of low Ru seemed to have been negated once the membrane was returned to 500°C. The hydrogen flux at 137.9 kPa and 400°C fell by 38.8% after the plating (0.98 mol/m$^2$·s during thermal cycle two versus 0.60 mol/m$^2$·s during thermal cycle three). This agrees very well with the theoretical flux decrease of 36.8% predicted by equation 2.1.

Examination of the ruptured region showed that it had become separated from the support. The region having bulged out suggests that the lattice constant of the material had expanded leading to weakness of the membrane, possibly due to hydride phase transition. It is unknown why one region of the membrane would develop the bulging and others would not.
Figure 4.3 Stable hydrogen flux of CSM 146 over the course of four thermal cycles (TC).

Figure 4.4 Stable nitrogen flux of CSM 146 over the course of four thermal cycles (TC).
Figure 4.5 Stable ideal separation factor of CSM 146 over the course of four thermal cycles (TC).

When attempting to reflect the membrane off the support with a razor, the bulging region was readily separated while non-bulging regions were found to be strongly adhered to the support and removal was found to be very difficult.

In summary, the testing of CSM 146 led to the conclusions that:

- Very thin (1.4 micron) membranes deposited using the low Ru bath can still have very high (>35,000) selectivity factors.
- Permeance of the membranes deposited with the low Ru bath is roughly equivalent to the permeance of membranes deposited with a pure Pd bath meaning that thin membranes will have high hydrogen flux.
- The membrane embrittled and failed after four thermal cycles and exposure to 600°C temperatures.
- Changes to the test module may need to be made for future high temperature testing.
4.4.1.2 GTC Supported Membranes of Equivalent Thickness

CSM 169, CSM 171, and CSM 172 were of roughly equivalent thickness after plating. Because of this, their performances were directly compared to each other.

In the pure gas permeation test, the low Ru membrane (CSM 172) had higher initial ideal hydrogen/nitrogen separation factors than the high Ru membrane (CSM 169) and pure Pd control (CSM 171) (separation factors of 5040, 2950 and 2150, respectively). These separation factors can be seen in Figure 4.6. At identical test conditions (400°C and 1.39 kPa differential hydrogen pressure), the pure hydrogen flux was 15% lower for the low Ru than the control pure Pd membrane (0.17 compared to 0.20 moles/m²-s). The pure hydrogen flux for the high Ru was 0.16 moles/m²-s under the same conditions. These fluxes can be seen in Figure 4.7. The higher thicknesses of the PdRu membranes partially account for the lower hydrogen fluxes. The permeability coefficients of the PdRu membranes relative to the pure Pd control are 0.89 for the low Ru and 0.90 for the high Ru membranes (relative permeabilities, defined as \( \frac{P_{\text{sample}}}{P_{\text{Pd}}} \), were obtained by using equation 2.1). Lowered hydrogen flux may also be due to higher Ru content than expected; the relative permeability of a 91.1 at% Pd-8.9 at% Ru alloy was reported to be 0.87\(^{15}\). In light of spectroscopy results, the latter explanation is not likely.

In order to test the thermal stability of PdRu, all three membranes were cooled from 400°C to room temperature over 12 hours under nitrogen without prior degassing of hydrogen. In doing so, the nitrogen leak rate of the pure Pd membrane increased 106%. The leak rate increase was 55% for the low Ru membrane and 20% for the high Ru membrane. The smaller increase in leak rates is consistent with claims that Pd-Ru is more thermally stable than pure Pd\(^{3}\). This smaller increase may be due to depression of
the critical temperature of the two phase hydride region in bulk. By avoiding the two phase hydride region, the membrane would not swell and develop leaks due to differences in lattice constants. A summary of results can be seen in Table 4-3.

The important results of testing these three membranes are that the:

- Permeabilities of the three materials were roughly the same.
- The nitrogen leak rate of the palladium membrane increased more than the nitrogen leak rates of the PdRu membranes upon being cooled after testing. This could mean that the PdRu membranes are more thermally stable or that the presence of Ru in the membrane depresses the critical temperature of the hydride phase transition.

![Graph showing hydrogen/nitrogen selectivity for three membranes](image)

Figure 4.6 Ideal hydrogen/nitrogen selectivity for the three membranes at 400°C, 137.9 kPa driving force.
Figure 4.7 Hydrogen flux through the three membranes at 400°C, 137.9 kPa driving force. Membranes were air purged within the first few hours and again after 24 hours of operation.

Table 4-3 Summary of the GTC ceramic ideal gas separation results

<table>
<thead>
<tr>
<th>Bath Type</th>
<th>Pure Pd</th>
<th>Low Ru</th>
<th>High Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>CSM 171</td>
<td>CSM 172</td>
<td>CSM 169</td>
</tr>
<tr>
<td>Ru at% in Bath</td>
<td>0.00</td>
<td>5.00</td>
<td>7.32</td>
</tr>
<tr>
<td>Thickness (micron)</td>
<td>2.15</td>
<td>2.26</td>
<td>2.41</td>
</tr>
<tr>
<td>Initial H₂/N₂ Selectivity</td>
<td>2150</td>
<td>5040</td>
<td>2950</td>
</tr>
<tr>
<td>H₂ Flux (mol/m²·s)</td>
<td>0.20</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td>Thickness Normalized Flux (mol·m/m²·s)</td>
<td>4.30·10⁻⁷</td>
<td>3.84·10⁻⁷</td>
<td>3.86·10⁻⁷</td>
</tr>
</tbody>
</table>
4.4.1.3 Membranes Deposited on the Planar Stainless Steel Supports

For seven different plating sessions of one cycle of the low Ru bath, the average nitrogen leak reduction was 74.2%. This was found to be higher than the average leak reduction of one cycle of the Pd bath (five sessions, average leak reduction of 28.2%) and of two consecutive cycles of the Pd bath (nine sessions, average leak reduction of 61.4%). Additionally, one cycle of the low Ru bath contributed much less to the membrane thickness than two cycles of Pd did. A proposed mechanism for the larger reduction in nitrogen leak rate compared to that of pure Pd is that the reported tensile strength of Pd-Ru is much higher than that of pure Pd. The increase in tensile strength would mean that a much thinner Pd-Ru membrane could be used to bridge a large pore in a support without mechanical failure leading to a defect in the film.

4.4.2 Characterization

The supports were characterized using the aforementioned variety of testing techniques.

4.4.2.1 Environmental Scanning Electron Microscopy

The CSM 169, CSM 171, CSM 172 and CSM 177 were examined with ESEM. CSM 169, CSM 171, CSM 172 had been operated under hydrogen at temperature. CSM 177 had been shattered after plating and had not been taken to temperatures above 130°C. Electron micrographs of the membranes can be seen in Figures 4.8 to 4.11 below. Care was taken to focus on an area of CSM 177 not affected by shattering.
The basic "cauliflower" pattern is clearly present in the Pd control, CSM 171. The presence of this pattern implies that palladium membranes deposited by our electroless deposition bath have similar surface structure to membranes deposited by other groups. This pattern, to a certain extent, is also present in the unannealed low Ru membrane, CSM 177. The unannealed low Ru membrane also has several large randomly dispersed artifacts ranging in size from roughly 2 to 5 microns.

Both of the annealed PdRu membranes, CSM 169 and CSM 172, have the appearance of several lumps fused together and are decisively non-cauliflower in appearance. It is possible that the fused lump surface resulted in lower surface area and in turn the slightly lower relative permeabilities of the membranes. While both of the membranes also have large artifacts present, the artifacts in the high Ru membrane, CSM 169, are much more pronounced: lobe-like structures, some greater than 10 microns in width. Despite these artifacts, the overall surface of the PdRu membranes is much smoother than that of the pure Pd. This smoothness is likely the reason why PdRu membranes have a brilliant and almost reflective light silver appearance while Pd membranes are dull and darker in comparison.

One proposed explanation for these artifacts is that before plating, examination of the PdRu solution under light reveals tiny particles suspended in solution. These particles vanish during the plating process with the used plating solution being completely homogenous to the naked eye. These particles could be adhering to the surface of the membranes during plating. The size of the particles seem to be related to the concentration of the ruthenium salt in solution; the particles of the high Ru bath were much larger than that of the low Ru bath.
Numerous black specs (possibly holes) can be seen scattered on both of the annealed PdRu membranes. If the black specs are indeed holes, they do not likely penetrate throughout the entire thickness of the membrane because visual leak testing did not show the presences of numerous small defects in ether of the PdRu membranes.

Figure 4.8 ESEM image of the annealed Pd control (CSM 171) at 4000x magnification.
Figure 4.9 ESEM image of an unannealed low Ru membrane (CSM 177) at 4000x magnification.
Figure 4.10 ESEM image of the low Ru membrane (CSM 172) at 4000x magnification after annealing under hydrogen at 400°C.
Figure 4.11 ESEM image of the high Ru membrane (CSM 169) at 4000x magnification after annealing under hydrogen at 400°C under hydrogen at 400°C.
4.4.2.2 Energy Dispersive X-ray Spectroscopy

EDX was performed on several locations of samples of the annealed low and high Ru membranes. Representative spectra and analysis can be seen in Figure 4.12 and 4.13. The results of the EDX were that there was no Ru present on the surface of the samples. This may be due to strong peak overlap between Pd and Ru or peak bleed from the strong Pd peaks; both are known to skew results. Also, EDX will not register a peak if the peak is not at least 50% larger than the surrounding noise. These results do not mean that there was no ruthenium present in the material \textit{per se} but rather that the actual ruthenium content is low and below detection. It is likely that the ruthenium content of this material is less than 2 wt%.

<table>
<thead>
<tr>
<th>Element</th>
<th>Wt%</th>
<th>ChiSquared</th>
<th>Z Corr</th>
<th>A Corr</th>
<th>F Corr</th>
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<td>Pd</td>
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<td>1.79</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>Ru</td>
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<td>1.83</td>
<td>0.993</td>
<td>1.054</td>
<td>1.000</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>0.55</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.12 EDX results for 2 micron spot on one of the lobe-like structures of the annealed high Ru membrane.
Figure 4.13 EDX results for 2 micron spot away from the lobe-like structures of the annealed high Ru membrane.

### 4.4.2.3 Ultimate Tensile Strength

UTS testing was performed on CSM 192 and CSM 195. Using proper safety equipment, the membranes were slowly internally pressurized with constant attention given to the bubble flow meter. While testing the pure Pd membrane, around 827.4 kPa a small nitrogen leak rate was noted. This leak rate was recorded and found to fall on the linear interpolation of the leak rate data from 137.9, 275.8, 413.7, and 551.6 kPa meaning that the nitrogen leak is identical for the membrane regardless of what side it is pressurized from. A similar observation was made for the PdRu membrane. Ultimately, both membranes were internally pressurized to 1379 kPa without failure at which point
the experiment was unable to be continued due to safety concerns and that 1379 kPa was
the upper limit of the regulator used. Visual leak tests confirmed that both membranes
had not ruptured or formed any major defects.

UTS values for pure Pd and a PdRu alloy from literature were used in conjunction
with equation 3.10 to calculate the theoretical pressure the membranes should have burst
at. Using literature values\(^3\), a non-thermally cycled, pure Pd membrane of the thickness
and diameter used (4.42 micron and 0.91 cm, respectively) should have ruptured at 178
kPa (25.85 psig) and a PdRu membrane of the thickness and diameter used (2.56 micron
and 0.90 cm, respectively) should have ruptured at 256 kPa (37.1 psig). Although this
experiment was inconclusive as to whether the PdRu had a higher UTS than the pure Pd
membrane, the UTS was determined to be much higher for both membranes than what
would be expected from literature. This leads to the conclusion that supported,
electrolessly deposited membranes may have higher relative tensile strength than cold
rolled membranes of equivalent thickness.

4.4.2.4 X-Ray Diffraction Spectroscopy

XRD was performed on the pure Pd, low Ru and high Ru discs to determine the
presence of Ru from the electroless deposition. The scan range was from 30° to 90° with
a scan rate of 0.75°/min. The spectra from the low Ru disc can be seen in Figure 4.14.
The spectra for the high Ru disc was nearly identical to that of the low Ru disc. The lattice constant for Pd was calculated using equations 3.3-5 to be 3.876 Å for the low Ru disc and 3.874 Å for the high Ru disc. The lattice parameter of the pure Pd disc was found to be 3.887 Å. The lattice constants for Ru for both discs were identical with a = 2.721 Å and c = 4.460 Å. The International Centre for Diffraction Data has the lattice constant for Pd known to be 3.88238 Å and the constants for Ru to be 2.6987 Å (a) and 4.2728 Å (c). This means, for the PdRu discs that there is a 0.19% average distortion in the lattice constant of Pd (compared to the 0.11% distortion in the lattice constant in the pure Pd disc), a 0.83% distortion in the “a” constant of Ru and a 4.38% distortion in the “c” constant of Ru. It should be noted that by using the lattice constant for palladium reported in Chapter 2, the distortion is 0.09% for the pure Pd disc and 0.36% average for the Ru discs. These distortions suggest that there are two separate phases present on the
surface of the PdRu membranes: a phase that is mainly palladium with a little ruthenium in it and a phase that is mainly ruthenium with a little palladium in it.

After XRD testing was performed, the high Ru disc was annealed for 20 hours at 400°C under nitrogen and another XRD spectra was obtained. Despite partially turning blue during annealing (it is possible that palladium oxide was formed), the lattice constants were calculated to 3.876 Å for palladium and 2.721 Å (a) and 4.360 Å (c), nearly identical to the constants before annealing. This suggests that the two phases formed during plating are thermally stable at 400°C.

The presence of Ru peaks in the XRD spectrum confirms that Ru is being deposited from the electroless bath along with Pd.

4.2.2.5 X-ray Photoelectron Spectroscopy

The low Ru disc was sent to Los Alamos National Labs for XPS testing to determine Ru content of the sample. Results of XPS testing were that the sample was 100% Pd in composition. Detection limits of XPS are usually 0.1 to 1.0 atom% but can increase to 5 to 10 atom% if a standard isn’t available for calibration. Additionally, XPS only measures the composition of the first 10 nm of a sample. Therefore, results of XPS testing can be used to conclude that there is less than 5 atomic% Ru in the electrolessly deposited membrane, if there is Ru on the membrane, it is not present on the surface of the membrane, or that there is the possibility that there actually is no Ru being deposited. The latter conclusion is contradicted by the XRD results.
4.4.3.3 Nanoindentation Testing

The result of microhardness testing performed using a nanoindentation tester was that the PdRu alloy was roughly twice as hard as pure Pd. This is important because hardness is an indicator of how much pressure a material can withstand before rupturing. A harder material should be able to bridge a pore of a certain size without failing at a thickness lower than what would be required of a softer material.

Nanohardness of the high Ru disc and the pure Pd disc were measured using a NanoIndentor XP™ (MTS Instruments) machine. Samples were taken 50 nm apart from each other from the center of the discs. Maximum sampling depth of the indentor was set to be 500 nm. The machine was confirmed to be properly calibrated by using a silicon standard (the modulus from unload of the standard averaged over nine indents was reported to be 72.7 GPa, well within the accepted range of 70 to 74 GPa)\textsuperscript{32}.

The hardness of the Pd sample was determined to be 2.11 GPa averaged over the indentation depth range (average over five sample points). The hardness of the PdRu sample was determined to be 3.77 GPa averaged over the indentation depth range (average over seven sample points). This means that the sample plated using the high Ru bath was 78.7% harder than the sample plated using the pure Pd bath. Comparison of the hardness of these materials to the hardness of sputtered PdAg foils can be seen in Figure 4.15.
Figure 4.15 Nanoindentation hardness for various materials. Values for the PdAg alloys from literature.

Because hardness measures a material's resistance to plastic deformation under mechanical stress, this result suggests that the membranes plated with the PdRu baths are stronger than those plated with the pure Pd bath. Also, the 78.7% difference in reported hardness is significant and suggests that membranes deposited with the PdRu bath are distinct from membranes plated with the pure Pd bath. The increased hardness of PdRu may make this alloy less attractive for manufacture through mechanical means such as cold rolling. The hardness of the alloy is significantly less than the hardness of the sputtered PdAg$_{68}$ foil. This may be due to differences in material preparation.
4.5 Conclusions

The carbonless, PdRu co-depositional electroless bath allowed fabrication of alloy membranes with many attractive properties including higher indentation strength, enhanced thermal stability and ability to better reduce nitrogen leak rate with thin coatings.

Performance of PdRu alloy membranes deposited using the carbonless, PdRu co-depositional electroless bath revealed that the permeability of the alloy was roughly equivalent to that of pure palladium membranes deposited using a similar plating technique. The alloy was initially stable at 500°C but started to fail after multiple thermal cycles before failing outright at 600°C. Still, possibly due to depression of the critical temperature of the two phase region, the alloy was found to be more thermally stable when cycling down to room temperature than the pure palladium. Additionally, the co-deposition bath reduced the nitrogen leak rate of palladium membranes significantly more than cycles of the pure palladium bath.

Characterization of the membranes with XRD confirmed the deposition of Ru by the electroless bath and suggested two separate phases existing in the membrane. EDX and XPS testing of the alloy did not detect any Ru on deposited membranes and suggest that the actual atom% in the alloy is low. Hardness of the alloy determined through nanoindentation testing was almost twice that of the hardness of pure Pd.
CHAPTER 5

CONCLUSIONS

It is concluded that the PdRu membranes deposited by the co-depositional bath are different in structure/composition from those deposited using the conventional pure Pd bath because:

- PdRu membranes look significantly different from the latter,
- the hardness of the PdRu is significantly higher than that of the Pd,
- the nitrogen leak rate increase upon returning to room temperature was substantially less for PdRu,
- the XRD spectra of PdRu contains observable Ru peaks while the spectra for Pd does not,
- a single cycle of PdRu decreased leak rate significantly more than two cycles of Pd in the Mott plate trial.

Furthermore, it is likely that the bath is forming a PdRu alloy because

- the membranes are different from pure Pd membranes for the above reason
- properties of increased mechanical and thermal stability noted for the membranes correspond to properties for PdRu alloys
- the non-palladium peaks in the XRD spectra correspond to known Ru peaks.

The alloy created by the co-depositional bath is desirable for hydrogen separations because

- the membranes deposited have roughly equivalent permeability to that of pure
palladium

- the deposited membranes can have very low nitrogen leak rates at very thin thicknesses leading to high hydrogen fluxes and selectivity factors
- the deposited membranes have resistance to defect formation upon cooling from operating temperature to room temperature without prior purging of hydrogen from the membrane
- the alloy is harder than pure palladium and is therefore more resistant to mechanical damage.

In summation, the proposed PdRu co-depositional plating bath results in the deposition of PdRu membranes that have comparable permeabilities and improved mechanical properties over those of a pure Pd membrane.
1) Because the PdRu alloy created with the electroless, co-depositional bath has extremely promising properties, further testing of the alloy is recommended.

2) Tertiary alloys with the PdRu binary and gold have been synthesized with some success and further testing of the alloy is recommended. PdAu binary alloys are known to have resistances to poisoning. Of special interest is whether the tertiary alloy would benefit from the poisoning resistance seen in PdAu alloys while retaining the strength and stability seen in PdRu alloys.

3) Because there appeared to be no significant difference between membranes plated with the high Ru and low Ru baths, it is recommended that the bath should be optimized to find a level of Ru salt in the bath that offers the same beneficial properties of the low Ru bath while using as little Ru as possible.

4) Because of the reported extra hardness and results of plating on the Mott platelets, it is recommended pursuing whether or not thin PdRu membranes can be used to create leak free membranes over supports with larger pores and lower flow resistances.

5) Because of the low ruthenium content of the membranes, it is recommended that more precise compositional analysis is performed on the alloy so that the exact ruthenium content of the alloy can be determined. This analysis could be performed by using a technique such as inductively coupled plasma mass
spectroscopy (ICP-MS). Specifically, samples of the alloy should be deposited onto an acid-resistant support, the sample should be digested in acid and the acid should be run through an ICP-MS machine. A standard for calibration would be needed.

6) Because of the failure of either membrane to rupture during the UTS testing, it is recommended that the test be repeated in a set-up that can safely be operated above 1400 kPa. Use of fittings designed for high pressure testing may be required for this test.
REFERENCES CITED

(10) Ash, R.; Barrer, R. M. Philosophical Magazine 1959, 4, 1197.


