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October 31, 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 July 1 through September 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/kal

Attachment

c/att: Andrea Holl Pfennig

LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION

Research Performance Progress Report (Quarterly)

(for the period of July 1, 2019, through September 30, 2019)

Prepared for:

Karlene Fine

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

Contract No. R-036-45

Prepared by:

Ted R. Aulich

Energy & Environmental Research Center
University of North Dakota
15 North 23rd Street, Stop 9018
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October 2019

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ACKNOWLEDGMENT

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LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION

PROJECT GOALS/OBJECTIVES

The project goal is to demonstrate an ammonia production energy reduction of 16% by replacing state-of-the-art (2018) 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 16% 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.

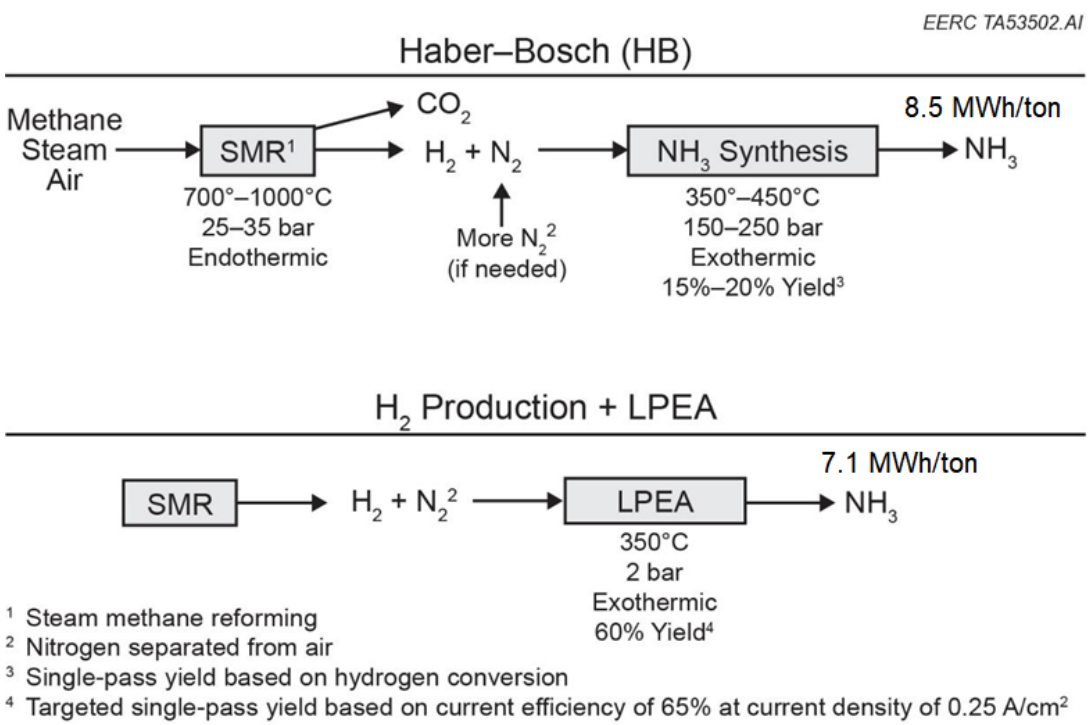

Figure 1. State-of-the-art (2018) HB versus LPEA-based NH_3 production.

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), Nel Hydrogen (Nel) (formerly Proton OnSite), 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 by project partner, NDSU.

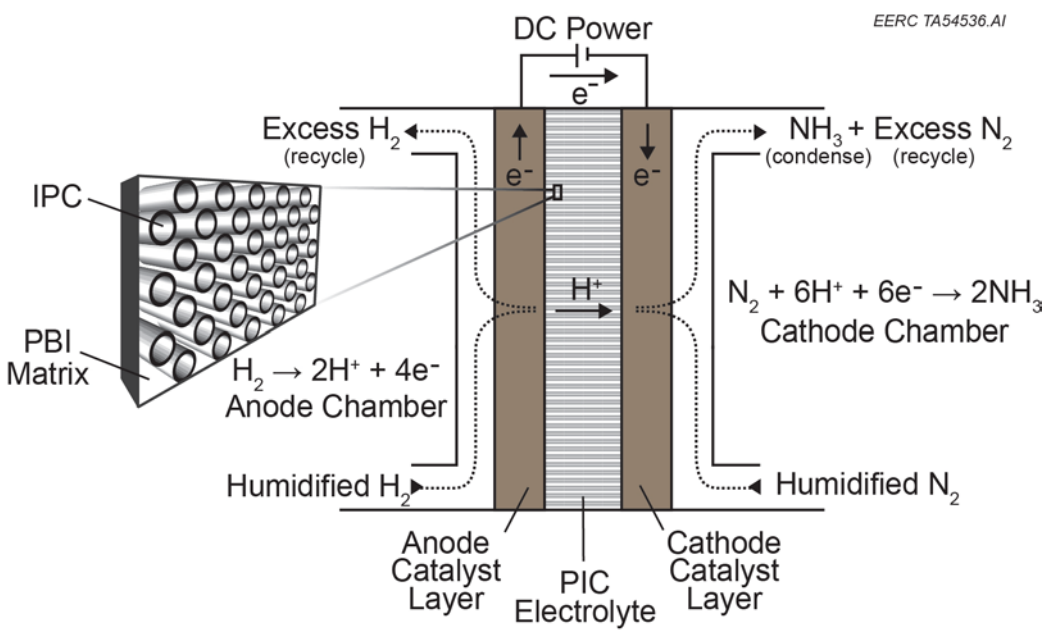

Figure 2. LPEA process.

Following fabrication of a PIC membrane that meets performance and durability 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 0.8 megawatt hours (MWh/ton), which would translate to a total (H_2 production plus NH_3 synthesis) LPEA-based NH_3 production energy input requirement of 7.1 MWh/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

- Synthesized an alternative IPC (referred to as "IPC2") with improved proton conductivity and stability versus the originally proposed IPC.

- Using IPC2 as a proton-conducting medium and PBI as matrix, fabricated a PIC membrane that met the three BP1 Go/No-Go Decision Point (DP1) performance metrics of:
  - Proton conductivity $\geq 0.75*10^{-2}$ S/cm
  - Gas permeability <10%
  - Thermal decomposition <10%

- Produced IPC2-based thin film (40–60-µm-thickness) PIC membranes containing up to 54 wt% IPC2 in PBI.

PROGRESS AND STATUS

Task 1 – Project Management

As shown in Table 1, the project is largely on schedule, with slight delays in Tasks 4 and 5. Although catalyst screening (Task 4) is currently behind schedule, addition to the project team of two postdoctoral researchers with electrocatalyst development experience should enable completion of screening and selection of promising catalysts for Budget Period (BP) 2 activities by the Task 4 completion date of 14 December 2019. As planned, all needed BP2 cathode catalyst work including performance improvement and/or particle-size optimization (to ensure compatibility with the Nel MEA fabrication technique) will be incorporated into Task 5. Although the catalyst-screening delay has translated to a delay in Task 5 progress, delivery to Nel of catalyst and membrane materials is planned for the week of 28 October 2019. This should enable meeting Milestone 5.1 (MEA fabrication method development) by the planned 14 March 2020 completion date.

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			40	
2	IPC Synthesis Method and Performance Improvement	14 Dec 2019			85	Shifted focus from IPC to IPC2
3	PIC Membrane Synthesis Method Development and Performance/Durability Optimization	14 Dec 2020			50	
4	Cathode Catalyst Screening	14 Dec 2019			70	Slightly delayed
5	PIC-Based MEA Fabrication Method Development and LPEA Unit Cell Performance/Durability Optimization	14 Dec 2020			20	15 June 2019 start, slightly delayed
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

A new IPC, temporarily referred to as IPC2, was identified, synthesized, and demonstrated to provide excellent proton conductivity—up to $4*10^{-2}$ S/cm at 300°C. In addition, IPC2 is water-insoluble, and all testing conducted to date indicates that IPC2 is stable at 300°C in the presence of steam (versus the highly problematic instability of the originally proposed IPC, cesium thiohydroxogermanate). Figure 3 illustrates the relationship of IPC2 proton conductivity to temperature as measured using a pressed disk PIC membrane (referred to as Membrane Configuration 4 or "MC4") comprising 94% IPC2–6% PBI.

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

As delineated in the statement of project objectives (SOPO), proceeding from BP1 to BP2 is contingent on producing a PIC membrane that exhibits the following properties at 300°C:

- Proton conductivity $\geq 0.75*10^{-2}$ S/cm
- Gas permeability <10%
- Thermal decomposition <10%

These three DP1 metrics were met using an MC4 sample comprising 94% IPC2–6% PBI. Proton conductivity was measured using a unit cell installed in a furnace, integrated with a potentiostat and frequency response analyzer and comprising a PIC membrane (MC4) sandwiched between an anode and cathode chamber equipped for controlled hydrogen and nitrogen flow, respectively. Both chambers were also equipped for controlled humidity injection. Following establishment of desired gas flow, furnace temperature was raised to 300°C. Humidity

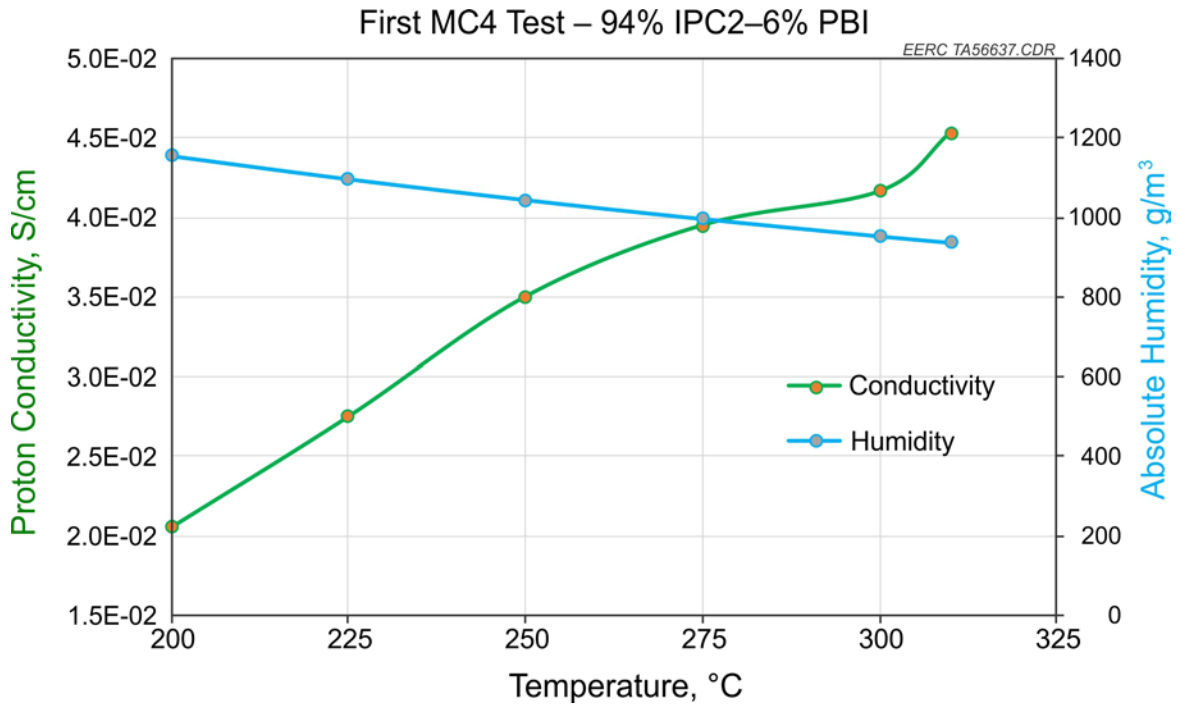

Figure 3. Proton conductivity versus temperature for 94% IPC2-based PIC membrane – Test 1.

was introduced into both chambers after the cell temperate reached 100°C. At test temperature, Nyquist plots were continually obtained and utilized to calculate membrane proton conductivity. Figure 4 shows proton conductivity measured over a 24-hour period, 19 hours of which were at 300°C. Over the several weeks following this demonstration, several more MC4 samples have been fabricated and tested, and all exhibited similar 300°C proton conductivities. Because early IPC2-based membrane performance results have indicated that humidity plays a critical role in conductivity magnitude and sustainability, major effort is focused on establishing an optimal humidity–temperature relationship.

To measure IPC2-based membrane gas permeability at 300°C, an online laser gas analyzer calibrated for hydrogen and nitrogen quantitation in volume percent (with a measurement precision of ±2 percentage points for each analyte) was connected to the cathode chamber outlet. During proton conductivity measurement at 300°C, hydrogen concentration in the cathode chamber exhaust stream was continuously monitored for 60 minutes. The measured amount of hydrogen in the cathode exhaust is indicative of the magnitude of hydrogen crossover from anode to cathode, which is defined as membrane gas permeability. As shown in Figure 5, gas permeability was well below the targeted 10% until 23:30 hours into the test, at which point a significant increase occurred. Thermal decomposition was measured by weighing the Test 2 PIC membrane before and after proton conductivity testing and accounting for 1) atmospheric moisture equilibration (PBI is highly hygroscopic, capable of absorbing up to 20% of its dry mass as moisture) and 2) loss of residual dimethylacetamide (PBI solvent utilized in MC4 preparation). Less than 8% loss of pretest PIC membrane mass was measured.

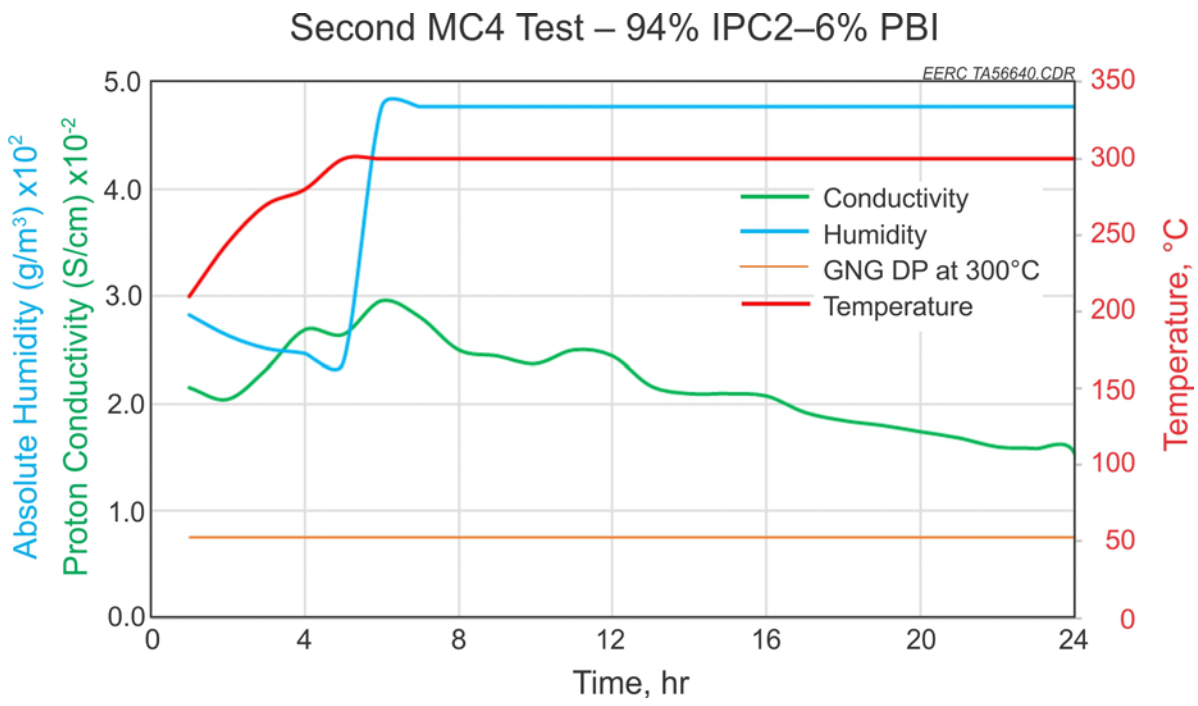

Figure 4. Proton conductivity versus temperature for 94% IPC2-based PIC membrane – Test 2.

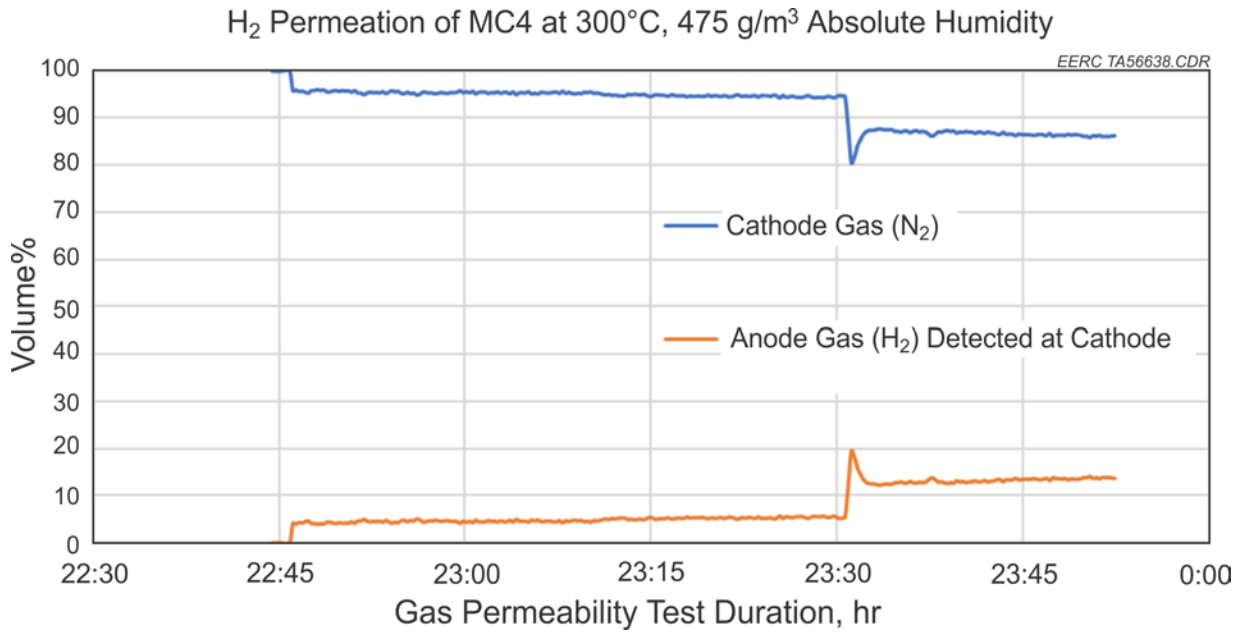

Figure 5. Gas permeability (measured during conductivity testing at 300°C) of MC4 – Test 2.

In addition to pressed disk membranes, IPC2-based cast film membranes were prepared for evaluation. Figure 6 compares a commercially produced PBI cast film with project-produced PBI and IPC2–PBI cast films. Although unit cell configuration modifications are being undertaken to enable accurate proton conductivity testing of these cast films, early gas permeability data are encouraging, as shown in Figure 7.

Task 4 – Cathode Catalyst Screening

Task 4 is focused on screening (preliminarily evaluating) cathode catalysts, with the goal of identifying a cathode catalyst for deployment in a PIC membrane-based MEA. The objective of Milestone 4.1 is to identify at least three catalysts with an ammonia synthesis faradaic efficiency (FE) of ≥50% and—if necessary—modify at least one catalyst to achieve an FE of ≥65%. More than three candidate catalysts with a reported ammonia synthesis FE of ≥50% have been identified, including $SmFe_{0.7}Cu_{0.1}Ni_{0.2}O_3$ (1), single-atom-Fe on N-doped C (2), Bi nanocrystals (3), and Au and Ni nanoparticles on N-doped C (4). However, difficulties in establishing an effective and reliable means of ex situ catalyst evaluation resulted in failure to validate catalyst performance and demonstrate the 65% FE milestone target. To address this problem, two alternative ex situ methods are being tailored for catalyst evaluation. Following establishment of protocols for most effectively deploying each method, one or both of the methods will be used for catalyst screening and/or validation of reported FE.

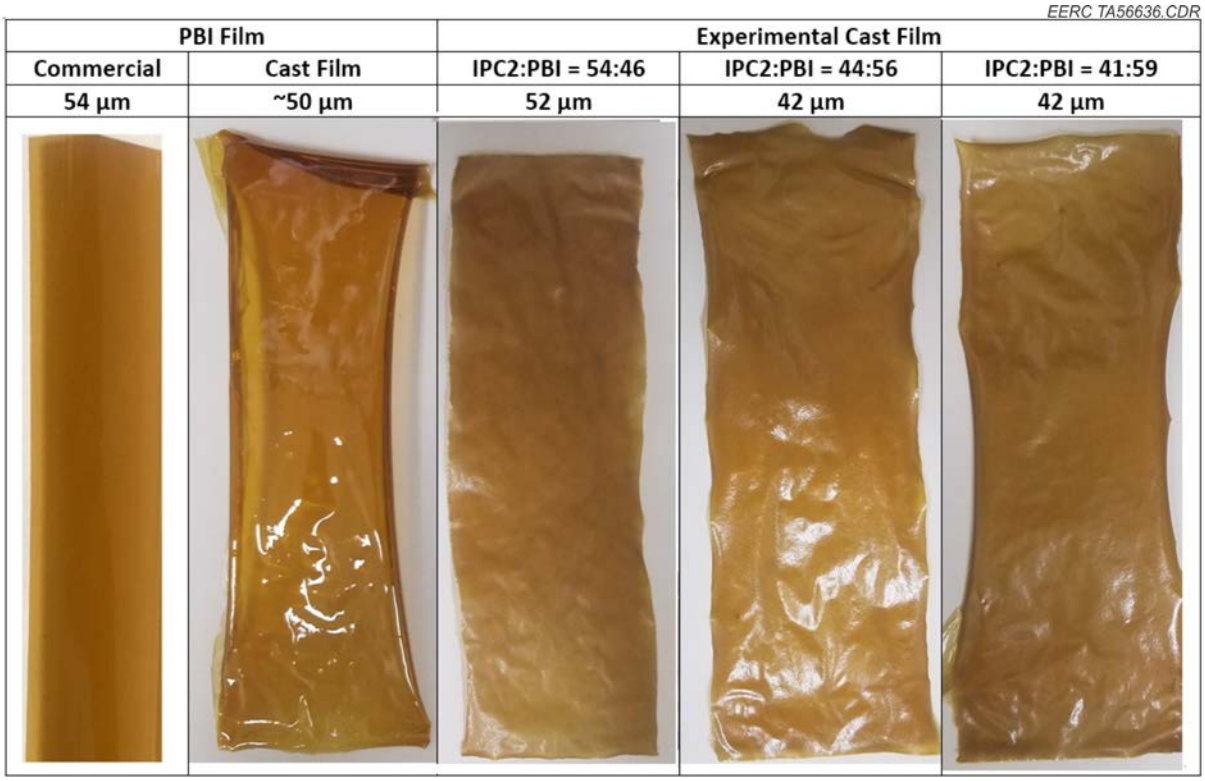

Figure 6. PBI and IPC2–PBI cast film membranes.

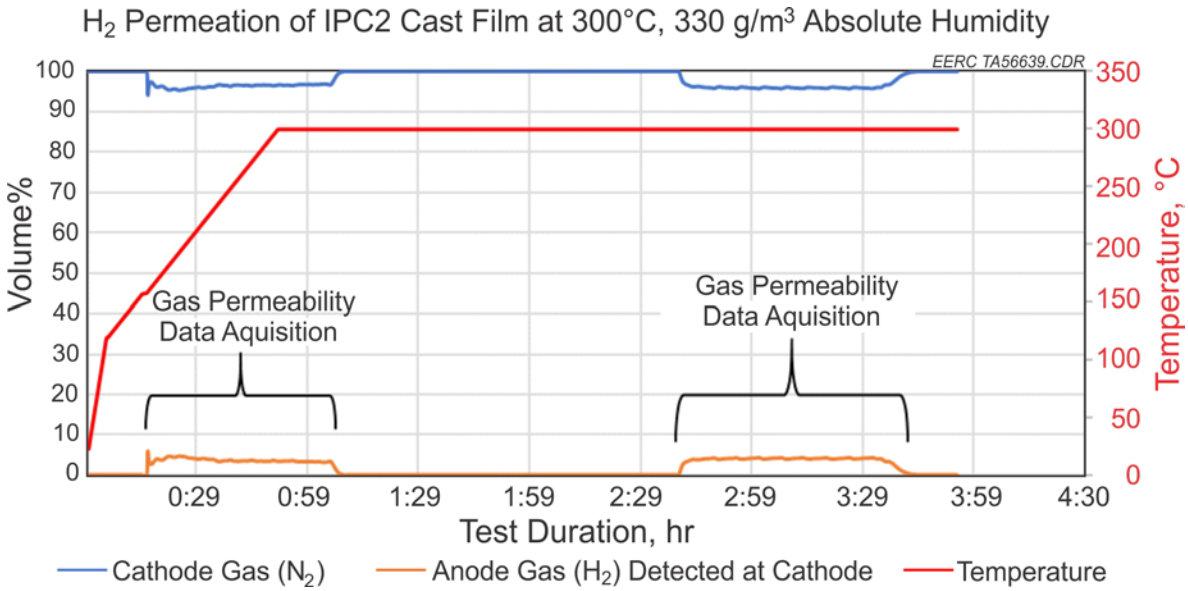

Figure 7. Gas permeability of 54% IPC2 cast film membrane at 300°C.

The originally proposed catalyst-screening method involved use of a rotating disk electrode (RDE) system to determine FE based on the amount of electrical current consumed in the synthesis of ammonia from protons and molecular nitrogen (N_2) dissolved in a measured volume of aqueous electrolyte. However, the very low solubility of nitrogen in conventional and safely manageable aqueous electrolytes (especially at room temperature) resulted in negligible levels of dissolved nitrogen for reaction, translating to undetectable levels of ammonia synthesis. The two alternative catalyst-screening methods being developed are:

- Single-chamber ammonia synthesis with continuous nitrogen sparging.
- H-cell (double-chamber) ammonia synthesis with continuous nitrogen sparging.

The single-chamber technique is similar to traditional RDE methods, with the most important difference being replacement of the small-surface-area RDE with an expanded-surface-area stationary gas diffusion electrode (catalyst layer deposited on carbon paper/cloth). Magnetic stirring of the electrolyte solution is used to facilitate reactant access to the electrode. Because the presence of anode and cathode in a single chamber introduces possibilities for unwanted reactions that could translate to inaccurate ammonia synthesis FE determination, double-chamber/H-cell testing will also be conducted, with the objective of generating corroborating FE data. The H-Cell system is built around an anode and cathode chamber, each filled with an acidic liquid electrolyte and separated by a proton exchange membrane. As shown in Figure 8, the system includes a cathode chamber gas inlet to enable continuous delivery of nitrogen for reaction. By bubbling a constant supply of nitrogen into the cathode chamber rather than relying only on the amount of nitrogen dissolved in a specific volume of electrolyte, ammonia synthesis is not limited by nitrogen supply depletion. With a continually replenished supply, screening tests can run as long as required to yield a sufficient amount of ammonia to enable its accurate quantitation and subsequent determination of ammonia synthesis FE.

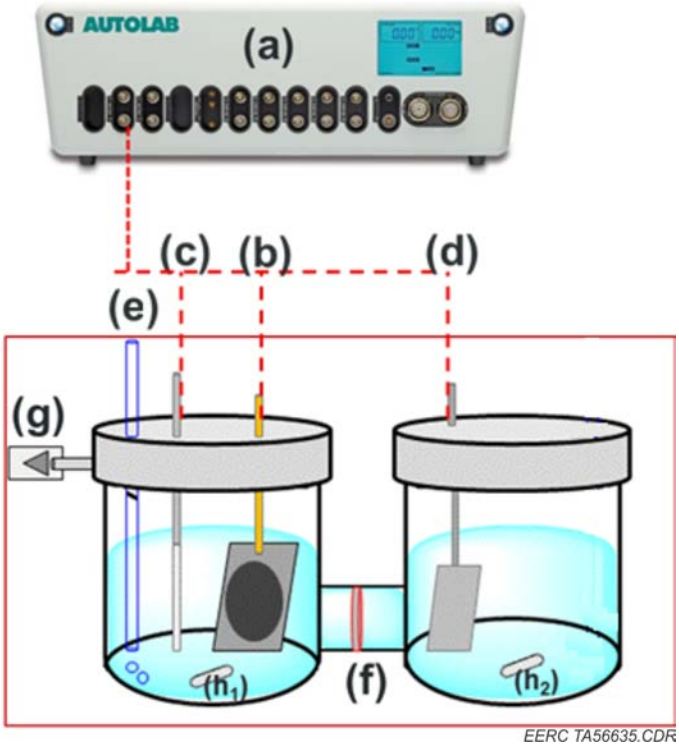

Figure 8. H-Cell system for cathode catalyst screening showing a) potentiostat, b) working electrode (candidate cathode catalyst), c) reference electrode (Ag/AgCl), d) counter/anode electrode (Pt wire/cage), e) N_2 inlet, f) Nafion membrane, g) following test completion, cathode chamber solution undergoes ultraviolet–visible light (UV–Vis) spectrophotometry analysis for ammonia quantitation, and h) magnetic stirrer.

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

Based on input from Nel, cast film PIC membranes, candidate cathode catalysts, and an ionomer material are being prepared for shipment to Nel.

Task 7 – Techno-Economic Analysis

Questions regarding the electricity input requirement for the LPEA process were addressed and tentatively resolved during the 2 October 2019 project team (including Bob Gemmer, Jeremy Leong, and John Winkel) meeting at the EERC.

PLANS FOR NEXT QUARTER

Task 1 – Project Management

Submit formal project continuation request.

Task 2 – IPC Synthesis Method and Performance Improvement

- Develop and deploy method for larger-batch production of IPC2.
- Explore IPC2 synthesis method alterations and evaluate their effects on IPC2 proton conductivity and structure.

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

- Improve the method for producing IPC2-based cast film PIC membranes to enable faster, cheaper, and optimal/consistent-quality membrane production.
- Complete proton conductivity test system modifications to enable accurate conductivity measurement of cast film membranes.
- Optimize cast film membrane based on proton conductivity, with optimization focus on IPC2 loading, absolute humidity input, and conductivity sustainability.
- Optimize cast film membrane based on gas (hydrogen) permeability and durability, with optimization focus on achieving maximum sustainability of minimum hydrogen permeation at operating conditions.

Task 4 – Cathode Catalyst Screening

Identify at least one catalyst that meets the Milestone 4.1 performance target.

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

Produce several MEAs for in situ evaluation.

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

Task initiation scheduled for 15 December 2019.

Task 7 – Techno-Economic Analysis

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 revise Milestone 4.1 completion date to 14 December 2019.

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.

BUDGETARY INFORMATION

No overall budget or nonfederal cost share issues occurred. Tables 4, 5, and 6 (milestone and budget tables) follow.

Table 2. Milestone Schedule

Milestone		Milestone Completion Date				
Task No.	**Title or Brief Description**	**Original Planned**	**Revised Planned**	**Actual**	**%**	**Milestone Progress Notes**
3.1	Complete PBI polymer identification literature review.	14 Sep 2018		14 Sep 2018	100	Under review by *Renewable and Sustainable Energy Review*.
3.2	ID ≥ two PBI formulations; evaluate mechanical strength, electrochemical and thermo-oxidative stability at 300°C.	14 Dec 2018		14 Dec 2018	100	Stability and strength adequate.
2.1	Synthesize ≥ one IPC composition with proton conductivity (PC) ≥$1.0*10^{-2}$ S/cm at 300°C.	14 Mar 2019		14 Mar 2019	100	Achieved PC target, became aware of IPC instability, hydration challenge.
3.3	Fabricate PIC membrane with PC ≥$0.5*10^{-2}$ S/cm, gas permeability (GP) <10% at 300°C.	14 June 2019		14 Aug 2019	100	Met PC and GP targets with PIC membrane made with initial IPC.
4.1	ID ≥ three catalysts with faradaic efficiency (FE) ≥50%, modify at least one catalyst to achieve ≥65% FE.	14 Sep 2019	14 Dec 2019		50	Utilizing new methods for catalyst screening.
2.2	Improve IPC PC to ≥$1.5*10^{-2}$ S/cm at 300°C (50% increase from Milestone 2.1).	14 Dec 2019		15 Sep 2019	100	Achieved 4*10-2 S/cm at 300°C with 94% IPC2.
DP1	Synthesize PIC membrane with PC ≥$0.75*10^{-2}$ S/cm, GP <10%, <10% thermal decomposition (TD) at 300°C.	14 Dec 2019		15 Sep 2019	100	Achieved >10^{-2} S/cm PC, <10% GP, <8% TD over 20 h at 300°C.
5.1	Develop method for MEA fabrication from PIC membrane and Task 4-selected catalyst(s).	14 Mar 2020				
3.4	Synthesize PIC membrane with PC ≥$1*10^{-2}$ S/cm, GP <2%, TD <3% at 300°C in optimal humidity.	14 June 2020				
5.2	Produce MEA with proton transport resistance (PTR) ≤150 mohms-cm^2, catalyst layer (CL) thickness of 5–10 µm.	14 Sep 2020				
CM	Demonstrate LPEA unit cell with current density ≥0.25 A/cm^2, current efficiency ≥65%, production energy efficiency ≥65%, ≤0.3% degradation/1000 h.	14 Dec 2020				
6.1	Complete techno-economic viability testing with 100-g/d multi-cell LPEA system.	14 Mar 2021				
7.1	Demonstrate ≥16% reduction in production energy versus state-of-the-art (2018) HB requirement of 8.5 MWh/ton of NH_3.	14 Jun 2021				

Table 3. Project Spend Plan

Quarter	From	To	Estimated Federal Share of Outlays	Actual Federal Share of Outlays	Estimated Recipient Share (Cost Share) of Outlays	Actual Recipient Share (Cost Share) of Outlays	Cumulative Actual Outlays (Federal + Recipient)
	6/15/2018	6/30/2018		$ -		$ -	$ -
FY18Q4	7/1/2018	9/30/2018	$ 59,587	$ 59,587	$ 95,383	$ 95,383	$ 154,970
FY19Q1	10/1/2018	12/31/2018	$ 197,222	$ 197,222	$ 37,900	$ 37,900	$ 235,122
FY19Q2	1/1/2019	3/31/2019	$ 260,548	$ 260,548	$ 29,252	$ 29,252	$ 289,800
FY19Q3	4/1/2019	6/30/2019	$ 258,299	$ 258,299	$ 26,242	$ 26,242	$ 284,541
FY19Q4	7/1/2019	9/30/2019	$ 168,252	$ 168,252	$ 78,378	$ 78,378	$ 246,630
FY20Q1	10/1/2019	12/31/2019*	$ 381,085		$ 70,959		
FY20Q2	1/1/2020	3/31/2020	$ 195,498		$ 54,652		
FY20Q3	4/1/2020	6/30/2020	$ 195,498		$ 54,652		
FY20Q4	7/1/2020	9/30/2020	$ 195,498		$ 54,652		
FY21Q1	10/1/2020	12/31/2020	$ 195,498		$ 54,652		
FY21Q2	1/1/2019	3/31/2019	$ 195,499		$ 54,652		
FY21Q3	4/1/2020	6/30/2020*	$ 195,499		$ 54,652		
Totals			$ 2,497,983	$ 943,908	$666,027	$267,155	$ 1,211,063
Approved Budget			$2,497,983		$666,027		$3,164,010

* End of budget period.

Table 4. Cost Category Summary

Category	Approved Budget Period 1	Federal Share	Cost Share	Total	Cummulative Federal Share	Cummulative Cost Share	Cummulative Total
Personnel	$409,507	$71,791	$34,647	$106,438	$292,944	$109,892	$402,836
Fringe	$249,320	$32,633	$16,760	$49,393	$138,674	$52,420	$191,094
Travel	$8,224	$93	$0	$93	$3,045	$2,043	$5,088
Equipment	$103,751	$0	$0	$0	$52,957	$0	$52,957
Supplies	$63,298	$4,387	$201	$4,588	$26,304	$10,191	$36,495
Contractual	$389,646	$46,312	$0	$46,312	$175,487	$0	$175,487
Other Direct Costs	$34,579	$2,187	$1,594	$3,781	$9,645	$6,211	$15,856
Indirects	$404,782	$10,849	$25,176	$36,025	$244,852	$86,398	$331,250
Total Costs	**$1,663,107**	$168,252	$78,378	$246,630	$943,908	$267,155	$1,211,063

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PARTNERS AND FINANCIAL INFORMATION

This project is sponsored by NDIC, DOE, UND Chemistry, NDSU, and Proton. Table 5 shows the initial 18-month budget of $1,663,107 for this project and expenses through the reporting period.

Table 5. Initial 18-month Budget and Expenses Through the Reporting Period

Sponsor	Budget	Current Reporting Period Expense	Cumulative Expenses as of 9/30/19	Remaining
DOE	$1,324,993	$168,252	$943,908	$381,085
UND Chemistry – In Kind	$34,514	$21,989	$33,101	$1,413
NDIC	$230,000	$56,067	$173,732	$56,268
NDSU – In Kind	$60,000	$0	$60,000	$0
Proton – In Kind	$13,600	$322	$322	$13,278
Total	**$1,663,107**	**$246,630**	**$1,211,063**	**$452,044**