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April 29, 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 January 1 through March 31, 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 January 1, 2019, through March 31, 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:

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April 2019

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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 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.

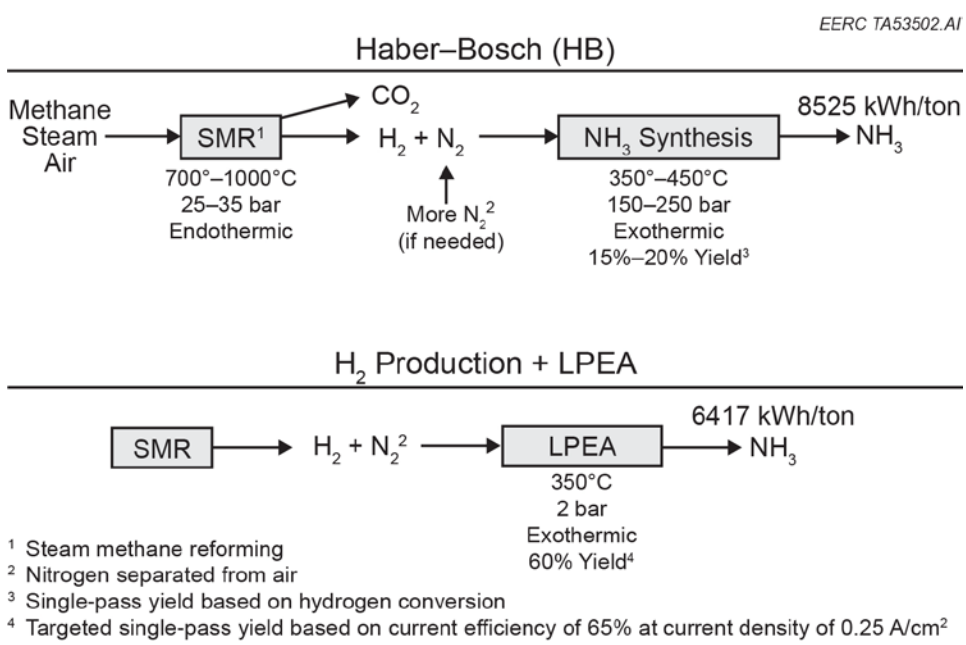

Figure 1. HB versus LPEA-based NH_3 production.

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.

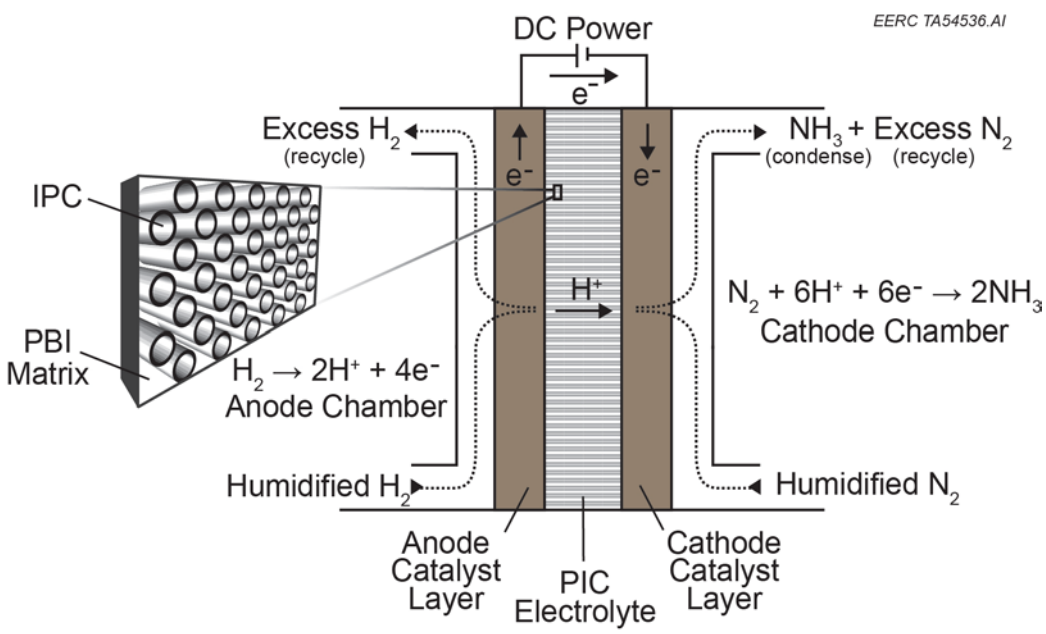

Figure 2. LPEA process.

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

- Completed third milestone (Milestone 2.1)—synthesize an IPC material with proton conductivity (PC) $\geq 1.0 \times 10^{-2}$ S/cm at 300°C—as described in Progress and Status (Task 2).
- Developed, implemented, and initially evaluated two new approaches for fabrication of IPC–PBI core–shell nanofibers:
  - Airflow-assisted core–shell nanofiber fabrication.
  - Three-step core–shell nanofiber fabrication using an initial "sacrificial" core.
- Validated alternating current impedance (ACI) spectroscopy technique for measuring membrane proton conductivity, and deployed technique in assessing two NDSU-fabricated PIC membrane samples. The membranes—which comprised heat-pressed matted core–shell nanofibers—were found to have proton conductivities of about 0.2×10^{-3} S/cm at 300°C and varying steam levels.
- Improved method for synthesis of ruthenium and ruthenium oxide on reduced graphene oxide ($Ru–RuO_2$/RGO) catalyst. The method enables preparation of catalyst with smaller and more highly dispersed Ru and RuO_2 nanoparticles than achievable with the previous method.

PROGRESS AND STATUS

Task 1 – Project Management (EERC)

- The tunable diode laser-based analyzer capable of online high-temperature quantitation of ammonia and water vapor was delivered, set up, and commissioned.
- Following discussions between the EERC and Proton contracting personnel, a draft project-teaming agreement has been prepared and submitted to Proton for review. A signed agreement is anticipated to be in effect prior to the proposed 15 June 2019 start date for Proton activities.
- 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			25	
2	IPC Synthesis Method and Performance Improvement	14 Dec 2019			50	
3	PIC Membrane Synthesis Method Development and Performance/Durability Optimization	14 Dec 2020			30	
4	Cathode Catalyst Screening	14 Dec 2019			50	
5	PIC-Based MEA Fabrication Method Development and LPEA Unit Cell Performance/Durability Optimization	14 Dec 2020				15 June 2019 start
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)

- Disks of solid IPC were prepared by evaporating water from IPC synthesis solution contained in a 30-mm-diameter plastic mold over several days in an oven containing nitrogen at an absolute pressure of 10 inches of mercury at up to 140°C. During ACI testing, IPC disks exhibited a conductivity of 5.27×10^{-2} S/cm at 200°C. However, as temperature increased above 225°C, released steam bubbles caused surface distortion and void formation, resulting in a steep performance drop between about 245° and 250°C, as shown in Figure 3. Disk samples were completely damaged before reaching 300°C. To avoid IPC disk distortion/void formation and enable conductivity measurement at 300°C, several different gradual drying methods were explored, all resulting in disks that exhibited a more gradual performance drop, as shown in Figure3. We believe that this loss of conductivity is due to the loss of IPC water of hydration at higher temperatures in the dry atmosphere.

- As an attempt to avoid steam release damage, pellets were prepared from IPC powder, since pellets were deemed likely to have higher porosity than solid disks. IPC solid was dried at 225°C for 2 hours (to drive off absorbed water, but not water of hydration), then ball-milled for 15 minutes to make a fine powder. IPC pellets were made by pressing 3 grams of IPC powder at 57,000 psi in a 1.25-inch-diameter die for 5 minutes. IPC pellets were tested for proton conductivity at increasing temperature in a humidified—at varying levels—atmosphere with the objective of minimizing water of hydration loss. Conductivity was unsustainable because of IPC erosion, likely resulting from IPC solubilization and removal from the pellet surface, leaving a gap between the pellet and ACI test cell electrodes (Figure 4).

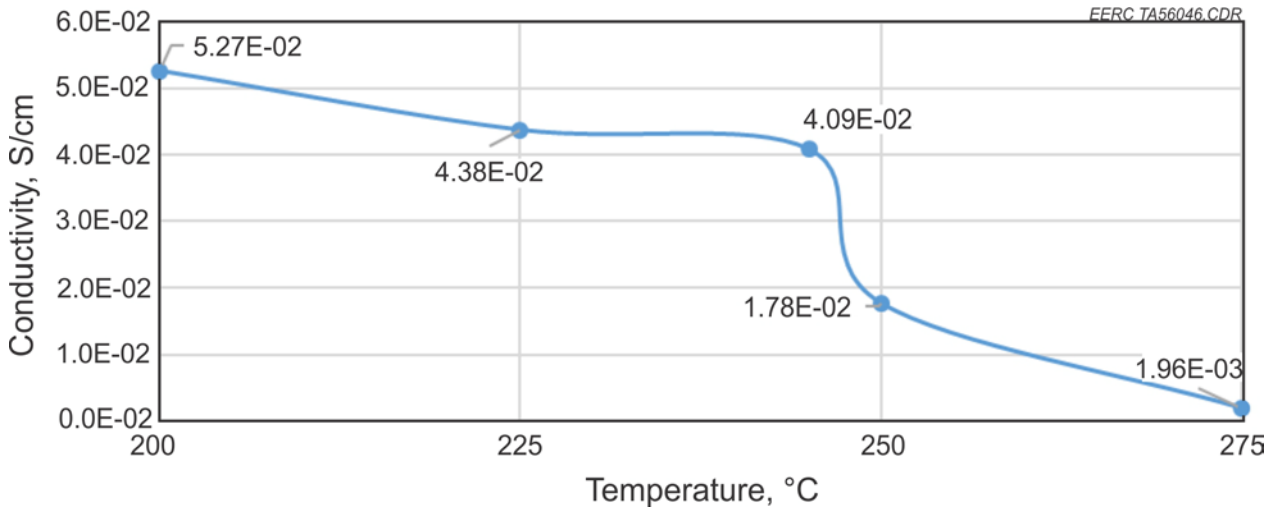

Figure 3. Conductivity of IPC disk as function of temperature.

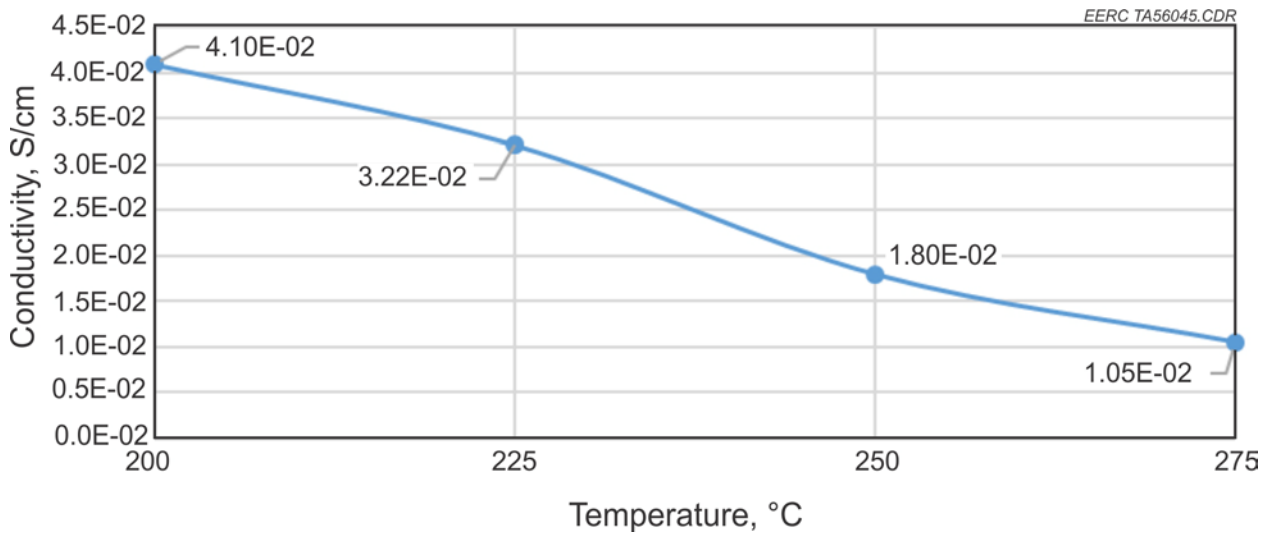

Figure 4. Conductivity of gradually dried IPC disk as function of temperature.

- To attempt mitigation of IPC surface erosion, pellets were pressed (via the above-described method) between top and bottom carbon cloth layers, with the objective of using the gas-permeable carbon layers as protective barriers against IPC erosion. Proton conductivities exceeding the milestone target of 10^{-2} S/cm were measured at 300°C and above, as shown in Figure 5.

- Data acquired to date indicate the importance of IPC humidity control to enable and sustain 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. For

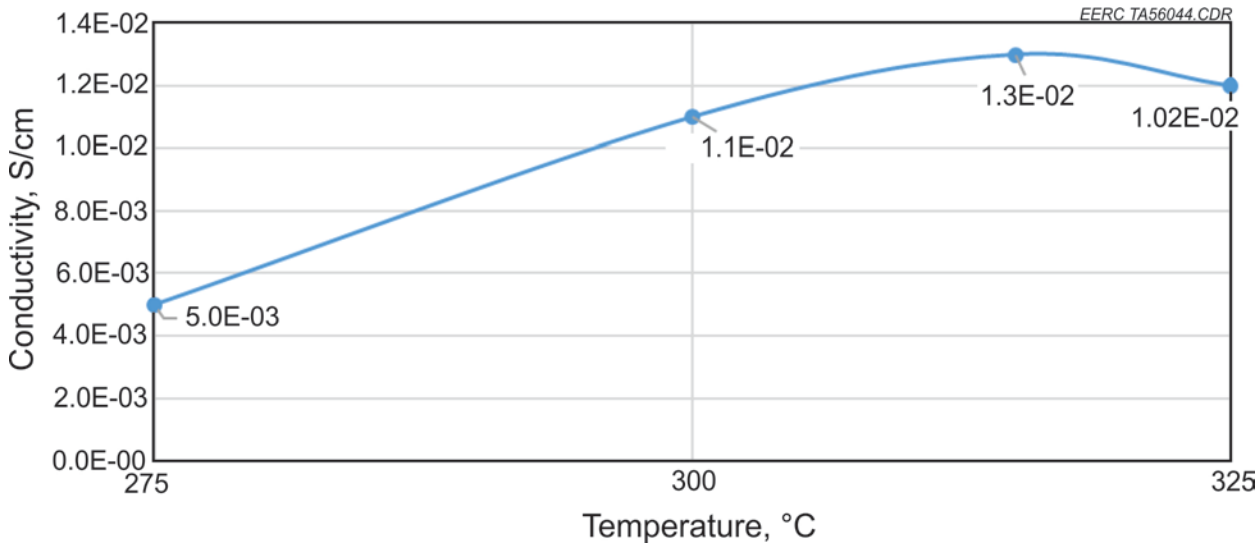

Figure 5. Conductivity of IPC pellet sandwiched between carbon cloth layers as a function of temperature.

this reason, upcoming work is focused on determining a humidity–temperature relationship that—if maintained—ensures both IPC integrity and maximum proton conductivity.

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

- An airflow-assisted processing technique was developed that enables fabrication of core–shell IPC–PBI nanofibers with improved structural quality and consistency at approximately 10 times higher productivity than the conventional (non-airflow-assisted) technique. A major challenge with the conventional technique was excessively fast PBI precipitation because of poor miscibility of the PBI and IPC processing solutions, which comprise PBI in dimethyl acetamide (DMAc) and IPC in water. Excessively fast PBI precipitation results in inconsistent structure and morphology of produced core–shell nanofibers. Prior attempts to address this challenge via solvent loading adjustment and/or use of a cosolvent with miscibility in both DMAc and water have been unsuccessful. However, it was found that use of an optimal-rate airflow during processing can effectively suppress premature PBI precipitation, enabling fabrication of high-quality nanofibers, as shown in Figures 6 and 7.

- A three-step process for core–shell nanofiber fabrication was explored. In the first step, nanofibers are fabricated with “sacrificial” cores of polymethylmethacrylate (PMMA). In the second step, PMMA cores are solvent-extracted to yield continuous hollow PBI nanofibers. Finally, the hollow PBI nanofibers are loaded with IPC via soaking in aqueous IPC solution followed by gradual drying. Figure 8 shows post-solvent-extracted hollow PBI nanofibers, and Figure 9 shows formerly hollow PBI fibers loaded with IPC.

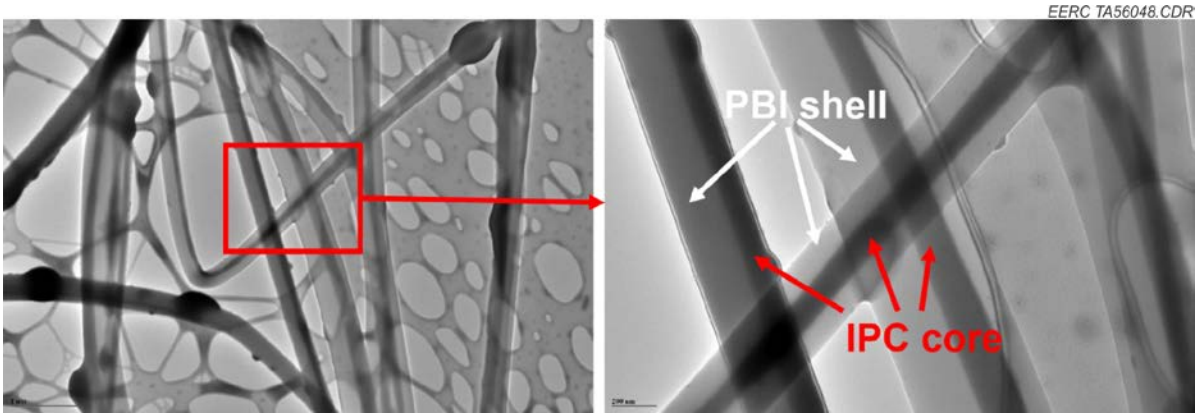

Figure 6. TEM micrographs of core–shell IPC–PBI nanofibers fabricated with airflow assistance. Right panel is a zoomed view of left. IPC core diameters are 100–200 nm.

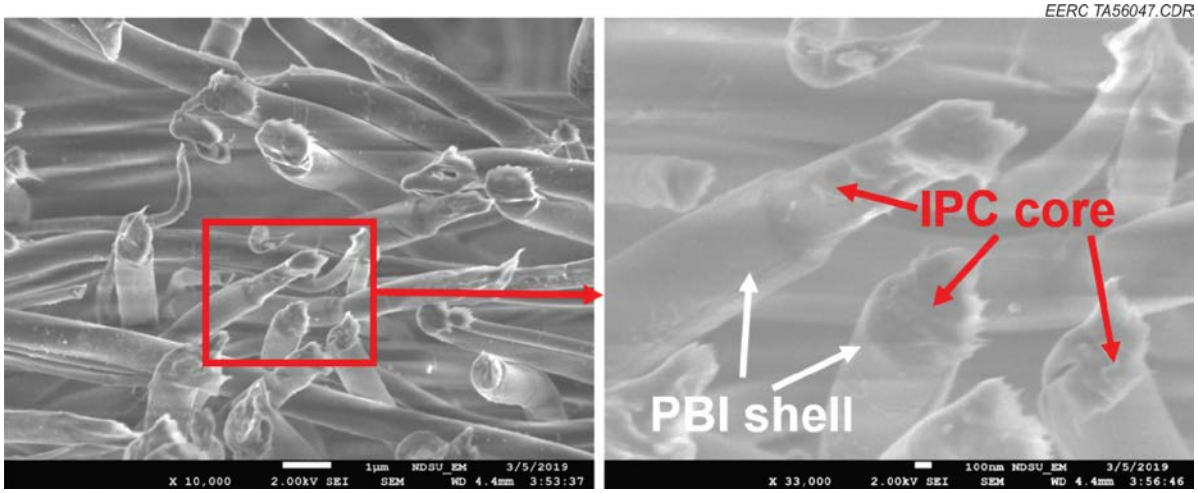

Figure 7. SEM micrographs of cross section of as-fabricated airflow-assisted core–shell nanofiber membrane. Right panel is a zoomed view of left.

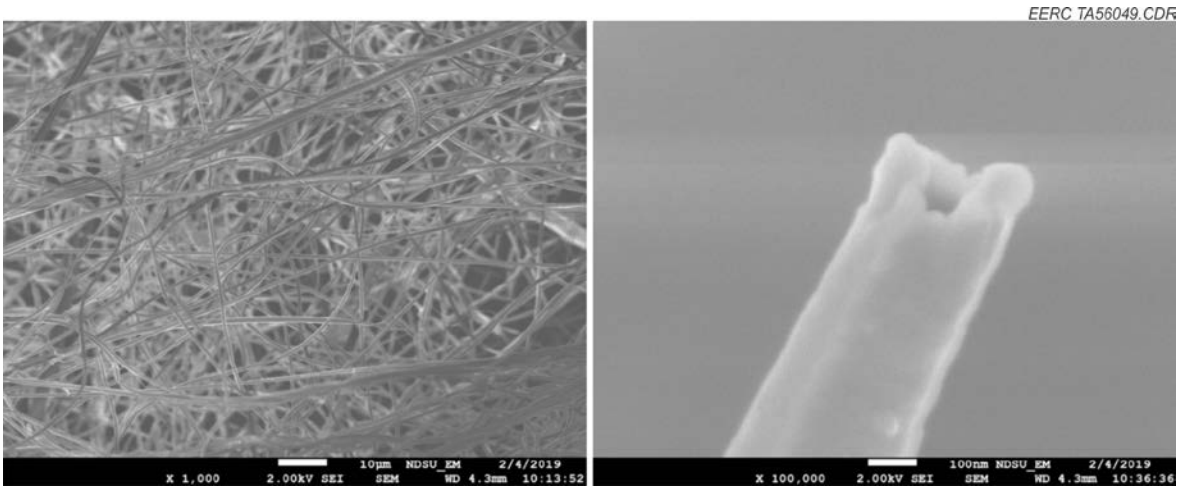

Figure 8. SEM (scanning electron microscope) micrographs of hollow PBI nanofibers after solvent extraction of PMMA cores.

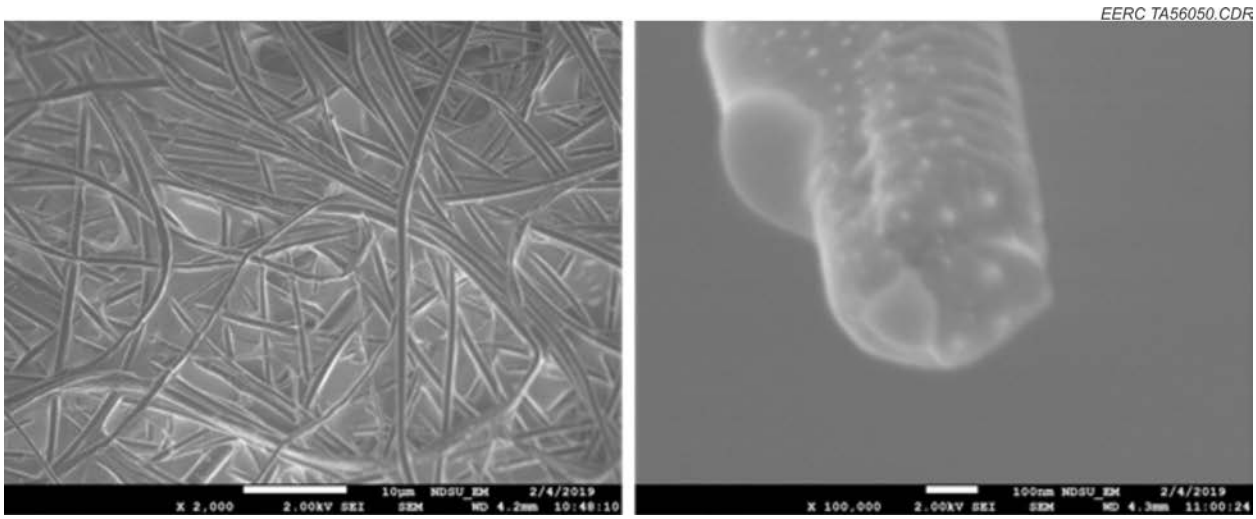

Figure 9. SEM micrograph of cross sections of formerly hollow PBI nanofibers filled with IPC.

- Thermogravimetric analysis (TGA) was utilized to examine the effect of heating rate (2°, 5°, and 10°C/minute) on release of water and DMAc from core–shell nanofiber membranes fabricated with airflow assistance. The TGA diagrams provided as Figures 10–12 show continuous mass loss with increasing temperature up to 350°C. A significant portion of the observed 12% loss is likely due to loss of water absorbed following membrane fabrication, since both PBI and IPC are highly hygroscopic. Loss of residual DMAc (boiling point of 165°C) is shown by the TGA plot derivative curves.

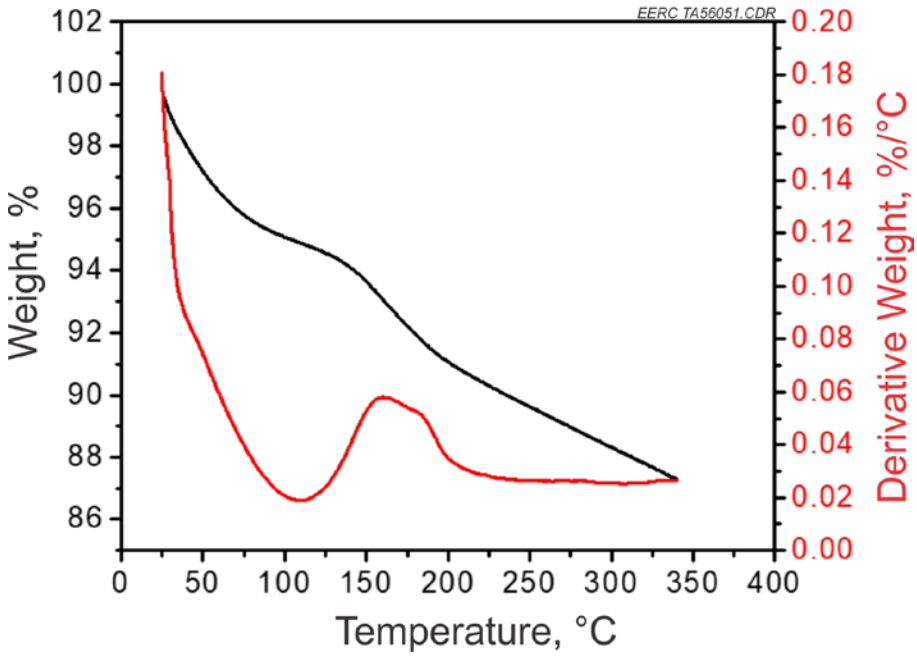

Figure 10. TGA and differential thermogravimetric (DTG) plots for core–shell nanofiber membrane dried at a heating rate of 2°C/minute under nitrogen.

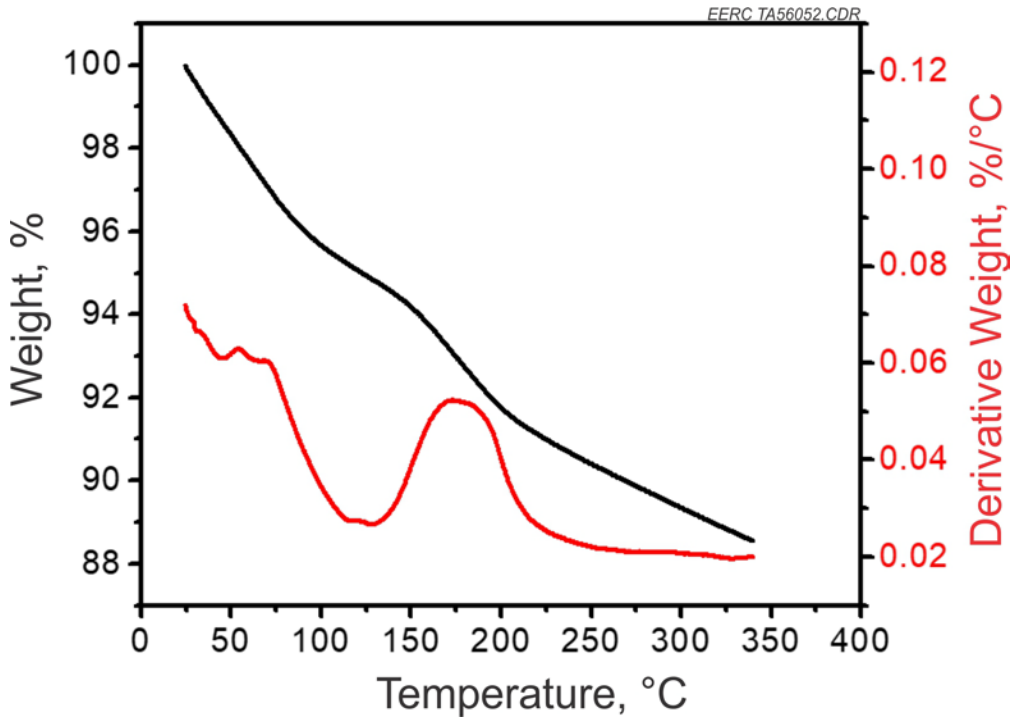

Figure 11. TGA and DTG plots for core–shell nanofiber membrane dried at a heating rate of 5°C/minute under nitrogen.

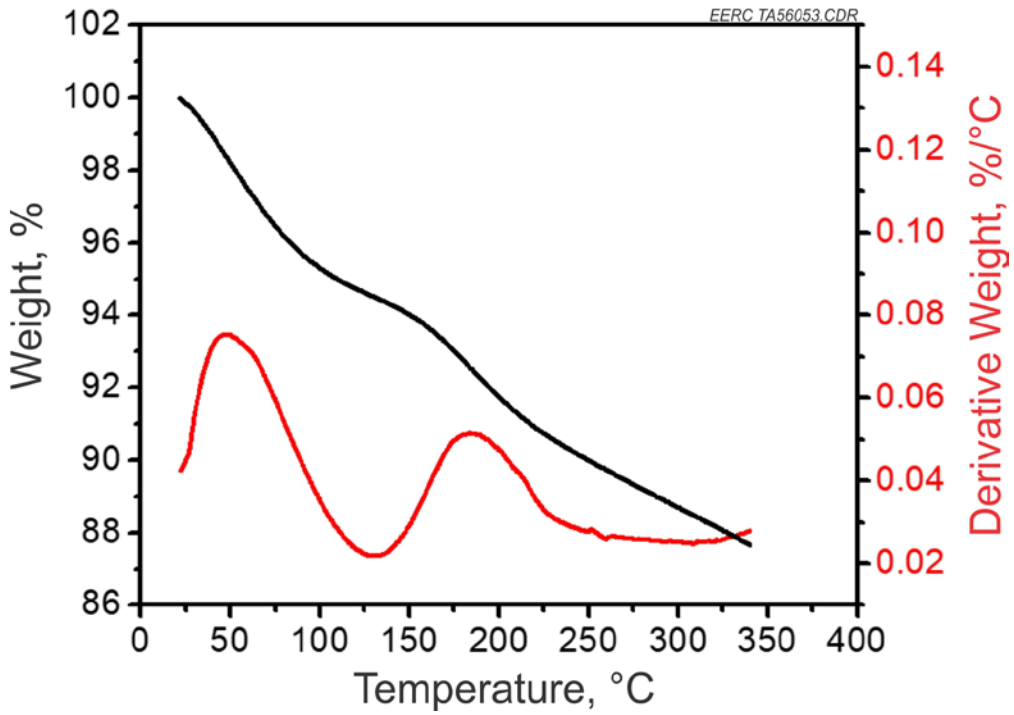

Figure 12. TGA and DTG plots for core–shell nanofiber membrane dried at a heating rate of 10°C/minute under nitrogen.

- An ACI spectroscopy technique for measuring proton conductivity was validated by conducting successful ACI tests with a commercial (Nafion 117) PEM. The tests—conducted at 75°C and 70% relative humidity—yielded proton conductivities of about 1.1×10^{-2} S/cm, closely matching literature-reported values acquired under the same conditions [1].

- Initial ACI tests on two NDSU-fabricated PIC membrane samples were completed. The membranes—which comprised heat-pressed matted core–shell nanofibers—were found to have proton conductivities of about 0.2×10^{-3} S/cm at 300°C and varying steam levels. Following both tests, brittleness was observed in several small regions within each membrane sample, likely due to water and/or DMAc interactions with membrane materials at higher temperatures. Methods for brittleness mitigation are being investigated.

Task 4 – Cathode Catalyst Screening (UND Chemistry)

- A rotating disk electrode (RDE) test station was configured and utilized (with palladium- and platinum-on-carbon electrodes) to develop a cyclic voltammetry procedure for cathode catalyst evaluation. Figure 13 shows the RDE test station. Additional work is needed to establish optimal parameters for evaluating candidate catalysts based on activity for nitrogen reduction.

- An improved method for synthesis of ruthenium and ruthenium oxide on reduced graphene oxide ($Ru–RuO_2$/RGO) catalyst was developed. The method enables preparation of catalyst with smaller and more highly dispersed Ru and RuO_2 nanoparticles than achievable with the previous method. Figure 14 shows Ru and RuO_2 nanoparticles on the surface of an RGO particle, and Figure 15 illustrates $Ru–RuO_2$ nanoparticle size and zeta potential distribution. Zeta potential provides a means of measuring particle surface charge, with a larger absolute-value zeta potential indicating a larger force of repulsion between particles. The observed zeta potential range of –30 to –40 millivolts (mV) indicates high potential for monodispersion (nonagglomeration and high dispersion) of $Ru–RuO_2$ nanoparticles in the aqueous catalyst preparation solution and subsequent monodispersion on RGO particle surfaces.

PLANS FOR NEXT QUARTER

Task 2 – IPC Synthesis Method and Performance Improvement

- Prepare additional IPC solutions as needed to support Task 3 efforts to optimize the process for producing consistent-quality core–shell nanofibers with continuous uniform-diameter IPC cores and continuous uniform-thickness PBI shells.
- 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.
- Explore IPC doping options and/or compositional adjustments to improve proton conductivity and durability.

Figure 13. RDE setup integrated with potentiostat for cyclic voltammetry data acquisition.

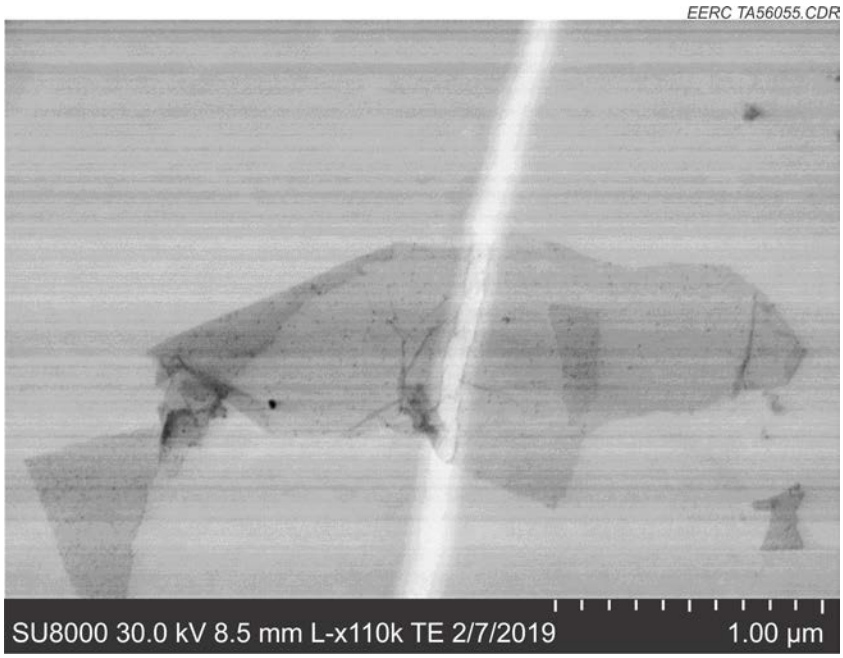

Figure 14. Micrograph showing highly dispersed (small, gray/black) Ru and RuO_2 nanoparticles on the surface of the RGO particle.

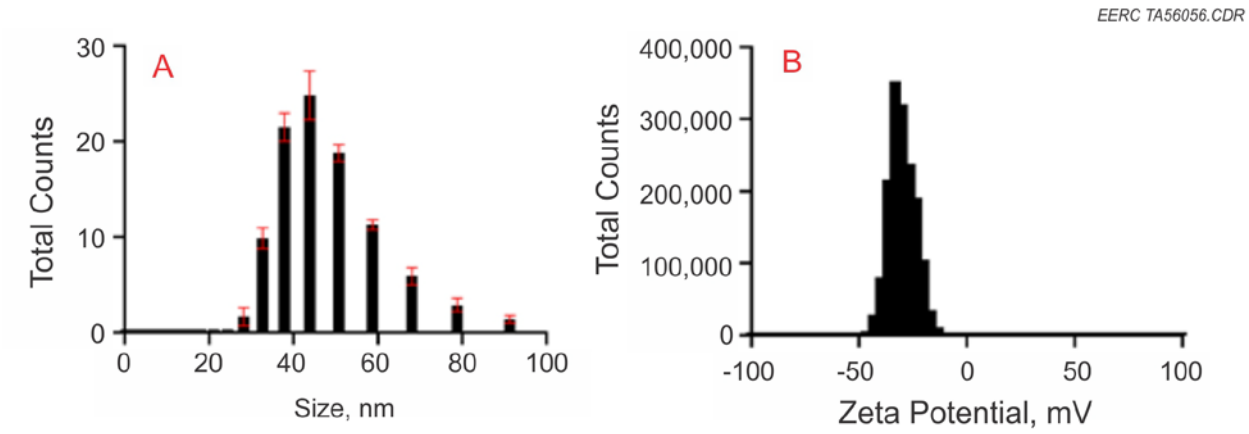

Figure 15. Size and zeta-potential distribution of Ru and RuO_2 nanoparticles.

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

- Further tailor PBI and IPC solutions (via solvent adjustment and/or surfactant introduction), process setup, and operating conditions to increase solution compatibility and enable improved production of high-quality core–shell nanofibers.
- Develop improved understanding of water/steam–IPC interactions over the temperature range of 100°–350°C, and use it to:
  - Optimize the overall heat-pressing process to improve the mechanical and thermomechanical properties of core–shell nanofiber-based membranes.
  - Establish a correlation between PIC membrane operation humidity and proton conductivity.
- Continue acquiring PIC membrane proton conductivity data (via ACI 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 0.5×10^{-2} S/cm at a temperature of at least 300°C.
- Utilize membrane morphology and thermal stability characterization techniques (including SEM, TEM [transmission electron microscopy], energy-dispersive x-ray spectroscopy [EDS], and TGA) as needed to correlate membrane structural and physical properties with membrane proton conductivity, durability, and tensile strength, and use correlative data to facilitate optimization of membrane production processing parameters.

Task 4 – Cathode Catalyst Screening

- Improve the procedure for applying experimental catalysts onto the RDE working electrode surface.
- Finalize procedures for utilizing the RDE test station for acquisition of the following data for candidate cathode catalysts:
  - Electrochemical surface area.
  - Nitrogen reduction reaction specific activity and mass activity.
  - Ammonia formation rate and Faradaic efficiency.

- Begin acquisition of cyclic voltammetry data for candidate catalysts, starting with Ru–RuO_2/RGO.

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

- No progress; task initiation scheduled for 15 June 2019.

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

- No progress; task initiation scheduled for 15 December 2019.

Task 7 – Techno-Economic Analysis (All)

- No activity during this quarter.

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

- None during this reporting period.

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

1. Sone, Y., Ekdunge, P., Simonsson, D. Proton Conductivity of Nafion 117 as Measured by a Four-Electrode AC Impedance Method. *J Electrochemical Society* **1996**, *143* (4), 1254–1259.

PARNTERS AND FINANCIAL INFORMATION

This project is sponsored by NDIC, DOE, UND Chemistry, NDSU, and Proton. Table 2 shows the initial 18-month budget of $1,663,107 for this project and expenses through the reporting period.

Table 2. 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	$260,548	$517,357	$807,636
UND Chemistry – In Kind	$34,514	$3,711	$9,258	$25,256
NDIC	$230,000	$11,606	$114,944	$115,056
NDSU – In Kind	$60,000	$13,935	$38,333	$21,667
Proton – In Kind	$13,600	$0	$0	$13,600
Total	**$1,663,107**	$289,800	$679,892	$983,215