EERC
Energy & Environmental Research Center
15 North 23rd Street, Stop 9018 • Grand Forks, ND 58202-9018 • P. 701.777.5000 • F. 701.777.5181
www.undeerc.org

July 30, 2019

Ms. Karlene Fine
Executive Director
North Dakota Industrial Commission
State Capitol, 14th Floor
600 East Boulevard Avenue, Department 405
Bismarck, ND 58505-0840

Dear Ms. Fine:

Subject: Quarterly Report Entitled "Low-Pressure Electrolytic Ammonia Production"
Contract No. R-036-45; EERC Fund 22946

Attached is a copy of the subject project status report for the period of April 1 through June 30, 2019.

If you have any questions, please contact me by phone at (701) 777-2982 or by e-mail at taulich@undeerc.org.

Sincerely,

Ted R. Aulich
Principal Process Chemist
Fuels and Chemicals

TRA/rlo

Attachment

LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION

Research Performance Progress Report (Quarterly)

(for the period of April 1, 2019, through June 30, 2019)

Prepared for:

Karlene Fine

North Dakota Industrial Commission
State Capitol, 14th Floor
600 East Boulevard Avenue, Department 405
Bismarck, ND 58505-0840

Prepared by:

Ted R. Aulich

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
Grand Forks, ND 58202-9018

July 2019

TABLE OF CONTENTS

LIST OF FIGURES ii

LIST OF TABLES ii

PROJECT GOALS/OBJECTIVES 1

BACKGROUND 2

ACCOMPLISHMENTS 3

PROGRESS AND STATUS 3
- Task 1 – Project Management 3
- Task 2 – IPC Synthesis Method and Performance Improvement 4
- Task 3 – PIC Membrane Synthesis Method Development and Performance/Durability Optimization 5
- Task 4 – Cathode Catalyst Screening 7
- Task 7 – Techno-Economic Analysis 8

PLANS FOR NEXT QUARTER 9
- Task 2 – IPC Synthesis Method and Performance Improvement 9
- Task 3 – PIC Membrane Synthesis Method Development and Performance/Durability Optimization 9
- Task 4 – Cathode Catalyst Screening 10
- Task 5 – PIC-Based MEA Fabrication Method Development and LPEA Unit Cell Performance/Durability Optimization (Proton and EERC) 10
- Task 6 – Design, Fabrication, and Operation of 100-g/d LPEA System 10
- Task 7 – Techno-Economic Analysis 11

PRODUCTS 11

IMPACTS 11
- Impact on Technology Transfer and Commercialization Status 11
- Dollar Amount of Award Budget Being Spent in Foreign Country(ies) 11

CHANGES/PROBLEMS 11
- Scope Issues, Risks and Mitigation Strategies 11
- Actual or Anticipated Problems or Delays and Corrective Actions or Plans to Resolve Them 11
- Changes That Have a Significant Impact on Expenditures 11

RECIPIENT AND PRINCIPAL INVESTIGATOR DISCLOSURES 11

CONFLICTS OF INTEREST WITHIN PROJECT TEAM 11

REFERENCES 12

PARNTERS AND FINANCIAL INFORMATION 12

LIST OF FIGURES

1 HB versus LPEA-based NH_3 production 1

2 LPEA process 2

3 Digital images of IPC–PBI core–shell nanofiber membrane before and after drying at 150°C in vacuum for 6 hours 5

4 TGA and DTG analysis of PBI nanofiber membrane at heating rate of 5°C/minute to 350°C, then 30 minutes at 350°C, all under nitrogen 6

5 TGA and DTG analysis of IPC–PBI core–shell nanofiber membrane at heating rate of 5°C/minute to 350°C, then 30 minutes at 350°C, all under nitrogen 6

6 Proton conductivity testing performed on an MC4 PIC membrane 7

7 Cyclic voltammograms for ECSA measurement of Pt electrode via surface oxide reduction and Cu UPD 8

LIST OF TABLES

1 Task Schedule 4

2 Measured Charge and Derived Surface Area for Pt Catalyst 8

3 HB-Based Ammonia Production Versus LPEA – Energy Consumption Comparison 9

4 Initial 18-month Budget and Expenses Through the Reporting Period 12

LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION

PROJECT GOALS/OBJECTIVES

The project goal is to demonstrate an ammonia production energy reduction of 25% by replacing state-of-the-art high-pressure Haber–Bosch-based ammonia synthesis with the Energy & Environmental Research Center (EERC)-developed low-pressure electrolytic ammonia (LPEA) process, as shown in Figure 1. To achieve the 25% production energy reduction target will require improving the LPEA process, which will require improving the polymer–inorganic composite (PIC) proton exchange membrane (PEM) on which the LPEA electrochemical cell is based. As a result, the proposed project is focused on improving the performance and durability of the PIC membrane, with the objective of producing a membrane that exhibits the following properties:

- Proton conductivity of $\geq 10^{-2}$ Siemens/centimeter (S/cm) and gas permeability of <2% at a minimum temperature of 300°C.
- Ability to sustain 10^{-2} S/cm proton conductivity for at least 1000 hours (h).
- Mechanical strength (at 300°C) comparable to that of a commercial proton exchange-based electrolyzer membrane.
- As measured in a membrane–electrode assembly (MEA) at a minimum temperature of 300°C, current efficiency of ≥65% for NH_3 formation at a current density of ≥0.25 amps/cm^2 (A/cm^2), NH_3 production energy efficiency of ≥65%, and ≤0.3% performance degradation per 1000 h of operation.

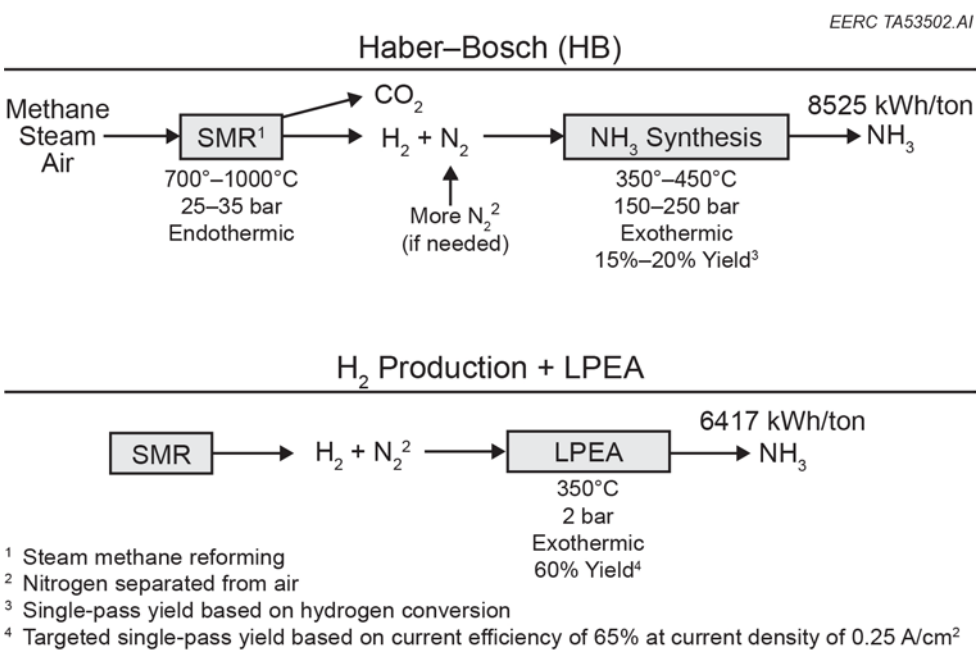

Figure 1. HB versus LPEA-based NH_3 production.

BACKGROUND

In support of U.S. Department of Energy (DOE) Energy Efficiency and Renewable Energy (EERE) Advanced Manufacturing Office (AMO) goals to reduce life cycle energy consumption of manufactured goods and more cost-effectively use hydrogen in manufacturing processes, this project is focused on optimizing and demonstrating the improved efficiency (versus HB ammonia production) of the EERC-developed LPEA production process. Because it does not require the high pressure and high recycle rate (because of low single-pass ammonia yield) of the HB process, LPEA offers the potential for significant reduction in both energy consumption and cost. Partners on the proposed project are North Dakota State University (NDSU), Proton OnSite (Proton), the University of North Dakota Chemistry Department (UND Chemistry), and the North Dakota Industrial Commission (NDIC). The LPEA process is based on an innovative EERC-developed PIC high-temperature PEM. The process operates at ambient pressure and a temperature of 300°C and uses inputs of hydrogen, nitrogen, and electricity to make ammonia. The EERC demonstrated LPEA process viability in ammonia formation tests conducted using a 0.2-watt electrochemical cell built around an early-stage PIC membrane.

To meet the above-listed membrane performance and durability specifications, the project will target development of a specifically configured PIC membrane that comprises “core–shell” inorganic proton conductor–polybenzimidazole (IPC–PBI) proton-conducting nanofibers contained within and aligned perpendicularly to the plane of a PBI matrix/membrane, as shown in Figure 2. Because each fiber core will comprise a chain of IPC particles in contiguous contact with one another throughout the chain length, each fiber will essentially function as a high-efficiency proton-conducting wire running straight through the membrane. Membrane production will utilize state-of-the-art nanofiber production/alignment and thermal pressing compositing techniques developed and deployed at project partner, NDSU.

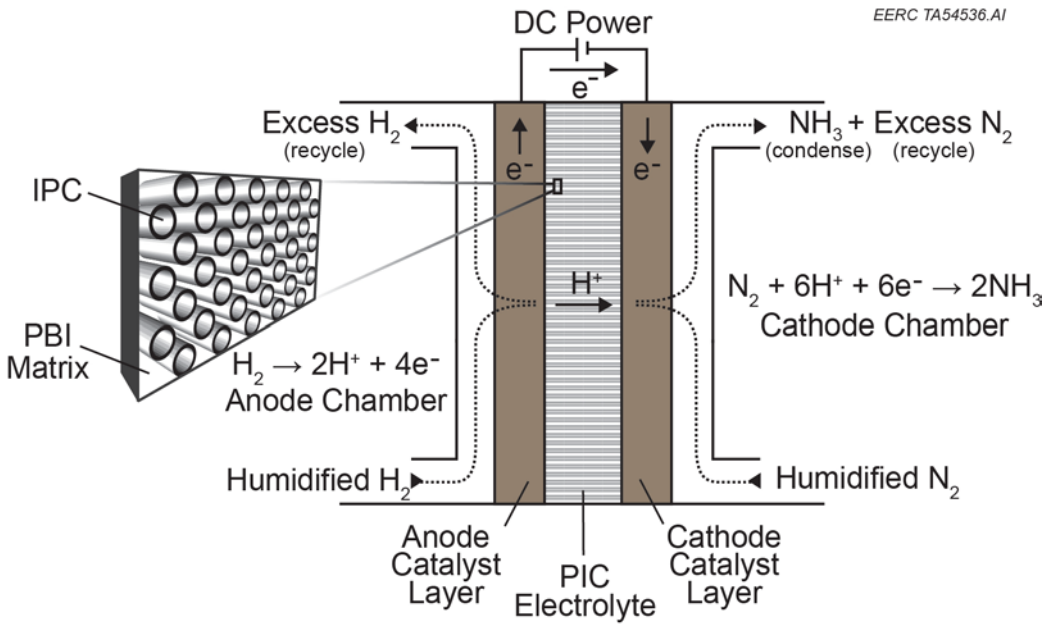

Figure 2. LPEA process.

Following fabrication of a PIC membrane that meets the above specifications, the membrane—along with selected anode and cathode catalysts—will be used to construct experimental MEAs. MEAs will be incorporated into LPEA unit cells that will be evaluated based on NH_3 formation efficiency and durability, with the objective of identifying an optimal MEA configuration. The optimal MEA configuration will be used as the basis for building a stack of several LPEA unit cells that will comprise an LPEA system capable of producing at least 100 grams/day (g/d) of NH_3. The 100-g/d LPEA system will undergo optimization and then be used to demonstrate NH_3 synthesis (from H_2) at the LPEA target production energy input requirement of 90 kWh/ton, which would translate to a total (H_2 production plus NH_3 synthesis) LPEA-based NH_3 production energy input requirement of 6417 kWh/ton, the project-targeted goal. LPEA system operation and performance data will be used to perform a techno-economic evaluation of the LPEA-based NH_3 production process.

ACCOMPLISHMENTS

- Devised, fabricated, and tested an alternative PIC membrane configuration—referred to as Membrane Configuration 4 (MC4)—comprising an IPC disk infiltrated with PBI.

- Partially completed fourth milestone (Milestone 3.3)—fabricate PIC membrane with proton conductivity $\geq 0.5\times10^{-2}$ S/cm and gas permeability <10% at 300°C—as described in Progress and Status (Task 3).

- Developed an alternative protocol for cathode catalyst screening, as described in Progress and Status (Task 4). Implementation of the protocol is contingent on DOE approval.

PROGRESS AND STATUS

Task 1 – Project Management (EERC)

- Subaward No. UND10759 with Proton was finalized, and Task 5 is active. The period of performance for this subaward is June 16, 2019, through December 14, 2019. During this period, Proton will initiate development of a method for PIC membrane-based MEA fabrication.

- The project is on schedule, as shown in Table 1.

Table 1. Task Schedule

Task No.	Task Title or Brief Description	Task Completion Date*				Task Progress Notes
		Original Planned	Revised Planned	Actual Complete	% Complete	
1	Project Management	14 June 2021			33	
2	IPC Synthesis Method and Performance Improvement	14 Dec 2019			67	
3	PIC Membrane Synthesis Method Development and Performance/Durability Optimization	14 Dec 2020			40	
4	Cathode Catalyst Screening	14 Dec 2019			67	
5	PIC-Based MEA Fabrication Method Development and LPEA Unit Cell Performance/Durability Optimization	14 Dec 2020				15 June 2019 start; under way.
6	Design, Fabrication, and Operation of 100-g/d LPEA System	14 March 2021				15 Dec 2019 start
7	Techno-Economic Analysis	14 June 2021				15 June 2020 start

* Unless otherwise noted, tasks start on 15 June 2018 project start date.

Task 2 – IPC Synthesis Method and Performance Improvement (EERC)

- The ability to regulate IPC humidity is critical to enabling and sustaining high proton conductivity at high temperature. With insufficient humidity, loss of water of hydration at increasing temperature results in conductivity loss, while too much humidity leads to excessive IPC water absorption and subsequent softening and erosion/attrition. We are preparing to use thermogravimetric analysis (TGA) to determine a humidity–temperature relationship that—if maintained—ensures both IPC integrity and maximum proton conductivity. A TGA system that allows testing with humidified gas was identified (at UND Chemical Engineering); however, the system needs a few minor modifications for application to our testing protocol. These modifications are under way.

- IPC compositional modifications are being made and evaluated with the objective of maximizing IPC proton conductivity. Modifications are selected based on their potential for establishing structural "vacancies" that facilitate proton transfer through the amorphous IPC matrix. Two modified IPC formulations have been prepared and will be evaluated for proton conductivity following completion of TGA testing to establish an improved IPC hydration management strategy.

- A new IPC material reported to offer higher proton conductivity at 300°C than our current IPC has been identified. Supplies for making the material have been procured, and material synthesis is under way. Following synthesis, the material will be evaluated for proton conductivity over a temperature range of 21°–350°C.

Task 3 – PIC Membrane Synthesis Method Development and Performance/ Durability Optimization (NDSU and EERC)

- Airflow-assisted coelectrospinning was utilized to fabricate core–shell IPC–PBI nanofibers with improved structural quality and consistency at approximately 10 times higher productivity than conventional (non-airflow-assisted) coelectrospinning. In the airflow-assisted technique, a pressurized tubular airflow around the coaxial spinneret is utilized to exert additional pulling force out of the jet. This decreases the rate of PBI precipitation at the coaxial spinneret tip, resulting in a more stable coaxial jet and formation of improved-quality (continuous and uniform-diameter/thickness core/shell) nanofibers. Figure 3 shows a PIC membrane (before and after drying) fabricated with airflow assist. The brown spots are standalone PBI deposits separate from IPC–PBI core–shell nanofibers, indicating the need for further improvement in coaxial jet stability as the jet emerges from the spinneret.

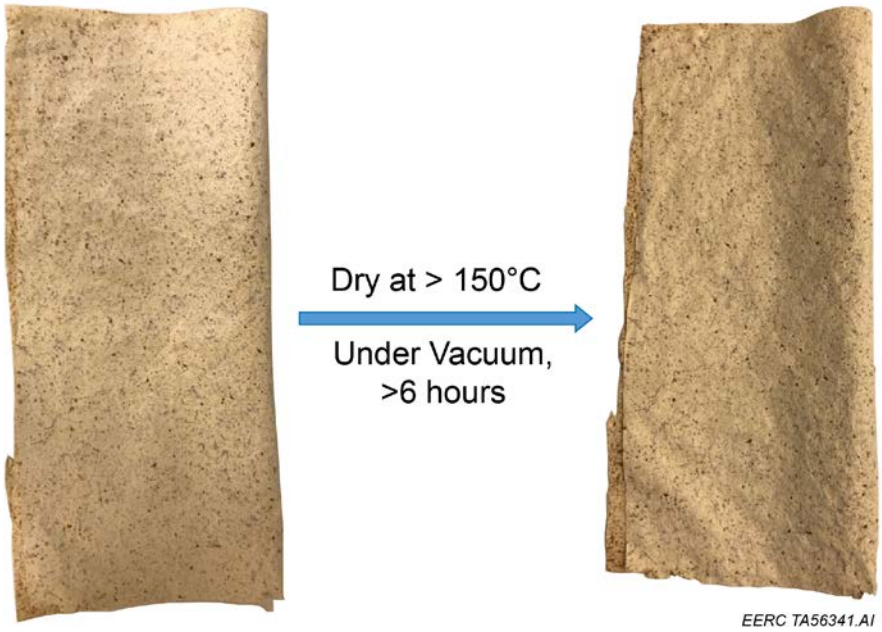

Figure 3. Digital images of IPC–PBI core–shell nanofiber membrane before (left) and after (right) drying at 150°C in vacuum for 6 hours.

- TGA was utilized to examine effects of increasing temperature on pure PBI nanofibers and IPC–PBI core–shell nanofibers fabricated with airflow assistance. The TGA tests were performed at a heating rate of 5°C/minute in N_2 environment. After reaching 350°C, temperature was maintained at 350°C for 30 minutes. Figures 4 and 5 show results for PBI and IPC–PBI core–shell nanofibers, respectively. The figures illustrate similar overall mass loss values, with loss rate differences likely due to differences in how moisture is associated within the two nanofiber materials. While the PBI nanofibers contain only absorbed moisture, the IPC–PBI core–shell nanofibers contain PBI-absorbed moisture as well as IPC-absorbed moisture and IPC water of hydration.

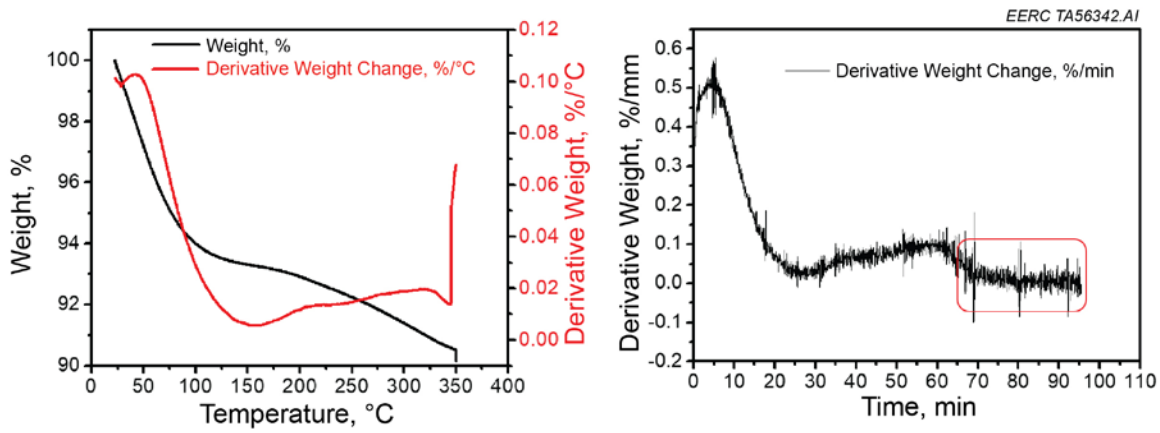

Figure 4. TGA and DTG (differential thermogravimetric) analysis of PBI nanofiber membrane at heating rate of 5°C/minute to 350°C, then 30 minutes at 350°C, all under nitrogen. Prior to analysis, membrane was washed with water, dried at 160°C for 6 hours under vacuum, and exposed to air at room temperature for 2 days.

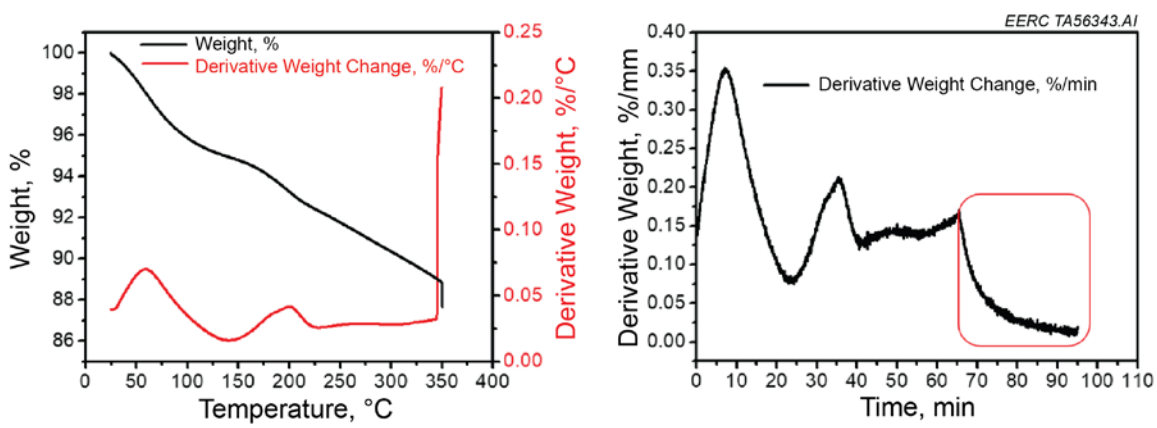

Figure 5. TGA and DTG analysis of IPC–PBI core–shell nanofiber membrane at heating rate of 5°C/minute to 350°C, then 30 minutes at 350°C, all under nitrogen. Prior to analysis, membrane was washed with water, dried at 160°C for 6 hours under vacuum, and exposed to air at room temperature for 2 days.

- Because PBI offers essentially zero proton conductivity (it is used to provide membrane flexibility, gas impermeability, and structural integrity), PIC membrane proton conductivity is a function of membrane IPC volume percentage. To increase membrane IPC loading, a core–shell IPC–PBI nanofiber membrane was soaked in 80 wt% aqueous IPC solution and then dried in air to yield an "enhanced-IPC-volume" membrane. Initial tests conducted with samples of this membrane were performed in a sealed cell, as opposed to an open cell with continuous gas flow. A proton conductivity reading of 4×10^{-2} S/cm was obtained at 250°C and a cell pressure of 15 psi, after which gasket failure resulted in test termination. Although a static cell is not an option for the LPEA process, analysis of these preliminary results may translate to a worthwhile idea for PIC membrane improvement.

- To investigate an alternative PIC membrane configuration (referred to as MC4), attempts were made to infiltrate the pores/void spaces of IPC disks (pressed from powdered IPC) with dilute PBI solution. When formed at a pressure of 20,000 psi, the IPC disks are approximately 78% dense, leaving 22% porosity for PBI infiltration. Initial infiltration attempts were made utilizing a slight vacuum to "pull" PBI solution into the porous IPC matrix. Figure 6 shows results of proton conductivity testing performed on an MC4 PIC membrane over a temperature range of 21°–325°C. The measured proton conductivity of 0.05 S/cm at 300°C illustrates that the proton conductivity target of the fourth project milestone (Milestone 3.3) has been met.

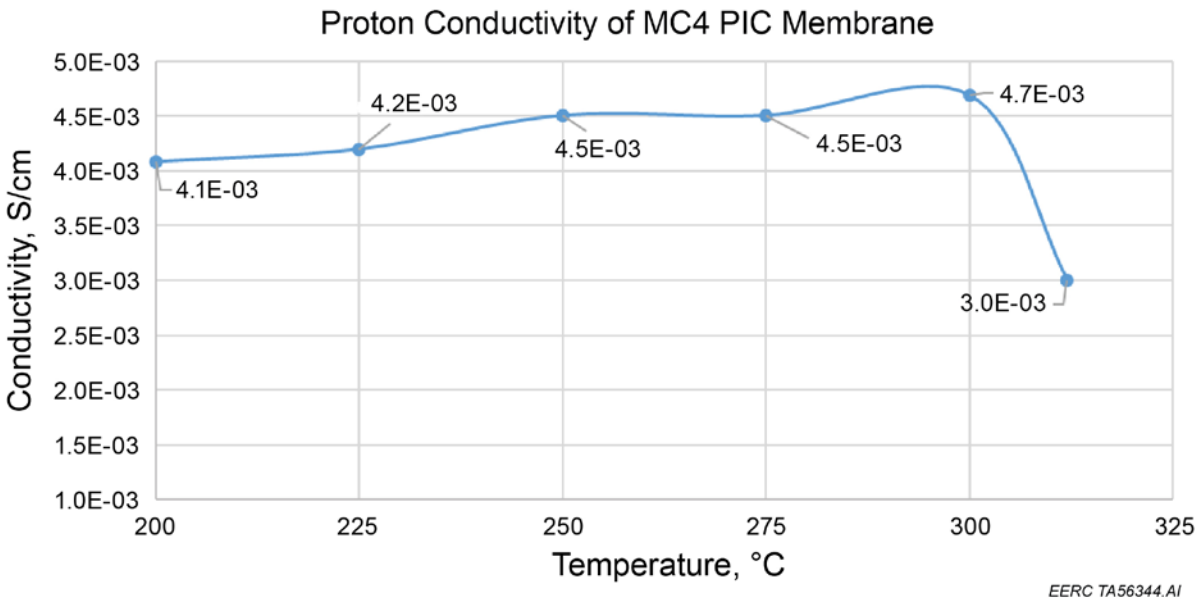

Figure 6. Proton conductivity testing performed on an MC4 PIC membrane.

Task 4 – Cathode Catalyst Screening (UND Chemistry)

- As described in the statement of project objectives (SOPO), cathode catalyst screening was to be conducted based on the electrochemical nitrogen reduction reaction (NRR). However, this approach has proven to be difficult, due in large part to the very low solubility of molecular nitrogen (N_2) in conventional and safely manageable aqueous electrolytes, especially at room temperature. This low solubility results in very low (undetectable) rates of nitrogen reduction and much higher rates of hydrogen evolution (via reduction of protons present in electrolyte solution). As a workaround, the catalyst team identified hydrazine (N_2H_4) as a surrogate for nitrogen. Hydrazine (procurable from commercial vendors as hydrazine sulfate) is readily soluble in dilute potassium hydroxide basic electrolyte. While hydrazine reduction requires breaking only a single N–N bond rather than the much stronger triple bond required for nitrogen reduction, both reactions comprise reduction of bonds between nitrogen atoms. It is proposed that catalyst screening be carried out by monitoring rates of hydrazine reduction and hydrogen evolution, with selection for further evaluation based on a strong inverse

relationship between the two competing reactions—a high rate of hydrazine reduction coupled with a low rate of hydrogen evolution. Selected catalysts will undergo in situ ammonia synthesis testing in MEAs to achieve Milestone M4.1. Use of this new plan for catalyst screening is contingent on DOE approval.

- Two methods were established for measuring electrochemical surface area (ECSA) and screening candidate catalysts by using ECSA to calculate catalyst current activity for hydrazine reduction and hydrogen evolution. The two methods are surface oxide reduction and copper "under potential deposition" (Cu UPD). Figure 7 shows cyclic voltammograms generated using the two methods with a platinum (Pt) electrode (cathode catalyst) and dilute H_2SO_4 electrolyte, and Table 2 shows ECSA values calculated for the Pt catalyst via the two methods. Catalyst screening tests will replace the Pt electrode with candidate catalyst electrodes.

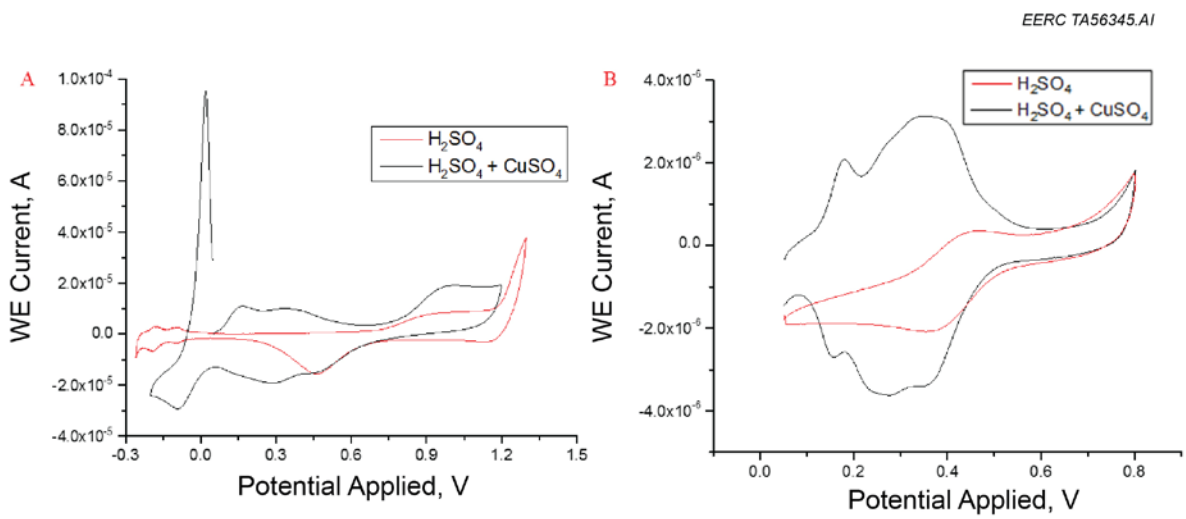

Figure 7. Cyclic voltammograms for ECSA measurement of Pt electrode via surface oxide reduction (A) and Cu UPD (B).

Table 2. Measured Charge (in millicoulombs [mC]) and Derived Surface Area for Pt Catalyst

Method	Charge, mC	Electrochemical Surface Area, cm^2
Surface Oxide Reduction	63.42	0.151
Cu UPD	69.72	0.166

Task 7 – Techno-Economic Analysis (all)

In response to reviewer input received at the June 11–12, 2019, U.S. DOE Advanced Manufacturing Office Program Review Meeting in Washington, D.C., work commenced on developing a strategy for LPEA process initial entry into the commercial ammonia industry. The

strategy will be designed to enable market-competitive ammonia production and distribution by optimal leveraging of key economic, location, and transportation factors, one of which is electricity cost. However, it is important to consider that in cases where LPEA is integrated with steam methane reforming (SMR) infrastructure—as proposed in the Market Transformation Plan and described in Figure 1 and Table 3 (originally provided in Appendix A of LPEA Project October–December 2018 quarterly report)—electricity represents about 3% (186 kWh/6417 kWh) of total ammonia production energy input, with the remaining 97% provided by natural gas.

Table 3. HB-Based Ammonia Production Versus LPEA – Energy Consumption Comparison

Process/Pathway	MWh/ton NH_3
SMR + HB – Theoretical Minimum	5587[1]
SMR + HB – State of the art	8525[2]
SMR – State of the Art (high-purity H_2 production only)	6231[3,4]
LPEA – Project Target (ammonia synthesis only)	90*
SMR + LPEA + Nitrogen Generation + Ammonia Condensation, Compression	6417**

* Based on achieving polymer–inorganic composite membrane performance targets (listed in statement of project objectives) and LPEA process operating at NH_3 production energy efficiency of 65%.

** Includes SMR and LPEA (target) energy inputs plus 10 kWh/ton for N_2 separation from air and 86 kWh/ton for NH_3 purification/condensation and compression.

PLANS FOR NEXT QUARTER

Task 2 – IPC Synthesis Method and Performance Improvement

- Perform TGA of IPC in varying-humidity atmospheres to establish an optimal temperature–humidity relationship that—if maintained—ensures IPC integrity/lifetime and maximum proton conductivity.

- Perform AC impedance (proton conductivity) testing to determine the effect(s) of IPC compositional modifications on proton conductivity. If any modifications are found to improve conductivity, additional testing will be conducted to determine the level of modification needed to provide maximum conductivity.

- Synthesize and evaluate the newly identified IPC material based on proton conductivity over a temperature range of 21°–350°C.

Task 3 – PIC Membrane Synthesis Method Development and Performance/Durability Optimization

- Improve the properties of MC4 by developing a means of increasing infiltration of PBI solution into IPC disks. The first approach will utilize a vacuum in combination with pressurized gas to force the dilute PBI solution into nearly 100% of the disk pore space.

- Acquire MC4 gas permeability data for complete fulfillment of Milestone 3.3.

- Optimize the configurations of the coelectrospinning system airflow tube and coaxial spinneret, and optimize operational parameters to reinforce laminar flow and further stabilize the coaxial jet for more uniform core–shell IPC–PBI nanofibers. One approach will investigate the performance impact of using gases other than air, including nitrogen and argon. Another potential approach involves the use of computational fluid dynamics modeling to devise a strategy for jet stabilization.

- Develop improved understanding of water/steam–IPC interactions over the temperature range of 100°–350°C, and use it to:
  - Determine needed moisture concentration in the PIC membrane and the H_2 and N_2 flows (employed during proton conductivity testing) to maximize proton conductivity and membrane integrity at 300°C.
  - Design experiments to investigate the impact of cell back pressure (up to 15–20 psi) on PIC membrane proton conductivity and integrity at 300°C.
  - Optimize the overall heat-pressing process to improve PIC membrane mechanical and thermomechanical properties.

- Continue acquiring PIC membrane proton conductivity data (via ACI [alternating current impedance] testing over an operating temperature range of ambient to 350°C), and utilize data to develop a strategy for improving membrane conductivity to meet the upcoming milestone of 0.75×10^{-2} S/cm at a temperature of at least 300°C.

Task 4 – Cathode Catalyst Screening

- Finalize procedures for applying candidate catalysts onto the surface of the glassy carbon working electrode needed for catalyst evaluation.

- Acquire ECSA measurements for candidate catalysts starting with ruthenium and ruthenium oxide on reduced graphene oxide (Ru–RuO_2/RGO) and then Ru on carbon (Ru/C).

- Finalize RDE (rotating-disk electrode) procedures for acquisition of additional data needed to derive/calculate the following characteristics for candidate cathode catalysts:
  - Hydrogen evolution activity
  - Hydrazine reduction activity

Task 5 – PIC-Based MEA Fabrication Method Development and LPEA Unit Cell Performance/Durability Optimization (Proton and EERC)

- Continue integration and active participation of Proton as project partner.

Task 6 – Design, Fabrication, and Operation of 100-g/d LPEA System (all)

- Task initiation scheduled for 15 December 2019.

Task 7 – Techno-Economic Analysis (all)

- Develop strategy/deployment scenario for economically competitive initial entry of LPEA into the commercial ammonia industry.

PRODUCTS

- None.

IMPACTS

Impact on Technology Transfer and Commercialization Status

- No commercialization impacts, progress, issues, or concerns to report during this quarter.

Dollar Amount of Award Budget Being Spent in Foreign Country(ies)

- No spending of any project funds in any foreign countries has occurred or is planned.

CHANGES/PROBLEMS

Scope Issues, Risks and Mitigation Strategies

- Request to utilize alternative cathode catalyst screening protocol, as described in Progress and Status (Task 4).

Actual or Anticipated Problems or Delays and Corrective Actions or Plans to Resolve Them

- None during this reporting period.

Changes That Have a Significant Impact on Expenditures

- None.

RECIPIENT AND PRINCIPAL INVESTIGATOR DISCLOSURES

- None.

CONFLICTS OF INTEREST WITHIN PROJECT TEAM

- None.

REFERENCES

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2. Incitec Pivot Limited. Half Year Results Presentation. Available at Incitec Pivot Limited, 2018. website: www.incitecpivot.com.au/.

3. Peng, X.D. Analysis of the Thermal Efficiency Limit of the Steam Methane Reforming Process. *Industrial & Engineering Chemistry Research* **2012**, *51*, 16385–16392.

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PARNTERS AND FINANCIAL INFORMATION

This project is sponsored by NDIC, DOE, UND Chemistry, NDSU, and Proton. Table 4 shows the initial 18-month budget of $1,663,107 for this project and expenses through the reporting period.

Table 4. Initial 18-month Budget and Expenses Through the Reporting Period

Sponsor	Budget	Current Reporting Period Expense	Cumulative Expenses as of 3/31/19	Remaining
DOE	$1,324,993	$258,299	$775,656	$549,337
UND Chemistry – In Kind	$34,514	$1,854	$11,112	$23,402
NDIC	$230,000	$2,721	$117,665	$112,335
NDSU – In Kind	$60,000	$21,667	$60,000	$0
Proton – In Kind	$13,600	$0	$0	$13,600
Total	**$1,663,107**	**$284,541**	**$964,433**	**$698,674**