January 30, 2020

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 Project Status 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, 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/bjr

Attachment

c/att: Andrea Holl Pfennig, North Dakota Industrial Commission
LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION

Quarterly Project Status Report

(for the period of October 1, 2019, through December 31, 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
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Grand Forks, ND 58202-9018

January 2020
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ACKNOWLEDGMENT

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EXECUTIVE SUMMARY

This quarterly report summarizes October–December 2019 progress made toward achieving milestones and objectives of the LPEA project under way at the University of North Dakota Energy & Environmental Research Center (EERC). Partners on the 3-year (June 2018–July 2021) project include North Dakota State University (NDSU) and Nel Hydrogen (formerly Proton OnSite). The project goal is to demonstrate an ammonia production energy reduction of at least 16% by replacing state-of-the-art (2018) high-pressure Haber–Bosch-based ammonia synthesis with the EERC-developed LPEA process. Achieving this energy reduction goal requires improving the proton conductivity, gas impermeability, and durability of the EERC–NDSU-developed polymer–inorganic composite (PIC) proton exchange membrane, a critical LPEA process component capable of high-rate proton transfer at 300°C. Key accomplishments of the October–December 2019 quarter include the following:

- Improved methods and equipment were utilized to fabricate Inorganic Proton Conductor 2 (IPC2)-based cast film PIC membranes with an IPC2 loading of 75 mass% (in a 25 mass% polybenzimidazole [PBI] matrix).
- Using a single-chamber electrochemical cell-based method, a project-synthesized ruthenium-nanoparticle-on-reduced-graphene-oxide catalyst was definitively shown to provide a faradaic efficiency (FE) for ammonia synthesis (at room temperature) of 13.6%. This result will be compared to the FE achievable under similar conditions with a double-chamber pressure-containing electrochemical cell to be delivered to the EERC in late January 2020.
- Gas diffusion layer-based electrodes (niobium nitride cathode and platinum anode) were prepared by Nel Hydrogen and delivered to the EERC for testing.
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 $\geq 65\%$ for NH₃ formation at a current density of $\geq 0.25$ amps/cm² (A/cm²), NH₃ production energy efficiency of $\geq 65\%$, and $\leq 0.3\%$ performance degradation per 1000 h of operation.

![Figure 1. State-of-the-art (2018) HB versus LPEA-based NH₃ production.](EERC_TAS3502.AI)
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 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 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 0.8 megawatt hours (MWh/ton), which would translate to a total (H₂ production plus NH₃ synthesis) LPEA-based NH₃ 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 NH₃ production process.

ACCOMPLISHMENTS

- Improved methods and equipment were utilized to fabricate IPC2-based film cast PIC membranes with an IPC2 loading of 75 mass% (in 25 mass% PBI).

- Using a single-chamber electrochemical cell-based method, a project-synthesized ruthenium-nanoparticle-on-reduced-graphene-oxide catalyst was definitively shown to provide a faradaic efficiency (FE) for ammonia synthesis (at room temperature) of 13.6%. This result will be compared to the FE achievable under similar conditions with a double-chamber pressure-containing electrochemical cell to be delivered to the EERC in late January 2020.

- Gas diffusion layer-based electrodes (niobium nitride cathode and platinum anode) were prepared by Nel and delivered to the EERC for testing.

PROGRESS AND STATUS

Task 1 – Project Management

Official notification of approval to proceed from Budget Period (BP) 1 (which ended on 14 December 2019) to BP2 was received on 21 January 2020. To maintain a modicum of project activity prior to this official notification, EERC management approved project spending up to a level of $20,000, somewhat limiting EERC activities during the approximate 5-week gap. As shown in Table 1, Task 2 is complete, with the understanding that if any additional work on IPC2 synthesis method improvement is needed, this work will be conducted under Task 3. Also shown is that uncompleted catalyst-screening work is shifted to Task 5. A patent application on IPC2 and its deployment in the PIC membrane was completed. Prior to submittal of the application to the U.S. Patent Office, the EERC is awaiting review and approval of the application by the U.S. Department of Defense.
Table 1. Task Schedule

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<tr>
<th>Task No.</th>
<th>Task Title or Brief Description</th>
<th>Task Completion Date*</th>
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<td>4</td>
<td>Cathode Catalyst Screening</td>
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<td>7</td>
<td>Techno-Economic Analysis</td>
<td>14 June 2021</td>
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* Unless otherwise noted, tasks start on 15 June 2018 project start date.

Task 2 – IPC Synthesis Method and Performance Improvement

Equipment was purchased to enable larger-batch synthesis of IPC2. With deployment of the new equipment and synthesis method improvements, batch size was increased from 3 to 15 grams of IPC2 product. In addition, three alternative IPC2 configurations/formulations were synthesized with the objective of ascertaining any possible effects on IPC2 proton conductivity. One synthesis method involved an attempt to increase the ratio of amorphous-to-crystalline material, since several technical papers suggest that IPC2 amorphous material may play a more significant role in proton conductivity than crystalline material. Another method involved an attempt to add OH groups to the IPC2 structure. The third involved development of a lower-temperature synthesis method that could facilitate easier blending of IPC2 with PBI solution, and subsequently easier membrane film casting. These new IPC2 configurations/formulations are awaiting proton conductivity testing.

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

Equipment upgrades and improvements made to the solution film casting method for PIC membrane fabrication enabled ramping up IPC2 loading from 33 to 75 wt% IPC2 (in 67 to 25 wt% PBI matrix). Figure 3 shows cast film PIC membranes comprising 75 wt% IPC2. Prior to membrane fabrication, IPC2 particles were ground/milled to an average particle size of about 700 nanometers, as shown in Figure 4.
Figure 3. Solution film-cast PIC membranes comprising 75 wt% IPC2.

Figure 4. Particle-size distribution of IPC2 milled for 10 minutes (left) and 30 minutes (right).

2129 ± 325-nm Average Particle Size

686 ± 99-nm Average Particle Size
Task 4 – Cathode Catalyst Screening

A project-prepared catalyst comprising ruthenium nanoparticles on reduced graphene oxide support (Ru/RGO) was preliminarily evaluated (screened) for application to nitrogen reduction/ammonia synthesis. Electrolysis measurements were conducted using an Autolab potentiostat and a single-chamber cell with a conventional three-electrode configuration. Each working electrode comprised a 1 × 2-cm tab of Toray carbon paper on which a catalytic ink (precisely 5 mg per cm²) was deposited. The catalytic ink was prepared by ultrasonically dispersing 10 mg of catalytic powder in a homogeneous mixture comprising 450 µL isopropyl alcohol (Sigma-Aldrich, 99.5%) and 50 µL Nafion® solution (10 wt% Sigma-Aldrich). The counter electrode was a slab of glassy carbon, and a saturated calomel electrode (SCE)—used as reference electrode—was connected to the cell through a Lugginn-Haber capillary tip to avoid working electrode potential shift that could result from SCE contamination. Prior to electrolysis, 0.1 mol L⁻¹ H₂SO₄ aqueous solution was saturated by N₂ for 30 minutes, after which electrolysis experiments were conducted (with constant N₂ sparging) at cathodic potentials ranging from −0.5 to −0.70 V (versus SCE) at room temperature. Figure 5 shows that a faradaic efficiency for ammonia synthesis of 13.6% was achieved at a potential of −0.60 V.

Figure 5. FE of Ru/RGO for ammonia synthesis at varying applied potentials in 0.1 mol L⁻¹ H₂SO₄ under ambient conditions.
Task 5 – PIC-Based MEA Fabrication Method Development and LPEA Unit Cell Performance/Durability Optimization

Nel-fabricated electrodes (niobium nitride cathode and platinum anode) were delivered to me EERC for testing. Electrodes were fabricated by spray deposition of a specially formulated ink (comprising IPC2 [as ionomer], PBI, dimethylacetamide, and catalyst) on a gas diffusion layer substrate, followed by spray deposition of an ionomer-dispersion top coating. Catalyst loading on each 128-cm²-active-area electrode—from which two 50-cm²-active-area electrodes will be cut for testing—was 3.0 mg/cm².

Task 7 – Techno-Economic Analysis

No activity this quarter.

PLANS FOR NEXT QUARTER

Task 1 – Project Management

• Get all subrecipient BP2 contracts in place.

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

• Acquire proton conductivity data for cast film PIC membranes and alternative IPC2 configuration/formulation materials.

• Evaluate viability of alternative IPC2 materials based on proton conductivity and compatibility with PIC membrane film-casting process.

• Optimize cast film membrane based on 300°C proton conductivity magnitude and sustainability, with optimization parameters including:
  – IPC2 material type (formulation/configuration).
  – IPC2 loading.
  – IPC2 particle size (a dry ball-milling process utilizing tungsten carbide balls may yield a smaller particle size than the currently achievable 700 nm).
  – Absolute humidity input.

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

- Using a double-chamber H-type cell (to be delivered to the EERC in late January 2020), evaluate Ru/RGO, single-atom Ru on nitrogen-doped carbon, niobium nitride, chromium nitride, and zirconium nitride catalysts based on faradaic efficiency for ammonia synthesis at room temperature. Select at least two catalysts for delivery to Nel.

- Fabricate and evaluate electrodes for ammonia synthesis at a temperature of about 160°C.

- Fabricate and evaluate MEAs (in unit cell) at temperatures of 160°–300°C.

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

- Initiate design of 100-g/d system.

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

None.
Actual or Anticipated Problems or Delays and Corrective Actions or Plans to Resolve Them

None.

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, NDSU, and Proton. Table 2 shows the initial 18-month budget of $1,663,107 for this project and expenses through the reporting period.

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