

Material Synthesis of Catalytic Membranes Used in Selective Alkane Oxidation

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Abstract - Within the field of natural gas, there has been a lot of interest to find ways to make lower carbon-chain molecules, such as methane, ethane, and propane, more profitable and usable. There are many reactions that can manipulate these gases into value-added chemicals. In order to perform these reactions, membrane reactors that transport oxygen ions are needed. With current state-of-the-art Oxygen Transport Membrane (OTM) technology, there are still many issues that inhibit the technological feasibility of their usage in partial oxidation reactions. One of these limitations is poisoning by carbon dioxide. This report explores an alternative membrane material, Cobalt doped Cerium Gadolinium Oxide (Co-CGO), and its potential usage in Oxidative Coupling of Methane (OCM). First, the synthesis steps for the production of the Co-CGO powder will be explored. Next, the steps for pressing the powder into a button-cell shape will be discussed. Finally, analysis of the powder with its gas-tightness, oxygen flux, selectivity, conversion, and operation in a carbon dioxide environment will be analyzed. This project was done in the Linic Lab as a University of Michigan College of Engineering Honors Program Capstone.

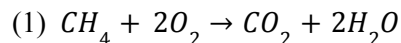
I. INTRODUCTION

A. Background

Methane is a single carbon hydrocarbon that is abundantly found in natural gas deposits. The gas itself is extremely efficient at trapping

heat, which when released into the atmosphere, can help contribute to global warming. It is highly detrimental to the environment, even more so than carbon dioxide is. Due to this, in 2016, the Obama Administration enacted the first national methane emissions cap for the oil and gas industry^[2]. This was to help reduce the amount of methane being released into the atmosphere from natural gas sites, as this gas is highly volatile and difficult to contain. To do so, it requires a lot of power to contain or use the gas. This power is expensive and also not readily accessible near most natural gas deposits, since they are in remote locations. On top of these things, methane gas also is very abundant, and there is a much higher supply than there is a demand for it.

Due to this issue of methane being unprofitable and bad for the environment, a lot of the oil and gas industry will burn it to produce carbon dioxide and water vapor. The chemical reaction for this process is described in Equation 1.

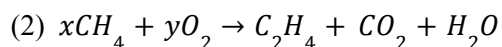


This chemical reaction will produce one molecule of carbon dioxide for every methane burned. Although this seems counterintuitive to burn the methane and produce carbon dioxide, an equivalent amount of carbon dioxide in the atmosphere is significantly less harmful to the environment than the same amount of methane. This way, these companies are able to meet the emission regulations set in place by the

government, yet not have to spend lots of money to capture it or convert it.

B. Oxidative Coupling of Methane

While methane presents a problem for the oil and gas industry as well as the environment, it also presents a large opportunity. There has been a lot of technology recently being developed that will convert methane into more usable, desirable, and profitable products. An example of this is converting methane to olefins, which is a molecule with double bonded carbons, through the Oxidative Coupling of Methane (OCM). This is a chemical reaction that will react methane with oxygen to create ethane or ethylene. Equation 2 shows the chemical reaction of creating ethylene from methane and oxygen.



The x and y in this equation represent the number of moles needed to balance this reaction. Here one can see that there are several products to this reaction such as ethylene, carbon dioxide, water vapor, and others not depicted like carbon monoxide and ethane. From all of the possible products, ethylene and ethane are used in a number of different materials and markets. With this chemical reaction the oil and gas industry is now able to stop burning methane and polluting the atmosphere with carbon dioxide and turn it into something profitable. There are other possible uses for methane as well, but this reaction is specifically studied by the Linic Lab.

Currently the OCM reaction is mostly being explored in a lab setting. There are several ways to run the OCM reaction, which will lead to different conversion rates and selectivities. Conversion in chemical reactions is the measurement of how much of the reactants, in this case methane, is actually reacted from the feed to form the products. Selectivity is the

measurement of the amount of one of the products produced compared to rest and taken as a percentage. There are two ways that have been explored so far, a packed bed reactor (PBR) and a membrane reaction. A packed bed reactor is a capsule that is full of catalysts or other materials and the feed gas (methane and oxygen) is sent through to perform the reaction. Catalysts are able to decrease the activation energy for certain reactions that will allow them to happen at lower temperatures. Catalysts can also affect the pathway of the reaction, leading to higher conversion rates and selectivities of certain products. This method has generally led to high conversion rates yet low selectivities. The second method is using a catalytic membrane, where the feed gas will have to diffuse through the membrane material to react and produce the products. This method has shown more promising results, as it has had higher conversion rates and selectivity^[1].

C. OCM Issues

The OCM reaction is a great achievement for the oil and gas industry in theory. It provides a profitable alternative to burning methane while reducing the environmental impact of the oil and gas industry. However, this reaction is difficult to perform in practice. The first reason being is that OCM generally happens at high temperatures, around 850 °C or above. A temperature this high requires a lot of energy, which as discussed earlier, is not cheap or readily available for a lot of natural gas sights. Another issue with OCM is that it is not yet an economically profitable process. There are certain techno-economic goals that are set for the conversion and yield of this reaction. OCM is a complex reaction that can lead to other products outside of equation 2, such as ethane, carbon dioxide, carbon monoxide, and others. Selectivity of the ethane and ethylene needs to be high for this reaction to be profitable, as

producing carbon dioxide or carbon monoxide are not useful.

In order to start tackling these issues, most current research has been looking at catalysts that are used for OCM. Catalysts are a way for us to make these difficult chemical reactions possible. There are different uses for catalysts. In the OCM reaction, we have two different uses for a catalyst. An “OCM catalyst” is a material that helps aid the reaction of methane conversion to the olefins. An example of this is the $Mn/Na_2WO_4/SiO_2$ compound. The other type of catalyst is a “membrane catalyst”, which is for oxygen transport through the membranes. These catalysts will react with oxygen to reduce it to its ionic form, O^{2-} , transport it and its electrons across the membrane to the methane gas, where it will then react. Two examples of current state-of-the-art catalysts are $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ (Lanthanum Strontium Cobalt Ferrite, or LSCF) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$ (Barium Strontium Cobalt Ferrite, or BSCF).

Although these catalysts are state-of-the-art currently, they still have their own issues as well. One primary issue is their behavior when carbon dioxide forms. The ability to transport the oxygen ion across its membrane is greatly inhibited by the presence of carbon dioxide. Figure 1 shows this with LSCF.

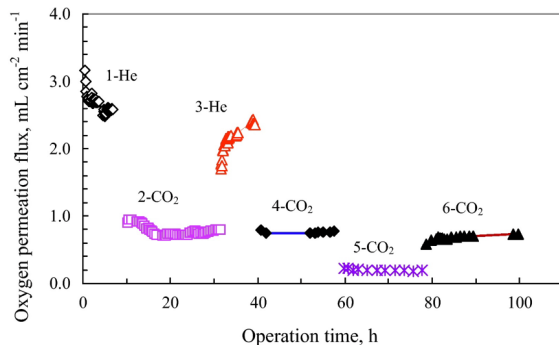


Figure 1. LSCF Oxygen Flux With and Without Carbon Dioxide^[5]

On the horizontal axis of the figure, the time of operation of the membrane is depicted, where on the vertical axis the oxygen flux is shown. Oxygen flux is defined as the amount of oxygen that is able to pass through a certain area of the membrane in a given amount of time. This is a great measurement to see how different environments are affecting the ability of the oxygen ions to diffuse. In the graph, you can see at time segment 1 that there is only a helium environment surrounding the membrane. In this environment the oxygen flux is high, at around 3 mL/(cm²*min). At time segment 2, the environment is switched to be only carbon dioxide, where you can see the flux has dropped down drastically to only 1 mL/(cm²*min). This relationship shows that even with these state-of-the-art catalysts being able to achieve their catalytic goals, there are inhibitors to their efficiency. The same relationship can be seen in Figure 2 which is exploring BSCF in carbon dioxide environments.

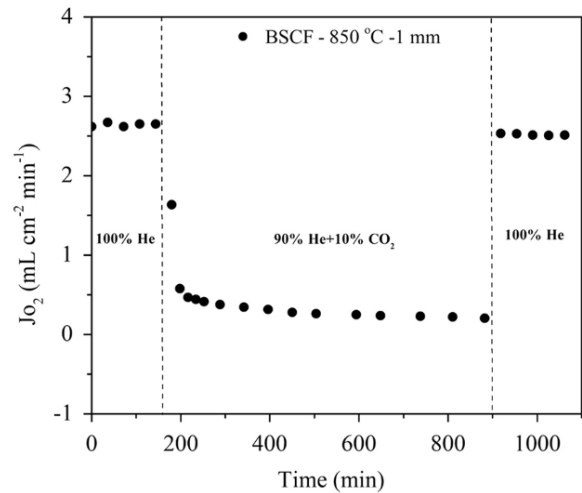


Figure 2. BSCF Oxygen Flux With and Without Carbon Dioxide^[4]

The reason that is expected for this to be happening is that carbon dioxide will react with Lanthanum and Barium to form a carbonate -

SrCO_3 or BaCO_3 - which affects the performance of the catalytic membranes.

D. Goal of Capstone Project

The goal of this project was to explore different catalytic membrane materials that would be able to provide the same level of oxygen diffusion across a catalytic membrane while being resistant to carbon dioxide in the atmosphere. The specific material we explored was Cobalt doped Cerium Gadolinium Oxide (Co-CGO). This report will discuss synthesis of the powder, button cell membrane pressing, test results, and conclusions/next steps going forward.

II. SYNTHESIS METHOD

A. Initial Synthesis

Throughout the course of this project we worked on our synthesis of the Co-CGO powder. The goal of the synthesis was to replicate literature values of the phases formed in the powder while also creating a homogenous mixture with particle sizes on the scale of microns to nanometers. These aspects are important as we want a powder that when formed into a membrane will have desirable properties for oxygen transport that is seen in the other state-of-the-art membrane..

Co-CGO is a useful catalyst for OCM as it is both ionic and electronically conductive^[3]. What this means is that the Cerium Gadolinium Oxide phases that form are great for reducing oxygen and transporting it along its grain boundaries, where the cobalt that is in between the particles is able to conduct electrons from the oxygen ion across the membrane as well^[3].

Our initial synthesis consisted of only five steps:

- (1) Solution-Gel (Sol-Gel) with Cerium (III) Nitrate Hexahydrate and Gadolinium (III) Nitrate Hexahydrate.
- (2) Calcine at 700 °C.
- (3) Incipient Wetness Impregnation of Cobalt (II) Nitrate Hexahydrate.
- (4) Calcine at 550 °C.
- (5) Sift with a 75 μm sieve.

Step 1 starts out with two nitrate compounds that contain cerium and gadolinium that will be mixed together in water. This solution will then be mixed with citric acid and ethylene glycol and the whole solution is mixed overnight at 105 °C. The goal of this synthesis step is to create a solution with our desired metal ions in it that will go from an aqueous mixture to a more gel-like mixture that has no water in it, hence “Sol-Gel”.

Step 2 is taking this gel and heating it up to 700 °C. This is important as we need to bake away the nitrate and help the Cerium Gadolinium Oxide form the correct phase. When this step takes place, ammonium, carbon monoxide, and nitrous oxides are being emitted from the mixture, therefore it is very important to have a well ventilated furnace.

Step 3 is now introducing cobalt into the mixture. This compound is added while being well mixed to form a homogenous mixture.

Step 4 is similar to step 2 where our goal is to bake off any undesirable compounds in our mixture to get the final Co-CGO powder.

Step 5 is necessarily to break apart any aggregates that formed during the synthesis. The 75 micron sieve is used to get aggregates of 75 microns or less in size.

B. Final Synthesis

Each step was chosen with the goal of getting a powder that could be pressed into a button cell and sintered for testing. Once completing this synthesis method and going forward with the button cell membrane pressing and testing, it was quickly seen that our synthesis method formed an undesirable membrane. Due to the results we received - which will be talked about in later sections - we knew we had to modify our synthesis method to help break down the particles more. With this information, we came up with our final synthesis method, which is also depicted in Figure 3:

- (1) Solution-Gel (Sol-Gel) with Cerium (III) Nitrate Hexahydrate and Gadolinium (III) Nitrate Hexahydrate.
- (2) Calcine at 700 °C.
- (3) Ball Mill in ethanol for 24 hours.
- (4) Incipient Wetness Impregnation of Cobalt (II) Nitrate Hexahydrate.
- (5) Calcine at 550 °C.
- (6) Ball mill in ethanol for 24 hours.
- (7) Sift with a 75 μm sieve.



Figure 3. Image Representation of the Synthesis of Co-CGO Powder

In this final method of synthesis, we introduced steps 3 and 6 to break down the powder more. This helped us form particles of Co-CGO that were to the scale of microns to nanometers in size, which have very high surface energy.

III. BUTTON CELL MEMBRANE PRESSING

A. Button Cell Press Process

Button Cell Membranes are small, cylindrical disks about 15 mm in diameter that are very effective for testing properties of a

membrane. This is an important step when it comes to testing the properties of Co-CGO, as we need the membrane to be “gas-tight” so that no gases besides oxygen are able to permeate through. This method was also worked on throughout the semester, as many issues were seen when trying to create the button cell membranes. The process for the final pressing method is described below and depicted in Figure 4.

- (1) Coat contact surfaces of press with WD40 and wipe off excess residue.
- (2) Assemble the base of the press and pour in 0.4 grams of powder.
- (3) Insert piston of press and twist to evenly distribute the powder.
- (4) Remove the piston carefully and wipe off any powder. Reapply WD40.
- (5) Press at desired tonnage and time.

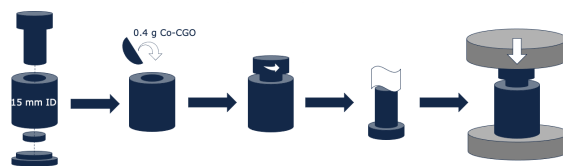


Figure 4. Image Representation of Button Cell Membrane Pressing Process.

Our original synthesis method was based on the process for a different powder called Yttria-Stabilized Zirconia (YSZ). YSZ powder is similar to Co-CGO, yet it is easier to densify due to its larger particle sizes. This creates less friction when pressing, therefore it is easier to compress. This requires a higher sintering temperature, so we modified our procedure to match this difference in material properties.

The process described above was not our initial synthesis method. Originally, we did not include WD40, the twist method of powder distribution, or any additional cleaning. These steps were added for a few reasons. WD40 was added due to the high surface energy of the

Co-CGO powder. Due to how fine the particle size was, there was too much friction between the press wall and the powder itself. Before using the WD40, we tried adding in a little bit of polyvinyl butyral (PVB). This was seen to work with the YSZ powder, however, did not for Co-CGO. The twist method for powder distribution was introduced in order to help form an even film inside the press. This is difficult through manipulation with a spatula or tapping the side of the press. Finally, removing the piston of the press and cleaning after twisting is a key part of the process. Due to the high surface energy, the powder sticks very easily to the press even with the minimal frictional force created through twisting. Cleaning this surface and reapplying WD40 helped prevent any sticking or breakage from pressing. Table 1 presents several synthesis methods with the steps of pressing as well as any deviations from the finalized procedure.

Table 1. List of Press Methods With Results

Synthesis of Powder	Press Tonnage (Metric Tons)	Time (min)	Notes
A. Not milled, No WD40, no polymer	0.5	2	Formed Cell
B. Not milled, No WD40, no polymer	2	2	Formed Cell
C. Not milled, No WD40, polymer added 1 wt%	0.5	2	Could not sinter
D. Not milled, No WD40, polymer added 1 wt%	2	2	Could not sinter
E. Milled, No WD40, no polymer	0.5	2	Stuck to press
F. Milled, No WD40, no polymer	2	2	Stuck to press

G. Milled, WD40, no polymer	0.5	2	Small chip, sealable cell
H. Milled, WD40, no polymer	4	0	Small chip, sealable cell
I. Full Synthesis steps	2	2	Formed cell

B. Button Cell Characterization

After successfully forming a button cell, we would sinter at 900 °C to form the final form of the membrane. This is an important step in the process, as sintering will cause the powder in the cell to become more dense as the grain boundaries become closer together and more compact. This is necessary for us to not only have good oxygen flux and electron transport, but to also ensure other gases are not able to permeate through. An image comparing a sintered cell to a pre-sintered cell can be seen in Figure 5.

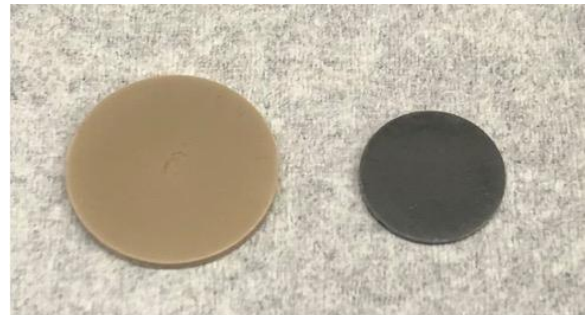


Figure 5. Pre-sintered Cell Depicted on Left with Sintered Cell Depicted on Right

The first characterization method we used was X-Ray Diffraction (XRD). This method will emit X-Rays towards the material and measure the intensity of the diffracted electrons in order to classify the material^[7]. This is necessary in determining if the proper phases were formed

during the button cell and powder synthesis. When we ran this test, we saw that our XRD graph matched literature. This graph can be seen in Figure 6.

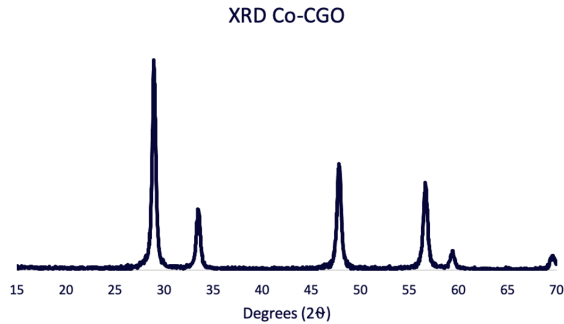


Figure 6. XRD Analysis of Co-CGO Powder

Next step in classifying the material was to perform a Scanning Electron Microscope (SEM) test on the sintered button cells. This test allows us to visualize the surface of the material as well as the bulk to see if the sintered cell formed is gas-tight. Press A SEM results can be seen in Figure 7.

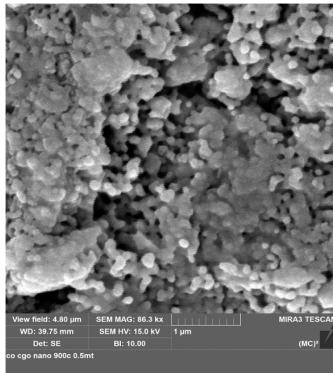


Figure 7. Press A SEM Results of Bulk

From these results, it can be seen that the first synthesis method did not form a gas-tight cell. There are many aggregates still within the bulk that did not form a homogenous phase, as well as many gaps being present. From this, we decided to increase the tonnage to see if this would help the cell compact more. Press B results can be seen in Figure 8 and 9 of the bulk and surface.

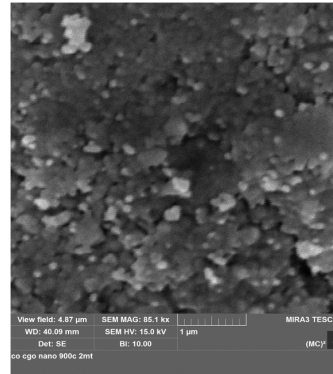


Figure 8. Press B SEM Results of Bulk

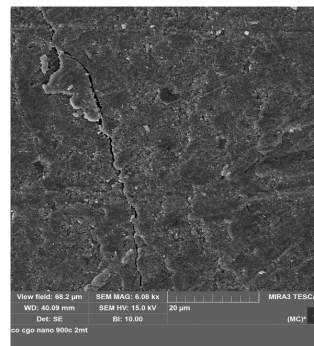


Figure 9. Press B SEM Results of Surface

The results from press B were a lot better, yet did not achieve our goal. We can see that still in the bulk there are larger aggregates as well as gaps in the cell, therefore not being gas-tight. On top of this, we saw on the surface there were cracks and fissures that we could not see after sintering. From these results, we determined to modify our initial synthesis method to include the ball mill steps to break apart the aggregates more, as well as modify our pressing method. With these steps accomplished, we were able to get a gas-tight cell with press I. This can be seen in Figure 10.

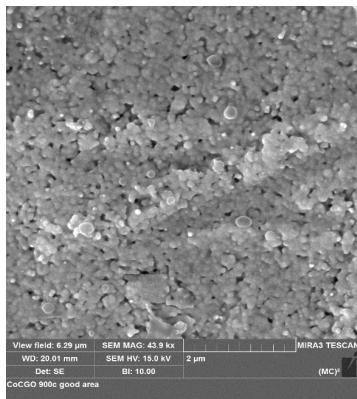


Figure 10. Press I SEM Results of Bulk

This shows that there is a homogenous phase that formed after pressing. This allows us to now start testing the cell to quantify the properties we are looking for.

IV. TESTING RESULTS OF Co-CGO BUTTON CELLS

A. Oxygen Flux Tests and Results

In order to ensure our cell properly works before testing further, we want to test its oxygen flux. To do this, we use an OCM membrane reactor and flow air through the membrane and classify the stream leaving through the other side. The classification is done through Gas Chromatography (GC). For us to quantify the flux from the GC, we need to use an equation that accounts for the oxygen flow as well as nitrogen across the cross-sectional area of the membrane. This is done by using Equation 3.

$$(3) \quad J_{O_2} \text{ for OCM } (\mu\text{mol cm}^{-2}\text{min}^{-1}) = \frac{0.5 * N_{H_2O} + 0.5 * N_{CO} + N_{CO_2}}{A_{outer}}$$

This equation reports the flux with micromoles instead of milliliters. This can easily be converted with the density of oxygen. The results from testing the oxygen flux can be seen in Figure 11.

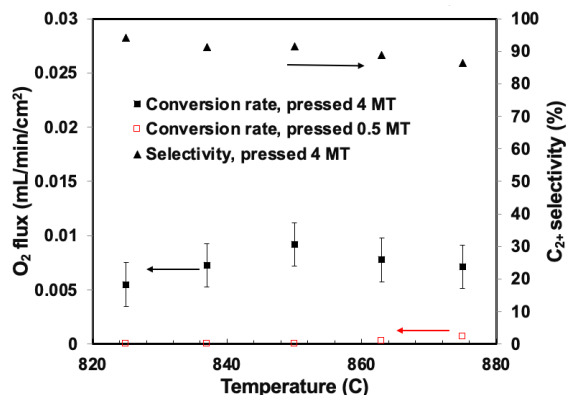


Figure 11. Oxygen Flux and Selectivity of OCM Membrane Reactor Using Co-CGO

The oxygen flux using this material can be seen to be very low compared to the state-of-the-art catalysts.

B. Conversion and Selectivity Tests and Results

To test the conversion and selectivity, we used the same reactor setup described in the oxygen flux tests. Instead, this time we used a methane and oxygen feed to run the actual OCM reaction. The results for conversion can be seen above in Figure 12, and for selectivity this can be seen in Figure 11 and 12 as well.

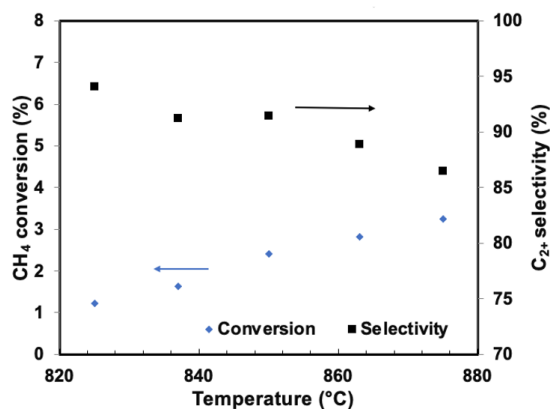


Figure 12. Conversion and Selectivity of OCM Membrane Reactor Using Co-CGO

Here we can see that our conversion rate is fairly low, like the oxygen flux. Our selectivity for the process is fairly high though, which shows that Co-CGO is promising.

V. CONCLUSIONS AND NEXT STEPS

A. Conclusions

When synthesizing this powder, it is very important to be able to control the particle size. This is important because too large will create large aggregates in the button cell and affect gas-tightness. Too small of particles can also become a problem when trying to press due to their high surface energy, which causes a lot of friction. In order to control these things, milling the powder at multiple stages in the synthesis is key, as well as the temperature the powder is calcined at. These things will alter the particle size which will affect the final results of the button cell membrane. From the steps described, we were able to make an effective synthesis method of Co-CGO powder.

With the particle size, this also affects the pressing procedure. By adding WD40 as well as additional cleaning steps, you can reduce the surface energy and friction between the press and the powder. This is important when it comes to removing the cell so that it does not stick to the press or crack. With the steps described, we were able to make an effective synthesis method of Co-CGO button cells.

Due to time constraints as well as results, we were unable to fully assess the effectiveness of Co-CGO in carbon dioxide. Because of the oxygen flux and conversion being so low, it would be difficult to assess the effects of carbon dioxide on the flux of oxygen through this membrane. Also with the low oxygen flux, we are below the techno-economical goal of 0.5 mL/(cm²*min). With the known information online we still expect that this powder will be stable in a carbon dioxide environment^[3].

B. Next Steps

The best way to progress with this project is by using Co-CGO as a thin, protective coating on state-of-the-art membrane materials. This way, we will have the combined effect of high oxygen flux as well as resilience to carbon dioxide poisoning. There are several ways to possibly do this, such as trying directly apply or having a gradient going from Co-CGO to bulk LSCF or BSCF.

This material can also be used outside of the OCM reaction. There are other reactions such as Oxidative Dehydrogenation of Ethane and Propane, as well as converting methane to syngas, that requires the use of oxygen transport membranes as well. These reactions will also produce carbon dioxide, therefore this technology will also be helpful in these fields as well^[6].

VI. REFERENCES

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