April 29, 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 January 1 through March 31, 2020.

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, North Dakota Industrial Commission
LOW-PRESSURE ELECTROLYTIC AMMONIA PRODUCTION

Quarterly Project Status Report

(for the period of January 1, 2020, through March 31, 2020)

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:

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April 2020
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ACKNOWLEDGMENT

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EXECUTIVE SUMMARY

This quarterly report summarizes January–March 2020 progress made toward achieving milestones and objectives of the low-pressure electrolytic ammonia (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), Nel Hydrogen (formerly Proton OnSite), and North Dakota Industrial Commission. 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 January–March 2020 quarter include the following:

- Initial testing of an alternative-formulation inorganic proton conductor (IPC) gave a proton conductivity of 1.2*10⁻² siemens/centimeter (S/cm), 20% higher than the 1.0*10⁻² S/cm target and worthy of further testing to validate.

- The first experimental membrane–electrode assembly (MEA) was prepared and tested for proton conductivity, yielding a stable value of 0.9*10⁻² S/cm at 300°C.

- Room-temperature chronoamperometric testing of a niobium nitride ammonia synthesis catalyst yielded an ammonia synthesis rate of 10.6 µg·h⁻¹·mg⁻¹ at a faradaic efficiency of 11%.

The EERC holds an unwavering commitment to the health and well-being of its employees, partners and clients, and our global community. As such, precautionary measures have been implemented in response to COVID-19. Staff continue to carry out project-related activities remotely, and personnel supporting essential on-site laboratory and testing activities are proceeding under firm safety guidelines. Travel has been minimized, and protective measures are being undertaken for those who are required to travel. At this time, work conducted by EERC employees is anticipated to progress with minimal disruption. Challenges posed by economic variability will be met with open discussion between the EERC, the DOE Project Manager, and other partners to identify solutions. The EERC is monitoring developments across the nation and abroad to minimize risks, achieve project goals, and ensure the success of our partners and clients.
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).

Figure 1. State-of-the-art (2018) HB versus LPEA-based NH₃ production.
• 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 NH₃ formation at a current density of ≥0.25 amps/cm² (A/cm²), NH₃ production energy efficiency of ≥65%, and ≤0.3% performance degradation per 1000 h of operation.

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.

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 compose 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

- Initial testing of an alternative-formulation IPC gave a proton conductivity of 1.2*10⁻² siemens/centimeter (S/cm), lower than the standard-formulation IPC peak measured value of 4*10⁻² S/cm but 20% higher than the 1.0*10⁻² S/cm target and worthy of further testing to validate.

- The first experimental MEA was prepared and tested for proton conductivity, yielding a stable value of 0.9*10⁻² S/cm at 300°C.

- Room-temperature chronoamperometric testing of a niobium nitride ammonia synthesis catalyst yielded an ammonia synthesis rate of 10.6 µg-h⁻¹-mg⁻¹ at a faradaic efficiency of 11%.
PROGRESS AND STATUS

Task 1 – Project Management

Table 1 summarizes task status and shows that Tasks 3, 5, and 6 are behind schedule. These progress delays resulted from 1) a tentative BP2 start at the front end of the quarter while awaiting official approval of BP2 funding and 2) a directive issued March 15 by UND President Dr. Joshua Wynne (in response to coronavirus spread concerns) instructing all nonessential EERC employees to work remotely till at least April 4, 2020, which restricted project laboratory activities. Similar restrictions were implemented at roughly the same time by project partners NDSU and Nel. Because the project is 15 months from its planned end date, the EERC and partners plan to intensify project effort when labs are reopened, get back on schedule, and avoid the need to request project extension.

<table>
<thead>
<tr>
<th>Task No.</th>
<th>Task Title or Brief Description</th>
<th>Task Completion Date*</th>
<th>Task Progress Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>Design, Fabrication, and Operation of 100-g/d LPEA System</td>
<td>Original Planned: 14 March 2021, Revised Planned: 14 March 2021, Actual Complete: 75% Complete</td>
<td>Planned 15 Dec. 2019 start didn’t happen</td>
</tr>
<tr>
<td>7</td>
<td>Techno-Economic Analysis</td>
<td>Original Planned: 14 June 2021, Revised Planned: 14 June 2021, Actual Complete: 15 June 2020 start</td>
<td></td>
</tr>
</tbody>
</table>

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

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

- As described in the October–December 2019 quarterly report, three alternative IPC2 configurations/formulations (IPC2-A1, IPC2-A2, and IPC2-A3) were synthesized. IPC2-A1 is 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. IPC2-A2 is an attempt to add hydroxy (OH) groups to the IPC2 structure, since OH groups are reported to enhance proton conductivity. IPC2-A3 was made using a lower-temperature synthesis method that could facilitate easier blending of IPC2 with PBI solution, and subsequently easier membrane film casting. Initial testing of
IPC2-A3 showed a proton conductivity of $1.2 \times 10^{-2}$ S/cm, lower than the IPC2 peak measured value of $4 \times 10^{-2}$ S/cm but 20% higher than the $1.0 \times 10^{-2}$ S/cm target and worthy of further testing to validate.

- Based on scanning electron microscope (SEM) analyses, as-synthesized IPC2 particles exhibit a relatively jagged (as opposed to spherical) morphology. In an attempt to reduce particle size and increase “sphericity,” new particle grinding techniques are being explored. Figure 3 compares as-synthesized IPC2 particles with particles ground for 60 minutes in a ball mill with tungsten carbide balls. During grinding, the particles were suspended in dimethylacetamide to inhibit agglomeration. As shown, the grinding regimen effected a significant reduction in particle size, with limited impact on particle shape.

![Figure 3. As-synthesized IPC2 particles (top) and particles ground for 60 minutes (bottom).](image-url)
Task 5 – PIC-Based MEA Fabrication Method Development and LPEA Unit Cell Performance/Durability Optimization

- An experimental MEA was prepared. The MEA embodied an 85% IPC2–15% PBI solution-cast membrane (70-µm thickness) sandwiched between two Nel-fabricated platinum electrodes. Each electrode comprised a carbon paper sheet coated with a catalyst ink comprising particles of platinum and IPC2 (serving as ionomer) suspended in a PBI-in-dimethylacetamide solution. The three MEA layers were squeezed together (not heat-pressed) in a metal holder and tested for proton conductivity at 300°C, yielding a stable value of 0.9*10^{-2} S/cm. This initial result with a crude MEA is significantly higher than the 300°C proton conductivities achieved to date with a solution-cast membrane only (not MEA), which range from 0.2–0.4*10^{-2} S/cm. Additionally encouraging is that because the use of platinum electrodes enables actual hydrogen oxidation at the anode and proton reduction at the cathode, the test result represents a measured value of actual (as opposed to inferred) proton conductivity, as confirmed by the distinctively different Nyquist plot obtained. Based on this finding, we are investigating the possibility that surface oxidation of the stainless steel membrane holder used for conductivity testing may be negatively impacting measured results.

- Niobium nitride (NbN), chromium nitride (CrN), and zirconium nitride (ZrN) were screened for use as cathode catalyst. Screening tests were conducted with an Autolab potentiostat using a divided H-type electrochemical cell separated by ion exchange membrane (Nafion® 117). The Nafion membrane was pretreated in 5% H2O2 solution for 1 hour, then in 0.5 mol L^{-1} H2SO4 for 1 hour at 80°C, and then rinsed in ultrapure water several times. Catalyst inks were prepared by ultrasonically dispersing 10 mg of catalyst powder in a mixture composed of 450 µL isopropyl alcohol and 50 µL 10-weight% Nafion® solution. A catalyst loading of about 3 mg catalyst-cm^{-2} was deposited onto Toray carbon paper (3.5-cm² geometric area). Reference and counter electrodes were Ag/AgCl (saturated KCl) and platinum wire, respectively. During electrolysis, N2 gas (99.99% purity) was continuously fed into the cathodic compartment. Figure 4 compares chronoamperometry curves obtained for the three catalysts at a constant potential of −0.60 V versus Ag/AgCl in N2-saturated 0.1 mol-L^{-1} H2SO4 electrolyte, at room temperature. Table 2 compares the three catalysts based on faradaic efficiency and ammonia production rate.

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

No activity this quarter.

Task 7 – Techno-Economic Analysis

No activity this quarter.
Figure 4. Chronoamperometry curves of thin-layer electrodes recorded at -0.60V in N₂-saturated 0.1 mol-L⁻¹ H₂SO₄ at room temperature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NH₃ Production Rate, µg-h⁻¹-mg⁻¹</th>
<th>NH₃ Synthesis Faradaic Efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbN</td>
<td>10.6</td>
<td>11.0</td>
</tr>
<tr>
<td>ZrN</td>
<td>9.8</td>
<td>2.3</td>
</tr>
<tr>
<td>CrN</td>
<td>10.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

PLANS FOR NEXT QUARTER

**Task 1 – Project Management**

- Devise plan for getting project back on schedule after lab shutdowns are lifted.

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

- For proton conductivity testing, investigate use of membrane holder made from graphite, titanium, or other electrically conductive material not susceptible to oxide layer build-up in high-temp steam. Objective is to see if gradual oxide buildup is possible reason for observed gradual conductivity loss at 300°C.

- Acquire proton conductivity data for IPC2 alternative formulations IPC2-A1 and IPC2-A2.
• Produce 85% IPC2 thin disk via hot-press method using PBI powder (rather than PBI in dimethylacetamide solvent) and IPC2. As per PBI Performance Products recommendation, press at 480°C (PBI glass transition temp is 427°C) and 20,000 psi. Objective is to eliminate voids/cavities and increase packing density of IPC2 particles. Test disk proton conductivity.

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

• Using double-chamber H-type cell, evaluate more candidate 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

Project is behind schedule due to social distancing directives aimed at minimizing coronavirus spread. A plan is being developed to ramp up project activity and get back on schedule when restrictions are lifted.

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 3 shows the total budget of $3,164,010 for this project and expenses through the reporting period.

Table 3. Project-to-Date Financial Report at March 31, 2020

<table>
<thead>
<tr>
<th>Funding Source</th>
<th>Budget</th>
<th>Current Reporting Period Expenses</th>
<th>Cumulative Expenses as of 3/31/20</th>
<th>Remaining Balance</th>
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<td>UND Chemistry – In Kind</td>
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<td>NDIC</td>
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<td>NDSU – In Kind</td>
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<td>Proton – In Kind</td>
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<tr>
<td><strong>Total</strong></td>
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<td><strong>$270,719</strong></td>
<td><strong>$1,765,893</strong></td>
<td><strong>$1,398,117</strong></td>
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