NDnano
Center for Nano Science and Technology

ND*nano* Summer Undergraduate Research 2019 Project Summary

1. Student name & home university:
Austin Booth
University of Notre Dame

2. ND faculty name & department:
Casey O'Brien
Chemical Engineering

3. Summer project title:
Intermetallic hydrogen separation membranes: towards unprecedented permeability and stability

4. Briefly describe new skills you acquired during your summer research:
Technical skills I acquired include using equipment such as micropipettes and vacuum pumps to prepare and deposit chemical solutions, depositing colloidal suspensions via dip coating, and programming and using a temperature-controlled furnace with gas input. I also learned to analyze data obtained from scanning electron microscopy and X-ray photoelectron spectroscopy. Finally, I gained the skill of communicating research findings clearly and concisely by presenting during the extended lunch hour and learning from group members' research presentations during group meetings.

5. Briefly share a practical application/end use of your research:
Palladium-based membranes are commonly used to separate hydrogen from other gases with extremely high selectivity. As such, our research in making defect-free, highly permeable Pd membranes has applications in hydrogen fuel cells and in production of chemicals such as ammonia and methanol, where very pure hydrogen is necessary.

6. 50- to 75-word abstract of your project:
Our goal has been to synthesize pure, defect-free palladium membranes using electroless plating and to test the effects of different preparation methods on membrane composition. Porous stainless steel disks were pretreated, coated with intermediate ceramic layers, then plated with Pd using both EDTA-free and EDTA baths. The EDTA-free bath was found to produce pure, defect-free membranes but was less stable at room temperature, although stability was improved by changing temperature and solution composition.

7. References for papers, posters, or presentations of your research:

Booth, A. (2019, July 18). *Intermetallic hydrogen separation membranes: towards unprecedented permeability and stability* [PowerPoint slides]. Presented at ND*nano* Presentation Lunch Hour.

One-page project summary that describes problem, project goal and your activities / results:

Demand for high-purity hydrogen is rapidly increasing due to hydrogen's importance in the chemical industry and potential as a clean energy source. Palladium membranes are a promising technology for hydrogen purification due to their ability to separate hydrogen with high permeability and nearly perfect selectivity. This property occurs because hydrogen gas in contact with a Pd membrane will dissociate into ions, pass through the membrane, and reform on the other side, while no other gases can permeate the membrane. A current focus of membrane research is the synthesis of thin, defect-free Pd-based membranes to maximize permeability and hydrogen purity and minimize cost. To provide stability, Pd membranes are typically synthesized on top of stainless steel supports. A ceramic intermediate layer is deposited on top of the steel to prevent metal ions from interfering with the membrane, then the Pd layer is deposited on top of the intermediate layer. One common method used to deposit the Pd layer is electroless plating, or autocatalytic deposition, which uses a chemical bath with a reducing agent to plate pure palladium onto a substrate without using electrical current. Advantages of this method include its simplicity, comparatively low cost, and low energy requirement. However, current electroless plating techniques face the challenge of maintaining solution stability while avoiding membrane impurities.

The project's goal so far has been to synthesize pure palladium membranes on porous stainless steel substrate disks using an electroless plating bath and to test the effect of different preparation methods on membrane composition and performance. EDTA (ethylenediaminetetraacetic acid) is commonly used in Pd plating baths to stabilize the solution at most temperatures, but it can introduce organic impurities into the membrane that decrease performance. As a result, we have focused on testing an EDTA-free plating bath composed of ammonia solution, hydrazine, and palladium nitrate and determining the optimal conditions for solution stability. The project has also focused on analyzing different intermediate layers and Pd seeding methods to determine how best to prepare the disks for palladium deposition.

The first step in the project was to prepare porous stainless steel disks by polishing them with fine sandpaper and then etching them with a mixture of hydrochloric and nitric acid. These treatments were intended to smooth the substrates and increase the number of open pores. Next, the intermediate ceramic layer was applied. Solutions of alumina, silica, and ceria were all tested on separate disks, as were two deposition methods: dip coating and vacuum-assisted deposition. Scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) were then conducted on the disks to analyze the surface texture and chemical composition. Analysis indicated that alumina deposition produced a smooth layer that filled most pores, while silica and ceria formed cracks that produced a rough surface and did not completely cover the stainless steel surface. Since this could cause membrane impurities through ionic interference, we chose to use alumina as the intermediate layer for future disks. We also decided to focus on dip coating, since vacuum deposition created a thick layer of alumina that would hinder permeability.

Once the intermediate layer was applied, a small amount of palladium seed solution was deposited onto the disks, and they were reduced under hydrogen at 450 °C to ensure adhesion. Pure palladium was then deposited on the disks using a plating bath; both EDTA and EDTA-free baths were tested. The plating bath was changed every few hours as it depleted until the Pd layer reached approximately 5 to 10 microns in thickness. SEM, XPS, and gas permeance tests were carried out on the finished membranes to check for impurities and observe membrane performance. It was found that the EDTA-free bath was able to create membranes approximately as smooth, permeable, and defect-free as those produced by EDTA baths without introducing any carbon impurities. The EDTA-free bath did face the problem of instability at room temperature; the solution would initially form precipitate on the sides of the beaker and did not deposit much Pd on the substrate. However, we were able to maintain stability either by reducing the amount of hydrazine (which slowed plating) or by refrigerating the bath at 4 ℃ (which would be less practical for industrial applications). We also found that the palladium adhered best to the substrate while using a seed solution with one-fourth of the $Pd(NO_3)_2$ concentration that was reported in literature. Higher concentrations caused excess seed to separate from the intermediate layer, destroying the membrane. Despite these challenges, the ability to produce high-performance palladium membranes without carbon impurities is a promising development for the field of hydrogen separation.

I plan to continue research with this project during the fall semester. In the future, we will expand the project to focus more on synthesizing intermetallic membranes such as palladium-copper membranes, which tend to be more stable, less expensive, and more resistant to membrane poisoning than pure Pd.

Figure 1. Beaker containing EDTA-free Pd bath solution, with Pd-coated disk inside