



January 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 October 1 through December 31, 2018.

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

Sincerely,

A handwritten signature in black ink, appearing to read "Ted R. Aulich", is written over a large, faint, stylized signature that also appears to be "Ted R. Aulich".

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 October 1, 2018, through December 31, 2018)

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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January 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 the Energy & Environmental Research Center (EERC)-developed low-pressure electrolytic ammonia (LPEA) process, as shown in Figure 1. (Note: The kilowatt-hours/ton [kWh/ton] ammonia production energy values shown are recently obtained and lower than values presented earlier, as explained in Appendix A). 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 $\geq 65\%$ for NH_3 formation at a current density of ≥ 0.25 amps/ cm^2 (A/cm^2), NH_3 production energy efficiency of $\geq 65\%$, and $\leq 0.3\%$ performance degradation per 1000 h of operation.

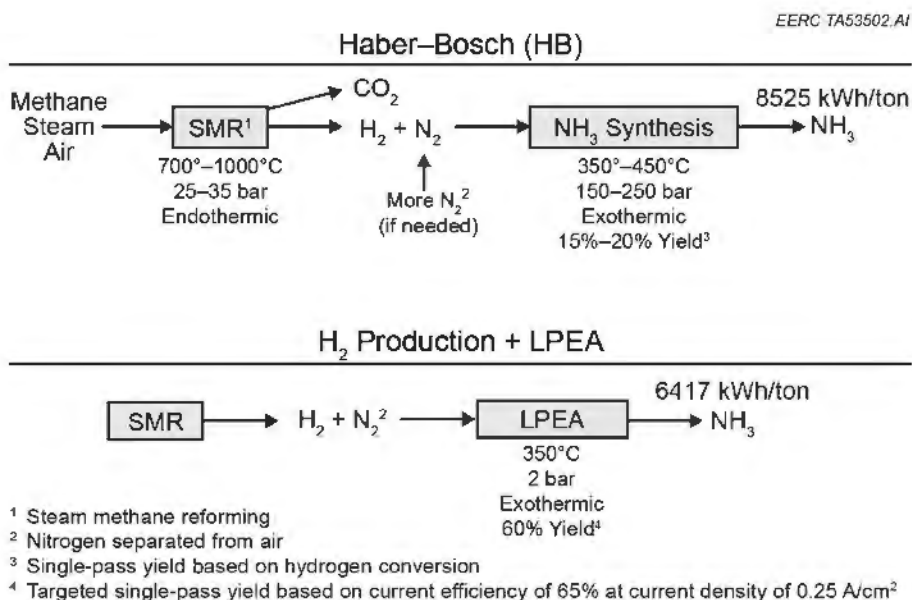


Figure 1. HB versus LPEA-based NH_3 production.

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 UND 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.

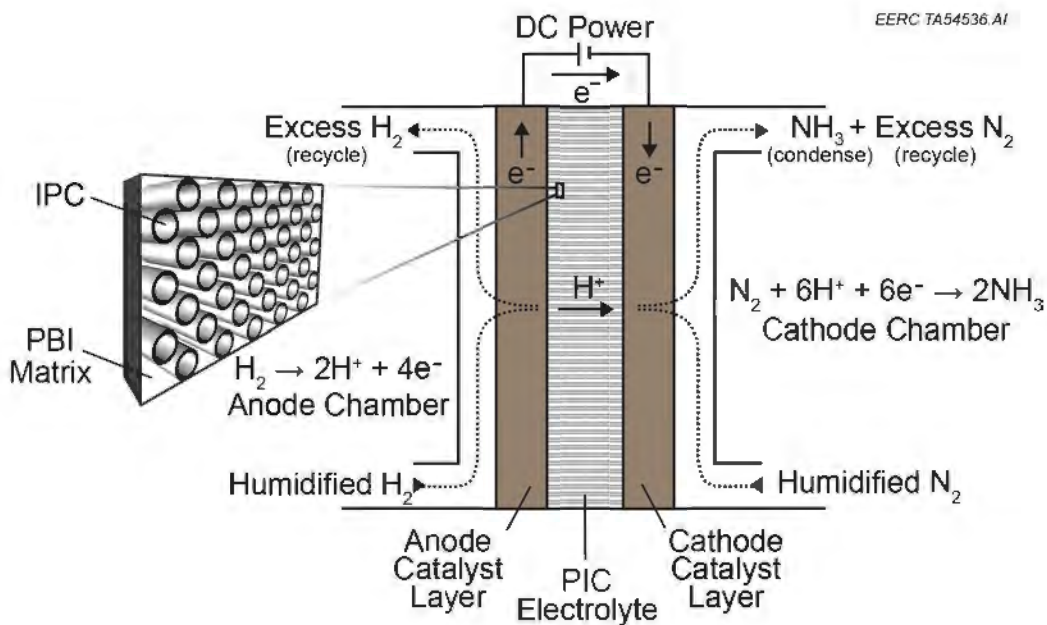


Figure 2. LPEA process.

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 NH₃ 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 NH₃. The 100-g/d LPEA system will undergo optimization and then be used to demonstrate NH₃ synthesis (from H₂) at the LPEA target production energy input requirement of 90 kWh/ton, which would translate to a total (H₂ production plus NH₃ synthesis) LPEA-based NH₃ 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 NH₃ production process.

ACCOMPLISHMENTS

- Completed second milestone (Milestone 3.2)—identification and evaluation of at least two PBI formulations—as described in Progress and Status (Task 3).
- Developed an improved IPC solvent (still undergoing optimization) and improved processing conditions, and used these developments to produce improved-quality core-shell (IPC-PBI) nanofibers and nanofiber-based membranes.
- Identified and prioritized four unique catalyst categories/types for empirical evaluation as LPEA cathode catalyst, and synthesized sample of first-priority catalyst material for initial characterization and rotating disk electrode (RDE) testing.
- Developed revised energy consumption target for LPEA process.

PROGRESS AND STATUS

Task 1 – Project Management (EERC)

The week of 28 January was confirmed for delivery, commissioning, and training in operation of the tunable diode laser-based analyzer procured for online high-temperature quantitation of ammonia and water vapor. 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			15	
2	IPC Synthesis Method and Performance Improvement	14 Dec 2019			30	
3	PIC Membrane Synthesis Method Development and Performance/Durability Optimization	14 Dec 2020			<20	
4	Cathode Catalyst Screening	14 Dec 2019			30	
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)

- Because Task 2 Leader Dr. John Hurley was out on medical leave for approximately 6 weeks of this quarter, progress was slower than normal. No milestone schedule impacts are anticipated.
- Work focused on improving miscibility of the solutions initially used for producing core–shell IPC–PBI nanofibers. The need for improved miscibility became apparent when analysis of initially prepared core–shell nanofibers showed discontinuity and nonuniform diameter of IPC cores, which indicated the occurrence of excessive interfacial surface tension between the IPC solution and PBI solution used for core–shell nanofiber production. The initially used solvents for IPC and PBI were water and dimethylacetamide (DMAc), respectively. Because PBI is notoriously difficult to solubilize and DMAc is widely recognized as the best PBI solvent, work focused on reducing the amount of water in the IPC solution to improve nanofiber processing compatibility between the PBI and IPC solutions. Experiments were conducted to establish the minimum amount of water needed—and/or identify a cosolvent (if needed)—to improve IPC–PBI solution compatibility sufficiently to enable improved core–shell nanofiber production. Cosolvents evaluated included DMAc, methanol, and DMAc–methanol combinations. As of the reporting date, the optimal IPC solution identified—based on core–shell nanofiber production tests—is 37 weight percent (wt%) IPC dissolved in a solvent comprising 70 wt% water and 30 wt% DMAc, which equates to an overall solution composition of 37 wt% IPC, 44 wt% water, 19 wt% DMAc.
- Task 2 work also included attempting to create 30-millimeter-diameter flat discs of dense IPC for proton conductivity and durability testing at various temperatures. The disk preparation approach includes evaporating water from IPC synthesis solution contained in a plastic mold. A variety of mold types/compositions and solution-heating methods and schedules have been

tested. Initial tests showed that the solid IPC is relatively clear but forms a meniscus at the sides of the mold and sticks to the mold, causing the disk to fracture when trying to remove it. Various mold release agents are being evaluated.

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

- Identified another commercially available PBI polymer formulation with potential for use as PIC membrane matrix. The formulation (referred to as GAZOLE 5000) is compared to the previously identified PBI formulation (available from PBI Performance Products, Inc.) in Figure 3.

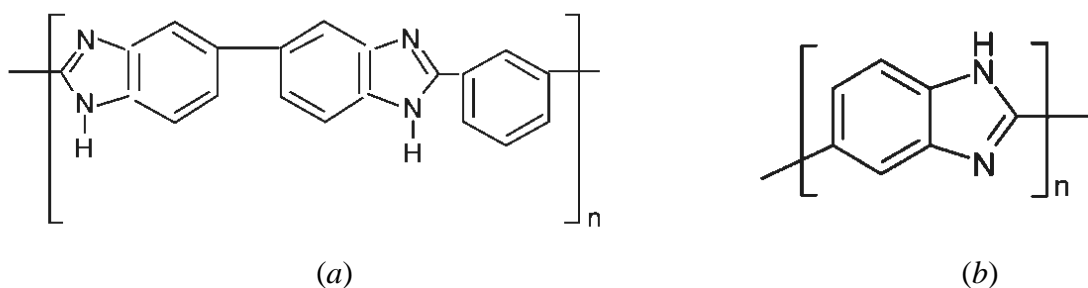


Figure 3. Commercially available PBI formulations. (a) Poly [2,2'-(m-phenylene)-5,5'-bibenzimidazole], with glass transition temperature (T_g) of 425°C, from PBI Performance Products, Inc. (b) Poly (2,5-benzimidazole), referred to as GAZOLE 5000, with melting temperature of 483°C, from Gharda Chemicals Limited.

- Using PBI solution (15 wt% PBI in 85 wt% DMAc) procured from PBI Performance Products Inc., monolithic matted PBI nanofiber-based membranes were fabricated and subjected to heat pressing. Figure 4 shows low- and high-magnification scanning electron microscope (SEM) photographs (micrographs) of PBI nanofibers with diameters of about 250 nanometers (nm). In the membrane fabrication process, nanofiber diameter is controlled by adjustment of material and process parameters, including PBI concentration in DMAc, voltage, and flow rate, while membrane thickness (prior to undergoing heat pressing) is controlled by adjustment of fiber collection time duration. Following membrane soaking in water to remove lithium chloride (added to PBI solution as a stabilizer), membranes undergo a controlled heat pressing process. Adjustment of heat pressing temperature, pressure, and duration is used to control membrane porosity, thickness, and mechanical properties. Figure 5 shows cross-sectional SEM photographs of a nominal 36-micrometer (μm) PBI nanofiber-based membrane after heat pressing at 200°C and 10,000 pounds per square inch (psi) for 1 minute. Prior to heat pressing, membrane thickness was about 50 μm .

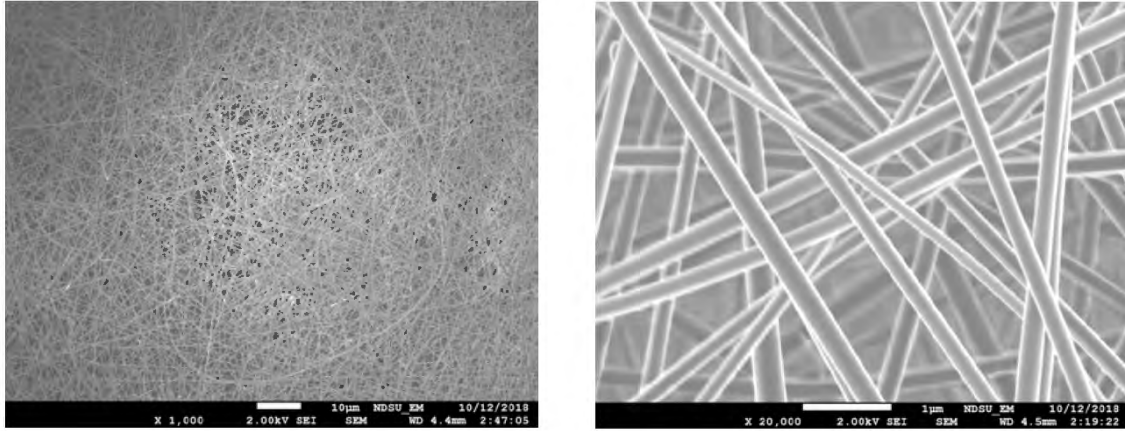


Figure 4. Low- and high-magnification ($\times 1000$ and $\times 20,000$) SEM micrographs of pure/monolithic continuous PBI nanofibers with diameters of about 250 nm.

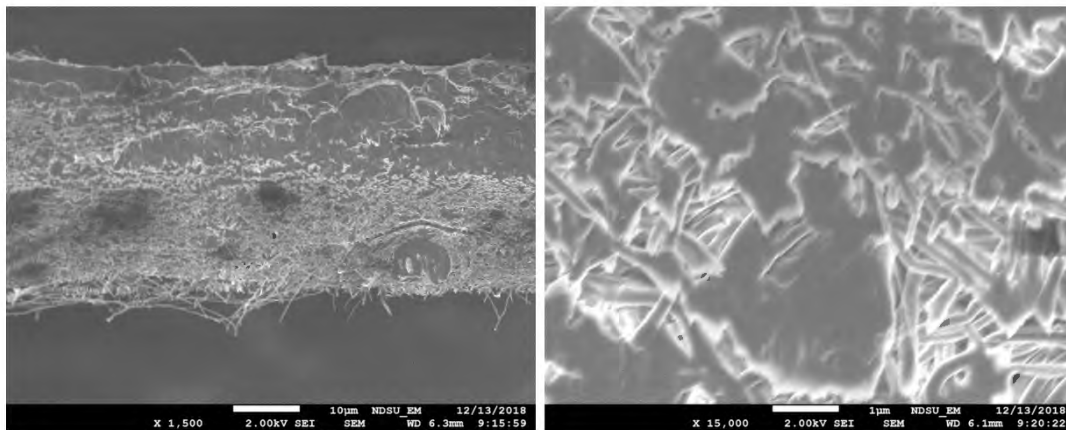


Figure 5. Low- and high-magnification ($\times 1500$ and $\times 15,000$) SEM micrographs of PBI nanofiber membrane after heat pressing at 200°C and 10,000 psi for 1 minute.

- Using PBI solution (15 wt% PBI in DMAc) and IPC solution (37 wt% IPC, 44 wt% water, 19 wt% DMAc), core-shell (IPC core in PBI shell) nanofiber-based membranes were fabricated and subjected to heat pressing. Figure 6 shows core-shell nanofibers with diameters of about 200 nm. As shown, IPC cores appear to be essentially continuous (important for optimal proton conductivity) but fairly variable (nonuniform) in diameter. Work is ongoing to ensure core continuity and more uniform core diameter throughout the entire length of each core-shell nanofiber. Critical to achieving these objectives is ensuring optimal compatibility between the IPC and PBI solutions during nanofiber processing. Progress has been made by adjusting IPC concentration in the IPC solution, and by adjusting the composition of the IPC solvent (initially, 100% water) as discussed earlier.

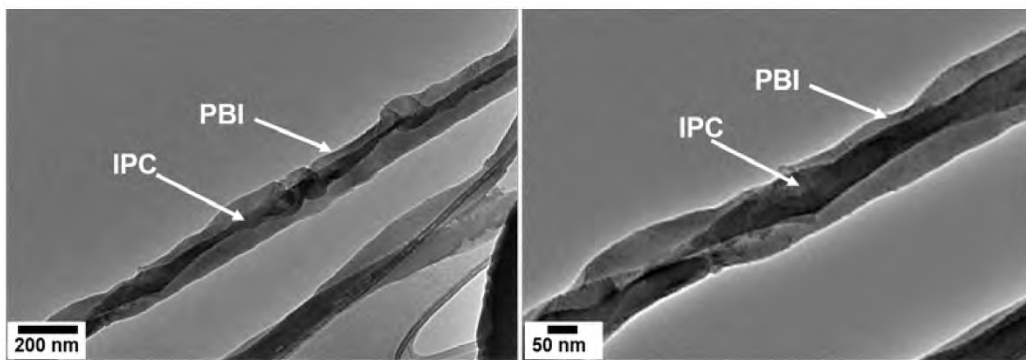


Figure 6. Transmission electron microscope (TEM) photographs of core-shell (IPC-PBI) nanofibers, showing continuity but nonuniform diameter of IPC cores.

- Using thermogravimetric analysis (TGA), the thermal stability of a PBI nanofiber-based membrane (with a thickness of about 35 μm) was compared to that of a procured (from PBI Performance Products) PBI film/membrane (with a thickness of 55 μm). Analysis was conducted under nitrogen. As shown in Figures 7 and 8, the two membranes displayed similar thermal stability. The higher mass loss for the commercial membrane is likely due to a higher content of absorbed moisture (PBI is hygroscopic).

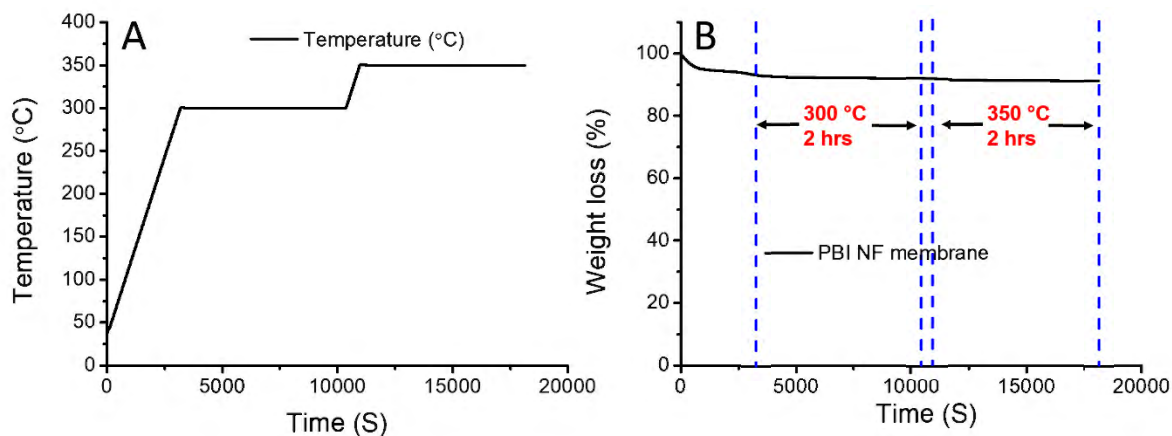


Figure 7. TGA-based thermal stability assessment of PBI nanofiber membrane. (A) TGA temperature program and (B) TGA profile, showing approximate 2% mass loss.

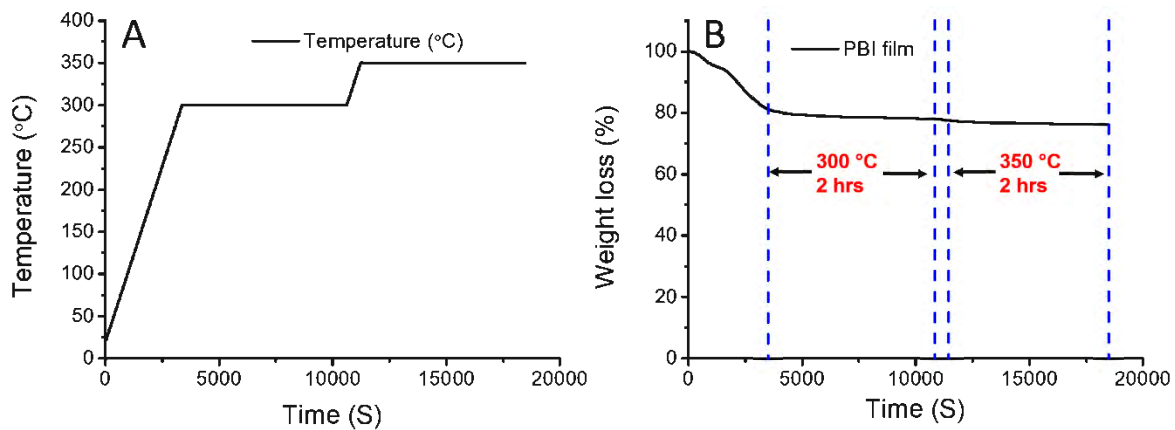


Figure 8. TGA-based thermal stability assessment of procured PBI film: (A) TGA temperature program and (B) TGA profile showing approximate 5% mass loss.

- PBI nanofiber membranes were compared to the procured PBI membrane based on tensile strength. Nanofiber membrane test samples included membranes comprising a single layer, two layers, and four layers of matted nanofibers. Prior to testing, all nanofiber membrane samples were heat pressed at 200°C and 10,000 psi for 1 minute. Figure 9 shows pretest membrane samples. Tensile strength test results are summarized in Figure 10 and Table 2.

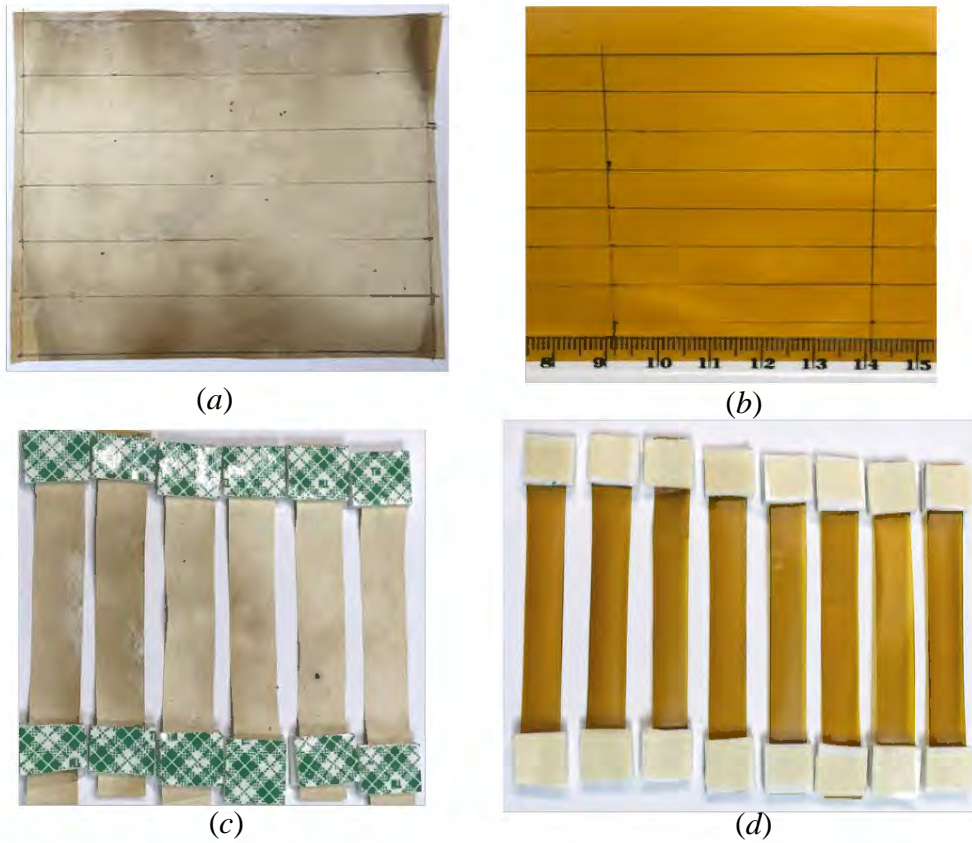


Figure 9. Pretest membrane materials: (a) PBI nanofiber membrane with marks for cutting, (b) procured PBI film, (c) nanofiber membrane test specimens, and (d) procured film test specimens.

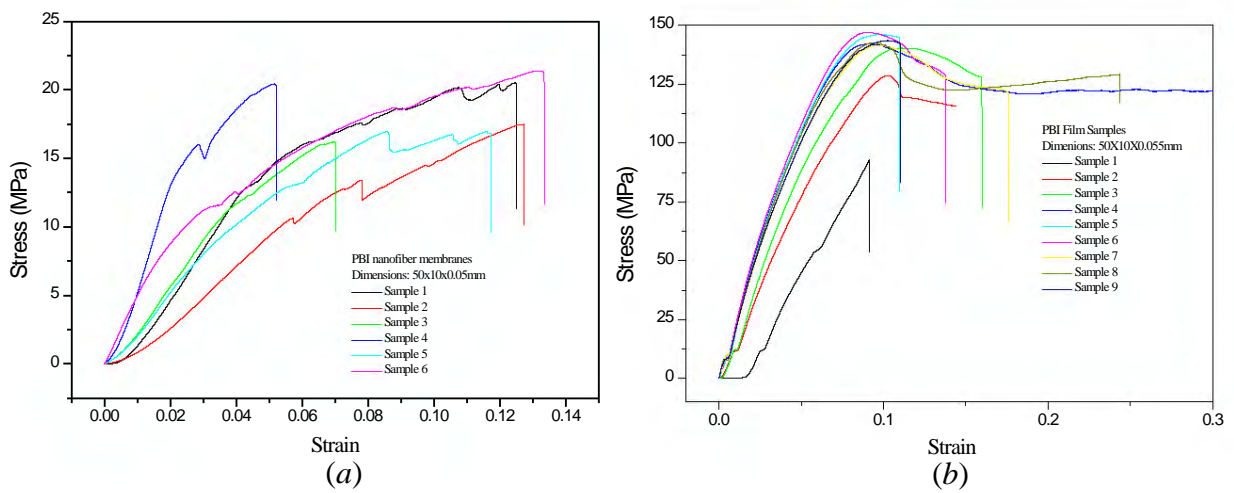


Figure 10. Stress–strain diagrams of PBI nanofiber membranes (a) and PBI film specimens (b).

Table 2. Tensile Strength of PBI Nanofiber-Based Membranes Versus Procured PBI Film

	Nanofiber membrane (single layer)	Nanofiber membrane (two-layered)	Nanofiber membrane (four-layered)	Solid PBI Film
Number of Tests	4	6	6	9
Length, Width, Depth, mm	50×10×0.04	50×10×0.04	50×10×0.05	50×10×0.055
Tensile Strength, MPa	17.89 ± 3.07	18.98 ± 2.17	18.83 ± 2.20	133.23 ± 18.23

- Installed a steam generator upstream of the LPEA test system for controlled humidification of LPEA reactant gases.
- Completed fabrication of the high-temperature sample holder for four-probe alternating current impedance (ACI) testing of membrane samples. The holder (shown in Figure 11) is a three-piece assembly (bottom plate, top plate, and wire holder) of high-temperature insulating material (zirconium oxide sheet) for positioning samples (PIC membrane or IPC material) within the LPEA test system at required temperature (up to 350°C) during ACI testing.

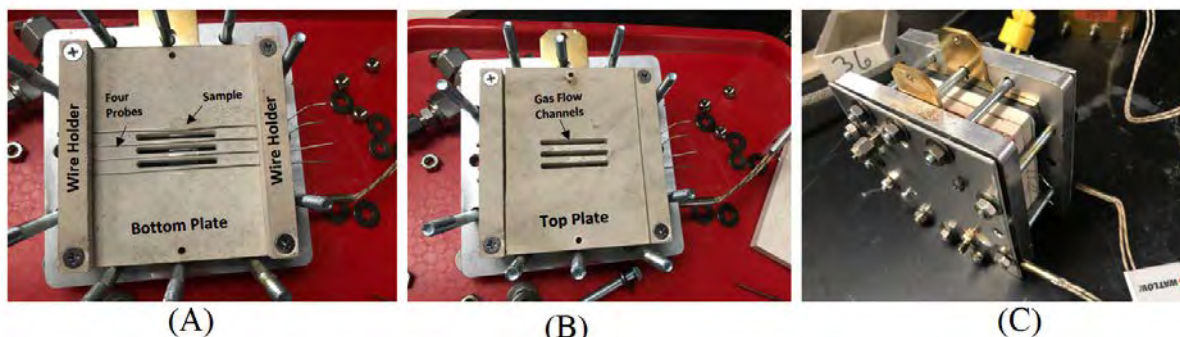


Figure 11. ACI sample holder: (A) bottom plate with membrane test sample and four probes in place, (B) top plate in place, and (C) assembled in unit cell hardware, ready for ACI testing.

Task 4 – Cathode Catalyst Screening (UND Chemistry)

- Through extensive literature review, four unique categories of cathode catalysts were identified for empirical testing and possible optimization. In order of priority for evaluation, the catalyst categories are:
 - Nano-scaled Ru on reduced graphene oxide (RGO) for enhanced electrical conductivity.
 - Perovskites, also called “SFCNs,” based on the formula $\text{SmFe}_{0.7}\text{Cu}_{0.3-x}\text{Ni}_x\text{O}_3$.
 - Transition metal nitrides.
 - Titanium-based hydrides.
- Using the draft standard operating procedure (SOP) for rotating disk electrode (RDE)-based catalyst evaluation as a starting point, needed supplies and hardware were procured for configuration of the RDE test station to enable catalyst evaluation via determination of:
 - Electrochemical surface area (ECSA).

- Nitrogen reduction reaction (NRR) specific activity and mass activity.
- Ammonia formation rate and Faradaic efficiency.
- SOPs were developed for synthesizing nanoscaled Ru- and perovskite-based catalysts.
- Nanoscaled Ru-based catalyst material, a composite of RGO, Ru, and Ru oxide—referred to as “RGO/Ru(oxide) composite”—was prepared and characterized. Figure 12 provides an overview of the synthesis process. Figure 13 provides evidence indicating the presence of Ru(oxide) particles on the RGO surface, and Figure 14 provides information regarding Ru(oxide) particle size and distribution.

PLANS FOR NEXT QUARTER

Task 2 – IPC Synthesis Method and Performance Improvement

- Prepare additional IPC solutions for core–shell nanofiber production testing, with the objective of establishing the optimal IPC solution composition for obtaining consistent-quality nanofibers with continuous uniform-diameter cores.
- Continue development of a method for production of consistent-quality IPC disks for proton conductivity testing.
- Using ACI testing and consistent-quality IPC disks, establish definitive proton conductivity values for IPC at various temperatures ranging from room temperature to 350°C.

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

- Further tailor PBI and IPC solutions (via adjustment of solvents and/or cosolvents) and process setup and operating conditions to enable better solution compatibility and improved production of core–shell nanofibers with continuous uniform-diameter cores.
- Optimize the overall heat pressing process—including a possible thermal annealing step—to improve core–shell nanofiber-based membrane mechanical properties.
- Acquire proton conductivity data (over an operating temperature range of ambient to 350°C) for core–shell nanofiber-based membranes.
- Utilize membrane morphology and thermal stability characterization techniques (including SEM, TEM, 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.
- Modify the LPEA test station as needed to enable integration with the online NH₃ analyzer.
- Conduct initial ACI tests on Nafion membrane samples to calibrate the ACI test setup and procedures.
- Conduct ACI tests on IPC samples and provide feedback for improving IPC proton conductivity if needed.
- Conduct ACI tests on PIC membrane samples and provide feedback for improving PIC membrane proton conductivity as needed.
- Update draft SOP for four-probe ACI testing based on test outcomes.

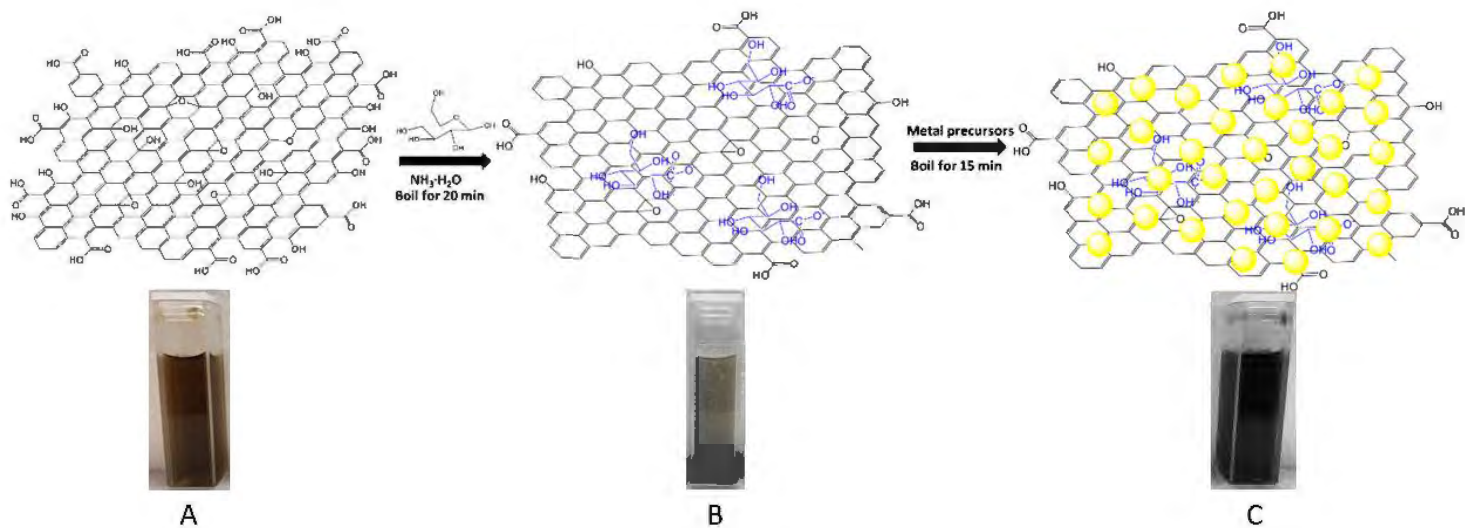
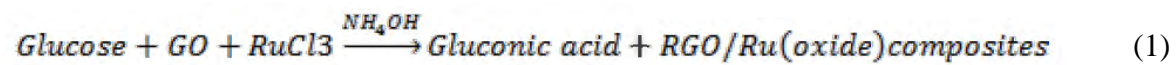


Figure 12. Synthesis of RGO/Ru(oxide) composites using glucose as reducing agent: (A) graphene oxide (GO) stirred with glucose, no heating; (B) GO reduced to RGO by glucose while boiling for 20 minutes; and (C) RGO/Ru(oxide) composites formed via addition of RuCl_3 while boiling for 15 minutes.

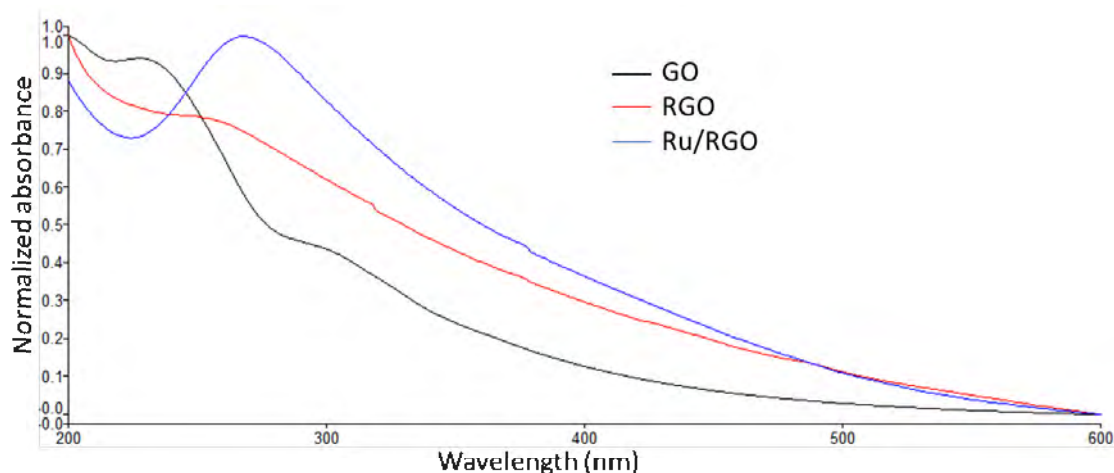


Figure 13. UV-vis absorption spectra comparison. The apparent peak at ca. 280 nm indicates the presence of Ru(oxide) on the RGO surface.

- Continue revision of the initial draft manuscript on high-performance, high-temperature polymers for electrochemical membrane applications, to include increased emphasis on $\geq 300^\circ\text{C}$ durability only, rather than durability plus proton conductivity.

Task 4 – Cathode Catalyst Screening

- Synthesize perovskite-based catalysts for evaluation.
- Validate RDE test station setup and procedures for determination of catalyst:
 - ECSA.
 - NRR specific activity and mass activity.
 - Ammonia formation rate and Faradaic efficiency.
- Evaluate performance of synthesized catalysts via RDE testing.
- Develop set of catalyst performance threshold values for use in screening experimental catalysts (selecting catalysts for more detailed evaluation and/or optimization).
- For selected catalysts, correlate performance with composition and morphology via use of SEM, TEM, EDS, x-ray diffraction (XRD), and x-ray photoelectron spectroscopy (XPS) as needed.

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.

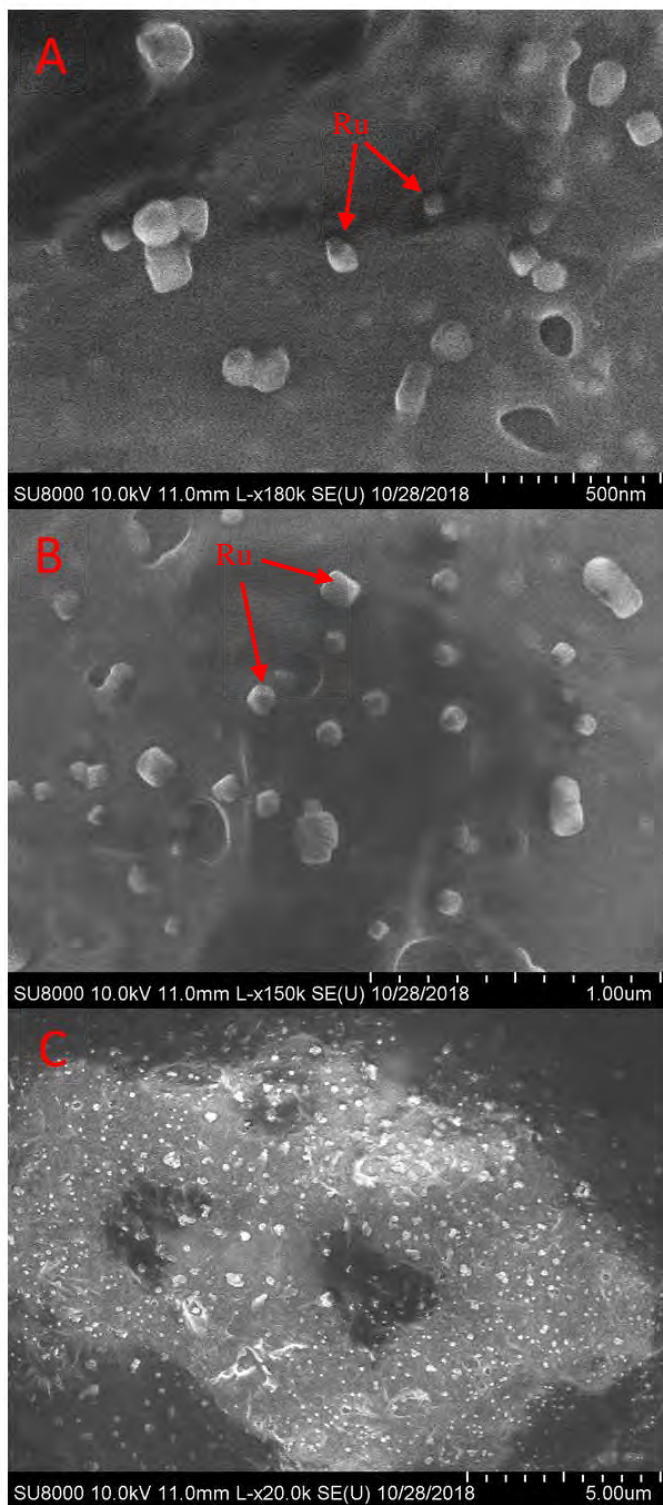


Figure 14. SEM images of RGO/Ru(oxide) composites, showing nominal Ru(oxide) particle size of 100–200 nm. In Image (C), milky-appearing material is likely RGO mixed with glucose and salt residuals.

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)

- Although Task 7 was not scheduled to start until 15 June 2020, the EERC initiated an effort to develop a revised energy consumption comparison between conventional HB-based and LPEA-based ammonia production. An initial draft of this revised comparison is included as Appendix A.

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.

PARTNERS AND FINANCIAL INFORMATION

This project is sponsored by NDIC, DOE, UND Chemistry, North Dakota State University, and Proton. Table 3 shows the initial 18-month budget of \$1,663,107 for this project and expenses through the reporting period.

Table 3. Initial 18-Month Budget and Expenses Through the Reporting Period

Funding Source	Budget	Current Reporting Period Expenses	Cummulative Expenses as of 12/31/18	Remaining Balance
DOE	\$1,324,993	\$197,222	\$256,809	\$1,068,184
UND Chemistry – In Kind	\$34,514	\$3,694	\$4,929	\$29,585
NDIC	\$230,000	\$9,190	\$103,338	\$126,662
NDSU – In Kind	\$60,000	\$16,302	\$16,302	\$43,698
Proton OnSite – In Kind	\$13,600	\$0	\$0	\$13,600
Total	\$1,663,107	\$226,408	\$381,378	\$1,281,729

APPENDIX A

REVISED TARGET FOR LOW-PRESSURE ELECTROLYTIC AMMONIA ENERGY CONSUMPTION

Revised Target for Low-Pressure Electrolytic Ammonia Energy Consumption
25 January 2019

During the 20 September 2018 visit to the Energy & Environmental Research Center (EERC) by the U.S. Department of Energy Advanced Manufacturing Office representatives, the EERC presented an energy consumption comparison of conventional ammonia production (steam methane reforming [SMR] followed by high-pressure Haber–Bosch [HB] ammonia synthesis) and ammonia production via SMR followed by low-pressure electrolytic ammonia (LPEA) for ammonia synthesis. In this comparison, the cited conventional ammonia production energy consumption value was an average for operating U.S. ammonia plants (rather than for a state-of-the-art plant) and the LPEA energy consumption target was incorrectly calculated. To provide a more meaningful comparison, the EERC undertook an effort to 1) acquire an accurate value for state-of-the-art ammonia production energy consumption and 2) develop a more accurate LPEA energy consumption target.

Table A-1 lists revised energy consumption values. In the table, the value for state-of-the-art ammonia production via SMR + HB is derived from a 2018 Incitec Pivot Limited/Dyno Nobel presentation to stockholders. The presentation lists a natural gas energy input requirement of 32 million Btu per metric ton of ammonia production (which translates to 8525 kilowatt-hours/ton [kWh/ton]) at the Waggaman, Louisiana, ammonia plant. The state-of-the-art Waggaman plant, with an annual ammonia production capacity of about 880,000 tons (about 2400 tons/day), was commissioned in September 2016. The 8525 kWh/ton value does not include electrical energy, which typically accounts for about 1% of total ammonia production energy consumption [1]. The SMR energy consumption value includes the total energy utilized (including hydrogen purification via pressure swing adsorption) to produce 0.1765 tons hydrogen, the amount needed to produce 1 ton of ammonia. The 90-kWh/ton LPEA target is based on an ammonia synthesis voltage of 0.12 V (at standard temperature and pressure) and a current efficiency of 65%. Figure A-1 compares the HB- and LPEA-based ammonia production pathways based on the Table A-1 energy consumption values.

Table A-1. Conventional 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	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 NH₃ production energy efficiency of 65%.

** Includes SMR and LPEA (target) energy inputs plus 10 kWh/ton for N₂ separation from air and 86 kWh/ton for NH₃ purification/condensation and compression.

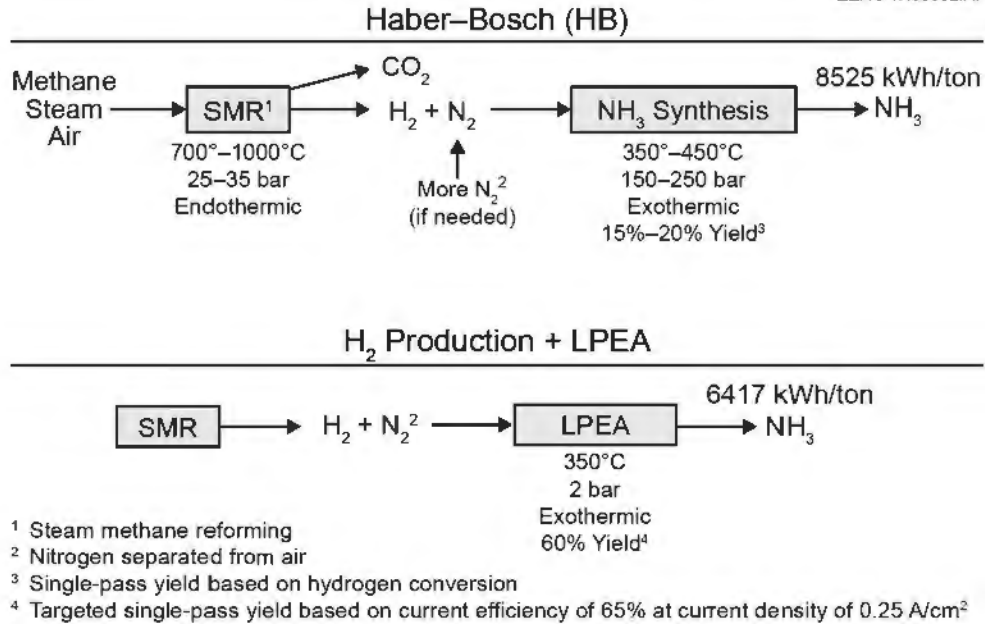


Figure A-1. HB versus LPEA-based NH₃ production (25 January 2019).

References

1. Noelker, K., Ruether, J., GmbH, U., Dortmund. Low Energy Consumption Ammonia Production: Baseline Energy Consumption, Options for Energy Optimization. Presented at the Nitrogen & Syngas Conference, Duesseldorf, Germany, 2011.
2. Incitec Pivot Limited, 2018, Half Year Results Presentation, available at Incitec Pivot Limited 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.
4. Rostrup-Nielsen, J.R. and Rostrup-Nielsen, T. Large-Scale Hydrogen Production, 2002, paper based on keynote lecture presented at 6th World Congress of Chemical Engineering, Melbourne, Australia, 2001. Available at Haldor Topsoe website: www.topsoe.com/.