Material Synthesis of Catalytic Membranes Used in Selective Alkane Oxidation

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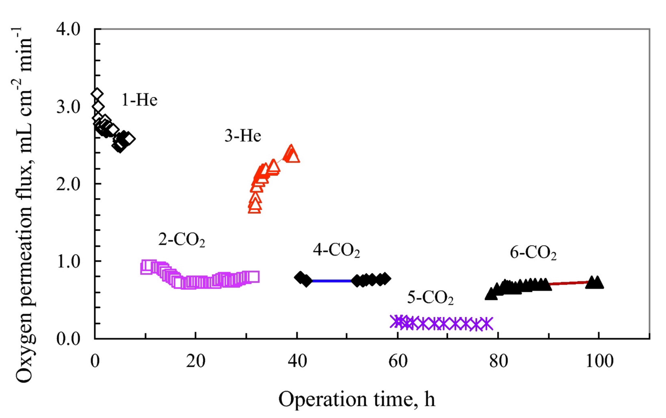
Challenges of Selective Alkane Oxidation

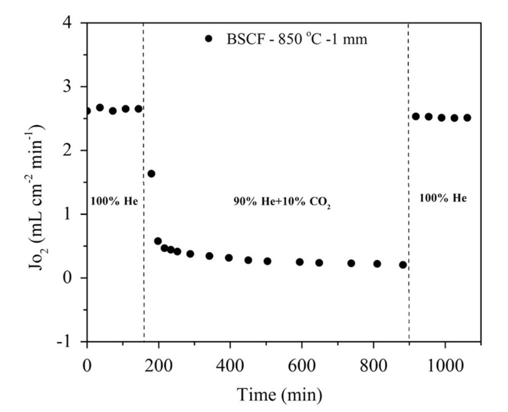
Oxygen Transport Membranes (OTMs) are an important material used in the separation of oxygen from air. We can utilize OTMs in many ways, including in the control of the selectivity in different partial oxidation reactions.

Methane to Syngas[3]	Oxidative Coupling of Methane (OCM) to Ethylene[3]	Oxidative Dehydrogenation of Ethane[3]	Oxidative Dehydrogenation of Propane[3]
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	$xCH_4 + yO_2 \rightarrow C_2H_4 + CO_2 + H_2O$	$xC_2H_6 + yO_2 \rightarrow C_2H_4 + CO_2 + H_2O$	$xC_3H_8 + yO_2 \rightarrow C_3H_6 + CO_2 + H_2O$

Materials used in OTMs for these reactions are a lot less effective in environments with Carbon Dioxide, which is a byproduct of a lot of these reactions. Because of this, it is our motivation to find materials that will not be affected by CO_2 while transporting oxygen.



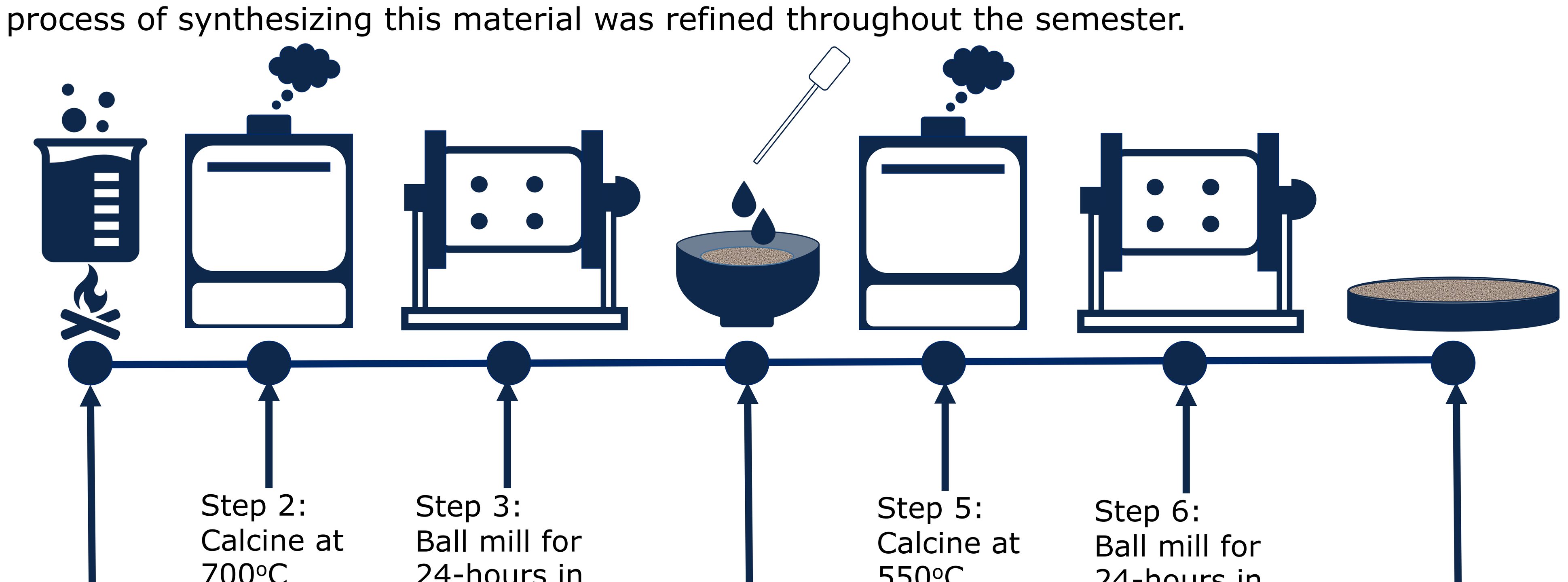
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-x}$ oxygen flux in different environments[2]



$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$ oxygen flux in CO_2 compared to Helium[1]

Cobalt Doped Cerium Gadolinium Oxide Synthesis

We want to investigate materials that will be stable in CO_2 conditions that can be used independently in an OTM or as a coating on other OTMs. Cobalt doped Cerium Gadolinium Oxide (Co-CGO) is possibly one of these materials. First, we need to create the powder. The process of synthesizing this material was refined throughout the semester.



Step 1 : Solution-Gel (So-Gel)
- Mix Cerium (III) Nitrate Hexahydrate and Gadolinium (III) Nitrate Hexahydrate in solution of water, citric acid, and ethylene glycol
- Heat overnight at 105ºC to evaporate water

Step 2: Calcine at 700ºC

Step 3: Ball mill for 24-hours in ethanol

Step 4: Incipient Wetness Impregnation
- Add 2 mol% Cobalt (II) Nitrate Hexahydrate to milled CGO powder dropwise and mix simultaneously
- Mole percent based on metal ions

Step 5: Calcine at 550ºC

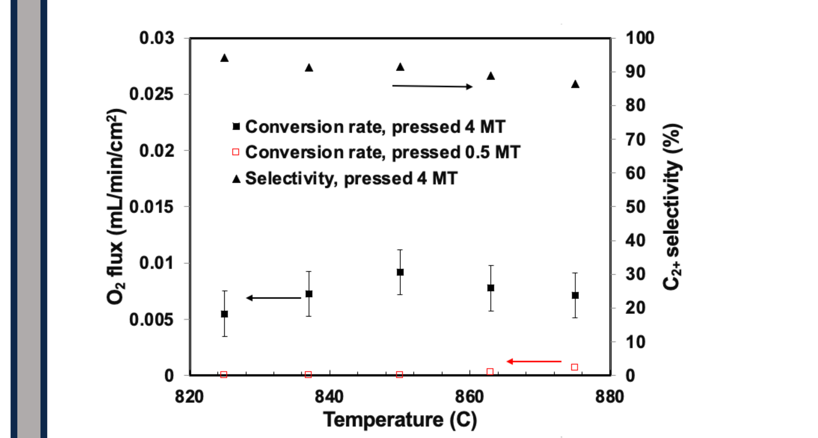
Step 6: Ball mill for 24-hours in ethanol

Step 7: Sift powder for size of 75 μm or less

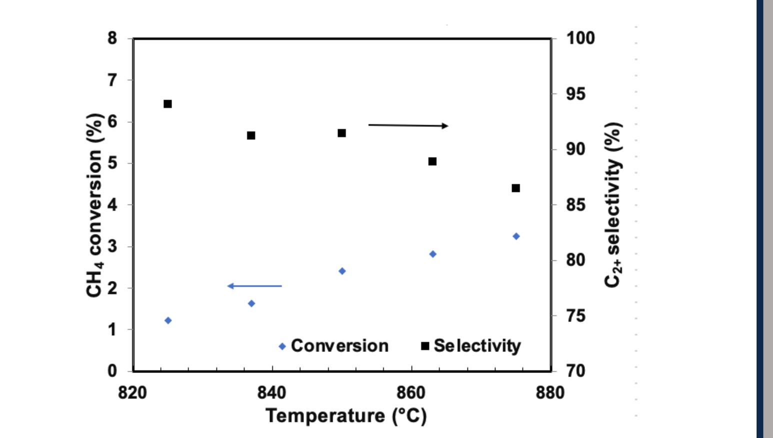
Button Cell Test Results

After analyzing our button cells through SEM, we ran gas-tightness testing and O_2 flux testing to see how the cell reacted. We needed to do this before testing in a carbon dioxide environment, as we wanted to make sure there was enough O_2 flux for us to get efficacious results.

These tests were done using an OCM reaction, where we are trying to create ethylene or ethane (C_{2+} compounds) from methane. Here, we want to track the C_{2+} conversion and selectivity of the overall reaction, as this process can create a lot of byproducts (CO_2 and CO).



O_2 flux and C_{2+} selectivity for Press G and H at different temperatures



CH_4 conversion and C_{2+} selectivity for Press H at differing temperatures

Mathematical Definitions *N_i is molar flowrate of species i*

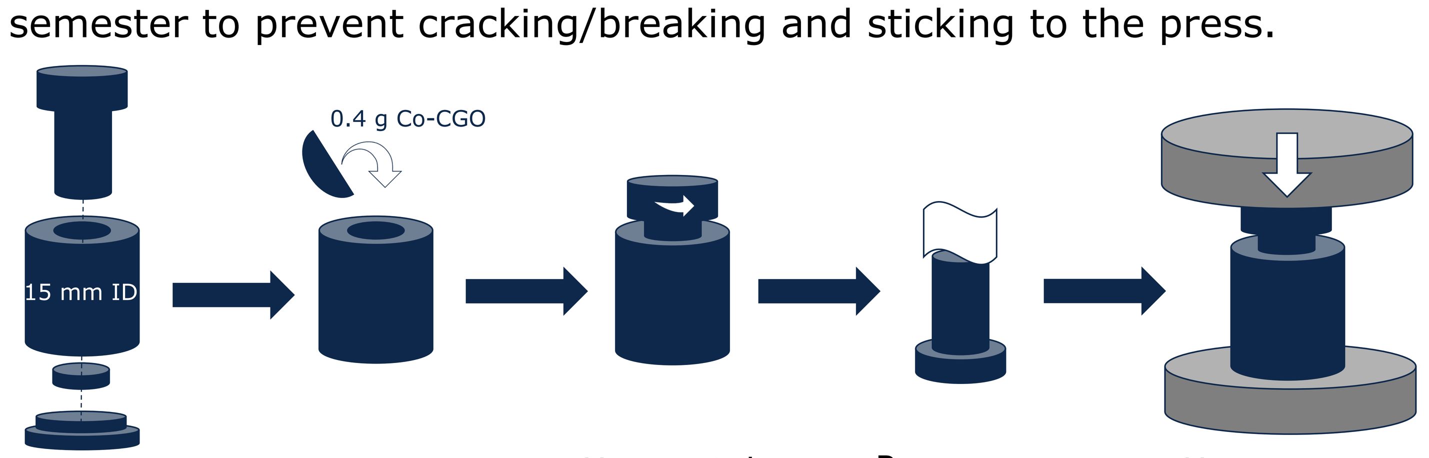
Conversion: $$X_{CH_4}(\%) = \frac{100[2(N_{C_2H_4} + N_{C_2H_6}) + 3(N_{C_3H_6} + N_{C_3H_8}) + N_{CO} + N_{CO_2})]}{\text{moles of } CH_4 \text{ fed}}$$

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

Selectivity: $$S_{C_{2+}}(\%) = \frac{[2(N_{C_2H_4} + N_{C_2H_6}) + 3(N_{C_3H_6} + N_{C_3H_8})]}{2(N_{C_2H_4} + N_{C_2H_6}) + 3(N_{C_3H_6} + N_{C_3H_8}) + N_{CO} + N_{CO_2}} \times 100$$

Button Cell Membrane Press Process

Next, we need to test our powder. Button Cell Synthesis is an important part of testing. This helps us test if the material can create a gas tight membrane that allows for O_2 flux without CO_2 poisoning the membrane. This process was refined over the course of the semester to prevent cracking/breaking and sticking to the press.



Coat surfaces that contact powder with WD40

Assemble base of press mechanism and pour in 400 mg Co-CGO

Use spatula to ensure even distribution and twist piston

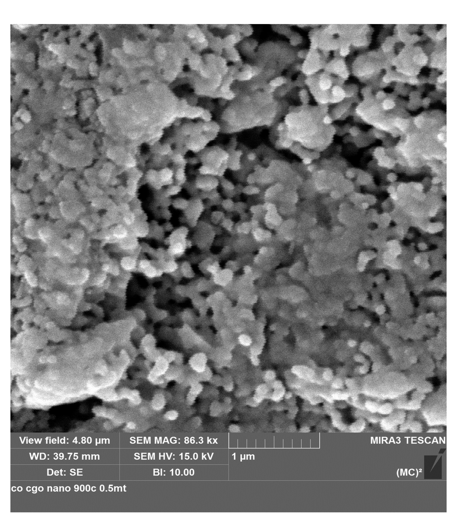
Remove piston carefully and clean surface. Reapply WD40

Use Hydraulic press at desired tonnage and time

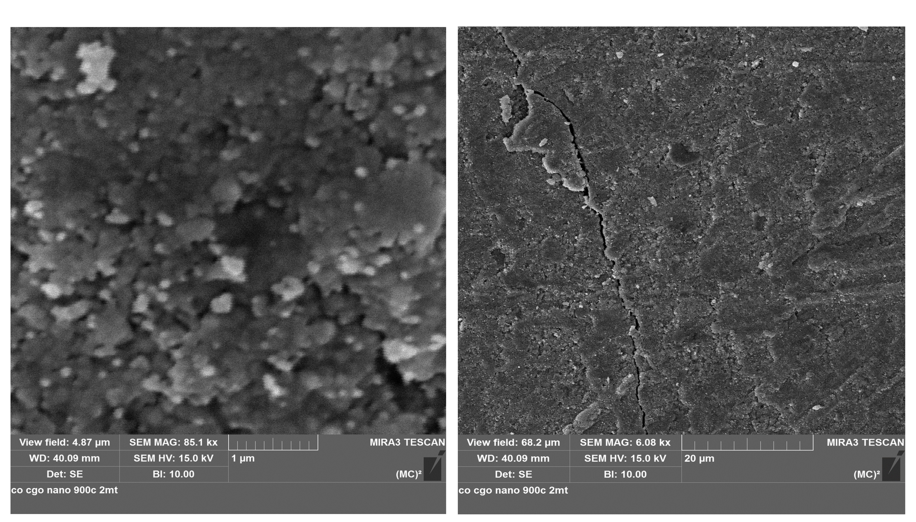
Synthesis of Powder	Press Tonnage (Metric Tons)	Time (min)	Notes
A. Not milled, No WD40, no polymer (PVB – Polyvinylbutyral)	0.5	2	Stuck to press, still loose powder
B. Not milled, No WD40, no polymer	2	2	Stuck to press, no loose powder
C. Not milled, No WD40, polymer added 1 wt%	0.5	2	Successfully formed cell, could not sinter
D. Not milled, No WD40, polymer added 1 wt%	2	2	Successfully formed cell, 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	Successfully formed cell

Button Cell Membrane Characterization

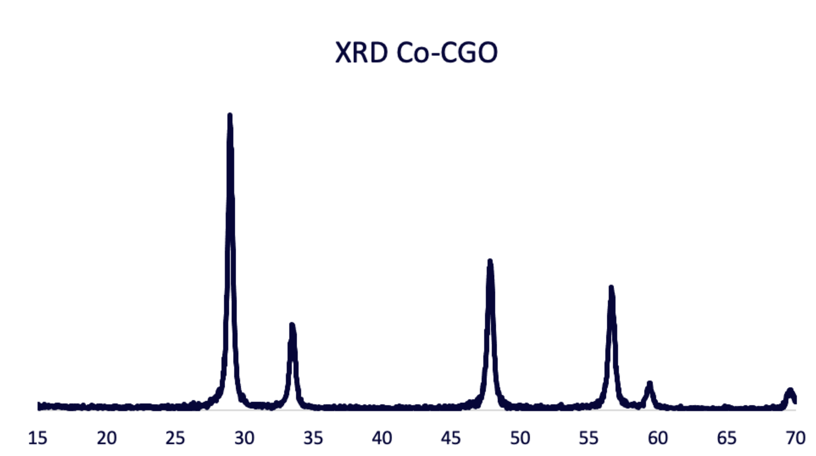
After creating a successful button cell, we need to analyze the structure of the cell before continuing testing. We would sinter the button cells at 900ºC and analyze them using Scanning Electron Microscopy (SEM). This helps us visualize grain boundaries, as well as other possible surface defects.



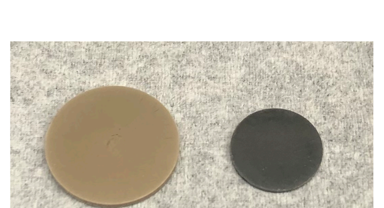
Press A SEM results. There are cracks in the surface and large aggregates, which indicates that the membrane is not gas tight. This is from too low of pressure to break apart aggregates.



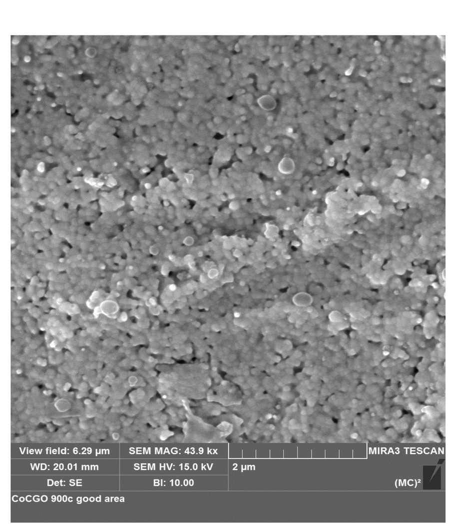
Press B SEM results. There are smaller aggregates, however, still have cracks and not gas tight. We see here that we need to mill the powder before pressing.



XRD classification of Co-CGO powder. This helps us see which phases formed. Matches literature values, therefore our synthesis method was effective.



Press G pre-sintered (left) and post-sintered (right)



Press I SEM results. This membrane would have been gas tight if not for mechanical breakage from defects. Defects propagated cracking effect from surface, results in minor gaps. Overall, this method was successful in our other trials.

Summary and Future Outlook

- An effective systematic process for creating Co-CGO was discovered for very fine particle size.
  - Particle size can be altered based on calcine temperature
  - Higher temperature for calcination would lead to larger particle size.
- Co-CGO powder was difficult to press, but ultimately a systematic process was created that led to reproducible results.
  - Small particle size created very high surface energy, which led to a lot of friction and sticking to press when applying pressure.
- For Press G and H test cases, both SEM and reactor testing showed gas-tightness of button cells.
  - Leaking of oxygen was less than .001 mL O_2/min/cm^2
- O_2 flux is too low for us to evaluate CO_2 stability results.
  - 0.5 mL O_2/min/cm^2 is minimum techno-economical goal
- Applying Co-CGO film to a more state-of-the-art OTM, like $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-x}$, might produce better results, as it will have higher O_2 flux and Co-CGO will provide CO_2 stability.

References and Acknowledgements

1. Zhenbao Zhang, Dengjie Chen, Yubo Chen, Yong Hao, Moses O. Tade, Zongping Shao, Facile fabrication and improved carbon dioxide tolerance of a novel bilayer-structured ceramic oxygen permeating membrane, Journal of Membrane Science, Volume 472, 2014, Pages 10-18, ISSN 0376-7388.
2. Xiaoyao Tan, Nan Liu, Bo Meng, Jaka Sunarso, Kun Zhang, Shaomin Liu, Oxygen permeation behavior of La0.6Sr0.4Co0.8Fe0.2O3 hollow fibre membranes with highly concentrated CO2 exposure, Journal of Membrane Science, Volume 389, 2012, Pages 216-222, ISSN 0376-7388.
3. X. Tan, K. Li, 8- Applications of dense ceramic membrane reactors in selected oxidation and dehydrogenation processes for chemical production, Handbook of Membrane Reactors, Woodhead Publishing, Volume 2, 2013, Pages 347-383, ISBN 9780857094155.

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