METHANE SYNTHESIS USING A SABATIER-ELECTROLYZER BASED ON 
PROTON-CONDUCTING CERAMICS

by
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ABSTRACT

The objective of this thesis is to study the performance of proton-conducting ceramics as a Sabatier-Electrolyzer in the synthesis of methane. The National Aeronautics and Space Administration seeks innovative space technology that can make use of resources in space via In-Situ Resource Utilization (ISRU). ISRU will enable sustainable human exploration and living in space by minimizing the materials carried from Earth. Available resources on Mars include carbon dioxide, which makes up 95% of the Martian atmosphere, and water, which is available in the form of ice within craters or regolith. Proton-conducting ceramics have unique properties that can enable simultaneous processing of these two feedstocks to produce methane and oxygen. Carbon dioxide and steam are fed on opposite sides of a proton-conducting membrane in a ceramic Sabatier-Electrolyzer cell. Electrolysis separates the steam into protons and oxygen. Oxygen continues to flow out the exhaust, and protons are driven across the electrolyte to react with the carbon dioxide to form methane using a nickel catalyst. Methane and oxygen have many potential uses on Mars. For example, these products can fuel ascent vehicles to send samples and humans back to Earth, or beyond. Presented are catalytic performance results using a proton-conducting ceramic cell, in which the cathode and electrolyte are based on Ni-BaCe$_{0.4}$Zr$_{0.4}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ and the steam anode is a triple-conducting BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$. High carbon dioxide conversion and methane selectivity with stability for more than 100 hours was demonstrated. Peak performance was obtained with 67% carbon dioxide conversion and 97% methane selectivity at 400° C and 4:1 hydrogen to carbon dioxide gas feed.
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CHAPTER 1

INTRODUCTION

The objective of this thesis is to study the performance of proton-conducting ceramics as a Sabatier-Electrolyzer in the synthesis of methane. Direct methane synthesis can be achieved by combining the methanation of $\text{CO}_2$ with $\text{H}_2\text{O}$ electrolysis within a proton-conducting Sabatier-Electrolyzer cell. The scope of this project is to characterize the performance of proton-conducting ceramics for catalytic conversion of $\text{CO}_2$ and $\text{H}_2$ feedstocks into $\text{CH}_4$. Future work will explore combined $\text{H}_2\text{O}$ electrolysis and $\text{CO}_2$ methanation.

1.1 Research Motivation

The National Aeronautics and Space Administration (NASA) Human Exploration of Mars Design Reference Architecture 5.0 calls for the development of In-situ Resource Utilization (ISRU) technology to be used on Mars. ISRU on Mars can enable life support for long-stay missions and return missions of samples and humans [1]. The Mars Atmospheric Processing Module (APM) was started in 2011 to construct a demonstration unit to show $\text{CH}_4$ and $\text{O}_2$ production in a simulated Mars environment. The APM is currently under active development at NASA. Upon completion, the APM is to be combined with the Mars 2024/2026 Pathfinder Mission: Mars Architectures, Systems, and Technologies for Exploration and Resources project to have a full test bed demonstration of ISRU. The test bed will test and move forward the technology for the Mars 2024/2026 Sample Return Mission to be powered by propellants manufactured from an ISRU payload [2]. In the development of ISRU technology for Mars, NASA seeks to support the development of low Technology Readiness Level (TRL) capabilities for the production of $\text{CH}_4$ and $\text{O}_2$ from $\text{CO}_2$ and $\text{H}_2\text{O}$.

Based on the available resources on Mars, rocket propellant can be produced in-situ through a $\text{CO}_2$ methanation process. The Martian atmosphere is mainly comprised of $\text{CO}_2$ (95.32%) and $\text{H}_2\text{O}$ have been observed in the form of liquid in shallow subsurface flow, ice
in craters, or in regolith [3–5]. Combining this abundant \( \text{CO}_2 \) resource with the available in-situ \( \text{H}_2\text{O} \), synthesis of \( \text{CH}_4 \) and \( \text{O}_2 \) is possible to produce propellant for rockets to send samples and humans to Earth.

1.2 State-Of-The-Art ISRU Technology

In contrast to the novel proton-conducting ceramics proposed in this project, NASA’s state-of-the-art Mars Oxygen In-Situ Resource Utilization Experiment (MOXIE) utilizes traditional oxygen-ion conducting ceramic membranes, called solid-oxide electrolysis cells (SOECs). The MOXIE project aims to electrolyze \( \text{CO}_2 \) to produce \( \text{O}_2 \). In contrast, the Sabatier-Electrolyzer based on proton-conducting ceramics presented here aims to fulfill multiple functions beyond oxygen production. Including oxygen production on Mars, the Sabatier-Electrolyzer have the potential to produce \( \text{CH}_4 \) as well. SOECs, however, are unable to form \( \text{CH}_4 \) directly due to their high operating temperatures around 800 °C. In addition, materials breakdown in SOECs can result in significant performance degradation at this temperature [6]. Proton-conducting ceramics, or protonic ceramics, operate at reduced temperatures between 500-550 °C, potentially reducing degradation and manifold packaging challenges while enabling simultaneous production of \( \text{O}_2 \) and \( \text{CH}_4 \).

Proton-conducting ceramics have numerous advantages in comparison to MOXIE’s state-of-the-art SOECs in addition to operating at a lower temperature. As mentioned above, degradation has been found to be problematic in solid-oxide electrolyzer cells. Root causes for such degradation remains an active area of research, but analysis of the fundamental properties of the novel proton-conducting ceramics proposed in this project show that some of the known key degradation mechanisms are relieved or eliminated. State-of-the-art SOECs based on yttria-stabilized zirconia (YSZ) composition, as in MOXIE, are comprised of a thick steam electrode made up of nickel and YSZ. This electrode encounters significant nickel sintering, coarsening, and depletion when high water-vapor partial pressures and temperatures are present. In contrast, protonic ceramic cells are comprised of a thin, nickel-free perovskite steam electrode, thus eliminating the nickel-degradation mechanism.
with water-vapor. The steam electrode can perform electrolysis, though with H$_2$O in this project, with improved stability. Nickel remains present in the counter electrode, which can then enable CO$_2$ methanation. Furthermore, chromium vaporization and deposition at three-phase boundaries is another important SOECs degradation mechanism. Since proton-conducting electrolyzer cells operate about 300 °C below YSZ-based solid-oxide electrolyzer cells, chromium vaporization is reduced by more than an order of magnitude [7]. As a result, chromium poisoning in protonic ceramics is greatly reduced. This lower-temperature operation also allows for less-expensive metallic manifold interconnects and supports, which increases reliability while lowering costs.

Another feature of proton-conducting ceramics, when used as a Sabatier-Electrolyzer, is the combination of two mechanisms into one reactor as a process intensification. Current NASA Mars Atmospheric Processing Module designs include proton exchange membrane electrolyzer cells (PEMECs) for splitting of H$_2$O into H$_2$ and O$_2$. Subsequently, a separate packed-bed Sabatier reactor uses the H$_2$ from the PEMECs to upgrade CO$_2$ to CH$_4$ [8]. In contrast, the Sabatier-Electrolyzer offers an advantage of combining the two reactors into one single reactor. This may serve as a benefit to NASA’s missions from a payload and operation perspective. Reducing the number of reactors for methane synthesis to one reactor can potentially reduce the overall quantity, as well as mass, of equipment necessary, and therefore reduce limitations in payload capacity. In addition, operation of the overall system may be simplified, which can reduce a number of failure points to prevent early termination of missions in case of a failure in the system. There are also advantages of using an electrolyzer based on protonic ceramics as compared to PEMECs. There is high activation polarization for H$_2$O electrolysis at low operating temperatures of PEMECs (50-100 °C), which limits the efficiency of PEMECs. Proton-conducting ceramic electrolyzers, however, operate at an intermediate temperature (400-600 °C) that enables a significantly higher efficiency than PEMECs [9]. These temperatures are also beneficial for methanation of CO$_2$, which operates at approximately 250-600 °C and is an exothermic reaction. Because protonic ceramics
can operate at temperatures optimal for CO₂ methanation, thermo-neutral operation of the Sabatier-Electrolyzer can be achieved. The endothermicity of H₂O electrolysis can be combined with the exothermicity of the Sabatier reaction.

1.3 Sabatier-Electrolyzer Cell

The approach to combining the Sabatier reaction and electrolysis takes advantage of the unique properties of proton-conducting ceramics. Specifically, using a proton-conducting ceramic electrolyte membrane can combine H₂O electrolysis and CO₂ methanation in a single device.

Figure 1.1: Conceptual diagram of electrochemical mechanism within a Sabatier-Electrolyzer cell.

The protonic ceramic Sabatier-Electrolyzer cells are made up of a Membrane-Electrode Assembly (MEA), which is comprised of a cathode, an electrolyte, and an anode as shown in Figure 1.1. The material composition of each MEA component is listed in Table 1.1. The electrodes are named Steam electrode and Fuel electrode for their processes of electrolysis and CO₂ methanation, respectively. The electrolyte is the proton-conducting ceramic mem-
brane, allowing protons to transport from the steam electrode to the fuel electrode as shown. Surrounding the MEA are metal manifolds that form gas channels over the electrodes and are connected to the gas lines to provide feed and exhaust gases. The assembly is encapsulated in a furnace to control the temperature. Supporting the reactor-manifold assembly is a test stand, equipped with gas lines, controllers, and measurement devices for the experiment. Alicat Mass Flow Controllers (MFCs) are used to precisely control the flow rate of each feed gases. Water-bubbler humidifiers control the steam concentration within the steam electrode for electrolysis. Power supplies are used to power the furnace, heat ropes, and instruments. A furnace temperature controller monitors the temperature of the furnace and controls the temperature and its rate of change. A MicroGC 3000 Gas Chromatograph measures the exhaust gas composition. Electrical communications are established with Lab-VIEW to monitor as well as control the test stand, e.g. measure voltage and temperature in real-time and control the MFCs. A Gamry Reference 600 is used for electrochemical measurements. A process flow diagram of the test stand is shown in Figure 1.2.

<table>
<thead>
<tr>
<th>MEA Component</th>
<th>Material Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam electrode</td>
<td>BaCo$<em>{0.4}$Fe$</em>{0.4}$Z$<em>{0.1}$Y$</em>{0.1}$O$_{3-\delta}$</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>BaCe$<em>{0.4}$Z$</em>{0.4}$Y$<em>{0.1}$Yb$</em>{0.1}$O$_{3-\delta}$ (+ 5 wt. % NiO)</td>
</tr>
</tbody>
</table>
| Fuel electrode      | 40 wt. % BaCe$_{0.4}$Z$_{0.4}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$  
|                     | 60 wt. % NiO (+20 wt. % starch)          |

The application of protonic ceramics for combined Sabatier and electrolysis concept has limited previous work demonstrating its capabilities. However, the concept has been demonstrated for CO$_2$ mitigation applications [10]. Hydrogenation of carbon dioxide has witnessed numerous studies, with elementary reaction mechanism proposed in Prairie et al. [11]. Past work also focused on CO$_2$ and H$_2$ mixtures, but instead this project involves electrochemical reaction using H$^+$ that may directly react with CO$_2$. Studies on effects of electrochemically
Figure 1.2: Piping and instrumentation diagram of test stand used for experimentation of Sabatier-Electrolyzer cells.
active reactant $H^+$ is minimal, but by controlling its potential in the proposed reactor, it has the potential to advance methane formation in the process known as Electrochemical Promotion of Catalysis (EPOC). However, it remains inconclusive whether hydrogen reacts with CO$_2$ in proton-conducting ceramics in the form of H$^+$ or molecular H$_2$. A study on electrochemical hydrogenation of CO$_2$ to produce CH$_4$ has shown promise. Kalaitzidou et al [10] found enhancement in methane production by four-fold, and a concomitant 50% suppression of the competing CO formation. This limited work indicates that protonic ceramics methanation processing may meet or exceed state-of-the-art methanation reactors, and this approach is able to integrate both Sabatier and water electrolysis to produce methane and oxygen within one reactor.

1.4 Water Electrolysis

Electrolysis of H$_2$O using proton-conducting ceramic electrolysis cells (PCECs) can produce H$_2$ according to the following global reaction:

$$H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2 \quad (1.1)$$

Electric, thermal, and total energy demand for H$_2$O electrolysis are dependent on temperature. The electric energy demand decreases considerably with increasing temperature, which is compensated by the thermal energy with increasing working temperature [12]. H$_2$ production using PCECs is thermodynamically favorable since PCECs operate at an intermediate temperature between 350-650 °C. The total energy demand for H$_2$O electrolysis decreases significantly at 100 °C, once the H$_2$O phase changes from liquid to steam. Also, at temperatures greater than 100 °C, the electric energy demand decreases, as compensated by thermal energy demand at temperatures between 350-650 °C. This lower consumption of electrical energy is important for space missions, in which power is scarce. The required thermal energy is typically provided from external sources, e.g. electric heating, in a PCEC running only H$_2$O electrolysis. Here, the thermal energy can be automatically provided by the heat generated within the Sabatier-Electrolyzer via the exothermic
Sabatier reaction. Additional heat can be provided by the ohmic heating generated by the entropy produced from electron flow through the electrodes and protons flow across the electrolyte of the Sabatier-Electrolyzer. The balance between endothermic H$_2$O electrolysis and exothermic CO$_2$ methanation can potentially enable thermo-neutral operation of the Sabatier-Electrolyzer. Furthermore, the Sabatier-Electrolyzer can be optimized and enable electricity-to-hydrogen efficiency greater than 100% [9].

The electrode composition used for H$_2$O electrolysis in the Sabatier-Electrolyzer cell in this project is a novel BaCo$_{0.4}$Fe$_{0.4}$Zr$_{0.1}$Y$_{0.1}$O$_{3-\delta}$ (BCFZY0.1), a triple-conducting electrode material that can conduct protons, oxygen ions, and electron holes simultaneously. BCFZY0.1 is an effective electrode for water electrolysis shown in [9].

1.5 Sabatier: CO$_2$ Methanation

The Sabatier reaction, or CO$_2$ methanation, synthesizes CH$_4$ from CO$_2$ and H$_2$ according to the global reaction:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$

(1.2)

It is highly exothermic, releasing 164 kJ per mole, which results in 1.8 kW heat produced for each 1 m$^3$ methane produced per hour (STP) [13]. This heat production would be useful in providing the thermal energy demanded by the H$_2$O electrolysis as described above.

Based on a study by Weatherbee and Bartholomew [14], the Sabatier reaction is effective within temperatures in the range of 250-600 °C in a packed-bed experiment. The optimal temperature, however, is shown to be approximately 400 °C, which exhibits the highest CO$_2$ conversion and CH$_4$ selectivity. Operating temperatures of PCECs range between 350-600 °C, and therefore would be able to meet the optimal temperature requirement by the Sabatier reaction. However, one tradeoff of a lower temperature operation is the reduction in electrochemical performance, as PCECs are typically operated between 550-600 °C. Such lower performance is manifested in the need for a higher applied voltage to drive the electrolysis process, leading to a reduced system efficiency.
Catalysts that offer significant activity and selectivity in CO\textsubscript{2} methanation are Ru, Ni, Co, Fe, and Mo. According to Mills and Steffgen, the order of catalyst activity for CO\textsubscript{2} methanation from highest to lowest is: Ru > Fe > Ni > Co > Mo, and the order of methane selectivity is: Ni > Co > Fe > Ru > Mo [15]. Ruthenium has been shown in literature to be the most active metal for methanation of CO, CO\textsubscript{2}, or mixtures [16]. Although Ru exhibits the highest CO\textsubscript{2} methanation performance, the catalyst used in the Sabatier-Electrolyzer cells in this project is nickel. Nickel has been used in the development of proton-conducting ceramic cells as the fuel electrode catalyst as well as an electron current conductor, and nickel is already implemented within state-of-the-art cells in concentrations of up to 60 wt.% Ni. This high catalyst loading greatly promotes high catalytic reactivity. Two BCZY(Yb) electrode compositions were explored at the start of the project, including BaCe\textsubscript{0.2}Zr\textsubscript{0.8}Y\textsubscript{0.2}O\textsubscript{3−δ} (BCZY26) and BaCe\textsubscript{0.7}Zr\textsubscript{0.1}Y\textsubscript{0.1}Yb\textsubscript{0.1}O\textsubscript{3−δ} (BCZY211), to compare catalytic activity and stability. Catalytic activity was tested since there is limited data of these novel protonic ceramic materials applied to CO\textsubscript{2} methanation. There are concerns regarding the instability of the protonic ceramic material in CO\textsubscript{2} according to Kreuer, specifically with cerates in the protonic ceramic material [17]. Independent stability tests showed cerates are “thermodynamically only slightly stabilized with respect to the decomposition into binary oxides, react to carbonates even with low levels of CO\textsubscript{2}, and form alkaline earth hydroxides at high water activities.” Ultimately, the electrode used for CO\textsubscript{2} methanation in the Sabatier-Electrolyzer cell presented here is based on a Ni-BaCe\textsubscript{0.4}Zr\textsubscript{0.4}Y\textsubscript{0.1}Yb\textsubscript{0.1}O\textsubscript{3−δ} (BCZYy4411) composition with 40 wt.% BCZYy4411 and 60 wt.% Ni, with an additional 20 wt.% starch pore former.

1.6 Summary

Proton-conducting ceramics used as a Sabatier-Electrolyzer have the potential to provide a positive impact on NASA’s In-Situ Resource Utilization on Mars. Current NASA ISRU technology relies upon solid-oxide electrolysis cells and proton exchange membrane electrolyzer cells to synthesize oxygen and hydrogen, respectively. Then, methane is synthesized downstream using a packed-bed reactor. The Sabatier-Electrolyzer, using the unique
properties of proton-conducting ceramics, however, can combine \( \text{H}_2\text{O} \) electrolysis and \( \text{CO}_2 \) methanation into one single reactor with high fuel utilization and efficiency. The first objective of this research is to quantify the performance of the Sabatier-Electrolyzer in terms of \( \text{CO}_2 \) conversion, \( \text{CH}_4 \) selectivity, Faradaic efficiency, electrical efficiency, and electrochemical production rate of \( \text{CH}_4 \). Second is to explore effects of operating parameters on performance, e.g. temperature, gas composition, and gas hourly space velocity. Third, explore the effects of electrochemical production of hydrogen on effectiveness of \( \text{CO}_2 \) conversion. Finally, demonstrate stability of protonic ceramics in \( \text{CO}_2 \) methanation.
To meet the objectives outlined for this project, in testing Sabatier-Electrolyzer based on proton-conducting ceramics, the Single-Channel Experiment is employed to characterize catalytic performance. The following chapter summarizes the fabrication and assembly methods used in preparing the proton-conducting ceramic cells and reactor for the Single-Channel Experiment.

2.1 Design of Single-Channel Reactor

Figure 2.1: Exploded view of Single-Channel Experiment Reactor showing gas manifolds assembly with sealing gaskets and cell.
The Single-Channel Experiment (SCE) was inspired by the Separated Anode Experiment (SAE), previously described by Richards in Ref. [18, 19]. The SCE consists of a manifolds assembly that encapsulate the Sabatier-Electrolyzer cell to form gas channels on the surface of the cell. As shown in the exploded view of the three-dimensional model in Figure 2.1, the Sabatier-Electrolyzer cell is placed at the center of the assembly. On either side, there are sealing gasket materials, which are then compressed by the gas channel manifolds that mate by using male and female geometries. Gas tubing are attached to the manifolds to provide gas inlet and exhaust down the length of the cell on either side.

Design of the SCE was based on Ph.D. candidate L. Le’s considerations to balance upstream diffusion, current density, and fuel utilization. Drawings of the Single-Channel Experiment manifolds can be found in Figure A.1 and Figure A.2, which are in Appendix A.2. In a developed cell stack, multiple gas channels are used to distribute gas feeds over the surface of the cell. The Single-Channel Experiment has gas channels on either side of the cell that mimic one single flow channel from that of a cell stack. The channel height of the fuel channel is nominal, and therefore has a high aspect ratio of channel width to channel height (W/D). With a high aspect ratio, fuel utilization is improved by minimizing the portion of gas flow over the porous electrode that remains in the gas channel and does not react with the catalyst. In addition, upstream diffusion of gases, which would be more prominent in very low flow rates, is also minimized. As a result, Single-Channel Experiment can improve the catalytic performance of the cell. More importantly, the SCE design facilitates a well-defined, two-dimensional geometry to increase accuracy of the study. This enables more in-depth examination of the tradeoffs between electrochemistry and thermal chemistry in the Sabatier-Electrolyzer cell.

2.2 Fabrication of Single-Channel Reactor

The Single-Channel Experiment gas channel manifolds were fabricated from Fecralloy steel stock. The Fecralloy material is made of 72.8% Fe, 22% Cr, 5% Al, 0.1% Y, and 0.1% Zr and is manufactured by Goodfellow [20]. This alloy of steel has unique properties
that enable the surface of the material to form an inert alumina oxide coating when heated above 1000 °C [21]. Fecralloy in literature have been shown to develop alpha-alumina on the surface with desirable low defect concentration, low volatility, and smooth surface finish when heated to 1200 °C for 2 to 40 hours [21, 22]. The alumina scales formed a thicker, more pure alpha-alumina layer when oxidized for a longer period of time, up to 6.1 µm after 40 hours of heating. Using Fecralloy as the material for the SCE would create an inert layer on the gas channel surfaces, isolating the cell electrochemistry from electrical shorts and reactivity between the gases and the gas channel surfaces. Additionally, the machinability of the metal and its ability to maintain dimensions true to the original design even after high temperature heating was desirable. Moreover, using metallic manifolds provided metal-metal interfaces that provided strong and durable gas-tight sealing when connecting to the stainless steel gas lines in the test stand.

Stainless steel tubing was used to create the gas inlet and outlet lines on each side by brazing the tubes onto the SCE manifolds. Ph.D. candidate L. Le had prepared the SCE manifolds with gold brazing of the tubing and oxidation of the Fecralloy manifolds. The brazing procedure used gold foil and heated the SCE manifolds and tubes to 1100 °C in pure hydrogen environment. The Fecralloy manifolds were sintered in air at 800 °C for 24 hours. This process resulted in hermetic sealing between the Fecralloy manifolds and the stainless steel gas plumbing.

2.3 Cell Fabrication

Cell material preparation and fabrication processes were performed by Ph.D. candidate L. Le using a solid-state reactive sintering method summarized below [23]. The supporting electrode was the fuel electrode based on Ni-BaCe₀.₄Zr₀.₄Y₀.₁Yb₀.₁O₃₋δ (BCZYb4411).

The powder for the fuel electrode green body is prepared from a powder mixture of BaCO₃, CeO₂, ZrO₂, Y₂O₃, Yb₂O₃, and NiO. Precursor composition is defined to produce a two-phase electrode comprised of 40 wt. % BaCe₀.₄Zr₀.₄Y₀.₁Yb₀.₁O₃₋δ phase with a 60 wt. % NiO phase, with an additional 20 wt. % starch pore former. The precursor powder
mixture is then ball-milled in isopropanol for 72 hours using 3 mm yttria-stabilized-zirconia beads and then dried in a drying furnace at 90 °C for 10 hours. The electrolyte precursor powder is prepared in the same manner with 5 wt. % NiO as a sintering aid. After drying of the precursor powders, the powders are then ball-milled again in a dry condition without the use of any solvent to form a homogeneous mixture of the precursor powder. Once ground in mortar and pestle. Then, the fuel electrode green body is formed by die-pressing the dry powder within a 57.15 mm stainless steel circular die. After pressing, the green body is dip-coated in an electrolyte solution made from electrolyte precursor powder suspended in isopropanol. Following dipping the cell is dried in air at room temperature for 30 minutes. The dipping procedure is repeated three times to achieve homogenous coverage of the anode surface and develop an electrolyte thickness of approximately 20 µm. The electrolyte coated fuel electrode green body is then sintered at 1500 °C for 5 hours with a ramping rate of 1 °C min⁻¹ to form a half-cell. The half-cell has a final diameter of approximately 40 mm, and one side of the assembly is polished to remove the excess electrolyte and reduce the cell thickness to approximately 1 mm.

2.4 Cell Preparation for Single-Channel Experiment

Typically, a BCFZY0.1 electrode would be painted on top of the dense electrolyte of the button half-cell and sintered at 900 °C to produce a full MEA button cell that would be ready for experimentation. However, to fit the cell within the Single-Channel reactor, the cell must be cut to match the geometry of the manifolds. This is done after the half-cell was sintered, when the fuel electrode green body and electrolyte formed a single ceramic body, which offers the most structural strength to prevent deformation or delamination. To ensure precise fitting of the cell inside the female manifold of the reactor, a cutting die in the exact dimensions of the Single-Channel sealing material (shown in Figure 2.1) is used to cut a mask from Kapton tape. The mask is applied onto the electrolyte side, across an area of the cell that has best flatness.
Flatness in the electrolyte side is critical in the cell-reactor assembly. Due to the fabrication approach of described above, the half-cell develops a concave curvature on the electrolyte side after being sintered. The nickel fuel electrode could be polished to form a flat surface. However, the electrolyte could not be polished without damaging the thin electrolyte layer. In addition, the mask forms a precise area in which the steam electrode could be applied. With the mask applied onto the half-cell electrolyte, the cell is cut using a diamond cutting wheel. Two cuts are made along the long side of the mask with a 1 mm margin on each side. To obtain the final dimensions, the perimeter of the cell is then polished to the edge of the mask using a polishing wheel with 120-grit silicon carbide sandpaper. Then, the fuel electrode surface is polished to form an even surface and reduce the thickness of the cell to approximately 1 mm. A BCFZY0.1 paste is hand-painted within the mask area. The mask is then peeled off to form the paste to precisely match the gas channel geometry. The cell is sintered at 900 °C, with a ramping rate of 1 °C min⁻¹, for 5 hours to form the full-cell MEA.

2.5 Electrical Connections for Single-Channel Experiment

Current and voltage wires were attached to the cell and fed through the inlet and exhaust tubing on both sides of the cell. A meticulous fabrication protocol was developed and used to enable accurate location and bonding of wires to the cell.

Once the MEA is formed, Kapton tape masks cutouts are applied again to both sides of the cell. First, a mask is applied to the BCFZY electrode, since the electrode itself fits within the inner perimeter of the mask. Second, a mask is applied on the fuel electrode, using the outer perimeter for alignment with the first mask. Finally, gold powder in isopropanol is painted on each of the cell electrodes within the masks.

Starting with either side of the cell, a paper mask with the gas inlet and outlet holes cutouts is then placed on top of the cell. This is used to align a wire directly under the gas inlet and outlet holes to provide clearance for silver paste to bond the wire to the cell without the wire making physical contact with the metal manifold. Silver paste is applied at
the center of the gas inlet and outlet cutout holes of the paper mask to mark the locations for the wire.

![Figure 2.2: Heat gun curing silver paste connecting wire to cell electrode.](image)

For current and voltage measurements, 0.25 mm diameter wires made of 99.9% silver by Alfa Aesar are fed through the inlet and outlet of the reactor, connecting to the surface of the cell. The wire is unspooled and cut into two pieces, each with a length of 90 cm. This length provides a single, continuous wire to route from manifold inlet, across the cell, and through the outlet to form two leads on each electrode. A total of four leads are then formed to enable Electrochemical Impedance Spectroscopy (EIS) measurements using a 4-point setup. Due to the coiling of the wire from the spool, the wires are straightened by hand. The wires are then bent to form a U-shape in the middle, matching to the length previously marked by the inlet and outlet holes mask. Fiber-glass sleeves fitted around the wire leads up until the 90° bends. These corners are then lined up precisely upon the silver paste marks on the electrode. Two strips of Kapton tape are used to hold the wire in place. Silver paste is then applied across the length of the wire that is in contact with the cell. With clearance provided by the alignment under the inlet and outlet holes, additional silver paste is applied at the 90° bends of the wire to provide additional strength. A heat gun is used to cure the silver
paste by flowing hot air at 200 °C over the cell for 20 minutes as shown in Figure 2.2. A thermocouple is used to monitor the temperature just above the surface of cell. Once cured, the Kapton tape mask was removed, shown in Figure 2.3. The procedure is then repeated for the other side of the cell, in which the completed cell wiring process is shown in Figure 2.4.

![Figure 2.3](image.png)

(a) Masked  
(b) Mask removed

Figure 2.3: (a) Cell wiring process with Kapton tape mask around Ni-BCZYYb4411 electrode, gold powder painted within mask, and silver wire applied onto electrode; (b) Kapton tape mask removed after silver paste was cured.

The cell wiring method described above was developed to limit potential issues in shorting of the cell through the metal Single-Channel reactor manifolds while minimizing significant effects on the gas flow. The procedure also maintains the height of the wire and silver paste within the gas channel to allow proper contact between the manifolds and sealing material. Although the Single-Channel reactor manifolds were made from Fecralloy that forms an inert oxide layer, any imperfections in the layer could allow the wiring to create an external short if the wires on both sides of the cell made contact with any conductive area of the metal. Routing the wire down the length of the cell in the center minimizes obstruction of the gas flow path while maintaining exposure of the cell surface to the gas stream. The wiring procedure also helps to enable repeatability in the integrity of the cells electronic connectivity to external instruments. Curing the silver paste for 200 °C for 20 minutes results in sufficient bonding strength to prevent delamination of the wire off of the electrode before and after experiments.
Figure 2.4: Final wire-cell assembly with wires bonded to either side of the cell forming four wire leads, with glass fiber sleeves around the wire for electrical insulation.

2.6 Cell-Reactor Assembly

The Single-Channel reactor is comprised of two manifold pieces, a male and a female counterpart. The female manifold forms the fuel channel with a 0.5 mm channel height, while the male manifold forms the steam channel with a 2.54 mm channel height. A 0.5 mm thick Thermiculite sealing material is cut using a cutting die and inserted into the female manifold. The wire leads on fuel electrode are out the gas inlet and outlet tubing of the manifold. Then, the cell is placed on top of the sealing material. The gold-painted area remains exposed to the gas channel. The height of the channel, in addition to the thickness of the sealing material, provides clearance for the wire without contacting the manifold. Then, a 1 mm thick Thermiculite sealing cutout is placed on top of the cell directly onto the electrolyte surface, while maintaining exposure the BCFZY0.1 electrode to the gas channel. The wire leads from the BCFZY0.1 electrode are then routed through the gas inlet and outlet of the Single-Channel reactor male manifold. The male manifold is assembled into the female manifold, compressing the sealing materials and the cell. Compression is achieved by using a hydraulic press. Wire leads protrude through the inlet and outlet tubing with
a Swagelok Tee fitting. The Tee fitting allows the wires to be sealed using Conax fittings while allowing gases to be fed through the reactor. Final assembly of the Single-Channel Experiment within the test stand is shown in Figure 2.5.

A fuel side sealing material thickness of 0.5 mm was selected in order to maintain the small channel height of the Single-Channel reactor design. The cell was able to accommodate this due to flatness of the fuel electrode formed from polishing. As for the electrolyte side, the sealing material was 1 mm to be able to accommodate the curvature of the electrolyte surface that was formed from the sintering process.

Figure 2.5: Final assembly of Single-Channel Experiment reactor within furnace, complete with air-side and fuel-side gas inlet and outlet lines. Reactor is compressed between two steel rods mounted to a spring on the top side and hydraulic press on the bottom side.
With the Cell-Reactor Assembly complete, the assembly was fitted into the test stand, in which steel rods were aligned on top and bottom of the reactor. The steel rods extend to a spring on one end and a hydraulic press on the other end to provide the necessary compression for gas sealing. Gas lines providing gases to the steam side and fuel side were connected to their respective side at each of the middle connection of the Swagelok Union Tee fittings beside the wire leads. Heat ropes were wrapped around the inlet lines, to preheat the feed gases, and the outlet lines, to prevent condensation from steam that was fed as well as steam produced from the Sabatier reaction.
CHAPTER 3
IMPLEMENTATION OF SINGLE-CHANNEL EXPERIMENT

After cell-reactor assembly was completed, the Single-Channel Experiment is verified for gas sealing and operation of the test stand. Heating of the cell and reduction of the nickel fuel electrode were initiated subsequently. Afterwhich, the electrochemical performance of the cell would be characterized by measuring Open-Circuit Voltage (OCV), impedance, and polarization curves as well as measure the Faradaic efficiency. Then, a Sabatier-Electrolyzer operation could be tested for electrolysis of H$_2$O and CO$_2$ methanation directly to CH$_4$.

3.1 Leak Testing Procedure

A simple test to check for the presence of leakage from either side of the SCE reactor assembly was to compare the flow rate between the inlet and the exhaust. Air flowed through each side of the Single-Channel Reactor one at a time, varying from 100 sccm to 200 sccm. At the exhaust, the flow rate was measured using a DryCal Defender 530+. Changes in the flow rate between the input and the exhaust measurement would indicate the presence and the rate of a leak. Using the assembly method described above, results showed a 99 sccm measurement with the DryCal under a 100 sccm Air input and a 198 sccm measurement with a 200 sccm Air input for each side of the reactor. Thus, leaking in the Single-Channel Reactor was minimal within a 1% leakage rate.

A second cross-flow leak test was used to monitor the gas composition of the exhaust streams using a gas chromatograph. This test was used to verify sealing between the gas channels on either side of the cell. 100% helium gas was fed into the steam side of the reactor at 100 sccm, while the fuel side was also fed 100% nitrogen at 100 sccm. Helium was selected for its higher diffusivity, which would be effective in detecting leakage. The fuel side exhaust was fed to a Agilent MicroGC 3000 gas chromatograph (GC), which measured the gas composition over time. GC results showed an average of 0.22 vol.% helium in the fuel gas
stream, an even smaller leakage rate than previously found with the DryCal. This indicated that the 1% leak rate was predominantly elsewhere in the test stand gas lines, while the cross-over leakage across the cell was less than 1%. This test was also performed for every cell tested in the Single-Channel Experiment. Execution of both tests were performed at high operating temperatures for the first few iterations of the SCE, and the sealing was consistent at both room temperature and at operating temperature. Since the sealing integrity demonstrated consistent sealing at both room temperature and high operating temperature, these tests were only performed at room temperature in later tests.

3.2 Cell Testing Procedure

After reactor leakage was verified, the SCE reactor assembly was heated to the target operating temperature. During heat up, air with 3% steam was fed to the steam electrode at a flow rate of 100 sccm. The fuel side was flushed with N₂ during the leak testing process, but the flow was stopped for the duration of the heating up process. The furnace was set to heat the reactor to 550 °C at a ramping rate of 1 °C min⁻¹. Reactor temperature was measured by placing the controller’s thermocouple on the outside surface of the reactor. During this process, the voltage of the cell and temperature of the reactor were monitored using an NI-DAQ USB Multifunction I/O device. Once the temperature has reached a steady 550 °C, the fuel side was fed 10% H₂, balance N₂ with a net 100 sccm flow rate to reduce the NiO in the Ni-BCZYYb4411 fuel electrode to Ni. A Gamry Reference 600 was used to monitor the OCV and perform Electrochemical Impedance Spectroscopy measurements every hour to measure the evolution of cell resistance during reduction. Reduction of the NiO to Ni is indicated by the decrease of resistance and polarization of the cell in the EIS spectra results. H₂ concentration in the fuel side was increased to 100% over the course of the reduction process. After a certain amount of time, typically 12-24 hours, the EIS results would no longer change, indicating steady-state and therefore show that the cell reduction process has been completed.
Once the fuel electrode was reduced, polarization curves were obtained in both fuel-cell mode and electrolysis mode. For this, the steam concentration in the air side was increased to 10% steam in air in order to provide a sufficient amount of steam for the electrolysis process. Operating the cell in electrolysis mode with target current densities above the amount of steam that can react with the steam electrode risks permanently damaging the cell. Provided the electrochemical performance of the cell was reasonable, electrolysis could be performed in the steam side to begin production of H$_2$ into the fuel side. Unfortunately, electrochemical performance of all cells tested within the Single-Channel Experiment showed significantly high resistances and were not able to drive a stable current.

Further testing of the cell would be followed with quantifying the Faradaic efficiency of the cell in electrolysis mode over a wide range of current and temperature. However, due to an unexpected high resistance in the cell, the experimental procedure could not move forward from this step. As such, the following step and subsequent steps continue to outline the procedure planned for the Single-Channel Experiment.

From the previous operating condition of 100% H$_2$ in the fuel stream at 100 sccm and 10% steam in air in the steam side, the exhaust flow rate and gas composition were monitored by the DryCal and GC as a baseline measurement. Then, electrolysis was performed to drive H$_2$ across. An increase in flow rate in the fuel side, and an unchanged 100% H$_2$ detection by the GC would indicate H$_2$ was being added into the stream from electrolysis. The difference in flow rate, therefore, quantified the H$_2$ produced. H$_2$ production rate divided by the theoretical H$_2$ produced for the given current resulted in the Faradaic efficiency. Faradaic efficiency is defined as:

$$FE = \frac{n_{H_2,\text{measured}}}{n_{H_2,\text{theoretical}}} \times \frac{n_{H_2,\text{measured}}}{i \times (n \times F)^{-1}} \times 100\%$$

(3.1)

where FE is the faradaic efficiency in electrolysis mode, the term $n_{H_2,\text{measured}}$ refers to the measured hydrogen production rate (units of mol s$^{-1}$), I is the applied current (units of A), n is 2 for the electrolysis of H$_2$O, and F is the Faradays constant (96,485 C mol$^{-1}$). The procedure was repeated for lower concentrations of H$_2$ in the fuel stream, in which both
DryCal measurements and GC results were factored into quantifying H₂ production rate. It was repeated further at lower temperatures where possible, until cell resistance became too significant to drive a sufficient amount of current to be able to detect a change in the fuel stream.

With the Faradaic efficiency characterized over the operating temperature range, H₂ flow rate can be precisely controlled when performing electrolysis using the Sabatier-Electrolyzer cell. For a given CO₂ flow rate in the fuel stream, the amount of current would be controlled to apply the desired ratio of H₂ to CO₂, beginning with stoichiometric 4:1. The ratio of H₂:CO₂ would subsequently be increased up to 6:1 to test the effect of H₂ concentration on CO₂ methanation. To test the effects of performing the Sabatier reaction in an electrochemical operation, versus chemical only, the H₂ feed can be mixed between 100% H₂ from electrolysis to 100% H₂ from gas feed.

3.3 High Resistance in Single-Channel Experiment Cells

Implementation of the Single-Channel Experiment faced challenges in performing electrochemistry with the proton-conducting cells. Specifically, cells used in the SCE exhibited instability according to the measured voltage data and too high of resistances. In attempting to isolate the potential causes, it was realized that the SCE fabrication processes were not correct. However, causes of high ohmic resistance were not able to be identified.

Observing the Open-Circuit Voltage of the cell during the reduction process, the OCV increased rapidly during the first few minutes. This could be attributed to the improved fuel utilization of the SCE reactor. However, it would still require an extended amount of time to reduce. Based on Ph.D. candidate L. Le’s experiments, his reduction process typically showed a steady ohmic resistance within 1-5 Ω cm² within 24 hours. Using the same cell composition and thickness, cells within the SCE required multiple days to achieve steady-state polarization curves when performing Electrochemical Impedance Spectroscopy (EIS) measurements. Even after an extended period of reduction, the SCE cells could not obtain an ohmic resistance and polarization within the expected range. Instead, EIS results showed
the resistance of the SCE cells were consistently greater than 6 Ω cm$^2$.

Figure 3.1: Impedance spectra captured from EIS during cell reduction, showing the spectra reaching a steady-state at approximately 6 Ω cm$^2$.

Results from the final Single-Channel Experiment performed showed that the OCV was able to reach a steady 1.16 V under 97% H$_2$ and 3% H$_2$O in the fuel side and 97% Air and 3% H$_2$O at 550 °C. Previous electrochemical cell performance was able to consistently achieve OCV measurements between 0.9 and 1.1 V and ohmic resistances between 12 and 20 Ω cm$^2$. In the final experiment, however, EIS results showed a consistent ohmic resistance of 6 Ω cm$^2$ as shown in Figure 3.1. Despite this, polarization curves in fuel cell and electrolysis modes were not able to exhibit higher current densities than previous experiments with higher ohmic resistances. Furthermore, when attempting to perform a galvanostatic test holding a low current density of 250 mA cm$^{-2}$, the cell could not hold the current for any significant amount of time. The voltage experienced a drop to 200 mV. Although this reduced OCV lasted for approximately 60 minutes, the voltage was able to recover back to a 1.12 V.
However, subsequent EIS results showed ohmic resistance measurements of $22 \ \Omega \ cm^2$ and did not recover to $6 \ \Omega \ cm^2$. This behavior indicated an instability within the cell.

Performing verification tests on measurement instruments and variation in experimental setup continued to show the same high resistance in the cell. Verification tests involved recalibrating the Gamry Reference 600, measuring other experiments, alternating EIS 4-point wire leads, and monitoring the voltage with an external multimeter. EIS results did not change. Experimental conditions were varied as well. Varying flow rates on either side of the cell only had minor effects on the EIS spectra, but resistance remained high. EIS spectra, when changing temperature and gas composition, behaved as expected and did not decrease to the desired resistance.

### 3.4 Investigation of Experimental Setup for Causes of High Cell Resistance

As mentioned above, the preparation and fabrication of the Single-Channel Experiment reactor, i.e. the mating manifolds and the brazing of the gas tubing, were completed before the beginning of this project. Although catalytic heterogeneous chemistry had been previously tested in an alumina Separated Anode Experiment reactor, testing of a full cell within the metallic SCE reactor has not yet been studied. As such, the SCE reactor were assumed to take on the desired properties. The surface of the reactor was assumed to have inert, non-conductive oxide scales, and the stainless-steel tubing had little to no effect on the experiment. Furthermore, the sealing achieved by compression of the sealing materials directly on either side of the cell was excellent. Thus, the compressive forces on the cell were not questioned as a potential cause for high cell resistance. Various approaches were executed in order to isolate the cause of high resistances in the cell and are outlined below.

#### 3.4.1 Effects of Metallic Single-Channel Reactor Assembly

Reviewing the heating procedure of the SCE reactor manifolds indicated that the oxide scales that formed were not the alpha alumina scales that were expected to form. The SCE reactor was oxidized in air at $800 \ ^\circ C$ for 24 hours. The required temperature, however, was
a minimum of 1000 °C, and the optimal temperature to form alpha alumina scales was 1200 °C. The duration of oxidation can range between 2 to 40 hours, with thicker scales and more pure alpha-alumina when oxidized for a longer period of time. Rallan, C. et al. performed analysis of alumina growth on Fecralloy wires of similar composition, also manufactured by Goodfellow, by oxidizing the wires between 800 °C and 1200 °C. X-Ray Diffraction results showed no presence of Al₂O₃ when oxidized at 800 °C for 16 hours [24]. Growth of alumina on Fecralloy surface only initiates at temperatures greater than 800 °C [25].

Performing oxidation tests on Fecralloy samples at 800 °C for 24 hours in air and at 1200 °C for 40 hours in air showed visible differences in scales formation in Figure 3.2:

![Image of Fecralloy samples sintered at different temperatures](image)

Figure 3.2: Fecralloy samples sintered at different temperatures; (left sample) un-sintered stock, (middle sample) 800 °C for 24 hrs in air, (right sample) 1200 °C for 40 hrs in air.

Surface finish is also important in surface coverage by the scales formed. Microscale areas in the sample surface did not have scales coverage, in which the bare metal was exposed. An electrical short was detected by a multimeter when contact was made between two exposed areas. The surface needed to be smooth for even coverage. Very smooth surfaces can be
achieved by polishing with diamond paste with particle size down to 1 \( \mu \text{m} \) and enable even surface scale coverage [24].

Figure 3.3: SEM image of Membrane Electrode Assembly after 72 hours in reducing environment; ohmic resistance \( >12 \ \Omega \ \text{cm}^2 \).

Despite the lack of alpha-alumina scales formation on the SCE reactor, effects from the manifolds on the cell were not observed. FESEM images of the fuel Ni-BCZYYb4411 electrode showed that the morphology of Ni and ceramic BCZYYb structures formed as expected, and Ni was totally reduced from the gas surface to the electrode-electrolyte interface. There was also no contamination detected when scanned with Energy Dispersive X-ray Spectroscopy. FESEM images of the steam BCFZY electrode and BCFZYYb4411 electrolyte showed similar results, with expected morphology and without contamination. Cross-section views of the MEA and the electrodes are shown in Figure 3.3 and Figure 3.4.
Figure 3.4: (a) FESEM image of BCFZY0.1 steam electrode after 72 hours under cell reduction process; (b) FESEM image of Ni-BCZYYb4411 fuel electrode near the gas channel after 72 hours of reduction.
Observations on the Ni-BCZYYb4411 near the electrode-electrolyte interface indicate that there may not be adequate reduction of the NiO in this area. This may be a contributor to the high resistance in the cell.

Although there were no effects from the metallic SCE manifolds on the cell, future research should repeat the oxidation process of the Single-Channel Experiment manifolds following the conditions demonstrated in literature. The alumina scales were assumed to have formed by simply oxidizing the manifolds in air at an elevated temperature. However, as shown in Figure 3.2, the scales did not form as desired. No alumina was formed on the surface of the manifolds, based on conditions tested in literature. Repeating the manifolds preparation process at 1200 °C would ensure the Single-Channel Experiment is independent of the reactor manifolds.

![Image](image_url)

**Figure 3.5:** Carbon powder accumulated inside the fuel side inlet line post 130 hours of operating time under CO$_2$ methanation at 4H$_2$:1CO$_2$ with temperatures between 350-550 °C and flow rates between 25-125 sccm.

The Swagelok 0.25" tubing used for the gas inlets and outlets of the Single-Channel reactor was not treated to prevent chemical reactivity, i.e. its stainless-steel surface was
exposed to the gas streams in the hot zone. It was assumed that the effect of reactivity at the tubing surface would be negligible. This may have been true for fuel cell or electrolysis cell only operation without the use of CO$_2$. As noted above, however, Fe and Ni are highly active for CO$_2$ methanation. Carbon powder was found in the fuel inlet after testing the cell in a CO$_2$ environment for 130 hours, as shown in Figure 3.5. An alumina coated tubing would be required to prevent chemical activity in the feed and exhaust tubing of the reactor.

In an effort to overcome the problem of high resistance, the metal manifolds were replaced with ceramic manifolds made of alumina. The reactor manifolds, as well as the gas tubing in the hot zone, were fabricated from alumina to minimize chemical activity with the gas channels and tubing. All other operating conditions remained the same, and sealing verification showed a similar seal integrity as previously demonstrated. In testing, however, measurements made on the cell, i.e. OCV and EIS, did not show any improvement to the cell electrochemical performance.

3.4.2 Cracking on Electrolyte From Compression

One potential cause of high resistance in the SCE cells was cracking in the electrolyte surface. Due to an applied compression on the surfaces of the cell, the stress induced may have formed cracks in the cell. Although the polishing of the fuel electrode of the cell enabled the surface to be flat to seat evenly across the sealing material, the electrolyte side remained curved, especially at the end edges where the cell was not cut. Areas of increased thickness due to the curvature would have concentrated stresses when compressed in the reactor, which would cause cracking if sufficient mechanical, as well as thermal, stresses were present. Observing the electrolyte surface after experiments were conducted, there were obvious cracks in the electrolyte surface as shown in Figure 3.6.

The cracks formed in a pattern, in which the three cracks shown are iterated at a similar gap and with a similar angle. This may have been caused by a stress concentration at the high points of the cells. The electrolyte surface curved upward, therefore the ends were most raised and interfaced with the compressive forces first. Stress here would be most
Figure 3.6: (a) FESEM image of electrolyte surface under compressed area at X300 zoom after 72 hours of reduction; (b) FESEM zoomed image of crack at X3,000.

Concentrated and thus propagated towards the middle of the cell. Thus, the pattern in the cracks may have been caused by this stress gradient formed from compression on the cell. Concerns about electrolyte cracking from cutting or polishing were assumed negligible since the fuel electrode and electrolyte were well bonded as a single-body ceramic component. Cross-section FESEM images showed no delamination in the electrode-electrolyte interface. However, these cracks may allow gases in either flow channels to cross. In the case that O\textsubscript{2} reaches the Ni-BCZYYb4411 electrode, the nickel may not be fully reduced as observed in the Figure 3.3. This would then increase the resistance in the cell.

To address the cracking of the electrolyte surface from compression, an experiment was performed with only the Fecralloy fuel manifold of the SCE reactor with no compression on the cell. The steam side was left open to the furnace environment, but with an alumina gas-feed tube placed beside the cell to provide a humidified air stream. Ceramabond was applied at the perimeter of the cell between the cell and manifold interface to seal the cell and to separate the steam side from the fuel side. Operating the cell under the same reduction procedure as previous experiments, the open-air experiment was able to achieve approximately reduction in the cells ohmic resistance and polarization. From 12 Ω cm\textsuperscript{2}, the
Ohmic resistance was then reduced to 6 \( \Omega \text{ cm}^2 \). While this was a significant improvement in the cell performance, the resistance was still too high to generate an adequate amount of current for either fuel cell or electrolysis operation. There was instability when attempting to hold a steady current in either electrolysis or fuel cell mode, in which the OCV would drop to approximately 200 mV, indicating instability in the cell.

Two experiments were performed to verify the effects of the potential causes of high resistance in the Single-Channel Experiment cells. The experiment with all alumina reactor eliminated the metal Fecralloy oxidation error as well as the stainless-steel gas tubing. Cell performance, however, remained unchanged. This indicated that the Fecralloy and stainless-steel did not have significant effects on the cell resistance. The open-air experiment removed compressive stresses on the cell and improved the performance of the cell by a factor of two. Although this provided valuable insight, the cause of the high resistance in the cell was not isolated. The open-air experiment removed the compressive forces, but it also removed the gas channel from the steam side of the SCE reactor. Further investigation is required to isolate the cause of the high resistance in the Single-Channel Experiment.

While electrochemical testing of the Single-Channel Experiment was not feasible, heterogeneous chemistry testing could be performed in the fuel side of the cell to characterize the catalytic performance within the SCE reactor. Two sets of experiments were conducted over a wide range of operating conditions to quantify CO\(_2\) conversion and CH\(_4\) selectivity. The first set was to characterize the effect of gas residence time within the fuel channel, which was quantified by Gas Hourly Space Velocity. Flow rate was varied between 7000-34000 h\(^{-1}\). The second set of experiment characterized the influence of increased ratio of H\(_2\) to CO\(_2\) (H\(_2\):CO\(_2\)) between 4:1 to 6:1. The temperature was varied between 350-550 °C across both sets of experiments, and fuel gas feed included 3% steam to remain consistent with typical cell operating conditions. The results were compared with thermodynamic equilibrium of the Sabatier Reaction.
CHAPTER 4
CO$_2$ METHANATION RESULTS IN SINGLE-CHANNEL EXPERIMENT

4.1 Thermodynamic Equilibrium of the Sabatier Reaction

![Figure 4.1: Thermodynamic equilibrium of Sabatier reaction with 80% H$_2$ and 20% CO$_2$ (+3% H$_2$O) between 200-800 °C showing volume percent of product species.](image)

Thermodynamic equilibrium of CO$_2$ methanation was calculated using Cantera, which is an open source chemistry library, and implemented within Python. The method used was equilibrate, which invokes Cantera’s chemical equilibrium solver. The solver uses an element potential method by default, which is a non-stoichiometric solver for single-phase solutions [26]. The results are shown in Figure 4.1. The mole fraction of 80% H$_2$ and 20 CO$_2$ (+3% H$_2$O) was used in the chemical equilibrium solver to match experimental conditions. Temperature ranged from 200-600 °C, and H$_2$:CO$_2$ ranged from 4:1 to 6:1.
As shown in Figure 4.1, thermodynamic equilibrium predicts that the presence of CO$_2$ and H$_2$ are minimal at 200 °C, which indicates the highest conversion of the CO$_2$ and H$_2$ input. The thermodynamic equilibrium solution is asymptotic below 200 °C. Thus, 200 °C is the optimal temperature. CO is also minimized at 200 °C, and the products are predominantly CH$_4$ and H$_2$O according to the stoichiometric Sabatier equation. Thus, CO$_2$ conversion and CH$_4$ selectivity is optimal at approximately 200 °C. Although thermodynamic equilibrium predicts an optimal temperature of 200 °C, the reaction is kinetically limited with reducing temperatures. As previously mentioned, the optimal temperature for the Sabatier reaction is 400 °C when tested within a packed-bed reactor [14]. Current optimal temperatures for proton-conducting ceramics are between 550 °C and 600 °C. While the protonic ceramics can operate at 400 °C, the electrochemical performance can be significantly limited.

![Figure 4.2](image-url)

Figure 4.2: Thermodynamic equilibrium of CO$_2$ methanation varying with temperature with H$_2$:CO$_2$ between 4:1 and 6:1; (a) CO$_2$ conversion; (b) CH$_4$ selectivity.
Figure 4.2 shows that increasing the concentration of H₂ relative to CO₂, or the ratio of H₂:CO₂, in the gas feed increases CO₂ conversion and CH₄ selectivity. This suggests that operating at an increased H₂:CO₂ could improve the fuel utilization of CO₂. For example, at 400 °C, increasing the H₂ to CO₂ ratio from 4:1 to 4.5:1 (by 12.5%) can improve the CO₂ conversion by 7%. CH₄ selectivity, however, is less dependent on H₂:CO₂, as shown by Figure 4.2(b).

![Figure 4.3: Thermodynamic equilibrium of CO₂ methanation showing H₂ conversion and CO₂ conversion varying with temperature at H₂:CO₂ between 4:1 and 6:1.](image)

Figure 4.3 compares the behavior of H₂ conversion with CO₂ conversion when the ratio of H₂:CO₂ is varied along with temperature. When increasing H₂ concentration relative to CO₂ to higher than 4:1, the conversion of CO₂ can be significantly improved. However, H₂ conversion decreases because the added H₂ content does not fully react proportionally to the additional CO₂ reacted. In a system in which high H₂ conversion is prioritized, then it is not beneficial to increase H₂:CO₂. However, a CO₂ methanation system can take advantage
of higher $H_2:CO_2$ because $CO_2$ conversion is prioritized. Furthermore, excess $H_2$ can be recycled back into the feed stream to maintain a higher $H_2:CO_2$ and continue to be utilized.

4.2 Packed-Bed Experiment Comparison between BCZY26 and BCZYYb711

Before the Single-Channel Experiment was conducted, a catalyst comparison was performed to down select between the two novel fuel electrode compositions, which were Ni-BaCe$_{0.2}$Zr$_{0.6}$Y$_{0.2}$O$_{3-\delta}$ (Ni-BCZY26) and Ni-BaCe$_{0.7}$Zr$_{0.1}$Y$_{0.1}$Yb$_{0.1}$O$_{3-\delta}$ (Ni-BCZYYb711). The catalyst comparison was performed in a packed-bed reactor using 0.25 inch diameter Swagelok stainless steel tubing with an inert alumina coating on the inside surface. Performance of the catalysts were measured by $CO_2$ conversion and $CH_4$ selectivity. Each catalyst was fabricated by sintering bulk electrode powder that was then crushed into granules. The granules were then sifted through micro-sieves of 250 and 180 $\mu$m to obtain a consistent target particle diameter of approximately 200 $\mu$m for optimal gas-surface reactivity based on a recommendation by Research Faculty Sandrine Ricote, Ph.D., at CSM.

The granules were weighed 1 gram for each experiment and packed within the tube using glass wool on either side of the powder to hold it in place. No additional packing compression was made on the bed of catalyst, which occupied 0.75 inch (1.91 cm) inside the reactor tube. The flow rate of the feed stream was normalized to the volume in which the catalyst granules occupied within the packed-bed reactor using Gas Hourly Space Velocity (GHSV) based on the flowing equation:

$$GHSV = \frac{\text{standard volumetric flow rate per hour}}{\text{volume of catalyst bed}} = \frac{\dot{V}}{V} = [h^{-1}]$$ (4.1)

GHSV has units of $h^{-1}$ and quantifies how many times the feed gas displaces the catalyst bed volume per hour. This helps compare the catalytic performance between different reactors by normalizing the flow rate to the volume of catalyst. The packed-bed experiment was performed by varying the flow rates between 5000 $h^{-1}$ and 35000 $h^{-1}$, and the reactor temperature ranged from 400 °C to 600 °C. Based on this catalyst height and the inner diameter of the tube of 0.18 in (0.46 cm), the GHSV of the packed-bed reactor had a conversion from
standard volume flow rate of 192.3 h⁻¹ sccm⁻¹. Using this conversion, the flow rates in sccm were input into the mass flow controllers for the packed-bed reactor.

![Graphs of CO₂ conversion and CH₄ yield](image)

Figure 4.4: Ni-BCZY26 and Ni-BCZYYb711 within packed-bed reactor at 5000 h⁻¹; (a) CO₂ conversion; (b) CH₄ yield.

Results from the packed-bed experiment comparing Ni-BCZY26 and Ni-BCZYYb711 showed significant instability in CO₂ environment when using Ni-BCZYYb711. The performance of Ni-BCZY26 was stable for the duration of each trial in the experiment. Each trial lasted approximately an hour because that was sufficient to see the difference in catalytic performance between the two catalysts. According to Figure 4.4 and Figure 4.5, the Ni-BCZYYb711 material had significant degradation in performance, with the greatest degradation rate when operating at 600 °C. Between increasing flow rate from 5000 h⁻¹ to 35000 h⁻¹, CO₂ conversion and CH₄ yield decreased due to a lower residence time of the gases within the packed-bed. In varying temperature, results showed, as expected according to equilibrium, conversion and yield decreases with increase in temperature. There was one exception with Ni-BCZYYb711 at 500 °C. At 500 °C and 5000 h⁻¹, Ni-BCZYYb711 had the best stability relative to the results at the other two temperatures.
Figure 4.5: Ni-BCZY26 and Ni-BCZYYb711 within packed-bed reactor at 35000 h\(^{-1}\); (a) CO\(_2\) conversion; (b) CH\(_4\) yield.

With the stability in Ni-BCZY26 and degradation in Ni-BCZYYb711 in CO\(_2\) shown above, the material of choice would be Ni-BCZY26 for CO\(_2\) methanation. However, BCZY26 based cells fall short of BCZYYb711 in terms of electrochemical performance in electrolysis mode, specifically with Faradaic efficiency in driving protons across the electrolyte. According to Ph.D. candidate L. Le, BCZY26 in electrolysis mode is expected to exhibit a Faradaic efficiency below 60\% at the target temperature 400 °C. As for BCZYYb711, a high Faradaic efficiency of 90-98\% can be obtained, with temperatures between 600-400 °C respectively [9]. Although there is higher Faradaic efficiency with BCZYYb711, its instability in CO\(_2\) can be attributed to its high Ce content. As previously mentioned above, cerates have been shown to be significantly unstable in a CO\(_2\) environment according to Kreuer [17]. As such, a balance of the two material properties was required to obtain high stability in CO\(_2\) methanation as well as high Faradaic efficiency. Hence, a novel BaCe\(_{0.4}\)Zr\(_{0.4}\)Y\(_{0.1}\)Yb\(_{0.1}\)O\(_{3-\delta}\) (Ni-BCZYYb4411) was fabricated at Mines in order to exhibit high CO\(_2\) stability as well as high Faradaic efficiency.
4.3 Ni-BCZYYb4411 Used in Single-Channel Experiment

Ni-BCZYYb4411 cells were used in the Single-Channel Experiment. However, due to high-resistances in the SCE reactor as described in Chapter 3, electrochemical operation in either fuel cell mode or electrolysis mode could not be performed. Instead, catalysis experiments were performed in the SCE to characterize the chemical performance and stability in CO\textsubscript{2} methanation of the novel Ni-BCZYYb4411. Presented below are results and analysis of the final Single-Channel Experiment that was able to be conducted during this project.

4.3.1 Catalysis Operating Conditions

As a result, the SCE was only able to run catalytic performance experiments. Using the Ni-BCZYYb4411 cell, the air side gas stream was maintained under reducing conditions of 97\% Air and 3\% H\textsubscript{2}O with a flow rate of 100 sccm, and the fuel side gas varied the net flow rate and H\textsubscript{2}:CO\textsubscript{2}. Maintaining a stoichiometric H\textsubscript{2}:CO\textsubscript{2} ratio of 4:1 according to the Sabatier reaction, the flow rate was varied from 7000 h\textsuperscript{−1} to 35000 h\textsuperscript{−1}. The temperature was varied between 350 °C and 550 °C. Although the Gas Hourly Space Velocity was defined above to use the catalyst bed as the volume, GHSV for the Single-Channel Experiment was calculated based on the fuel gas channel volume directly above the nickel fuel electrode. Testing of H\textsubscript{2}:CO\textsubscript{2} maintained the net fuel flow rate in the fuel channel at 14000 h\textsuperscript{−1} and varied H\textsubscript{2}:CO\textsubscript{2} from 4.5:1 to 6:1. The temperature was also varied between 350 °C and 550 °C. Each experimental condition was performed in subsequent to one another using the same cell, provided the performance did not show any degradation for the duration of each condition.

Each condition ran for approximately 2 hours to allow the system, specifically the gas chromatograph, to reach a steady-state. Cell performance showed no degradation during each run, thus, results from subsequent experiment conditions were independent of the previous condition. To verify this, the experiment was operated at a previously completed set of conditions to determine if the performance has changed. The CO\textsubscript{2} conversion and CH\textsubscript{4}
selectivity showed no loss in performance in the final run versus the initial run under the operating conditions of 14000 h\(^{-1}\) flow rate, 4:1 H\(_2\):CO\(_2\), and temperature of 400 °C. Thus, there was no degradation. After 100 hours of catalysis testing by changing flow rate and H\(_2\):CO\(_2\) with temperature, the condition with 14000 h\(^{-1}\) flow rate at 400 °C was not only repeated, but also extended for 35 hours to verify stability in performance and repeatability.

Results from varying the fuel flow rate and temperature show a balance between thermodynamic equilibrium, kinetic limitations, and gas transport. While equilibrium predicted CO\(_2\) conversion would increase with a decrease in temperature from 550 °C to 350 °C, Figure 4.6(a) shows that the general behavior of each flow rate was that the CO\(_2\) conversion decreased with temperature. As the temperature decreased, the chemical reaction became kinetically limited, which explained the disagreement between experimental results and thermodynamic equilibrium. However, this is prominent only at temperatures below 400 °C, as shown by CO\(_2\) methanation results in a packed-bed reactor according to Weatherbee and
Bartholomew [14]. Another attribute to the decrease in CO₂ conversion in experimental data at temperatures above 400 °C was the gas diffusion rate becoming limited with a decrease in temperature from 550 °C to 400 °C and below. This was especially true for higher flow rates, in which the decrease in CO₂ conversion was more significant at lower temperatures.

At higher flow rates, the residence time of the gases in the fuel channel was reduced. However, the divergence in CO₂ conversion from 7000 h⁻¹ to 35000 h⁻¹ indicated gas transport limitations in conjunction with kinetic limitations. The proportion with which the gas was able to diffuse into the porous Ni-BCZYYb4411 electrode versus the gas that continued down the channel to the exhaust was greatly lowered, thus the exhaust gas stream observed a lower CO₂ conversion. CO₂ conversion for 7000 h⁻¹ exhibited the best accordance with equilibrium. At this flow rate, the chemical reaction did not appear limited by gas diffusion rate as much as higher flow rates due to a higher residence time that accommodated the gas diffusion limitations to a larger extent. CO₂ conversion at 7000 h⁻¹ flow rate continued to improve as the temperature decreased to 400 °C, while conversion at higher flow rates decreased after 450 °C and 500 °C for flow rates of 14000 h⁻¹ and 21000 h⁻¹, respectively.

Figure 4.6(b) shows the behavior of CH₄ selectivity of each flow rate condition following the predicted behavior of thermal equilibrium when varying the temperature between 350 °C and 550 °C. At the flow rate of 7000 h⁻¹, the experiment followed equilibrium closest to its predictions. With increasing flow rates, the results deviated away from equilibrium and therefore were lower in performance. The matching of CH₄ selectivity between experimental results and thermodynamic equilibrium indicated that the Ni-BCZYYb4411 catalyst did not exhibit kinetic or gas transport limitations in CH₄ selectivity with regard to temperature. As for CO₂ conversion, however, catalytic performance was highly dependent on temperature with lower performance with decrease in temperature. In order to optimize Ni-BCZYYb4411 cells for combined electrolysis and methanation, the Sabatier-Electrolyzer cell would need to operate at a lower temperature to obtain optimal CH₄ selectivity as well as CO₂ conversion with a lower flow rate.
Figure 4.7 shows the influence of increasing the ratio of H$_2$:CO$_2$ from 4:1 to 6:1. Equilibrium calculations predicted that CO$_2$ conversion increased within the temperature range between 350 °C and 550 °C. Experimental results followed the same kinetic limitation relative to equilibrium as previously discussed with a 4:1 H$_2$:CO$_2$. This behavior could be explained by the CO$_2$ methanation mechanism favoring CH$_4$. In the presence of increased concentrations of H$_2$, there is more H$_2$ readily available to react with CO$_2$ in the methanation reaction. According to Figure 4.7(b), CH$_4$ selectivity followed the same relative behavior as predicted by equilibrium. CH$_4$ selectivity was more dependent on the ratio of H$_2$:CO$_2$ with increasing temperatures above 400 °C. Below 400 °C, however, CH$_4$ selectivity was no longer dependent on H$_2$:CO$_2$ and converged to the maximum selectivity of 100%. Here, the experimental results matched the equilibrium trend in varying H$_2$:CO$_2$ and temperature. However, the magnitude by which CH$_4$ selectivity was dependent on the ratio of H$_2$:CO$_2$ is nominal between each step of H$_2$ increase.
Figure 4.8 shows the evolution of CO$_2$ conversion and CH$_4$ selectivity over 35 hours, after the cell had previously operated CO$_2$ methanation for 100 hours over a range of operating conditions. The final condition tested was with flow rate of 14000 h$^{-1}$ at 400 °C, using an H$_2$:CO$_2$ ratio of 4:1. The results were able to match the first CO$_2$ conversion and CH$_4$ selectivity results tested under the same conditions an initial condition of the experiment. Thus, the cell did not undergo any noticeable degradation after 100 hours of CO$_2$ methanation. Furthermore, Figure 4.8 shows that the cell was able to maintain this CO$_2$ conversion and CH$_4$ selectivity for an additional 35 hours. These results suggest that the Ni-BCZYyYb4411 electrode material is highly stable in a CO$_2$ methanation environment. However, extended studies are required to characterize the degradation behavior of the material composition in CO$_2$ over a period of >1000 hours.

4.4 Performance in Single-Channel Experiment versus Packed-Bed

Based on the results in Figure 4.9, performance within the Single-Channel Experiment was not as optimized as a packed-bed reactor in terms of catalytic performance. Both of the experiments were conducted under the same operating conditions of 35000 h$^{-1}$ respective to their flow channel. Ni-BCZY26 and Ni-BCZYyYb4411 were similar catalysts in CO$_2$
methanation, so their CO$_2$ conversion performance were expected to also be similar under the same conditions. Within a packed-bed reactor, catalytic performance nearly reached thermodynamic equilibrium. At 400 °C, packed-bed Ni-BCZY26 was able to convert 76% of the CO$_2$ feed, which was within 8% equilibrium. At 500 °C, packed-bed Ni-BCZY26 exhibited a CO$_2$ conversion performance that was within 3% of equilibrium with 67%. Ni-BCZYYb4411 within the Single-Channel Experiment, however, had less than half the CO$_2$ conversion at 400 °C, but within 8% at 500 °C. These results further support that CO$_2$ conversion within the SCE reactor at these temperatures was limited by gas transport into the porous electrode, rather than limited by kinetics alone.

As previously described above, the CH$_4$ selectivity performance within the SCE reactor was not as dependent on kinetic or gas diffusion limitations when changing temperature. Thus, the behavior between the packed-bed Ni-BCZY26 and SCE Ni-BCZYYb4411 did not diverge as CO$_2$ conversion did. However, there was still a lower CH$_4$ selectivity with the
SCE overall of 16% on average between the two temperatures.

4.5 Conclusions

By fitting a BCZYYb4411 cell within a Single-Channel Experiment reactor, high catalytic performance was demonstrated for CO\textsubscript{2} methanation over a wide range of operating conditions. Characteristic CO\textsubscript{2} conversion and CH\textsubscript{4} selectivity followed thermodynamic equilibrium predictions closely. For CO\textsubscript{2} conversion, however, the experimental results diverged from equilibrium as the performance experienced kinetic as well as transport limitations with a decrease in temperature. Performance was enhanced by reducing the gas hourly space velocity of the fuel gas feed, thereby increasing the gas residence time within the channel. Where gas transport limitation was prominent at lower temperatures, increasing residence time within the gas channel helped sustain CO\textsubscript{2} conversion and CH\textsubscript{4} selectivity rates. Excellent stability of the Ni-BCZYYb4411 electrode in CO\textsubscript{2} was demonstrated, with stable CO\textsubscript{2} conversion and CH\textsubscript{4} selectivity for more than 100 hours. Peak performance was obtained with 67% carbon dioxide conversion and 97% methane selectivity with operating conditions of 400°C, 4:1 H\textsubscript{2}:CO\textsubscript{2} gas feed, and flow rate of 7000 h\textsuperscript{−1}.

Catalytic performance within the Single-Channel Experiment was lower than that of a packed-bed reactor. The channel design was fundamentally different in its gas transport mechanism. Gas flowing through the channel could bypass the porous electrode to the exhaust without reacting with its catalyst. In addition, fuel diffusion into the electrode is limited by its pore properties. The starch content in the BCZYYb4411 at 20 wt.\% and sintering procedure were optimized for 550 °C based on Ph.D. candidate L. Le’s Separated Anode Experiments. The diffusivity could, therefore, be significantly limited at lower temperatures. In contrast to the channel flow, gas flow in a packed-bed reactor must flow through the catalyst bed. The fuel was therefore unable to simply bypass the reactive catalyst volume as it did in the SCE gas channel. Furthermore, the particle diameter could be optimized to enhance the surface reaction. To improve the catalytic performance within the Single-Channel Experiment, the porosity of the fuel electrode may require an optimization based
on the target operating temperature. Starch content could be increased to enable larger pore diameters at lower temperature operation to reduce gas transport limitations.

The BCZYYb4411 cell in the Single-Channel Experiment was unable to achieve a reasonable cell resistance, instead it consistently manifested a high resistance beyond typical cell operation. Approaches used in isolating the cause of the high resistance remained inconclusive. The Single-Channel Experiment reactor may require a redesign or use of a different reactor in order to reduce the cell resistance and enable electrochemical operation to test Sabatier-Electrolyzer CO$_2$ methanation.

4.6 Scale-Up Analysis for Mars ISRU Methane Synthesis

A case study on ISRU propellant production system has been modeled to generate mass and power estimates to produce fuel for a Mars Ascent Vehicle based on [8]. The MAV is capable of transporting 4 crew members off the surface of Mars. Its engines use liquid oxygen and liquid methane with mixture ratios between 3:1 and 3.5:1 (oxygen:methane). Total propellant for a single launch of the MAV is 7.0 mT of methane and 22.7 mT of oxygen. The launch window is every 26 months, of which 9 months are transit and 16 months (480 days) of allowable fuel production time. Assuming continuous fuel generation for those 480 days, the requirement for CH$_4$ is a rate of 0.61 kg hr$^{-1}$, which would produce a total of 6978 kg CH$_4$. The amount of O$_2$ produced simultaneously from electrolysis is 2.43 kg hr$^{-1}$, providing an excess of 5184 kg O$_2$ for the MAV. Thus, CH$_4$ production is the driving metric for the Sabatier-Electrolyzer system.

Based on the selected peak performance with the operating condition of 400 °C, 7000 h$^{-1}$ (25 sccm), and H$_2$:CO$_2$ of 4:1, the catalytic performance results from this project can be scaled up to estimate the total Sabatier-Electrolyzer stack size and power required to produce the methane and oxygen required for the MAV. However, various assumptions are made in the analysis. A Faradaic efficiency of 100% at 400 °C with a current density of 1.43 A cm$^{-2}$ is assumed, based on model predictions of BCZYYb-based PCEC performance outlined in [9]. The voltage required for 1.43 A cm$^{-2}$ at 400 °C was extrapolated from
j-V data from 500 °C to 600 °C, which resulted in a voltage of 1.75 V. For simplicity, it is assumed the Sabatier-Electrolyzer stack will not exhibit degradation in performance for the 480 days. Additionally, the CH₄ production rate from combined steam electrolysis and CO₂ methanation follows the same rate purely from heterogeneous chemistry in the Single-Channel Experiment as shown above. Scale-up analysis calculations are detailed in Appendix A.1 and are summarized below. Scale-up analysis results show a total required area needed to meet the 0.61 kg-CH₄ hr⁻¹ is 0.961 m². Assuming each cell within the Sabatier-Electrolyzer stack has dimensions of 10 cm² x 10 cm², the total number of cells required are 97 cells. The electric power demand for the stack can be calculated from the equation:

\[ P_{\text{stack}} = V_{\text{cell,avg}} \times N_{\text{cell}} \times I \]  

(4.2)

\(V_{\text{cell,avg}}\) refers to the average voltage applied to each cell, \(N_{\text{cell}}\) is the total number of cells within the stack, and \(I\) equal the total current driven. For a 97-cell Sabatier-Electrolyzer stack to fuel the MAV, the total power required is 24.2 kW, for a total of 278,000 kWh per MAV.

4.7 Future Work

Future work on Sabatier-Electrolyzer based on protonic ceramics will extend the catalytic performance characterization from this project to operating the cell in combined H₂O electrolysis and CO₂ methanation. The results obtained in the Single-Channel Experiments performed here are highly useful in establishing the performance of BCZYYb proton-conducting ceramics in the synthesis of methane from carbon dioxide and hydrogen. Next steps include resolving challenges in reducing the cell resistance in order to enable electrolysis operation within the Single-Channel Experiment. Further analysis of experimental data obtained from this thesis may serve to isolate the cause of high resistance in the cells tested, i.e. Electrochemical Impedance Spectroscopy results. Next, the electrochemical performance of the BCZYYYb4411 cell needs to be quantified, i.e. Faradaic efficiency, to control the H₂ to CO₂ ratio for optimal synthesis of CH₂. Finally, performance of methane synthesis using
a Sabatier-Electrolyzer protonic cell can be characterized in combined H\textsubscript{2}O electrolysis and CO\textsubscript{2} methanation operation.

In further development and analysis of the Sabatier-Electrolyzer in implementation, a system level model will be analyzed. The behavior of the Sabatier-Electrolyzer in a stack configuration interfaced with other components necessary for operation of the stack in methane synthesis can be analyzed. In addition, more accurate scaling up and sizing analysis of the overall system can be determined, which would be useful in implementation with NASA’s Mars Atmospheric Processing Module.

Beyond methane synthesis, proton-conducting electrolysis cells operation can be extended to synthesize higher hydrocarbons (C\textsuperscript{2+}) fuels using novel catalysts within the cell MEA as well as increased pressure operation. Active work is being performed at the Colorado Fuel Cell Center to apply proton-conducting ceramics for this purpose.
REFERENCES CITED


A.1 Scaling-Up Analysis Calculations

Input Flow = 7000 h\(^{-1}\) = 25 sccm

Required CH\(_4\) = \(\dot{m}_{CH_4,required} = 0.61 \text{ kg CH}_4 \text{ hr}^{-1}\)

Output Flow Measured = \(\dot{V}_{exh,measured} = 11 \text{ sccm}\)

Exhaust \(X_{CH_4} = 0.288\)

\[
\dot{V}_{CH_4} = \dot{V}_{exh,measured} \times X_{CH_4} = 3.17 \text{ sccm}
\]

\[
\dot{N}_{CH_4} = \dot{V}_{CH_4} \times 2.36 \text{ mol CH}_4 \text{ sccm sec}^{-1}
\]

\[
\dot{m}_{CH_4} = \dot{N}_{CH_4} \times M_{CH_4} = 3.79 \times 10^{-8} \text{ kg sec}^{-1} = 1.36 \times 10^{-4} \text{ kg hr}^{-1}
\]

\[
\dot{m}''_{CH_4} = \frac{\dot{m}_{CH_4}}{A_{cell}} = 6.34 \times 10^{-5} \text{ kg hr}^{-1} \text{ cm}^2
\]

\[
A_{cell,required} = \frac{\dot{m}_{CH_4,required}}{\dot{m}''_{CH_4}} = 9610 \text{ cm}^2 = 0.9610 \text{ m}^2
\]

Voltage at 400 °C = \(V = 1.75\)

Current density required = \(j = 1.43 \frac{A}{\text{cm}^2}\)

Power = \(P = V \times j \times A = 24 \text{ kW}\)

Total Energy Per Launch = \(P \times t = 277000 \text{ kWh}\)

A.2 CAD Drawings of Single-Channel Manifolds
Figure A.1: CAD drawing of SCE female manifold.
Figure A.2: CAD drawing of SCE male manifold.