Intermediate Temperature Hybrid Fuel Cell System for the Conversion of Natural to Electricity and Liquid Fuels

Final Scientific/Technical Report

***Chemical Sciences and Engineering Division**

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Prepared for U.S. Department of Energy Advanced Research Projects Agency-Energy
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Final Scientific/Technical Report

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Public Executive Summary

This goal of this project was to develop a new hybrid fuel cell technology that operates directly on natural gas or biogas to generate electrical energy and to produce ethane or ethylene from methane, the main component of natural gas or biogas, which can be converted to a liquid fuel or high-value chemical using existing process technologies. By taking advantage of the modularity and scalability of fuel cell technology, this combined fuel cell/chemical process technology targets the recovery of stranded natural gas available at the well pad or biogas produced at waste water treatment plants and municipal landfills by converting it to a liquid fuel or chemical. By converting the stranded gas to a liquid fuel or chemical, it can be cost-effectively transported to market thus allowing the stranded natural gas or biogas to be monetized instead of flared, producing CO₂, a greenhouse gas, because the volumes produced at these locations are too small to be economically recovered using current gas-to-liquids process technologies.

The research conducted in this project led to the development of new catalyst technology for converting propane, a major component found in shale gas, to propylene, a major feedstock in the polymer chemistry industry; new anode and electrolyte materials that enabled the development of a proton-conducting fuel cell technology that operated at temperatures ranging from 500-700°C; and a method for integrating the catalyst technology into the fuel cell. Overall, the project led to a better understanding of how to develop hybrid systems that perform multiple operations in a single-unit operation. Such knowledge is critical for process intensification technologies that will allow the development of new process technologies for utilizing stranded resources. While a proof-of-concept of the hybrid technology was demonstrated operating on propane, we were unable to meet the overall project goals of developing methane catalyst coupling technology with carbon efficiency of 50% or greater; a fuel cell that is capable of operating at 500°C with a cell voltage of >780 mV at 200 mA; and manufactured at a cost of \$2000/kW. Due to a drop in the price of crude oil from a high of over \$100 per barrel when this project was awarded in 2014 to around \$50 per barrel in 2017 when this project was completed, a technoeconomic analysis showed this hybrid fuel cell technology, even if successful in meeting performance targets, would not be able to produce a liquid fuel at a cost-competitive price.

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Accomplishments and Objectives

This award allowed Argonne National Laboratory and the Illinois Institute of Technology to develop and demonstrate key technologies such as catalyst technology for dehydrogenating propane to propylene and for the non-oxidative coupling of methane to higher hydrocarbons, new anode and cathode materials for a proton-conducting solid oxide fuel cell that operates at 500-600°C, and demonstrate at the button-cell level a hybrid fuel cell system with the propane dehydrogenation catalyst technology integrated into the anode compartment of the fuel cell.

A number of tasks and milestones were laid out in Attachment 3, the Technical Milestones and Deliverables, at the beginning of the project. The actual performance against the stated milestones is summarized here:

Table 1. Key Milestones and Deliverables

Tasks	Milestones and Deliverables
Task 1 Catalyst Development 1.1 Non-oxidative propane dehydrogenation (NOD) catalyst development 1.2 Non-oxidative coupling of methane (NOCM) catalyst development	<p>Milestone 1.1.1. Identify candidate dehydrogenation catalysts and down select composition for optimization (Deliverable is report)</p> <p>Actual Performance: (Completed 3/31/2015) Single-site metal atom and bimetallic catalysts supported on the three candidate anode materials, $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF), $(\text{La}_{0.25}\text{Sr}_{0.75})_{0.95}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ (LSMT), and $\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ were investigated as catalysts for propane dehydrogenation. While all three unmodified anode materials displayed some catalytic activity for propane dehydrogenation, depositing single-metal atom or bimetallic catalysts resulted in more active catalysts with higher propylene selectivity. In general, the bimetallic catalysts exhibited higher activity than the single-site metal atom catalysts. Four bimetallic catalyst formulations, Pt-Ga, Pt-Re, Pd-Ga, and Ru-Co exhibited a turnover frequency (TOF) $> 10^{-2} \text{ s}^{-1}$ which is estimated to be the minimum TOF necessary to meet the fuel cell performance targets for methane conversion and power density.</p> <p>Milestone 1.1.2 Kinetic rate of NOD catalyst demonstrated</p> <p>Actual Performance: (Completed 9/30/2015) Pt/Ga was down selected as the composition for the catalyst for the propane dehydrogenation test based on its ability to maintain a turnover frequency (TOF) greater than 10^{-2} s^{-1} (based on the Pt loading) after 9 h on stream. Propene selectivity approached 90% and does not include CH_4 and C_2H_6 that was produced as cracking hydrocarbons indicating the $>95\%$ gaseous hydrocarbon products is achievable.</p>

	<p>Milestone 1.2.1 Interim status report on the development of the NOCM catalyst</p> <p>Actual Performance: (Completed 12/31/2015) A status report on the development of the non-oxidative methane coupling catalyst technology was provided in the quarterly report.</p> <p>Milestone 1.2.2 Identify candidate dehydrogenation catalysts and down select composition for optimization (Deliverable is report)</p> <p>Actual Performance: (Not completed) We have identified two NOCM catalysts for optimization - a Pt bimetallic and a Ru-bimetallic. Initial effort focused on PtMo and RuMo, both catalysts were shown to exhibit initial catalytic activity that exceeded the TOF (turnover frequency) milestone with product yields approaching equilibrium-predictions at temperatures ranging from 550-650°C. Coking, which deactivates the catalyst, is the major issue we are addressing and optimizing the formulation to address.</p> <p>Milestone 1.2.3 Kinetic rate of NOD catalyst demonstrated</p> <p>Actual Performance: We demonstrated that a LSCF supported-Pt/Ga catalyst demonstrated a turnover frequency (TOF) greater than the targeted TOF of $10^{-2} \cdot \text{s}^{-1}$ in powder form in a microreactor study.</p>
<p>Task 2 Proton-Conducting Electrolyte Development</p> <p>2.1 Electrolyte material synthesis and characterization</p> <p>2.2 Electrolyte stability testing</p> <p>2.3 Electrolyte film fabrication</p> <p>2.4 Electrochemical characterization of electrolyte films</p> <p>2.5 Conductivity stability</p>	<p>Milestone 2.1.1 Synthesize and characterize 3 electrolyte compositions.</p> <p>Actual Performance: (Completed 3/31/2015) Three electrolyte compositions ($\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_x$, $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_x$, and $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$) were synthesized and the compositional phase purity was evaluated by X-ray powder diffraction. All three powders synthesized showed phase purity.</p> <p>Milestone 2.2.1 Demonstrate 100 h composition stability at 500°C in simulated shale gas.</p> <p>Actual Performance: (Completed 3/31/2015) Powders for three electrolyte compositions ($\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_x$, $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_x$, and $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$) were exposed to a simulated shale composition at 500°C for 100 h. $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ was observed to be the most stable whereas both $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_x$ and $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_x$ reacted with the shale gas resulting in the formation of a significant amount of BaCO_3.</p>

	<p>Milestone 2.3.1 Fabricate 3 dense solid solutions of Y-doped cerates and zirconates and Pr-doped zirconate films with thickness $\leq 10\text{-}\mu\text{m}$.</p> <p>Actual Performance: Button cells with a NiO/BZY with a thickness of $8\text{-}\mu\text{m}$ were produced.</p> <p>Milestone 2.4.1 Electrolyte that passes earlier Task 2 milestones has proton conductivity of $>4\text{ mS/cm}$ and proton transference number of >0.90 at 500°C in hydrogen</p> <p>Actual Performance: (Completed 7/10/2015) Demonstrated a proton conductivity of 4.1 mS/cm at 500°C in hydrogen with BZPY electrolyte. The proton transference number was determined to be 0.92 exceeding the milestone target of 0.90.</p> <p>Milestone 2.4.2 Electrolyte that passes earlier Task 2 milestones has proton conductivity of $>8\text{ mS/cm}$ and proton transference number of >0.90 at 500°C in hydrogen</p> <p>Actual Performance: (Completed 12/31/2015) Measured total conductivity of $9.3 \times 10^{-3}\text{ S/cm}$ at 500°C with BZY electrolyte. The proton transference number is >0.95 at 500°C equivalent to a proton conductivity of $>8.8\text{ mS/cm}$.</p> <p>Milestone 2.5.1 Demonstrate $>8\text{ mS/cm}$ for 50 h stability in presence of simulated shale gas at 500°C</p> <p>Actual Performance: (Completed 3/31/2016) We have demonstrated the stability of the electrolyte in presence of simulated shale gas for 100 h at 500°C which we reported in our Q2 Report. We reported conductivity $>8\text{ mS/cm}$ and transference number >0.90 at 500°C in hydrogen in our Q5 Report. We have shown the 100 h stability and $>8\text{ mS/cm}$ conductivity of the electrolyte. We believe that we have met this milestone although we didn't measure conductivity in simulated shale gas.</p>
<p>Task 3 Anode Development</p> <p>3.1 Electron-conducting anode component development</p> <p>3.2 Composite anode development</p> <p>3.3 Catalyst integration into anode</p>	<p>Milestone 3.1.1 Synthesize and characterize phase structure of 3 electron-conducting anode components.</p> <p>Actual Performance: (Completed 12/3/2014) Three candidate electron-conducting anode materials, $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF), $(\text{La}_{0.25}\text{Sr}_{0.75})_{0.95}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ (LSMT), and $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$ (CSO), were synthesized, characterized by x-ray diffraction, and their electrical conductivity measured. Of the three materials, LSCF exhibited a conductivity of 1.71 S/cm at 493°C in 4% H_2 which is sufficient to achieve the</p>

	<p>targeted ASR of $0.06 \Omega \text{ cm}^2$ at $\sim 500^\circ\text{C}$ with a 0.1 cm thick anode layer.</p> <p>Milestone 3.1.2 Demonstrate composition stability of electron-conducting ($> 60 \text{ mS/cm}$) anode material at 500°C in hydrogen and then in simulated shale gas for 50 h.</p> <p>Actual Performance: (Completed 3/31/2015) $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ (LSCF) exhibited an electrical conductivity of $\sim 1.7 \text{ S/cm}$ in the presence of 3% humidified H_2 and an electrical conductivity of 2.58 S/cm in the presence of a simulated shale gas over 80 hours.</p> <p>Milestone 3.2.3 Electrode with ASR of $<3 \Omega\text{-cm}^2$ at 500°C in hydrogen.</p> <p>Actual Performance: (Completed 6/30/2015) A Cu/BZY cermet anode exhibited an electrical conductivity of $1.1 \times 10^{-4} \text{ S/cm}$, which was stable for 95 h in a humidified hydrogen steam (3 vol % H_2O, 3.5% H_2 balance He).</p> <p>Milestone 3.2.4 Electrode with ASR of $<1.5 \Omega\text{-cm}^2$ at 500°C in hydrogen.</p> <p>Actual Performance: (Completed 12/31/2015) Measured electrical conductivity of $1.1 \times 10^{-4} \text{ S/cm}$ with 40 vol% Cu/BZY composite anode at 500°C in hydrogen. Based on the measured conductivity of Cu/BZY composite, the ASR is estimated at $9 \times 10^{-6} \Omega\text{-cm}^2$ for a 0.1 cm thick 40 vol % Cu/BZY composite anode. The ASR is estimated to be $\sim 10^{-1} \Omega\text{-cm}^2$ for a Ni/BZY composite substrate consisting of $>59 \text{ wt\% Ni}$.</p> <p>Milestone 3.2.5 Demonstrate $<3 \Omega\text{-cm}^2$ at 500°C for 50 h in presence of simulated shale gas at 500°C.</p> <p>Actual Performance: (Completed 3/31/2016) Milestone 3.2.5 was set as an intermediate goal toward reaching Milestone 4.2.3. We met Milestone # 4.2.3 – Demonstrate single cell operating on hydrogen; current density $>200 \text{ mA/cm}^2$ for 100 h at 500°C with less than 10% decrease in power density over 100 h. The fact that we have met Milestone 4.2.3 effectively demonstrates that we have met Milestone 3.2.5. If we had not achieved the performance of $<3 \text{ ohm-cm}^2$, we would not have been able to achieve Milestone 4.2.3.</p> <p>Milestone 3.3.1 Identify optimal process for integrating NOD catalyst into anode.</p> <p>Actual Performance: Integration has been pursued with the</p>
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	<p>Pt/Ga dual-metal catalyst supported on $\text{LaSrCr}_{0.7}\text{Fe}_{0.3}\text{O}_3$ (LSCF) physically mixed with $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_3$ (BZY). We have addressed the adhesion issue previously reported. However, the processing conditions were found to deactivate our dual-metal catalysts in parallel testing. A pretreatment protocol was developed for the catalyst/LSCF that overcame this issue to produce active catalyst compatible with the sintering procedure.</p> <p>Milestone 3.3.2 Determine the maximum NOD catalyst loading ; demonstrate that loading of NOD does not impact ASR of anode nor catalyst reactivity (Deliverable is report]</p> <p>Actual Performance: Task not started.</p> <p>Milestone 3.3.3 Identify optimal process for integrating NOCM catalyst into anode.</p> <p>Actual Performance: Task not started.</p> <p>Milestone 3.3.4 Determine the maximum NOCM catalyst loading ; demonstrate that loading of NOCM catalyst does not impact ASR of anode nor catalyst reactivity [Deliverable is report]</p> <p>Actual Performance: Task not started.</p>
<p>Task 4 Fuel Cell Development</p> <p>4.1 Fuel cell test stand development</p> <p>4.2 Single cell performance testing</p>	<p>Milestone 4.1.1 Develop conceptual design for single cell test stand and procure test stand equipment.</p> <p>Milestone 4.1.2 Commission single cell test stand.</p> <p>Actual Performance: Construction and commissioning of test stand completed.</p> <p>Milestone 4.2.1 Demonstrate single cell operating on H_2 with cell size of 25 cm^2; current density $> 100\text{ mA/cm}^2$ for 50 h; 500°C; with less than 10% decrease in power density over 50 h.</p> <p>Actual Performance: (Completed 9/30/2015) Button cells, which were 19 mm in diameter, consisting of 10-20 μm dense BCY-BZY layered electrolyte films on a 1-2 mm thick porous NiO/BZY composite anode substrate were fabricated and tested. A power density of 110 mW/cm^2 at a current density of 250 mA/cm^2 at 600°C was measured for a cell with an 18 μm-thick electrolyte layer. The performance was relatively stable over a 100 h with no observable loss in performance. At 500°C, a maximum power density of 45 mW/cm^2 at a current density of 80 mA/cm^2 was measured.</p>

	<p>Milestone 4.2.2 Demonstrate single cell operating on propane dehydrogenation - cell size of 25 cm²; current density > 50 mA/cm² for 24 h; 500°C; product yield ≥50% (< 10% decrease in yield over the course of the 50 h test); selectivity >95% to gaseous carbon-containing species.</p> <p>Actual Performance: Task initiated but not completed. Tests were conducted using button cell with a LSCF-supported Pt/Ga as the anode given that the NiO/BZY anode used in the H₂ test coked severely when exposed to propane. Tests were conducted in the hydrogen pump mode. A major problem was making good electrical contact between the anode and the current collector. Maximum currents observed were 20 mA for the cell when using propane or H₂ as the feed.</p> <p>Milestone 4.2.3 Demonstrate single cell operating on H₂ - cell size of 25 cm²; current density > 200 mA/cm² for 100 h; 500°C; with less than 10% decrease in power density over 100 h.</p> <p>Actual Performance: (Completed 6/30/2016) Measured stable current density (~200 mA/cm²) for 101 h at 500°C at the cell voltage of 0.62 V using a cell with 14 μm-thick electrolyte. Overall decrease in power density was less than 10%. We conducted the test using a button cell instead of a 25-cm².</p> <p>Milestone 4.2.4 Demonstrate single cell operating on methane coupling - cell size of 25 cm²; current density > 100 mA/cm² for 100 h; 500°C; product yield ≥50% (< 10% decrease in yield over the course of the 100 h test), carbon efficiency ≥50% ; selectivity >95% to gaseous carbon-containing species.</p> <p>Actual Performance: Task not started..</p>
<p>Task 5 Tech-to-Market (T2M)</p> <p>5.1 T2M Lead/IP Agreements</p> <p>5.2 Technical Economic Agreement (TEA)</p> <p>5.3 Technology-to-Market (T2M) Plan</p> <p>5.4 Pitch Plan</p>	<p>Milestone 5.1.1 Identify Technology-to-Market Lead/POC.</p> <p>Actual Performance: Elizabeth Jordan, a staff member of Argonne Technology Development and Commercialization (TDC) Office, was assigned as the Technology-to-Market Lead/POC by senior TDC management.</p> <p>Milestone 5.1.2 IP agreement between Argonne and IIT in place (Deliverable is IP Management Plan).</p> <p>Actual Performance: IP agreement between Argonne and IIT was completed. A document outlining the agreement was submitted in November 2014.</p>

	<p>Milestone 5.2.1 Preliminary TEA including Performance-Cost Model for producing electricity and fuel (Deliverable is report).</p> <p>Actual Performance: A preliminary technoeconomic analysis (TEA) was conducted to provide an estimate of the cost of producing electricity and liquefied petroleum gas (LPG), which have determined to be the optimal fuel product for our technology. Since the optimal compositions for our fuel cell and catalyst materials were not determined at this time nor was an integrated system, a TEA analysis for a 275 kW solid oxide fuel cell developed by Pacific Northwestern National Laboratory was used to estimate the manufacturing cost for the proton-conducting ceramic-based fuel cell. The project performance targets for the production of electricity and LPG were used. The estimated levelized cost of producing electricity and liquefied petroleum gas is \$0.087/kW and \$2.23/gal, respectively, which is competitive with the current market prices for electricity and LPG based on information available through the U.S. Department of Energy Energy Information Agency.</p> <p>Milestone 5.2.2 Updated TEA including Performance-Cost Model for producing electricity and fuel (Deliverable is report).</p> <p>Actual Performance: Task was initiated but not completed. A more indepth TEA was initiated building upon the TEA conducted in the previous year. Due to a drop in the price of crude oil from a high of over \$100 per barrel when this project was initiated in 2014 to around \$50 per barrel in 2017 when this project ended, the technoeconomic analysis, although not complete, showed this hybrid fuel cell technology, even if successful in meeting performance targets, would not be able to produce a liquid fuel at a cost-competitive price.</p> <p>Milestone 5.3.1 Preliminary Technology-to-Market Plan (Deliverable is report).</p> <p>Actual Performance: The Preliminary Technology-to-Market Plan was submitted. The key changes and updates to the initial document are as followed: (1) Flared gas capture has been added as a potential market for this hybrid fuel cell technology. (2) The key players, competitive landscape, and market needs and requirements have been expanded. (3) Summary of commercialization activities to date has been added. (4) The IP Strategy has been updated. (5) The Manufacturing and Scalability section has been updated to include the TEA.</p>
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	<p>Milestone 5.3.2 Updated Technology-to-Market Plan (Deliverable is report).</p> <p>Actual Performance: The preliminary Technology-to-Market Plan submitted in Q3 has been updated and submitted to John Tuttle for review on July 15, 2016. Major addition to the report involves our focus on "propylene-on-purpose" for producing propylene from propane (natural gas liquids) as a new potential market opportunity based on our discussions with the petrochemical industry representatives and venture capitalists that fund technology development targeting the petrochemical industry.</p>
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Background

This research results presented in this report targeted the development of intermediate temperature (500-700°C) fuel cell technology that could operate on excess natural gas being produced at a natural gas wellpad or on renewable biogas from an anaerobic digester to generate electrical power and liquid fuel that is more readily transported to market than the gas. The fuel cell could also operate as a hydrogen-pump utilizing excess electricity produced by a variable energy resource generator such as wind or solar to produce a liquid fuel that could be fed into a power-generating device at a later time to meet local power demands. The technical targets for the project based on the requirements in the FOA announcement, DE-FOA-0001026, are listed in **Table 2**.

Table 2. Technical Targets for hybrid fuel cell system that operates on natural gas to produce a liquid fuel and power.

Metric	State of the Art	Proposed
Proton-conducting solid electrolyte fuel cell	Cell Voltage of 625 mV at 200 mA/cm ² and 500°C	Cell Voltage of >780 mV at 200 mA/cm ² and 500°C
Methane coupling carbon efficiency	<30%	50%
Fuel cell manufacturing cost	\$4000/kW	\$2000/kW

Our approach was to integrate catalyst technology for the non-oxidative coupling of methane (NOCM), i.e., to convert methane to ethylene and hydrogen, in the anode compartment of a proton-conducting fuel cell (PCFC) as shown in **Figure 1**. The hydrogen would be oxidized within the anode generating protons which will migrate to the cathode where they react with oxygen, thus driving the thermodynamically-unfavorable methane coupling reaction by reducing the hydrogen partial pressure in the anode and by providing heat generated by the fuel cell to drive the endothermic reaction. When operated in the hydrogen-pump mode, part of the electrical energy input was to be “stored” in chemical bonds formed in the production of ethylene and hydrogen. Ethylene would serve as an intermediate reaction product undergoing further reactions, such as oligomerization, to yield benzene or with additional methane to yield a liquid fuel in a separate unit operation downstream of the fuel cell.

Figure 1. Schematic of our proposed hybrid proton-conducting fuel cell system with the NOCM catalyst incorporated in the anode.

The technical benefits of our proposed integrated technology are: (1) higher levels of methane conversion can be realized at a lower temperature than in a conventional chemical reactor by using a fuel cell to consume the hydrogen thus helping to overcome the thermodynamic limitations of the NOCM reaction and (2) using a proton-conducting electrolyte eliminates the loss of carbon due to the formation of CO and CO₂ that occurs when oxygen is either co-introduced with methane, as in conventional oxidative methane coupling (OCM), or when an oxide ion-conducting solid oxide fuel cell is employed. The key technology developments required were the development of (1) NOCM catalyst technology that is highly active at 500-700°C, (2) a proton-conducting fuel cell (PCFC) that is capable of operating efficiently at 500-700°C and (3) the integration of the NOCM catalyst within the anode without negatively impacting the performance of the NOCM catalyst nor the performance of the fuel cell.

We proposed a 3-year, \$4,100,266 project with the U.S. Department of Energy providing \$3,900,000 in funding. The deliverables for this project were: (1) a prototype PCFC with a minimum cell area of 100 cm² operating on natural gas continuously for 100 h co-generating electrical power and ethylene with a current density of >200 mA/cm²; (2) a process design that integrates the PCFC with a chemical process for converting the ethylene to a liquid fuel with a conversion and carbon efficiency of >50%, and (3) estimates for the PCFC manufacturing cost and for the capital and operating costs of the integrated PCFC/chemical process design. After the award, the scope and budget of the project were reduced to a 2-year, \$2,000,000 project with the size of the prototype PCFC reduced from a minimum cell area of 100-cm² to 25-cm² and the elimination of the process design for converting the ethane/ethylene to a liquid fuel. In addition, the fuel cell material effort was now focused only on the anode and electrolyte materials.

The revised project was divided into five tasks, four R&D tasks and a Tech-to-Market task, with each task have well-defined milestones and deliverables at shown in **Table 1**. A summary of the primary objectives of each of the five tasks as follows:

Task 1: Non-oxidative Propane Dehydrogenation (NOD) and Coupling of Methane (NOCM) Catalyst Technology. This task was to develop new NOD and NOCM catalyst technologies that exhibit higher reaction rates at 500-700°C and with longer lifetimes and greater resistance to deactivation by coking than current NODH and NOCM catalyst technologies.

Task 2: Proton-Conducting Electrolyte and Task 3: Anode Development. This task was to develop (1) a new proton-conducting solid oxide electrolyte with the requisite conductivity, transference number, and stability in the presence of shale gas levels of H₂O and CO₂ and (2) anodes with the requisite low overpotential for hydrogen oxidation and which were compatible with the NODH and NOCM catalysts. The goal was to achieve an overall cell performance of >200 mA/cm² at >780 mV at 400-500°C to achieve >70% of the thermodynamic potential.

Task 4: Fuel Cell Development. This task will test and demonstrate the performance of the integrated components developed in Tasks 1-3. The deliverable was to be a hybrid PCFC operating on natural gas with a minimum cell area of 25-cm² operated continuously in the fuel production mode at 100 mA/cm² for >100 h.

Task 5: Tech-to-Market. This task was to conduct a technoeconomic analysis of our technology to define its market potential and define its market opportunity, a marketing plan that developed a strategy for marketing our technology to potential investors; and a pitch plan for presenting our technology to potential investors.

While the overall goal of the project was to utilize natural gas, i.e. primarily methane, as the feed, we had proposed first developing and integrating non-oxidative catalyst technology for dehydrogenating propane to propylene as a “proof-of-concept” for our ability to integrate catalyst technology into a proton-conducting fuel cell with minimal impact on the performance of the fuel cell. We had chosen this pathway based on promising results from our effort to develop single-site alkane dehydrogenation catalysts^{1,2,3} that we were pursuing as part of a U.S. Department of Energy Office of Science-funded catalysis program at Argonne National Laboratory. In the end, as part of our Tech-to-Market effort, we came to conclusion that there was a greater interest in our technology for dehydrogenation C₃-C₄ alkanes typically found in wet shale gas to produce olefins such as propylene and butenes for the polymer industry than to produce a liquid fuel such as gasoline or diesel based on numerous discussions with two major petroleum companies over the course of this project.

Background Catalytic Activity of Candidate Anode Materials

As previously noted, a main concern was that the anode material would be catalytically activity. To evaluate the catalytic activity of the anode material, we tested the three candidate anode materials, (La_{0.75}Sr_{0.25})_{0.95}Cr_{0.7}Fe_{0.3}O_{3-δ} (LSCF), (La_{0.25}Sr_{0.75})_{0.95}Mn_{0.5}Ti_{0.5}O_{3-δ} (LSMT), and

¹ N. M. Schweitzer, B. Hu, U. Das, H. S. Kim, J. Greeley, L. A. Curtiss, P. C. Stair, J. T. Miller, and A. S. Hock, *ACS Catal.* 2014, **4**, 1091–1098

² B. Hu, N. M. Schweitzer, G. H. Zhang, S. J. Kraft, D. J. Childers, M. P. Lanci, J. T. Miller, and A. S. Hock, *ACS Catal.* 2015, **5**, 3494–3503

³ B. Hu, A. “Bean” Getsoian, N. M. Schweitzer, U. Das, H. S. Kim, J. Niklas, O. Poluektov, L. A. Curtiss, P. C. Stair, J. T. Miller, and A. S. Hock, *J. Catal.* 2015, **322**, 24–37

$\text{Sm}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (SDC10) for dehydrogenating propane to propylene. The tests were conducted in a microreactor system by contacting 0.5-1 g of the anode material with a gas mixture consisting of 2% propane in argon flowing at a rate of 30-50 cc/min over the temperature range of 500-600°C. The product gases were analyzed using gas chromatography. Tests were conducted under differential reaction conditions to maintain conversion levels far from the equilibrium-predicted yields to accurately assess the intrinsic catalytic rate and selectivity of each anode materials. All three anode materials exhibited some degree of activity for dehydrogenation propane to propylene and for cracking propane or propylene to yield ethylene and methane as shown in **Table 3**. SDC10 and LSCF exhibited some degree of stability over the course of the test whereas LSMT rapidly deactivated. As will be discussed later in the section on Fuel Cell Materials Development, LSCF was selected for the anode material based on its favorable performance under fuel cell conditions.

Table 3. Product yields observed when passing propane over the three candidate anode materials.

Catalyst	Initial Rate (mmol·h ⁻¹ ·g ⁻¹ cat)	Surface Area (m ² /g)	Carbon balance (%)	C ₃ H ₆ selectivi ty (%)	CH ₄ selectivi ty (%)	C ₂ H ₄ selectivi ty (%)	Temperatur e (°C)
SDC10	0.110	25	102	50	30	20	550
	0.320		99.3	38	40	22	600
LSMT	0.430	2.5	106	18	42	40	550
	0.620		103	13	43	44	600
LSCF	0.100	2.0	101	23	42	35	550

Propane dehydrogenation catalyst development

Commercial propane dehydrogenation processes, such as UOP's Oleflex™ Process, uses an alumina-supported bimetallic Pt-Sn catalyst. In our BES-funded catalysis program, we had observed that silica-supported Pd deactivated rapid when exposed to propane at temperatures around 500-600°C forming most CH₄ instead of the desired propylene product. However, the addition of a second non-reducible metal under reaction conditions, such as Zn, to Pd resulted in a stable propane dehydrogenation catalyst that exhibited a high selectivity for propylene and little evidence of propane/propylene cracking as shown in Table 4. For example, a 3 wt% Pd-1.8 wt% Zn catalyst exhibited a selectivity to propylene of >98% and a steady-state TOF = $8.8 \times 10^{-3} \text{s}^{-1} = 31.68 \text{h}^{-1}$. Other non-reducible metals, such as Ga, were shown to exhibit a similar effect on the performance of silica-supported Pt-based propane dehydrogenation catalysts.

Table 4. Comparison of the propane dehydrogenation activity and product selectivity for silica-supported Pd and Pd/Zn bimetallic catalysts.

Catalyst	TOF (s ⁻¹)	Product Distribution			
		CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₆
2% Pd	Rapid deactivation	75	6.3	8.1	10.7
3%Pd-1.8%Zn	8.8×10^{-3}	0.3	0	1.7	98.3
2%Pd-10%Zn	1.9×10^{-3}	1.2	0	0.7	98.4

Since Pt is often the preferred choice for the electrocatalyst in many fuel cell systems and the beneficial results from the addition of a non-reducible second metal, we identified a number of potential bimetallic Pt catalyst candidates, such as Pt/Zn, Pt/Ga, Pt/Re, and Pt/In, for evaluation as well as a number of other bimetallic Pt-based formulations based on a survey of the literature as shown **Table 5**. While Pt alone showed favorable performance in terms of high selectivity for propylene and low activity for cracking, the addition of the second metal was shown to improve the rate while only slightly impacting the selectivity to propylene. All catalysts deactivated over the 9-10 h reaction run. The most active catalyst formulation was the Pt/Ga with a higher atomic ratio of Ga to Pt. This catalyst formulation was selected for incorporation into the hybrid fuel cell.

A series of X-ray absorption experiments was conducted at the Materials Research-Collaborative Access Team (MR-CAT) Beamline located at Sector 10 of the Argonne Advanced Photon Source was conducted to gain insight into the nature of the Pt-Ga interaction. Pt is only partially reduced under 4%H₂ in He at 650°C or 2% C₃H₈ in N₂ at 500°C as shown in the Pt X-ray Absorption Near Edge Structure (XANES) spectrum as shown in **Figure 2**. Both Pt-O and Pt-Pt scatterings were observed in the Extended X-Ray Absorption Fine Structure (**EXAFS**) spectrum, but not Pt-Ga scattering indicating that a Pt-Ga alloy is not formed. The Ga XANES spectrum (**Figure 3**) showed only Ga(+3) even under reducing conditions and coupled with the EXAFS results showed suggested that 6-coordinated Ga(+3) was present.

Table 5. Propane dehydrogenation results for selected LSCF-supported bimetallic-Pt and Pd catalysts. wt% is based on Pt or Pd loading only.

Catalyst	Initial Rate (mmol·h ⁻¹ ·g ⁻¹ cat)	Carbon balance (%)	C ₃ H ₆ selectivity (%)	CH ₄ selectivity (%)	C ₂ H ₄ selectivity (%)	C ₂ H ₆ selectivity (%)
0.1 wt% Pt-LSCF	0.107	98.2	94.6	1.0	2.2	2.1
0.1wt% Pt/Zn-LSCF-3	0.427	97.5	79.7	17.4	2.6	0.4
0.03wt% Pt/Zn-LSCF	0.073	95.3	91.8	4.6	2.1	1.5
0.1wt% Pt/Ga-LSCF-1	0.419	97.2	74.4	22.5	2.9	0.2
0.03 wt% Pt/Ga-LSCF-1	0.073	> 99	75.7	1.5	0.9	1.9
0.1 wt% PtGa/LSCF (high-Ga loading)	1.213	94.7	88.4	9.3	1.2	1.2
PtIn/LSCF-4	0.730	97.9	91.2	5.3	1.8	1.8
0.1 wt% Pt/Sn-LSCF-2	0.214	96.3	80.8	16.9	2.1	0.2
0.1% wt% Pt ₃ /Sn-LSCF- 2	0.214	96.6	80.0	17.6	2.3	0.1
0.1wt%% Pt/Re-LSCF-4	0.427	96.1	85.6	13.5	3.2	0.1
0.1wt% Pt/Co-LSCF	0.092	97.8	94.0	2.7	1.6	1.7
PtCo/LSCF-4	0.911	97.0	87.5	9.4	1.6	1.6
PtNi/LSCF-4	0.965	93.7	81.7	14.1	1.4	2.8
PtRu/LSCF-3	0.663	96.9	85.4	9.8	2.4	2.4
PdGa/LSCF-4	0.951	97.0	87.8	9.5	1.4	1.4

Figure 2. The Pt XANES (top) and EXAFS (middle and bottom) spectra for the freshly prepared Pt/Ga catalyst as well as the catalyst heated under 4% H₂ in He at 650°C or 2% C₃H₈ in N₂ at 650°C.

Figure 3. The Ga XANES (top) and EXAFS (bottom) spectra for the freshly prepared Pt/Ga catalyst and as the catalyst heated under 4% H_2 in He at 650 °C or 2% C_3H_8 in N_2 at 650 °C.

Methane Coupling Catalyst Development

The development of non-oxidative methane coupling catalyst technology that would convert the CH_4 present in natural gas to C_{2+} alkanes and olefins with both high overall conversion (little to no coke formation) and selectivity to gaseous products was initiated in the first year. Given that the development of a methane coupling catalyst represented a far greater challenge than the development of propane dehydrogenation catalyst; this was the major focus during the first year of the project. However, due to the accelerated time schedule for the project with the need to demonstrated a hybrid fuel cell system for dehydrogenating propane as a near-term GO/NO GO decision point and the greater interest expressed by representatives of the petroleum and chemical industries for this technology for dehydrogenating propane than coupling methane, effort was scaled-back.

While we are unaware of any commercial non-oxidative methane coupling catalyst, studies have shown that both Ta/SiO_2 and W/SiO_2 have been reported to exhibit non-oxidative methane

coupling at temperatures as low as 250°C^{4, 5}. Given that C-H bond breaking is a critical step in methane coupling, we evaluated SiO₂-supported versions of our bimetallic Pt propane dehydrogenation catalysts. Two other bimetallic Pt catalysts, PtMo/SiO₂ and PtW/SiO₂, were evaluated as were Ta/SiO₂, W/SiO₂ and Mo/SiO₂. Due to time constraints, the use of LSCF as a catalyst support was not evaluated.

Evaluating the performance of methane coupling catalysts at 500-700°C is very challenging because the equilibrium conversion in the absence of removing H₂ or coke formation results in extremely low conversion, ~1%, with individual product yields of C₂'s, C₃'s, etc.), being significantly lower as shown in **Figure 4**.

Figure 4. Thermodynamically-predicted product yields for non-oxidative methane coupling for temperatures ranging from 400-700°C based on our reaction test conditions.

SiO₂-support propane dehydrogenation catalysts, Pt/Ga/SiO₂ and Pt/CO/SiO₂, exhibited some activity for methane coupling at 600°C as shown in **Figure 5**. Both Pt/Ga and Pt/Co yielded primarily C₂H₆ and C₂H₄ at a C₂H₆:C₂H₄ ratios of ~2:1 and 1:1.5, respectively. Both catalysts coked severely.

⁴ D. Soulivong, S. Norsic, M. Taoufik, C. Coperet, J. Thivolle-Cazat, S. Chakka, and J.-M. Basset *J. Am. Chem. Soc.*, 2008, **130** (15), 044–5045

⁵ K. C. Szeto, S. Norsic, L. Hardou, E. Le Roux, S. Chakka, J. Thivolle-Cazat, A. Baudouin, C. Papaioannou, J.-M. Basset and M. Taoufik, *Chem. Commun.*, 2010, **46**, 3985–3987

Figure 5. Methane coupling product selectivity for Pt/Ga/SiO₂ (left) and Pt/Co/SiO₂ (right) test using 5% CH₄ in Ar at 600 °C.

2 wt% Ta/SiO₂, 2 wt% W/SiO₂, and 2 wt% Mo/SiO₂ all exhibited some degree of activity for methane coupling at 650 °C. The Ta and W catalysts produced C₂H₆ and C₃H₆ whereas the Mo catalyst produced only C₂H₆. Adding 0.1wt% Pt to Mo/SiO₂ and W/SiO₂ catalysts resulted in a slight increase in the methane conversion with C₂H₆ and C₃H₆ still being the major gas-phase products. For the Pt/Mo/SiO₂ catalyst, C₃H₆ was the major product in the first 2 h with C₂H₆ beginning to increase in yield after about 1 h and eventually becoming the primary product as shown in Figure 24. All catalysts deactivated rapidly. Attempts at regenerating the Pt/Mo/SiO₂ catalyst by burning the coke off in air resulted in a different product yield, with C₂'s being the major products as shown in Figure 24.

Figure 6. Methane coupling product selectivity for Pt/Mo/SiO₂ (left) and after regeneration by calcining in air (right) using 5% CH₄ in Ar at 650 °C.

Other formulations such as Pt/Mn, Ru/Mn, and Ru/Mo supported on SiO₂ as well as carbon-supported PtMn alloy were investigated. All of these catalysts produced C₂ and/or C₃'s under the reaction conditions utilized; however, like the catalysts previously discussed they all deactivated rapidly. While the ability of all the catalysts studied to produce C₂ and/or C₃ at temperatures ranging from 550-650°C were encouraging, all of the catalysts deactivated within a few hours on stream and were not viable options for incorporating into the hybrid fuel cell system.

Task 2: Proton-Conducting Electrolyte and Task 3: Anode Development

Proton-Conducting Electrolyte Development

Three electrolyte compositions, BaCe_{0.7}Zr_{0.1}Y_{0.2}O_x (BCZY712), BaCe_{0.5}Zr_{0.3}Y_{0.2}O_x (BCZY532), and BaZr_{0.7}Pr_{0.1}Y_{0.2}O_x (BZPY712), were prepared by a combustion synthesis process. The combustion synthesis process involved mixing an aqueous solution containing dissolved nitrate salts of the desired constituent oxides, Ba(NO₃)₂, Ce(NO₃)₃, ZrO(NO₃)₂, Y(NO₃)₃, or Pr(NO₃)₃, with a fuel such as glycine, hydrazine, or citric acid. The mixture was heated using a hot plate to evaporate the water. Once the water evaporated, a solid was generating consisting of the nitrates and fuel which reacted rapidly (<10 min). Because the reaction was so rapid and generated a large volume of gaseous byproducts, particle growth had little time to occur and was disrupted by the evolution the gas leading to the formation of fine-grained oxide particles. These fine-grained particles were easily sintered. The XRD patterns of the three electrolyte compositions, - BaCe_{0.7}Zr_{0.1}Y_{0.2}O_x, BaCe_{0.5}Zr_{0.3}Y_{0.2}O_x, and BaZr_{0.7}Pr_{0.1}Y_{0.2}O_x, are shown in **Figure 7**.

Figure 7. XRD patterns of the three electrolyte compositions investigated - $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_x$ (BCZY712), $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_x$ (BCZY532) and $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ (BZPY712).

The chemical stability of the three electrolyte compositions, $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_x$, $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_x$, and $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$, was evaluated by exposing samples of each powder to a simulated shale gas with a composition representative of Marcellus shale gas⁶: 1% CO_2 , 4% C_3H_8 , 15% C_2H_6 , 80% CH_4 , at 500°C for 100 h. For the test, 0.1-0.2 g samples of each composition were loaded onto a dense Al_2O_3 tray. The tray was placed into a tube furnace and the furnace was purged with dry N_2 for ~30 min. The furnace temperature was increased at a rate of 180°C/h to 500°C. Once the furnace temperature reached 500°C, the feed gas was switched from N_2 to the simulated shale gas which was humidified to 3% by bubbling it through a water reservoir. After the powders had been exposed to the humidified shale gas for 100 h, the feed gas was switched back to dry N_2 and the furnace was cooled to room temperature. X-ray diffraction patterns of the powders were taken using a Bruker D8 AXS diffractometer with a General Area Detector Diffraction System and compared to the patterns obtained for the as-prepared samples to evaluate their stability.

Figure 8 shows the XRD patterns of the three electrolyte compositions after exposure to simulated shale gas. For reference, the peak positions and relative intensities are also shown for BaCO_3 (PDF #44-1487). Two of the compositions, $\text{BaCe}_{0.7}\text{Zr}_{0.1}\text{Y}_{0.2}\text{O}_x$ and $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Y}_{0.2}\text{O}_x$, clearly decomposed during the exposure to shale gas as seen by the presence of strong peaks for BaCO_3 . The dominant peaks in the diffraction pattern for $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ are due to the presence of the perovskite phase with only a relatively minor amount of BaCO_3 being present based on the relative intensities of the peaks. We suspected that the presence of the small amount of BaCO_3 in $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ might have resulted from a slight excess of Ba. A new batch of $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ was prepared with a slightly lower Ba content (~5 mol. %). Figure 9 shows the x-ray pattern for $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ with reduced Ba content after its exposure to humidified simulated shale gas at 500°C for 100 h. Only a very minor amount of BaCO_3 was present after exposure to the simulated shale gas indicating that $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ is stable.

⁶ Keith Bullin and Peter Krouskop “Composition Variety Complicates Processing Plans for US Shale Gas”, Bryan Research and Engineering Inc., Bryan, Tex.

Figure 8. XRD patterns of the three electrolyte compositions. BCZY712, BCZT532, and BZPY712, after exposure to humidified simulated shale gas (1% CO_2 , 4% C_3H_8 , 15% C_2H_6 , 80% CH_4) at 500°C for 100 h.

Figure 9. XRD pattern of $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ with reduced Ba content after exposure to humidified simulated shale gas (composition: 1% CO_2 , 4% C_3H_8 , 15% C_2H_6 , 80% CH_4) at 500°C for 100 h.

Anode Development

Three candidate anode materials, two A-site-deficient perovskites, $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF) and $(\text{La}_{0.25}\text{Sr}_{0.75})_{0.95}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ (LSMT), and Sm-doped ceria, $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$ (SDC10), were synthesized and their electrical conductivity evaluated. Single-phase powders of LSCF and LSMT were prepared by solid state synthesis from La_2O_3 (Aldrich, 99.9%), SrCO_3 (Aldrich 99.9%), Mn_2O_3 (Aldrich, 99%), TiO_2 (Aldrich, 99.8%), Cr_2O_3 (Fisher, 99%), and Fe_2O_3 (Alfa Aesar 99.945%). To prepare the powders, a mixture of the desired metal oxide powders in the appropriate stoichiometric ratios were ball-milled, dried, and calcined in air at $800\text{--}1200^\circ\text{C}$ with intermediate regrinding. Sm-doped ceria ($\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$), was obtained from Rhodia Chimie. The phase purity and crystal structure of these powders were determined by XRD. **Figure 10** shows the XRD spectra of the LSCF and LSMT and the Sm-doped ceria having cubic fluorite structure. XRD analysis confirmed that the powders are single phase.

The electrical conductivity of the LSCF and LSMT was measured using a 4-probe DC method. For the measurement, a sample of the powder was uniaxially pressed into a disk which was then sintered at 1550°C for 10 h in air. The sintered disk was cut into a bar using an ISOMET low speed diamond saw. Electrical contacts were made to rectangular bar using platinum wires. The conductivity was measured at temperatures ranging from 450 to 600°C in flowing air and humidified (3% H_2O) 4% H_2 .

Figure 11 shows the electrical conductivities of LSCF and LSMT measured in air. For comparison, the electrical conductivities of LSCF and LSMT reported by Kolotygin⁷ are included. The conductivity of our LSCF measured in air is comparable to the conductivity for LSCF reported by Kolotygin and co-workers, but the conductivity of our LSMT is about a factor of 5 lower than that obtained by Kolotygin and co-workers. It should be noted that Kolotygin and co-workers measured the electrical conductivities of LSCF and LSMT at 950°C and 800°C, respectively. Since we measured the electrical conductivity of LSCF and LSMT at a much lower temperature range than Kolotygin and co-workers, we extrapolated their high temperature data to the temperature range at which we performed our measurements. It should also be noted that Kolotygin and co-workers used a different processing condition to make their LSMT which could account for differences in electrical conductivity observed between our LSMT and theirs.

Figure 12 shows the conductivity of LSCF measured in air and humidified 4% H₂. The conductivity of LSCF decreased about an order of magnitude when the atmosphere was switched from air to humidified 4% H₂. The total conductivity of doped lanthanum chromium oxide is known to be mainly p-type electronic conductivity. Therefore, the conductivity of LSCF is expected to decrease when the oxygen partial pressure (pO₂) is decreased when switching from air to humidified H₂. The conductivity of LSCF in humidified 4% H₂ was measured to be 1.37, 1.71, and 2.36 S/cm at 443, 493 and 593°C, respectively. Based on these results, we concluded that the electronic conductivity of 1.71 S/cm at 493°C would be sufficient to meet the performance and result in a ASR of 0.06 Ω cm² at ~500°C for a 0.1 cm thick LSCF anode.

The conductivity of LSMT could not be measured because LSMT crumbling into pieces when the air was switched to humidified 4% H₂ at ~600°C. The instability of LSMT may be related to the mechanical stress that developed as a result of the volume increase of the Mn cation when it undergoes reduction in reducing atmosphere.

⁷ V.A. Kolotygin, E.V. Tsipis, M.F. Lü, Y.V. Pivak, S.N. Yarmolenko, S.I. Bredikhin, and V.V. Kharton, Solid State Ionics, 2013, **251**, 28-33

Figure 10. XRD pattern of (a) $(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{Cr}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$ (LSCF) sintered disk, (b) $(\text{La}_{0.25}\text{Sr}_{0.75})_{0.95}\text{Mn}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$ (LSMT) sintered disk, and (c) $\text{Ce}_{0.9}\text{Sm}_{0.1}\text{O}_{2-\delta}$ powder.

Figure 11. Total conductivity of LSCF and LSMT measured in air.

Figure 12. Total conductivity of LSCF measured in air and wet (3% H₂O) 4% H₂.

The electrical conducting property of SDC10 was also evaluated. Acceptor-doped cerias, such as SDC10, are known to exhibit electronic conductivity under low oxygen partial pressure (pO_2) at high temperatures. They have also been shown to be resistant to sulfur poisoning and coking which are two major concerns when utilizing natural gas as the fuel. A sample of SDC10 powder

was uniaxially pressed into a disk and sintered at 1250°C for 10 h in air. The relative density of the disk was determined to be 98% of the theoretical density of SDC10. The electrical conductivity was measured as a function of oxygen partial pressure, pO_2 , at 500°C and 600°C using an AC impedance method. **Figure 13** shows the total conductivity of SDC10 as a function of the measured at 500°C and 600°C. At moderate oxygen partial pressure, $pO_2 = 10^{-15}$ atm, the conductivity is predominantly ionic and remains constant. As the oxygen partial pressure was decreased to lower values, $pO_2 = 10^{-20}$ atm, the total conductivity increased by factor of about three, from 2.1×10^{-2} to 6.5×10^{-2} S/cm, at 600°C, but increased only slightly at 500°C. At these lower oxygen partial pressures the total conductivity increases due to an increase in the electronic conductivity resulting from the reduction of Ce^{4+} to Ce^{3+} . The electronic conductivity of SDC10 observed at low pO_2 at 500°C and 600°C was considered not to be high enough to use SDC10 as the anode.

Figure 13. Total electrical conductivity of the SDC10 versus oxygen partial pressure (pO_2). Oxygen partial pressure was measured *in-situ* using an YSZ oxygen sensor.

The composition stability of LSCF was investigated at 500°C by measuring the electrical conductivity of a sintered disk of LSCF in 4% H_2 and simulated shale gas. To prepare the sintered disk, a sample of LSCF powder was uniaxially pressed into a disk and sintered at 1550°C for 10 h in air. The relative density of the disk was determined to be 92% of the theoretical density of LSCF. The sintered disk was cut into a bar using an ISOMET low speed saw. Contacts were made to the rectangular bar using platinum wires and the electrical conductivity was measured using a 4-probe DC method. **Figure 14** shows the time dependence

of the total electrical conductivity of LSCF in humidified (3 vol% H₂O) 4% H₂ and in simulated shale gas at 500°C. After switching from air to humidified 4% H₂, the conductivity continually decreased with time until it reached 1.66 S/cm and then remained stable at this value for >50 h. The feed gas was switched to the humidified (3 vol% H₂O) simulated shale gas and the electrical conductivity was measured. The conductivity began to increase, reaching a conductivity level of 2.58 S/cm where it remained stable for about 50 h. The higher electrical conductivity of LSCF in simulated shale gas compared to 4% H₂ is due to the shale gas having a higher pO₂ than 4% H₂.

Figure 14. Electrical conductivity of LSCF versus time in wet (3 vol% H₂O) 4% H₂ and wet (3 vol% H₂O) simulated shale gas at ~500°C.

Composite anode development

Based on the selection of LSCF as the anode material, three composite anode materials were prepared, LSCF/BaCe_{0.7}Zr_{0.1}Y_{0.2}O_x (LSCF/BCZY712), LSCF/BaCe_{0.5}Zr_{0.3}Y_{0.2}O_x (LSCF/BCZY532), and LSCF/BaZr_{0.7}Pr_{0.1}Y_{0.2}O_x (LSCF/BZPY712), and their phase stability evaluated. To prepare a composite disk, a 50:50 vol% ratio of LSCF and a sample of the candidate electrolyte material were mixed and the resulting mixture ground using a mortar and pestle. The ground powder was uniaxially pressed into a disk which was sintered at 1300°C for 5 h in air. **Figure 15** shows the XRD patterns for the three sintered composite disks. For comparison, the XRD patterns of BCZY712, BCZY532, and BZPY712 are also shown. Based on these results, it was observed that LSCF reacted with BCZY532 and BCZY712 forming new unidentified phases whereas LSCF/BZPY712 exhibited the least amount of reaction.

Given that we anticipated having to sinter the electrolyte thin film at a temperature above 1300°C, the phase stability of the LSCF/BZPY712 composite was evaluated at sintering temperatures above 1300°C. **Figure 16** shows the XRD pattern of LSCF/BZPY712 sintered at 1400°C for 5 h in air. For comparison, the XRD pattern of BZPY712 and LSCF/BZPY712 sintered at 1300°C are also shown. The XRD pattern of LSCF/BZPY712 sintered at 1400°C showed that a significant amount of reaction had occurred between LSCF and BZPY712 as evident by the increase in the intensity of the unidentified peaks when compared to the XRD pattern of LSCF/BZPY712 sintered at 1300°C. Based on these results, it was determined that the BZPY712 thin-film electrolyte with the LSCF/BZPY712 electrode (support) had be sintered at temperatures below 1400°C.

Figure 15. XRD spectra of LSCF/BZPY712 sintered disk (top), LSCF/BCZY532 sintered disk (middle), and LSCF/BCZY712 sintered disk (bottom). Disks were sintered at 1300°C for 5 h in air. For comparison, the XRD pattern of BCZY712 and LSCF powders are also shown.

Figure 16. XRD patterns of (a) LSCF/BZPY712 composite disk sintered at 1400°C for 5 h in air, (b) LSCF/BZPY712 composite disk sintered at 1300°C for 5 h in air, and (c) BZPY712 and LSCF powders.

The electrical conductivity of a LSCF/BZPY composite disk at 50 and 60 vol% of LSCF/BZPY was measured to determine the effect of LSCF content on the electrical property. **Figure 17** shows the XRD patterns of the LSCF/BZPY composite disks sintered at 1300°C for 5 h in air. Both composite disks show similar XRD patterns except increased peak intensity of LSCF phase in the 60/40 vol% composite.

The electrical conductivity of the LSCF/BZPY composite electrode was measured as a function of the LSCF content at 500°C using the 4-probe DC method as shown in **Figure 18**. The total conductivity of the composite increased with increasing the LSCF content both in air and H₂ atmosphere which was not unexpected since LSCF dominates the conductivity of composite electrode. Electrical conductivity of 4.6×10^{-2} S/cm was measured with 60 vol% LSCF/BZPY composite anode at 500°C in hydrogen. With this conductivity, an ASR of $2.2 \text{ } \Omega\text{-cm}^2$ was estimated for a 0.1 cm thick 60 vol % LSCF/BZPY composite anode.

Figure 17. XRD patterns of 50/50 LSCF/BZPY (top) and (b) 60/40 LSCF/BZPY (bottom).

Figure 18. Total conductivity of the LSCF/BZPY composites as a function of LSCF content measured at $\sim 500^{\circ}\text{C}$.

We also investigated both Ni/BZY and Cu/BZY composites for the thin-film electrolyte substrate as well as an anode. Based on the electrical conductivity of Ni metal, the ASR of the Ni/BZY (>59 wt % of Ni) composite substrate is expected to be on the order of $10^{-1} \Omega\text{-cm}^2$, which is considerable smaller than the milestone target of $1.5 \Omega\text{-cm}^2$ at 500°C in hydrogen; however, we have not measured its conductivity. The electrical conductivity of the 40 vol % Cu/BZPY composite anode was measured at $\sim 500^{\circ}\text{C}$ using 4-probe DC method. **Figure 19** shows the total conductivity of the Cu/BZY composite anode as function of time. A very high electrical conductivity, $1.1 \times 10^4 \text{ S/cm}$ was measured and was relatively stable for more than 90 h in humidified (3 vol % H_2O) 3.5% H_2 balance He. Based on the measured conductivity of Cu/BZY composite, ASR of the 0.1-cm thick 40 vol % Cu/BZY composite anode is estimated to be approximately $9 \times 10^{-6} \Omega\text{-cm}^2$.

Figure 19. Electrical conductivity of the Cu/BZY cermet anode measured at $\sim 500^{\circ}\text{C}$ in humidified 3.5% H_2 .

Electrolyte Film Fabrication

Based on our previous reactivity study of LSCF and BZPY there was concern that they would react at 1400°C to form side products that could degrade the electrical conductivity of the anode as well as the electrolyte. Therefore, the BZPY electrolyte film on LSCF/BZPY substrate should be sintered at temperatures below 1400°C . Doped barium zirconates; however, require a higher sintering temperature ($1600\sim 1700^{\circ}\text{C}$) to obtain highly density electrolyte. The disk of $\text{BaZr}_{0.7}\text{Pr}_{0.1}\text{Y}_{0.2}\text{O}_x$ (BZPY) sintered at 1600°C reached 96% of the theoretical density, but it reached only 89% of the theoretical density when it was sintered at 1450°C for 5 h, which indicated that higher sintering temperature would be required for film processing. This raised the concern that BZPY film on a LSCF/BZPY substrate that was sintered at temperatures $>1450^{\circ}\text{C}$ may not work due to the reaction between the LSCF and BZPY.

To fabricate electrolyte films on porous electrolyte substrates required introducing an electrical conducting material, such as LSCF or a conductive metal that is free from coke formation to be infiltrated into the pores of a sintered substrate. To prepare a porous substrate, a powder mixture of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_x$ (BZY, Praxair Specialty Ceramics) and carbon (Fisher Scientific) was ball-milled in isopropyl alcohol using zirconia media. After milling, the isopropyl alcohol was evaporated yielding a dry powder. The dried powder was uniaxially pressed into a disk which was then partially sintered for 4 h at 1100°C in air. A thin film of BZPY electrolyte was fabricated using a colloidal dip coating process. The partially sintered porous substrate was dipped into the colloid solution containing BZPY electrolyte powder and the solvent removed by drying the film/substrate on a hot plate. The film was sintered in ambient air at temperatures $1350\text{--}1600^{\circ}\text{C}$ using heating and cooling rates of 180°C/h .

Figure 20 shows the SEM micrographs of the BZPY film sintered at 1600°C for 5 h. The film was still porous even at after sintering at this high temperature. Sintering at a temperature above

1600°C may help further densify the electrolyte, but it was not attempted due to concerns over evaporation of barium oxide and the temperature limitation of our furnace. It is well-known that barium oxide evaporates from barium zirconates and barium cerates at temperatures above 1500°C. To minimize the loss of barium oxide due to evaporation during high-temperature sintering, the disk is covered with the same powder as the disk constituent, then the surface of a sintered disk is polished off. This practice; however, is impractical for a thin-film process, but a crucible containing the powder can be placed next to the film sample inside the furnace during high temperature sintering to minimize/eliminate barium loss from the film.

Doped barium cerates are known to have high proton conductivity and they can be sintered at much lower temperatures ($\approx 1400^\circ\text{C}$) than the doped barium zirconates. Adding a doped barium cerate layer on top of BZPY is one approach to reduce the sintering temperature of BZPY and increase densification at lower sintering temperature. We used a yttrium doped barium cerate, $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_x$ (BCY), for this purpose.

Figure 20. SEM micrographs of BZPY film on a BZY substrate; a) fracture and b) film surface. Film was sintered at 1600°C for 5 h in air.

To investigate the proof of concept of using a BCY as a sintering aid, the BCY film was first fabricated on a porous BZY substrate. **Figure 21** shows the SEM micrographs of the BCY film on a porous BZY substrate. The film was sintered at 1350°C for 10 h in air. A dense BCY film having a film thickness of $\approx 11\ \mu\text{m}$ formed on the porous BZY substrate with the film surface having relatively well-defined grain boundaries.

Figure 21. SEM micrographs of BCY film on a BZY substrate; a) fracture and b) film surface. Film was sintered at 1350°C for 10 h in air.

Figure 22 shows the SEM micrographs of the BCY/BZPY composite film sintered at 1350°C for 10 h in air. To fabricate the composite film, the BZPY green film was first made by dipping the substrate into a BZPY colloid solution. After drying the solvent, the substrate was dipped into a BCY colloid solution to put a BCY coating on top of the BZPY and then the green film was sintered. The SEM micrograph of the fracture surface showed a ~5 μm thick dense BCY layer at the top of the film and ~4 μm thick BZPY layer with some isolated pores. The SEM micrograph of the surface showed a dense film with relatively well-defined grain boundaries similar to the BCY film shown in the **Figure 21**. This result clearly showed the benefit of using BCY as a sintering aid allowing a dense composite film of BCY/BZPY to be fabricated at much lower sintering temperature than a film of BZPY. BCY is known to be chemically unstable toward CO₂, forming barium carbonate, that could cause degradation of the electrolyte. Since the BCY side of the electrolyte will be located at the cathode (air) side and the chemically stable BZPY layer will be located at the anode (hydrocarbons) side, the chemical instability of the BCY in the electrolyte is not expected to be problematic.

Figure 22. SEM micrographs of BCY/BZPY composite film on a BZY substrate; a) fracture and b) film surface. Film was sintered at 1350°C for 10 h in air.

The electrical property of the BZPY electrolyte was characterized using a BZPY disk that was prepared by compressing the powder using an uniaxially press to form the disk which was then sintered at 1600°C for 10 h in air. The relative density of the sintered disk was measured to be 96% of the theoretical density of BZPY. Electrical conductivity of the sintered BZPY was measured as a function of temperature using the AC impedance method with a porous platinum electrode. **Figure 23** shows the total conductivity of BZPY measured at temperatures from 450 to 650°C in dry and wet (3 vol % H₂O) air. Below temperature 650°C, the conductivity in wet air is higher than in dry air indicating proton conductivity development in wet atmosphere by proton charge carrier incorporation through the reaction below.

The ionic transference number measurement was evaluated using a concentration cell. The equations used to calculate the transference number are shown below:

$$OCV_{Nernst} = -(t_H + t_O) \frac{RT}{2F} \ln(P_{H_2}''/P_{H_2}') + t_O \frac{RT}{2F} \ln(P_{H_2O}''/P_{H_2O}')$$

$$t_{ion} = t_O + t_H = (OCV_{observed}) / (OCV_{Nernst})$$

When the p_{H_2O} is the same on both sides, the equation for OCV reduces to:

$$OCV_{Nernst} = -(t_H + t_O) \frac{RT}{2F} \ln(P_{H_2}''/P_{H_2}')$$

$t_H + t_O$ was determined to be 0.98. When the p_{H_2} is the same on both sides, the equation for OCV reduces to:

$$OCV_{Nernst} = t_O \frac{RT}{2F} \ln(P_{H_2O}''/P_{H_2O}')$$

t_O was determined to be 0.06. Thus t_H was determined to be 0.92.

Figure 23. Total conductivity of the BZPY in dry and wet (3 vol % H₂O) air.

Figure 24 shows the total conductivity of BZPY measured at temperatures from 450 to 650°C in wet (3 vol %) air and wet 4 % H₂. Yttrium-doped barium zirconate is a mixed conductor (mixed oxygen-, proton-ion and electron conductor) and the main charge carrier depends on the temperature, oxygen partial pressure, and moisture concentration. The total conductivities in H₂ and Ar are similar to those in air at temperatures below 550°C, but lower than those in air above 550°C because the electron hole conductivity dominates in air. Total conductivity of 4.1×10^{-3} S/cm was measured at 500°C in H₂.

The electrical conductivity of the BZY (BaZr_{0.8}Y_{0.2}O_x) electrolyte was measured in wet air and wet hydrogen atmospheres. The BZY powder was uniaxially pressed into a disk and sintered for 10 h at 1600°C in air. To increase the sinterability of the disk, 0.3 wt % of CuO was used as a sintering aid. The relative density of the sintered disk was measured to be 97% of the theoretical density of BZY. Electrical conductivity of the sintered BZY electrolyte was measured as a function of temperature and atmosphere using AC impedance method. **Figure 25** shows the total conductivity of BZY measured at temperatures from 450 to 650°C in wet (3 vol % H₂O) air and wet 3.6% H₂.

The total conductivity of 9.3×10^{-3} S/cm is measured at 500°C in hydrogen. The total conductivity in H₂ is similar to that in air below 550°C, but lower at temperatures above 550°C. Similar conductivity behavior was observed in the BZPY electrolyte [FY2015-Q3]. Electromotive force (EMF) measurements under hydrogen atmosphere showed that the BZY is almost pure proton conductor (proton transference number >0.95 at 500°C).^{8,9} This shows a proton conductivity $>8.8 \times 10^{-3}$ S/cm (>8.8 mS/cm) for the BZY electrolyte at 500°C in hydrogen.

⁸ K. Katahira, Y. Kohchi, T. Shimura, H. Iwahara, *Solid State Ionics*, 2010, **138**, 91-98

⁹ T. Schober, H. G. Bohn, *Solid State Ionics*, 2000, **127**, 351-360

Figure 24. Total conductivity of the BZPY in wet (3 vol % H₂O) atmosphere. Conductivity was measured using AC impedance method.

Figure 25. Total electrical conductivity of the BZY measured as function temperature in wet air and wet hydrogen atmospheres.

Task 4: Fuel Cell Development

A test stand capable of testing either button cells or a single 5-cm x 5-cm (25 cm²) cell was constructed as shown in **Figure 26**. A manifold system allowed the anode to operate on H₂, propane, or a simulated shale gas. A potentiostat/impedance analyzer capable of dc currents up to 3 amps was used for the cell testing. The 25 cm² cell holder/manifold (**Figure 27**) was purchased from FuelCellMaterials.com.

Figure 26. Design of the single cell test stand.

Figure 27. A 5 cm x 5 cm Test Fixture Kit for anode or electrolyte-supported solid oxide fuel cells from Fuel Cell Materials.com (a division of NexTech Materials, Ltd.).

Single cell performance testing operating on H_2

The goal of this task was to demonstrate a 25-cm² single cell operating on H_2 with cell size of; current density > 100 mA/cm² for 50 h; 500°C; with less than 10% decrease in power density over 50 h. Given the size of our large press, we attempted to fabricate 6-cm x 6-cm (36-cm²) cells consisting of dense BaCe_{0.8}Y_{0.2}O_x / BaZr_{0.8}Y_{0.2}O_x (BCY/BZY) layered electrolyte films on ~1-mm thick porous NiO/BaZr_{0.8}Y_{0.2}O_x composite anode substrate. To prepare the anode substrate, a powder mixture of BaZr_{0.8}Y_{0.2}O_x (BZY, Praxair Specialty Ceramics), NiO (Alfa Aesar), carbon lamp black (Fisher Scientific), and binder was ball-milled in isopropyl alcohol using zirconia media. After milling, the isopropyl alcohol was evaporated and the dried powder was then sieved. The sieved powder was uniaxially pressed into a disk and partially sintered for 5 h at temperatures ranging from 100 to 1225°C in air. Pressing a substrate a square die (**Figure 28**) proved to be challenging because of the difficulty in packing powder uniformly into the die and then releasing the pressed disk without breaking. Partially sintering a flat and crack-free large anode slab was another challenge. **Figure 29** shows an example of the partially sintered anode slab with cracks at the corners that developed during sintering. We optimized the powder preparation process and packing, pressing, and sintering conditions to eliminate the defects in the partially sintered porous anode slabs. **Figure 30** shows the partially sintered anode substrates using the improved process conditions.

Figure 28. 3"x 3" square die set used to press large anode slabs.

Figure 29. Partially sintered anode slab showing cracks at the corners.

Figure 30. Partially sintered anode substrates using improved processing conditions.

Thin films of layered BCY-BZY electrolyte was fabricated by colloidal dip coating process using a home-made dip-coater (**Figure 31**). To fabricate the layered film, the BZY film was first deposited by dipping the substrate into a BZY colloid. After drying the solvent the substrate was dipped into a BCY colloid to get the BCY coating on top of the BZY, then the film was dried

and sintered. Dipping and drying steps were repeated to obtain proper film thickness for both BZY and BZY coating. The film was sintered in an ambient air at temperatures ranging from 1350 to 1485°C using heating and cooling rates of 180°C/h.

Figure 31. Home-made dip coater setup.

Electrolyte film fabrication was initially done using a substrate containing 55 wt% NiO in the NiO/BZY mixture. The sintered substrate, however, was insulating when the resistance of the substrate was measured at room temperature after reducing the NiO phase using 4% H₂ at 600°C. This result indicates that the amount of NiO in the substrate was not enough to make percolated network of Ni grains in the substrate after reduction of the NiO. A sintered substrate made with 60 wt% of NiO was also insulating after reduction. To ensure good electronic conductivity of the substrate, 69 wt% NiO was used to prepare the NiO and BZY mixture. The sintered substrate made with 69 wt % of NiO was conducting after the reduction treatment.

Figure 32 shows the SEM micrographs of the fracture surfaces of the layered BCY-BZY films. Both films were made on a circular 1" NiO/BZY composite substrate and were sintered at 1420°C for 5 h in air. Films were made on the NiO/BZY substrate with (a) 60 and (b) 69 wt% NiO, respectively. The SEM micrographs show the porous substrates and dense electrolyte films with film thickness of 10-11 μm .

Figure 32. SEM micrographs of layered BCY-BZY electrolyte films on NiO/BZY porous substrates; fracture surfaces of film on a substrate with (a) 60 and (b) 69 wt% NiO. Both films were sintered at 1420°C for 5 h.

Figure 33 shows the partially sintered porous anode substrate and the electrolyte film after drying the solvent. The dried film was then sintered in air for 5 h at 1485°C. During sintering, four alumina bars were used as weights (**Figure 34**) to prevent warping of the sample. **Figure 35** shows the photographs of the surfaces of fully sintered electrolyte film and the porous anode. The dimension of the sintered electrolyte film/anode substrate is $\approx 6.1\text{-cm} \times 6.1\text{-cm} \times 0.01\text{-cm}$.

The performance of the 25 cm^2 fuel cell is currently be measured using the fuel cell test stand. The single cell is sandwiched between two metal blocks with a ceramic gasket on each side of a cell as shown in Figure 17. The dimensions of the cell blocks are 6-cm x 6-cm with an active area of 5-cm x 5-cm after the sealing gasket is applied.

Figure 33. Partially sintered porous anode substrate (left) and the electrolyte deposited on anode substrate after drying the solvent (right).

Figure 34. Alumina bars are used as weight to prevent warping of the sample during sintering.

Figure 35. Fully sintered layered BCY-BZY electrolyte film on porous NiO/BZY anode substrate.

We tested the cell but it exhibited extremely poor performance which was attributed to the inability to achieve a good seal due to warping along the edges of the cell and the presence of cracks that allowed H_2 cross-over, which was observed to be fairly significant. We produced a second 5 cm x 5 cm cell but it cracked while we were preparing to initiate the test. Given the aggressive timeline for this project, we made the decision to conduct the test using 1-in. diameter button cells.

To prepare the 1-in. diameter button cells, a thin film of layered BCY-BZY electrolyte was fabricated on an anode substrate by a colloidal dip coating process discussed above. The sieved powder was uniaxially pressed into a disk with 1" size die and partially sintered for 5-10 h at 950-1000°C in air. To fabricate the layered film, the BZY film was first deposited by dipping the substrate into a BZY colloid. After drying the solvent the substrate was dipped into a BCY colloid to get the BCY coating on top of the BZY, then the film was dried and sintered. Dipping and drying steps were repeated to obtain proper film thickness for both BZY and BCY coating. The film was sintered in an ambient air at temperatures of 1400~1420°C using heating and cooling rates of 180°C/h. Fuel cell performance of the button cell was measured using a platinum electrode as the cathode. To prepare the cathode, a platinum paste (Heraeus) was brush-painted on the electrolyte and was heated for 1 h at 850°C in air. The film side of a disk was then sealed to an alumina tube with a gold O-ring. A gas-tight seal formed when the assembly was heated to 900°C or above, and spring-loaded rods squeezed the gold O-ring between the cell and the alumina tube.

Figure 36 and **Figure 37** show the current-voltage characteristics and the power densities of a cell measured at 500 and 600°C. Humidified (3 vol % H_2O) H_2 and air were used as a fuel and an

oxidant, respectively. At 600°C, a power density of $\sim 110 \text{ mW/cm}^2$ was measured at a current density of $\sim 250 \text{ mA/cm}^2$. The cell performance was fairly stable over a 100 h. At 500°C, a maximum power density of $\sim 45 \text{ mW/cm}^2$ was measured at a current density of $\sim 80 \text{ mA/cm}^2$. SEM analysis of the cell after test shows (Figure 38) a dense electrolyte with a thickness of about 18- μm . The measured open circuit voltage (OCV) of $\sim 1.01 \text{ V}$ at both 500 and 600°C were little lower than the theoretical OCV of $\sim 1.1 \text{ V}$. The lower OCV might be due to the gas leak by an imperfect gas-tight seal. Because of the high-temperature sintering process required for the electrolyte film, it was difficult to prevent the button cell from warping during sintering. The warping of a cell caused an imperfect seal which lowered the OCV. Gas leakage was also another concern that would lead to an increase in resistance of both ohmic and electrode polarization resistances, and thereby lowering the cell performance.

Figure 36. Current-voltage characteristics and power density of a cell measured at 600°C in wet hydrogen and air. The electrolyte thickness is $\sim 18\text{-}\mu\text{m}$.

Figure 37. Current-voltage characteristics and power density of a cell measured at 500°C in wet hydrogen and air. The electrolyte thickness is ~18- μm .

Figure 38. SEM micrograph of the fracture surface of a button cell after fuel cell test.

Figure 39 shows the impedance plots of a cell measured under open circuit condition. The high frequency intercepts represent the ohmic resistance of the electrolyte, wires, and wire contacts. The low frequency portions of the spectra represent the sum of the anode and cathode polarization resistances of the cell. The ohmic and electrode polarization resistance of the cell at 600°C were measured to be 0.82 and 1.9 $\Omega \text{ cm}^2$, respectively. At 500°C, much higher electrode polarization resistance of 10 $\Omega \text{ cm}^2$ was measured. Impedance analysis of the cell shows that the electrode polarization mainly limits the cell performance at both temperatures. The main

contribution of the electrode resistance is not known at this point, but it is believed to be mainly due to the Pt cathode. The thickness of the anode, 1.3 mm, could also be the cause of the high electrode polarization resistance of the cell.

Figure 39. Impedance plot of a cell measured under open circuit condition.

The fuel cell performance of the cell with $\sim 18\mu\text{m}$ thick electrolyte was not as high as we expected to achieve. We believed that the performance could be increased by decreasing the thickness of the anode thickness and reducing the electrolyte thickness from $18\mu\text{m}$ to $10\mu\text{m}$. We produced a cell with an electrolyte thickness of $\sim 8\mu\text{m}$ and tested it. The new cell showed a significant increase in performance with a peak power density of about 180 mW/cm^2 at 500°C and 280 mW/cm^2 at 600°C as shown in **Figure 40**. The long-term stability of the cell was tested over a 100 h period with the current density only decreasing slightly from about 200 to 187 mA/cm^2 as shown in **Figure 41** with about a 10% decrease in maximum peak power density as shown in **Figure 42**.

Figure 40. I-V and Power density of a button cell with a $\sim 8\text{-}\mu\text{m}$ thick electrolyte layer tested in H_2 .

Figure 41. Long-term stability of a button cell with a $\sim 8\text{-}\mu\text{m}$ thick electrolyte layer measured at 500°C in H_2 .

Figure 42. I-V and Power density of a button cell with a ~8- μm thick electrolyte layer before and after 100 h durability test at 500°C in H_2 .

Demonstrate a single cell operating on propane

The goal of this task was to demonstrate a 25 cm^2 single cell operating on propane (to dehydrogenate the propane to propylene) at 500°C exhibiting a current density $> 50\text{ mA/cm}^2$ for 24 h with a product yield $\geq 50\%$ (and less than a 10% decrease in yield over the course of the 50 h test) and selectivity to propylene of $> 95\%$. Key to achieving this goal was to integrate the NOD catalyst into the anode so that the performance of the anode and the catalyst was not negatively impacted.

The NiO/BYZ anode composite which was utilized in the Milestone 4.2.1 demonstration promoted severe coking when exposed to propane at 500°C which we attributed to the formation of large Ni particles that promote carbon deposition under reducing conditions. Given that we had planned to incorporate a bimetallic Pt-Ga propane dehydrogenation catalyst onto this composite anode substrate and that Pt, itself, can serve as an electron-conductor capable of replacing Ni, we proceeded with replacing the NiO with Pt/Ga to yield a PtGa/BYZ composite anode that will serve both as the anode and the propane dehydrogenation catalyst. We observed that calcining PtGa/LSCF in air to temperatures similar to the sintering process ($> 1100^\circ\text{C}$) resulted in a material that was not active for NOD. However, we found that pretreatment of the calcined PtGa/LSCF with H_2 at 500°C produced an active catalyst.

Testing was conducted using a single button cell operating on propane in the hydrogen pump mode. A number of problems plagued the experiments including poor electrical conductivity between the anode and the current collector. By coating a very thin porous gold foil onto gold mesh being used as the anode current collector resulted in a slight improvement in performance

with currents of up to 20 mA observed. In the limited number of experiments that we were able to accomplish before the project ended, both hydrogen and propane feeds produced the same current. The fact that we observed a current when exposed to propane suggests that propane was being dehydrogenating providing a proof-of-principle.

Task 5: Tech-to-Market

The project targeted developing a technology that would be economically competitive with conventional gas-to-liquids technology for producing liquid fuels at the small-scale production level of 1000 barrels per day or less compatible with production levels that could utilize stranded natural gas or biogas sources. We had targeted the production of C₃-C₄ alkanes/alkenes within the hybrid fuel cell system with an additional chemical process train downstream of the fuel cell which converted the C₃-C₄ alkanes/alkenes to hydrocarbons in the gasoline/diesel range (C₈-C₂₀).

Given the high manufacturing cost of hybrid fuel cell system coupled with the additional capital cost for the downstream chemical process train, there was concern that electricity and the liquid fuel could not be produced at a market competitive prices. The decision was made to eliminate the downstream process train and to market the C₃-C₄'s as liquefied petroleum gas (LPG). A very simplistic technoeconomic analysis was conducted within the first six months of the project which estimated that electricity and liquefied petroleum gas (LPG) could be produced at levelized cost of producing is \$0.087/kW and \$2.23/gal, respectively, assuming all the FOA targets were achieved.

When the project was initiated in October of 2014, the price of WTI crude oil was \$90.74/barrel.¹⁰ By October 2016, the price of WTI crude oil had dropped by nearly a factor of two to \$47.42/barrel. Given the drop in the price of crude oil coupled with the increasing need for significant capital investment in downstream separation processes, it became clear as we began updating the preliminary technoeconomic analysis that liquid fuels and electricity could not be produced at a cost-competitive price.

As part of our Tech-to-Market activities, we had numerous discussions with representatives of two major petrochemical companies as well as venture capital managers who funded technology development in the petrochemical industry. Based on these discussions, it was clear that there was interest in our technology for dehydrogenating propane to propylene but not for producing a liquid fuel.

¹⁰ Price data available on the U.S. Department of Energy Energy Information Administration website.

Project Activities

The goal of this project was to develop a hybrid fuel cell system that integrated a chemical process, either the dehydrogenation of propane to propylene or the non-oxidative coupling of methane to higher alkanes and alkenes, into a proton-conducting solid oxide fuel cell system that operated at temperatures ranging from 500-700°C to produce a liquid fuel and electrical power. The project targeted developing a technology that would be economically competitive with conventional gas-to-liquids technology for producing liquid fuels at the small-scale production levels (1000 barrels per day or less) required for deployment at stranded natural gas or biogas sources. The advantage of such a hybrid system is the fuel cell consumes the H₂ produced by the chemical reaction allowing higher conversion to be achieved at a lower temperature than is possible in the absence of the proton-conducting fuel cell. Among the new technologies developed were a novel highly-active bimetallic propane dehydrogenation catalyst technology capable of achieving equilibrium-predicted conversion at temperatures in the range of 500-600°C with selectivity to propylene >95%, new anode and electrolyte materials for the proton-conducting fuel cell that was able to achieve a power density of 285 mW/cm² (~500 mA/cm²) at 500°C operating on hydrogen, and a methodology for integrating the propane dehydrogenation catalyst into the fuel cell anode. A “proof-of-concept” of the hybrid fuel cell system operating on propane was demonstrated at the button cell level. Due to the accelerated schedule, the overall goal of developing and integrating methane coupling catalyst technology into the fuel cell was not completed.

Project Outputs

A. Journal Articles

No articles currently in publication. Articles being prepared for publication after patent applications are filed.

B. Papers

The following papers were presented at scientific and technical conferences:

Theodore Krause, Uthamalingam (Balu) Balachandran, Deborah Myers, Adam Hock, Carlo Segre, “Intermediate Temperature Hybrid Fuel Cell System for the Conversion of Natural Gas to Electricity and Liquid Fuels,” Presented at the 16th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting, Pittsburgh, PA, July 14-16, 2015.

U. (Balu) Balachandran, T. H. Lee, S. E. Dorris, T. R. Krause, and D. J. Myers, Intermediate Temperature Hybrid Fuel Cell System for the Conversion of Natural Gas to Electricity and Liquid Fuels, Presented at *2015 Fuel Cell Seminar*, Los Angeles, CA, November 16-19, 2015.

Theodore Krause, Uthamalingam Balachandran, Adam Hock, Debbie Myers, Carlo Segre, “Intermediate Temperature Hybrid Fuel Cell System for the Conversion of

Natural Gas to Electricity and Liquid Fuels,” Presented at the U.S. Department of Energy Hydrogen and Fuel Cells Program 2016 Annual Merit Review, Washington, DC, June 6-10, 2016.

Theodore Krause, Uthamalingam (Balu) Balachandran, Deborah Myers, Adam Hock, Carlo Segre, “Hybrid Fuel Cell Technology For Producing Chemicals, Fuels, And Electricity,” Presented at the 17th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting, Pittsburgh, PA, July 19-21, 2016.

Theodore Krause, Uthamalingam (Balu) Balachandran, Steve Dorris, Tae Lee, Deborah Myers, Adam Hock, Guanghui Zhang, Yunjie Xu, Carlo Segre and Kamil Kucuk, “Hybrid Fuel Cell System for Producing Chemicals and Electricity from Natural Gas,” Presented at the 2016 American Institute of Chemical Engineers (AIChE) Annual Meeting, San Francisco, CA, November 13-18, 2016.

Theodore Krause, Uthamalingam (Balu) Balachandran, Deborah Myers, Adam Hock, Carlo Segre, “Intermediate Temperature Hybrid Fuel Cell System for the Conversion of Natural Gas to Electricity, Liquid Fuels, and Chemicals,” Presented at the U.S. Department of Energy Hydrogen and Fuel Cells Program 2017 Annual Merit Review, Washington, DC, June 5-9, 2017.

C. Status Reports

No status reports were released.

D. Media Reports

No media reports were released other than the announcement of the award.

E. Invention Disclosures

The following two invention disclosures were filed:

ANL IN-15-105 “Multi-layered Proton-Conducting Electrolyte”
(DOE Case #: S-141,875)

ANL IN-16-071 “Alkane Activation with Single and Bi-Metallic Catalysts on Crystalline Mixed Oxide Supports” (DOE Case #: S-143,911)

F. Patent Applications

Provisional Patent application for the “Alkane Activation with Single and Bi-Metallic Catalysts on Crystalline Mixed Oxide Supports” filed September 2017.

G. Licensed Technologies

No technologies have been licensed to date.

H. Networks/Collaborations Fostered

No formal collaborations have been established; however, we have established dialogues with two major chemical companies, one solid oxide fuel cell manufacturer, and one ceramics manufacturer.

I. Websites Featuring Project Work Results

None.

J. Other Products (e.g. Databases, Physical collections, Audio/Video, Software, Models, Educational Aids or Curricula, Equipment or Instrumentation)

No other products were developed.

K. Awards, Prizes, and Recognition

No awards, prizes or recognition to date.

Follow-On Funding

No additional funding has been committed or received from other sources after the effective date of the APRA-E award.

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