



August 3, 2022

Ms. Karlene Fine
Executive Director
North Dakota Industrial Commission
600 East Boulevard Avenue
State Capitol, 14th Floor
Bismarck, ND 58505-0310

Dear Ms. Fine:

Subject: EERC Final Report Entitled “Low-Pressure Electrolytic Ammonia (LPEA) Production”
Contract No. R-036-45; EERC Fund 23228

Attached is the final report for the period of December 15, 2019, through June 30, 2022.

If you have any questions, please contact me by phone at (701) 777-2982, by fax at (701) 777-5181, or by e-mail at taulich@undeerc.org.

Sincerely,

DocuSigned by:

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Ted R. Aulich
Principal Process Chemist, Fuels and Chemicals

TRA/rlo

Attachment

c/att: Reice Haase, North Dakota Industrial Commission



LOW-PRESSURE ELECTROLYTIC AMMONIA (LPEA) PRODUCTION

Final Report

(for the period December 15, 2019, through June 30, 2022)

Karlene Fine

North Dakota Industrial Commission
State Capitol, 14th Floor
600 East Boulevard Avenue, Department 405
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Contract No. R-036-45

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August 2022

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LOW-PRESSURE ELECTROLYTIC AMMONIA (LPEA) PRODUCTION

EXECUTIVE SUMMARY

Project Purpose – The project goal was to advance and demonstrate the techno-economic viability of the low-pressure electrolytic ammonia (LPEA) process developed by the University of North Dakota Energy & Environmental Research Center (EERC) for producing ammonia from electricity, hydrogen, and nitrogen. The critical enabling technology of the LPEA process is an EERC-developed proton-exchange electrolyte (PEE) capable of high proton conductivity (at least 1×10^{-2} [0.01] siemens/centimeter [S/cm]) at 200°–300°C. An affordable PEE that works at 200°–300°C has been a major and elusive goal of the global electrochemistry industry for over 25 years because of the techno-economic benefits it would bring to ammonia, fuel cell, electrolyzer, and other electrochemical technologies capable of operating on and maximizing the value of renewable energy and hydrogen. Also critical to LPEA performance is a cathode catalyst capable of ammonia synthesis at a rate of at least 1×10^{-10} moles/second-cm² catalyst surface area (mol-s⁻¹cm⁻²) in viability/screening tests conducted at room temperature and 1×10^{-7} mol-s⁻¹cm⁻² at 200°–300°C (for commercial viability). The project focused on these two goals.

Work Accomplished – Project work included 1) identifying appropriate materials for formulating, optimizing (for proton conductivity and durability), and filing a patent application for a 200°–300°C-capable PEE; 2) identifying, synthesizing or procuring, and screening the performance of candidate cathode catalysts based on ammonia synthesis rate at room temperature; 3) using optimized PEEs, best-performing cathode catalysts, and a platinum anode catalyst to fabricate membrane-electrode assemblies (MEAs); and 4) evaluating the MEAs based on ammonia synthesis rate and electrical current efficiency.

Project Results – The most important project result is development of a PEE based on cerium ultraphosphate (CUP), an easily synthesized (at low cost) material with a unique physical arrangement (crystalline structure) of phosphorus and oxygen atoms that enables high-rate transport of protons (proton conductivity) over a temperature range of 200–300°C. CUP-based PEEs (C-PEEs) fabricated using two different project-developed techniques were demonstrated to provide proton conductivities (at 200–300°C) exceeding the 1×10^{-2} -S/cm target for up to 100 hours. In room-temperature catalyst-screening tests, a project-synthesized cathode catalyst was demonstrated to produce ammonia at 1.7×10^{-10} mol-s⁻¹cm⁻², exceeding the target by 70%. However, when deployed in an MEA (in combination with an optimized C-PEE and a proven platinum anode catalyst) and tested at 300°C, the cathode catalyst gave an ammonia synthesis rate of only 1×10^{-10} mol-s⁻¹cm⁻². Because both the C-PEE and cathode catalyst were demonstrated to meet performance targets when tested separately, their inadequate performance when combined (with a proven anode catalyst) in an MEA indicates the need for an improved MEA fabrication technique that yields more intimate integration of C-PEE, anode, and cathode.

Potential Applications of Project – Ongoing post-project work is focused on improving the MEA fabrication technique to enable optimum performance and deployment of the C-PEE in commercial ammonia production. This work includes 1) improving C-PEE and MEA fabrication methods to both increase MEA performance/efficiency and ensure that the fabrication methods are

cost-effectively scalable to output capacities needed for commercial viability, 2) maximizing cathode catalyst ammonia synthesis performance via enhancement of currently available catalysts or identifying and procuring/synthesizing a better catalyst, and 3) planning for pilot-scale demonstration of electrochemical ammonia production at a North Dakota utility site. Initial techno-economic projections based on project data show that North Dakota renewable and/or coal-based electricity could be used to produce ammonia at a cost of about \$700/tonne (2200 pounds), half the May 2022 Tampa spot price of \$1400/tonne.

LOW-PRESSURE ELECTROLYTIC AMMONIA (LPEA) PRODUCTION

PROJECT DESCRIPTION AND PURPOSE

The Energy & Environmental Research Center (EERC) technology development project entitled “Low-Pressure Electrolytic Ammonia (LPEA) Production” was funded by the U.S. Department of Energy (DOE) Office of Energy Efficiency and Renewable Energy (EERE) Advanced Manufacturing Office (AMO) and the North Dakota Industrial Commission (NDIC) Renewable Energy Program, with in-kind contributions provided by project partners North Dakota State University (NDSU), Nel Hydrogen (formerly Proton OnSite), and the University of North Dakota Chemistry Department. The project goal was to advance the EERC-developed LPEA process sufficiently to demonstrate ammonia production at an energy consumption of 16% less than state-of-the-art (2018) high-pressure Haber–Bosch (HB)-based ammonia production, as shown in Figure 1. Critical to achieving this energy reduction was improving the 300°C-capable proton exchange electrolyte (PEE) on which the LPEA process is based. As a result, the project was focused on PEE improvement to achieve the following performance metrics:

- Proton conductivity of $\geq 10^{-2}$ siemens per centimeter (S/cm) and gas permeability of $< 2\%$ at a 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) operating at 300°C, an electrical current efficiency of $\geq 65\%$ for ammonia formation at current density of ≥ 0.25 amps/cm² (A/cm²), ammonia production energy efficiency of $\geq 65\%$, and $\leq 0.3\%$ performance degradation per 1000 h of operation.

BACKGROUND

In support of DOE–AMO goals to reduce life cycle energy consumption of manufactured goods and more cost-effectively use hydrogen in manufacturing processes, the LPEA project was focused on optimizing and demonstrating the improved efficiency (versus HB ammonia production) of the EERC-developed LPEA production process. Because ammonia fertilizer is a critical input to North Dakota agriculture and ammonia is rapidly gaining recognition around the globe as a carbon-free hydrogen carrier and fuel (see Figure 2), LPEA process commercialization would offer significant benefits to the North Dakota economy, especially as a means of monetizing North Dakota renewable energy—at maximum value—by using it in-state for producing an increasingly valuable commodity.

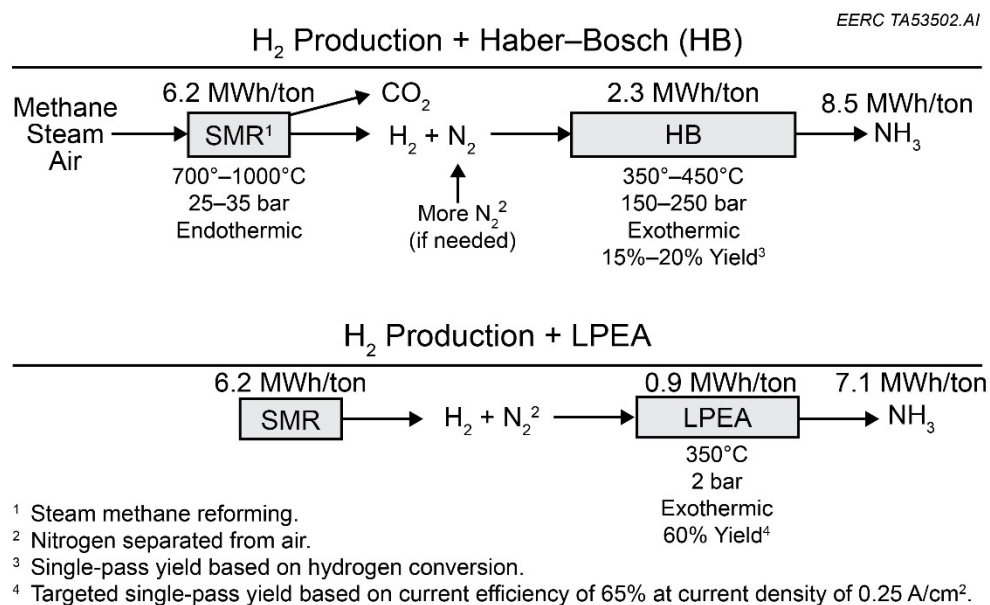
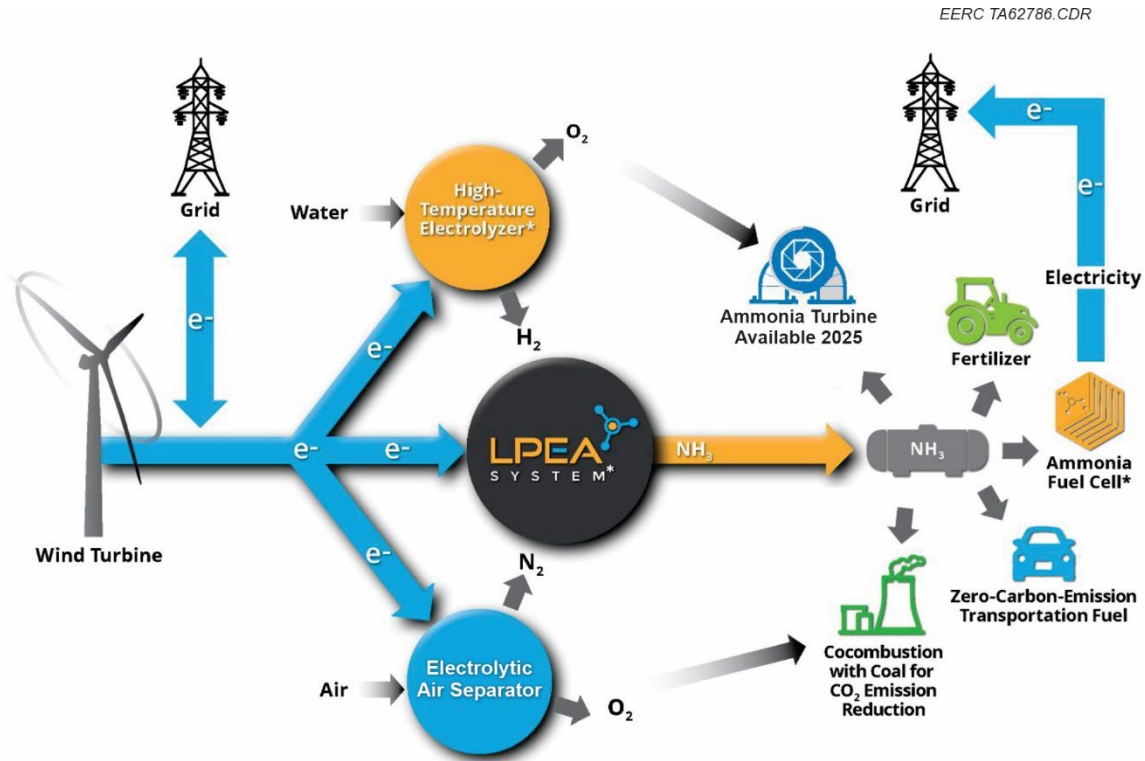


Figure 1. State-of-the-art (2018) HB versus LPEA-based ammonia production.

As illustrated in Figure 3, the LPEA process is built around an innovative high-temperature PEE; operates at ambient pressure and temperature of 200°–300°C; and uses inputs of hydrogen, nitrogen, and electricity to make ammonia. While the HB process is driven by high pressure (which translates to high capital cost that necessitates building huge plants that operate constantly to achieve a commercially viable economy of scale), the LPEA process is driven by electricity. In addition to reducing capital cost, replacing pressure with electricity enables viable economics at smaller scale and intermittent operation, which means that ammonia plants could be built where ammonia is needed and operated on renewable and/or lower-cost off-peak fossil-based electricity.

ATHG as Proton Conductor

To meet the above-listed PEE performance and durability specifications, the project was initially focused on fabricating a PEE by compositing alkali thio-hydroxogermanate (ATHG)—an inorganic material with >0.01-S/cm proton conductivity at 200°–300°C—in high-temperature-tolerant polymer polybenzimidazole (PBI) via a technique called coelectrospinning. This approach derived from past EERC work (limited in scope and depth) in which several experimental ATHG–PBI electrolytes were used to produce ammonia at low yield rates. However, after about 6 months of work comprising ATHG synthesis, coelectrospinning varying combinations of ATHG and PBI to yield matted-fiber membranes, and evaluating the membranes based on proton conductivity at different temperatures and under varying humidity levels, it became obvious that 1) ATHG lacked the thermal stability (in steam at 300°C) needed for sustaining high proton conductivity and 2) encapsulating ATHG in PBI fibers to protect ATHG from thermal/steam degradation was technically unachievable. In response to this setback (which was accompanied by valuable



*Technology based on EERC-NDSU-developed proton-exchange electrolyte (PEE).

Figure 2. Ammonia as fertilizer, fuel, energy carrier, and energy storage medium.

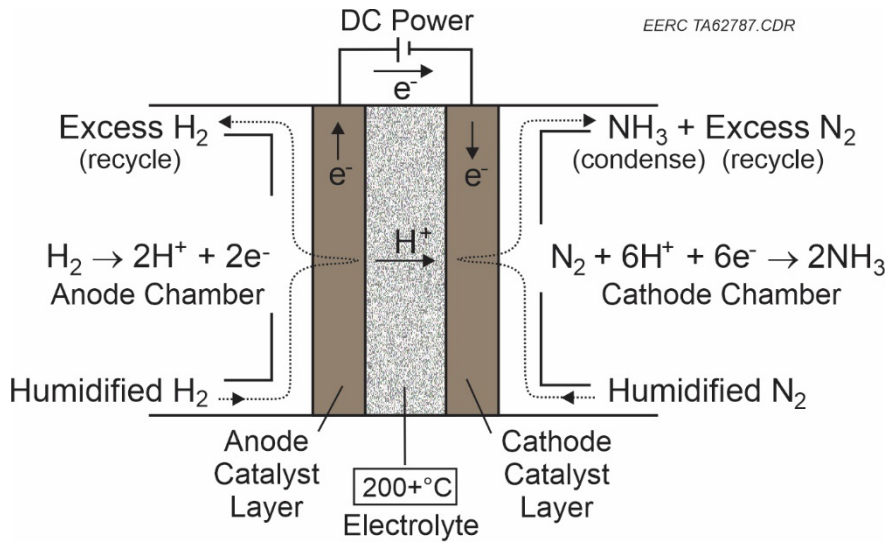


Figure 3. LPEA process.

learnings regarding requirements for operating an ammonia synthesis electrochemical cell at 300°C), a concerted effort was made to identify an alternative proton conductor. An extensive literature review and numerous communications with PEE researchers around the globe led to the identification of cerium ultraphosphate (CUP) as a viable candidate, based in large part on work conducted by Dr. Tatiana Anfimova. Her work and findings regarding use of CUP as an intermediate-temperature (200°–300°C) proton conductor are described in her Ph.D. dissertation, published in 2014 by the Technical University of Denmark.

Validation of CUP as Proton Conductor

After identifying CUP as a promising basis for an intermediate-temperature PEE, a global search was conducted for a possible vendor (chemical supplier) from which CUP could be purchased. Because no vendor was found, the EERC developed a method for CUP synthesis based on technical literature search findings. Synthesized CUP then underwent extensive characterization, analysis, and testing to ensure that 1) the synthesis method was correct, in that it yielded high-purity CUP (based on stoichiometry, structure/crystallinity, and the presence of functional groups needed for proton conductivity) and 2) CUP is thermally and chemically stable under LPEA operating conditions in the presence of steam, hydrogen, and ammonia. After establishing—via x-ray diffraction (XRD) and Fourier-transform infrared (FTIR) analytical techniques—that the synthesis method was correct, a series of heated-stage XRD tests were conducted to assess CUP thermal/chemical stability. CUP particles were mounted on the XRD stage, temperature was ramped up to 600°C in 30° intervals, and XRD patterns were acquired at each 30° increment. Temperature was then ramped down in 30° intervals and data acquired accordingly. Throughout the complete up–down cycle, CUP particles were exposed to steam (carried by flowing nitrogen) by bubbling nitrogen through a 50°C water bath. Figures 4 and 5 indicate that exposure to high-temperature steam has no impact on CUP crystallinity or composition.

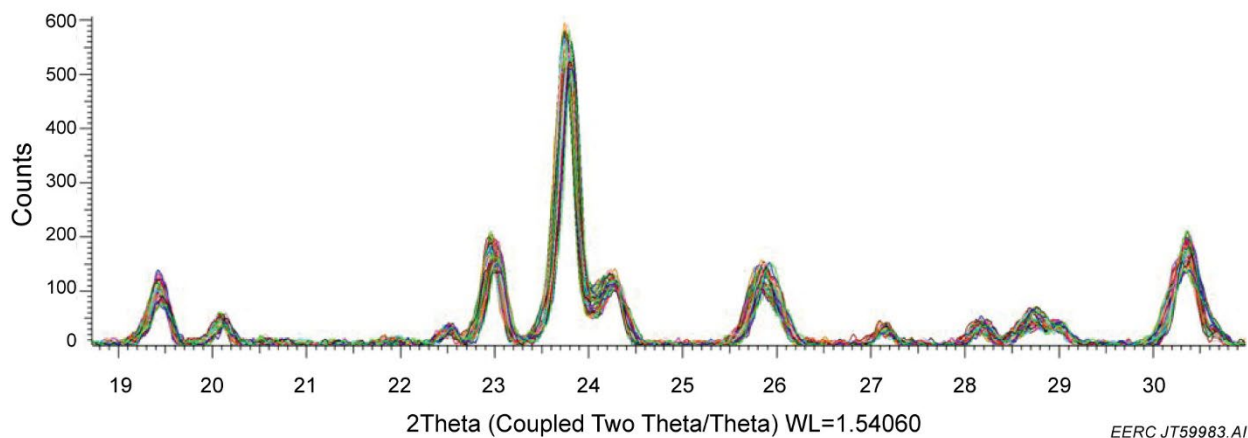


Figure 4. Overlaid diffraction patterns for CUP from 30° to 600° to 30°C (in 30° increments) under humidified nitrogen. Lateral shift is due to thermal expansion of CUP crystals.

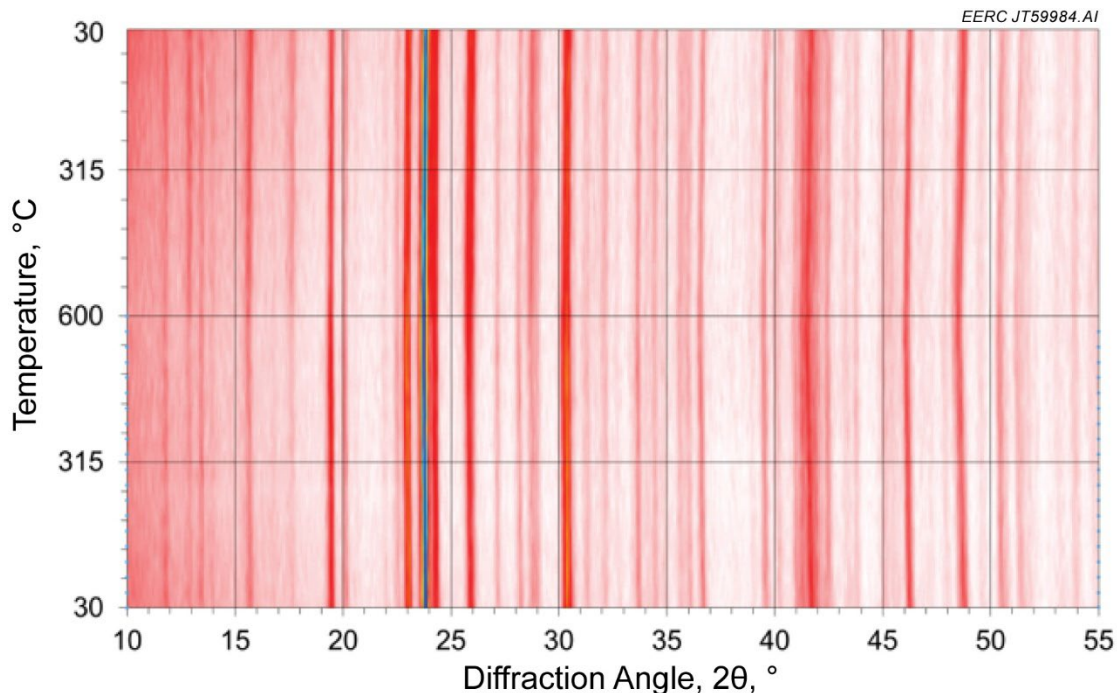


Figure 5. XRD history of CUP from 30° to 600° to 30°C. Color indicates diffraction signal height. No new phases form; CUP structure appears stable, exhibiting only thermal expansion.

CUP Deployment in Pressed Disk Electrolyte

Because of major differences in the chemical and physical properties of CUP versus the originally proposed proton conductor ATHG, the originally proposed PEE fabrication method—coelectrospinning with PBI—was found to be unworkable with CUP. Initial efforts to deploy CUP in a 300°C-capable PEE centered on compositing CUP with PBI via a method that involved 1) preparing a viscous PBI “dough” by partially evaporating a solution of 26% PBI in dimethylacetamide (DMAc) procured from PBI Performance Products, 2) blending CUP particles (at varying proportions) into the PBI dough, 3) putting the dough into a 1-inch-diameter stainless steel die and—using a hydraulic press—compressing the dough at 10,000 psi to yield an approximate 1-mm-thick disk, and 4) drying the disk to remove any residual DMAc. Numerous disks were fabricated and tested for proton conductivity. Figure 6 shows the effect of temperature on proton conductivity for a disk comprising 94% CUP–6% PBI, and Figure 7 shows the effect of time at 300°C on proton conductivity for a similar (94% CUP–6% PBI) disk. Figure 7 shows that although conductivity at 300° is initially 0.03 S/cm—300% higher than the project target of 0.01 S/cm—after about an hour conductivity starts a gradual decline and eventually (after 40–50 hours) falls below the target. In addition to failure to sustain conductivity, the pressed disks exhibited unacceptably high hydrogen permeability at 300°C, as shown in Figure 8. These findings indicated that the pressed-disk method for PEE fabrication yielded insufficient bonding between PBI and CUP, and an alternative method for CUP deployment was needed.

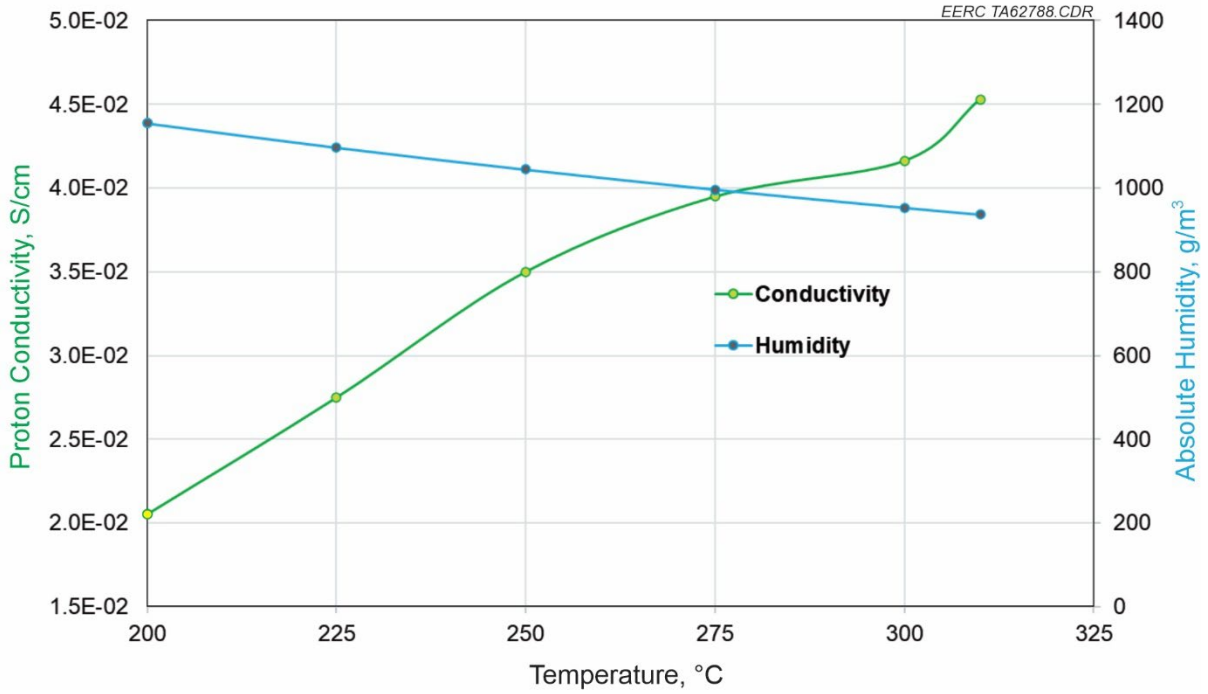


Figure 6. Proton conductivity of 94/6 CUP/PBI pressed-disk electrolyte versus temperature.

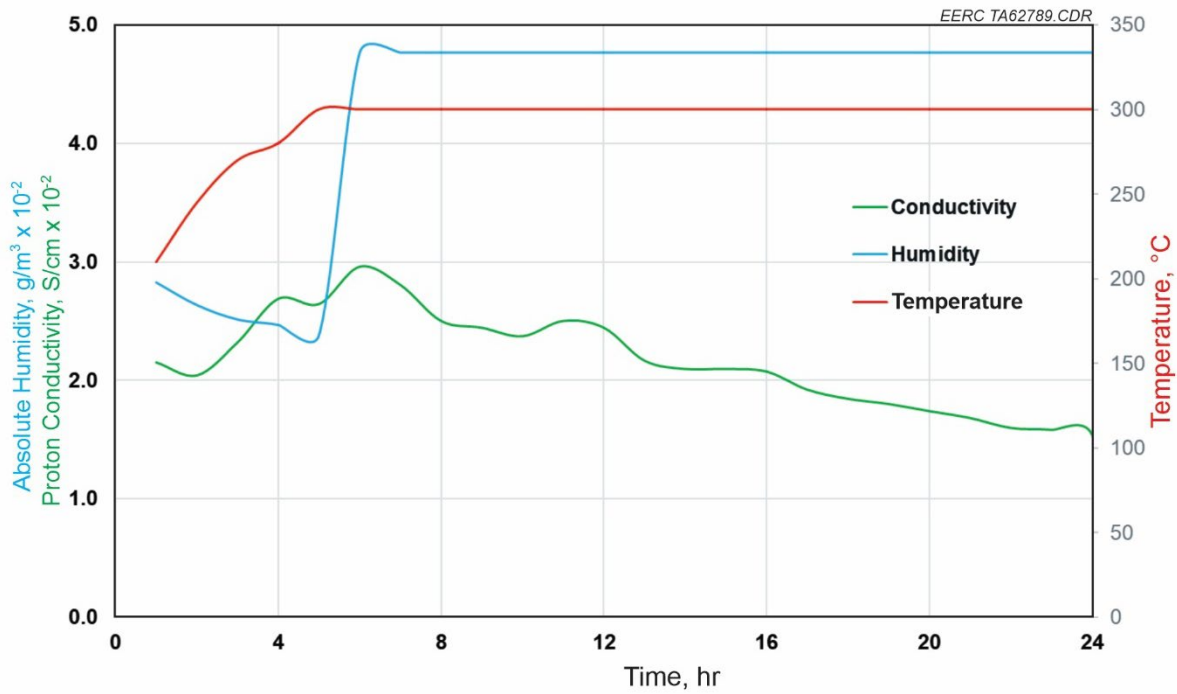


Figure 7. Proton conductivity (at 300°C) of 94/6 CUP/PBI pressed-disk electrolyte versus time.

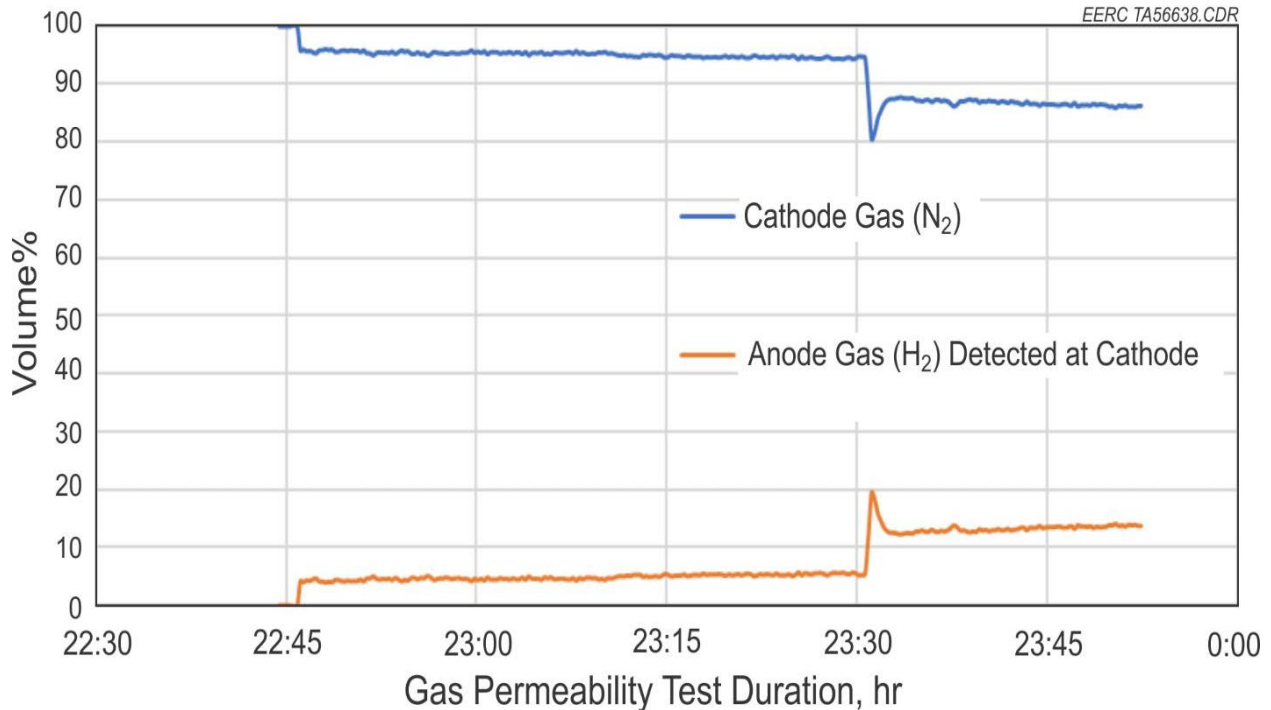


Figure 8. Hydrogen permeability of 94/6 CUP/PBI pressed disk at 300°C.

Two-Track Strategy for CUP Deployment in PEE

After project team discussions, tests of various ideas, and analysis of findings, a two-track strategy was devised with the objective of leveraging NDSU and EERC strengths in developing a fabrication method that would enable optimal deployment of CUP as an intermediate-temperature proton conductor. As a world leader in polymer engineering, NDSU would pursue a deployment method based on compositing CUP and PBI in a membrane via “film casting,” a well-established technique utilized in the fuel cell industry. The EERC would leverage its high-temperature materials expertise in pursuit of a non-PBI-based method for CUP deployment. One approach involved compositing CUP particles in a suitable matrix/binder, with initial focus on a glass with a melting point above 300°C but below the CUP decomposition temperature of 830°C. For context, the fact that CUP decomposes at 830° but does not actually melt until about 1200°C is the reason a method for its deployment in a PEE is needed. If CUP could simply be melted (without losing its proton-conducting functionality through decomposition) and formed into PEEs, no special deployment method would be needed. After roughly 6 months of literature review, materials synthesis, and testing, a potentially suitable material for use as CUP matrix/binder was identified. The material is referred to as “PCN glass” and encompasses varying mixtures of oxides of phosphorus, calcium, and sodium. In addition to having melting points of 330°–730°C (well below the 830°C CUP decomposition temperature), several PCN glasses exhibited moderate proton conductivity at 300°C, a definite attribute for deployment in an intermediate-temperature PEE.

A second CUP deployment approach investigated involved use of a “sintering” aid to join/bond CUP particles together at a temperature below the CUP decomposition temperature. The

idea for this approach derives from the use of sintering in preparation of high-temperature electrolyte materials for deployment in solid oxide fuel cells (SOFCs). However, unlike CUP, SOFC electrolyte materials are generally stable and do not decompose at temperatures well below their melting points, which enables heating SOFC electrolyte material particles up to slightly below their melting point, where—with an effective sintering aid—particle surfaces or “grain boundary layers” become sufficiently malleable and liquid-like to bond with each other, yielding—after cooling—a dense, strong electrolyte. Achieving the same strong bonding of CUP particles at a temperature of about 350°C below CUP melting point would prove to be challenging.

Film-Cast CUP-Based PEE Membrane: Fabrication and Testing

A film-casting procedure was developed and utilized to fabricate C-PEE (CUP-based PEE) membranes from CUP and PBI at thicknesses ranging from about 80 to 150 μm (versus the 1-mm thickness of the pressed-disk C-PEEs described above). In the course of procedure optimization, it was found that in order to ensure membrane integrity and flexibility, PBI loadings of at least 15% were required, versus the 6% loading typically used for the approximately 10-times-thicker pressed-disk PEEs. Because PBI has no measurable proton conductivity, membrane conductivity decreases linearly with increasing PBI loading, which means an optimum balance between membrane integrity and conductivity is needed. Based on iterations of membrane fabrication and evaluation, an optimum PBI loading range of 15%–25% was established. The film-casting procedure is summarized and illustrated in Figure 9.

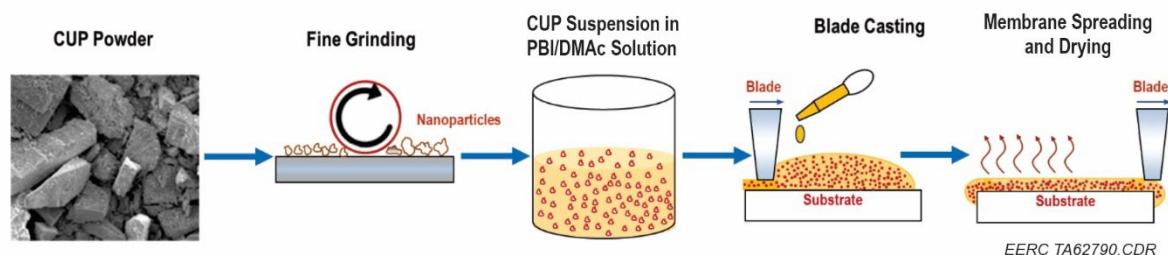


Figure 9. Procedure for film-casting C-PEE membrane.

1. Grind CUP powder into particles with an approximate size distribution of 200–500 nanometers via use of planetary ball milling technique.
2. Disperse the CUP particles into DMAc to form a stable CUP–DMAc nanocolloid. Lab devices of analog vortex stirrer, sonication bath, and magnetic stirrer are utilized for effective and uniform dispersion.
3. Based on the targeted mass ratio of CUP to PBI in the finished membrane, add the appropriate amount of 26% PBI-in-DMAc solution (S26 solution, PBI Performance Products Inc., Charlotte, NC) into the CUP–DMAc dispersion under vigorous stirring. Analog vortex and magnetic stirrers are utilized to accelerate the dissolution of PBI into the CUP–DMAc nanocolloid to form a stable triphase CUP–PBI–DMAc mixture.

4. Cast the CUP–PBI–DMAc mixture onto a steel panel (e.g., Q-panel, Q-Lab Co., Westlake, OH) using a drawdown bar with the desired wet layer thickness: typically in the range of 0.200 millimeters (mm).
5. Bake the as-cast membrane on the steel panel (e.g., Q-panel) in an air-circulating oven at 125°C for 6 minute to evaporate a portion of the DMAc.
6. Wash/rinse the baked/dried solution-cast membrane (on the steel panel) in deionized water to peel off the membrane from the steel-panel substrate.
7. Anneal the free-standing membrane in the air-circulating oven at 125°C for 1 minute. The resulting solution-cast C-PEE membrane is ready for use.

Film-cast C-PEE membranes ranging in CUP concentration from 75% to 85% were fabricated and evaluated based on proton conductivity, durability, and hydrogen permeability. Figure 10 shows a 75% CUP PEE membrane. While the film-cast membranes gave reasonable proton conductivities ranging from 0.002 S/cm to near the project target of 0.01 S/cm, consistently achieving acceptable conductivity along with high integrity (no leakage/gas permeation) proved difficult. Acquisition of a planetary ball mill that enabled reducing CUP particle size to a monomodal size distribution of 200–500 nanometers was helpful but not sufficient. Figure 11 shows an MEA (comprising the 75% CUP membrane, platinum anode, and ruthenium cathode) that was tested for ammonia synthesis, with no success. While unsuccessful (so far) in application to ammonia synthesis, the C-PEE membrane concept is of major interest to the global electrochemistry research community because of its unique approach to achieving high proton conductivity with a membrane at 200°–300°C. This interest is evidenced by the project-prepared peer-reviewed articles published on the topic,^{1,2,3} one of which—a comparative experimental study of the hygroscopic and mechanical behaviors of electrospun nanofiber membranes and solution-cast films of polybenzimidazole—was selected as the cover story in the 15 October 2020 issue of the *Journal of Applied Polymer Science*.



Figure 10. Film-cast PEM comprising 75% CUP–25% PBI.



Figure 11. MEA comprising film-cast C-PEE membrane, platinum anode, and ruthenium cathode.

Sintered CUP-Based PEE: Fabrication and Testing

Sintering refers to the process of coalescing discrete particles into a solid mass of material through heat without melting the particles to the point of liquefaction. The process involves atoms diffusing across particle/grain boundaries and fusing together, thereby bonding particles together, with bond strength dependent on the level of cross-particle-boundary atom-to-atom fusing. Assessment of sintering as a means of C-PEE fabrication involved the use of sintering aids, which can significantly reduce (in some cases by 200°C or more) the temperature at which sintering occurs. Several sintering aids were investigated, with the most effective being cobalt oxide (Co_3O_4). To make a sintered C-PEE, a well-dispersed mixture of 97–98 wt% CUP powder and 2–3 wt% sintering aid was heated to 635°C and pressurized to 2000 psi in a round (disk-shaped) carbide steel die—until mixture volume compression rate dropped below 0.2 $\mu\text{m}/\text{minute}$, when pressure was released and the mixture allowed to cool. The resulting C-PEE disk was then tested for proton conductivity. Figure 12 shows the relationship of proton conductivity to temperature for a C-PEE disk made with Co_3O_4 as sintering aid, and Figure 13 compares C-PEE disks (made with different sintering aids) based on proton conductivity at 300°C. As referenced in the figure, the temperature during the first 14 hours of the “0.73 M Sintering Aid 2” test was 275°C. During all tests, disks were exposed to an atmosphere of humidified nitrogen. These and other tests showed that sintered C-PEEs consistently provide conductivities that often exceed the 1×10^{-2} -S/cm target by a wide margin. In addition, several sintered C-PEEs were able to sustain target-exceeding conductivities for more than 100 hours.

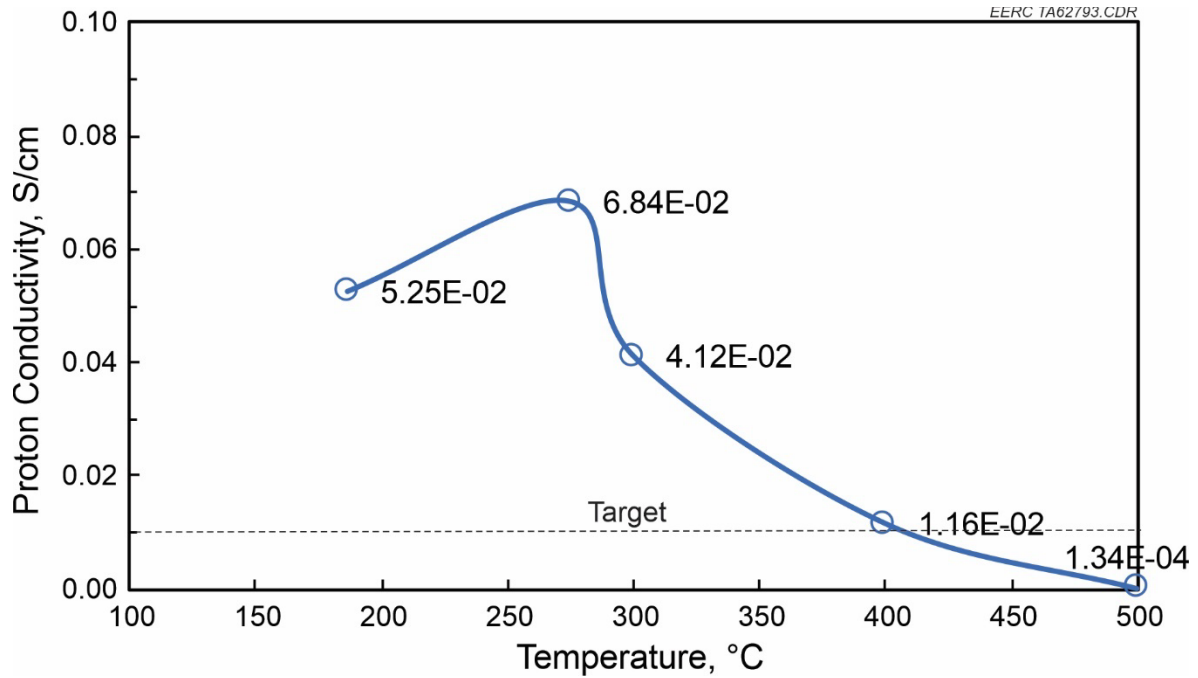


Figure 12. Proton conductivity versus temperature for sintered (with 2% cobalt oxide) C-PEE.

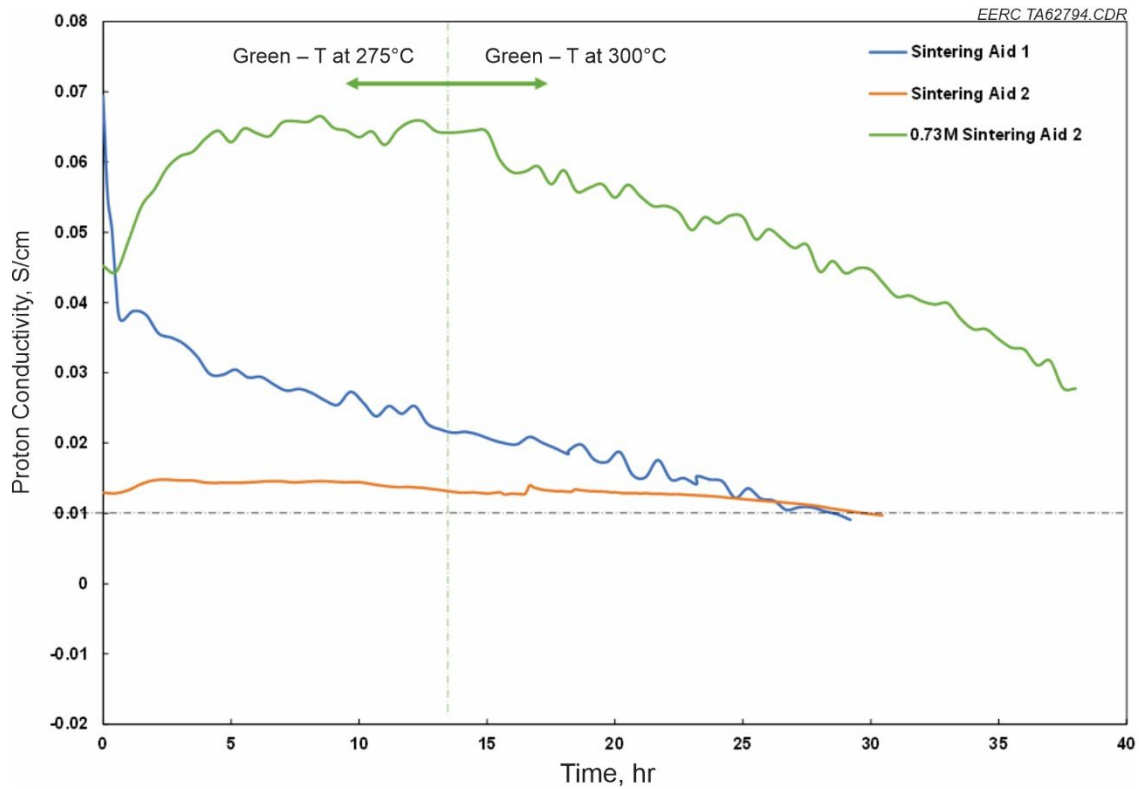


Figure 13. Proton conductivity at 300°C versus time for sintered C-PEEs made with 3% cobalt oxide/97% CUP (blue and brown lines) and 2% cobalt oxide/98% CUP (green line).

CUP–PCN PEE: Fabrication and Testing

After several moderately proton-conductive and low melting-point PCN glass formulations were identified as potentially viable matrix materials for C-PEE fabrication, work focused on 1) developing an efficient, replicable method for PCN synthesis; 2) analyzing each synthesized PCN glass to confirm its melting point; and 3) developing a method for combining/fabricating CUP and PCN into a dense, strong C-PEE. Systematic development and optimization of a method for PCN matrix-based electrolyte fabrication led to the following technique: a mixture of 80–90 wt% CUP and 10–20 wt% PCN is blended, ground to a –400-mesh particle size, formed into a 1-inch (25-mm)-diameter 1-mm-thick pellet using a hydraulic press, and heat-treated under an experimentally derived protocol to yield a hard, dense, durable C-PEE disk. Figure 14 is a photo (taken through an optical microscope) of an approximate 25-mm-diameter, 1-mm-thick C-PEE disk comprising 85% CUP–15% PCN. Based on evaluations that yielded sustainable (60 hours) proton conductivity values ranging from 1 to 3×10^{-2} S/cm, the PCN matrix approach appears to offer high potential for fabrication of high-performance/durability C-PEEs.



Figure 14. CUP–PCN PEE disk as viewed through optical microscope.

Cathode Catalyst Screening

Candidate cathode catalyst screening tests were conducted at room temperature using an Autolab potentiostat and two-chamber H-type electrochemical cell separated by a Nafion® 117 proton-exchange membrane (see Figure 15). The Nafion membrane was pretreated in 5%

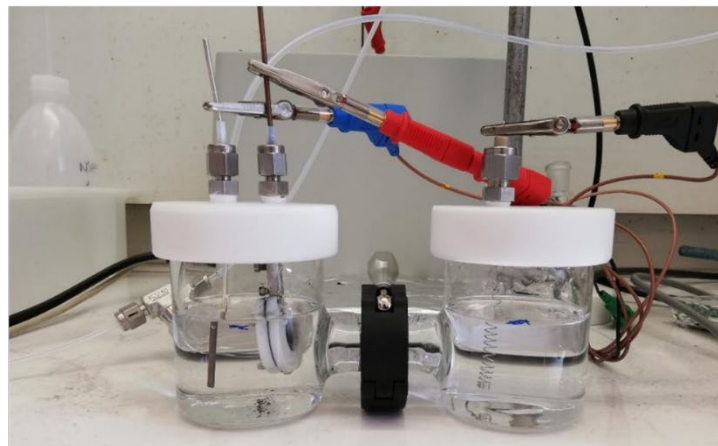
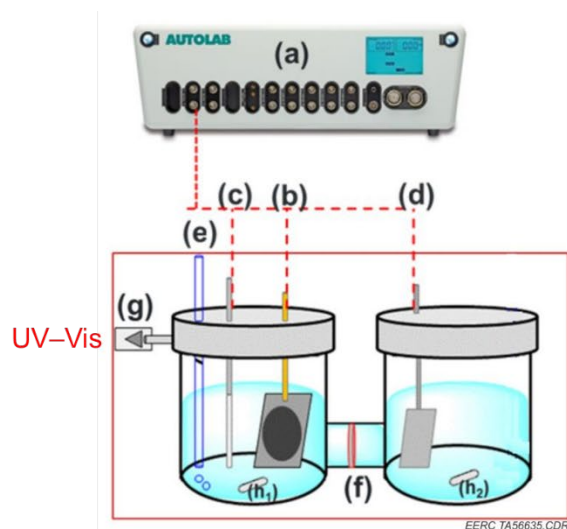


Figure 15. H-cell system for cathode catalyst screening showing a) potentiostat, b) working electrode (candidate cathode catalyst), c) reference electrode (Ag/AgCl), d) counter/anode electrode (Pt wire/cage), e) N₂ inlet, f) Nafion membrane, g) following test completion, cathode chamber solution undergoes ultraviolet–visible light (UV–Vis) spectrophotometry analysis for ammonia quantitation, and h) magnetic stirrer.

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 wt% Nafion® solution. A catalyst loading of about 3 mg catalyst-cm⁻² was deposited onto Toray carbon paper (1.57-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.

A partial list of candidate cathode catalysts identified, synthesized/procured, and screened for ammonia synthesis rate at room temperature includes a project-developed/synthesized ruthenium oxide-on-reduced graphene oxide (RuO_x/rGO) catalyst, two additional Ru-based materials (Ru2 and Ru3), bismuth on carbon black (Bi/C_b), and niobium nitride (NbN). Performance data for the catalysts are summarized in Table 1.

Table 1. Cathode Catalyst Screening Results

Catalyst	Applied Potential, V vs. RHE	Current Density, mA/cm ²	Coulombic Charge, C	Current Efficiency, %	Production Rate, $\mu\text{g}\cdot\text{h}^{-1}\text{ mg}_{\text{cat}}^{-1}$	Production Rate, $\text{mol}\cdot\text{s}^{-1}\text{ cm}^{-2}$
Catalyst Mass Loading: 2 mg; Catholyte Volume: 40 mL						
Electrolysis Time: 1 hour, Electrode Area: 1.54 cm², Potential: Voltage vs. Reversible Hydrogen Electrode						
RuO _x /rGO	-0.1	1.7	9.4	1.9	5.2	1.1E-10
	-0.2	2.4	13.5	2.0	8.0	1.7E-10
	-0.3	32.5	180.0	0.1	3.9	8.4E-11
	-0.4	63.6	352.8	<0.1	2.4	5.1E-11
Ru2	-0.2	7.8	43.2	0.1	1.8	3.9E-11
Ru3	-0.2	0.6	3.6	1.9	2.0	4.3E-11
Bi/C _b	-0.5	0.5	2.7	7.1	2.39	1.2E-10
	-0.6	0.6	3.3	5.6	2.34	1.2E-10
	-0.7	0.8	4.4	8.4	4.57	2.2E-10
	-0.8	1.7	9.4	2.2	2.63	1.3E-10
NbN	-0.6	10.4	57.6	<0.1	0.7	1.4E-11

MEA Fabrication and Ammonia Production Performance Assessment

Using a C-PEE as electrolyte, the RuO_x/rGO catalyst as cathode, and a platinum (Pt) catalyst as anode (Pt has a long commercial history as a high-efficiency anode for PEE-based fuel cells), MEAs were fabricated for evaluation based on the three primary metrics defined below:

- Ammonia production rate – Amount of ammonia produced per unit time, expressed as:
 - 1) Moles (number of molecules) ammonia produced per second per square centimeter of catalyst active surface area ($\text{mol}\cdot\text{s}^{-1}\cdot\text{cm}^{-2}$).
 - 2) Micrograms of ammonia produced per hour per milligram catalyst ($\mu\text{g}\cdot\text{h}^{-1}\cdot\text{mg}^{-1}$).
- Ammonia production current efficiency – Percentage of total number of electrons (quantified as amps [A] or milliamps [mA]) supplied to the MEA (essentially, the reactor) actually used/consumed in the production of ammonia.
- Ammonia production current density – Amount of electrons supplied to the MEA per square centimeter of catalyst active surface area, expressed as $\text{mA}\cdot\text{cm}^{-2}$.

MEAs were fabricated using two slightly different techniques. In the simplest technique, anodes and cathodes (collectively referred to as electrodes) were prepared via a procedure similar to that used to make the electrodes deployed in the room temperature catalyst screening tests. A key difference was the replacement of Nafion as ionomer (used to facilitate proton transport from catalyst layer to electrolyte) with CUP, which required additional changes to the catalyst ink formulation. Once prepared, electrodes were simply pressed tightly against either side of the electrolyte (C-PEE) using a stainless steel “unit cell holder” and appropriate gaskets. Because of its simplicity, this approach was used to facilitate relatively quick evaluation of MEA performance

at operating temperature. To achieve the more intimate anode–electrolyte–cathode integration needed to maximize MEA performance at 300°C, an improved technique was needed to yield an MEA with gradual/near-seamless transitions from one layer to the next, thereby minimizing resistance to inter-layer proton transport. Development of an “integrated fabrication” technique involved attempts to lay down an anode powder layer, apply a C-PEE powder layer on top of the anode, apply a cathode powder layer on top of the C-PEE, and heat-treat the resulting assemblage to yield a tightly bonded, highly integrated three-layer MEA.

Figure 16 shows an approximate 30-mm-diameter, 1.5-mm-thick MEA made by the above-described layering–heat-treating process. Although the three layers emerged from the fabrication process well-integrated and tightly bonded, after exposure to steam (needed to sustain proton conductivity) at 300°C during ammonia synthesis testing, the layers gradually dissociated, resulting in reduced proton transport and reduced current density, current efficiency, and production rate. At project conclusion, optimization of the MEA integrated fabrication technique was (and is, at the time of this report) ongoing.



Figure 16. C-PEE-based MEA fabricated via simultaneous three-layer heat-treating process.

PROJECT OUTCOMES VERSUS TARGETS

As stated in the Project Description, the project goal was to demonstrate ammonia production via the LPEA process at an energy consumption of 16% less than state-of-the-art (2018) high-pressure Haber–Bosch-based ammonia production. The two critical enabling technologies needed to achieve this goal are:

- 1) A PEE capable of meeting the performance targets listed in the Project Description.

- 2) A cathode catalyst capable of room temperature ammonia synthesis a rate of at least $1 \times 10^{-10} \text{ mol-s}^{-1}\text{-cm}^{-2}$.

Although the cathode catalyst target was met, not all of the PEE performance targets were met. As a result, the 16% energy reduction goal was not achieved. While not the level of success envisioned, the primary project outcome (the partially optimized C-PEE) is a major step toward an intermediate-temperature (200°–300°C) PEE, a goal pursued—with increasingly higher intensity and investment—by the global electrochemistry and energy industries for over 25 years. With continuing success in ongoing and planned C-PEE optimization activities, the C-PEE is a legitimate contender to being one of the first and best commercially available 200+°C PEEs.

The PEE performance targets are listed below, along with an account of whether and/or to what extent each target was achieved.

Target 1 – Proton conductivity of $\geq 10^{-2} \text{ S/cm}$ and gas permeability of $< 2\%$ at 300°C. This target was achieved.

Target 2 – Ability to sustain 10^{-2}-S/cm proton conductivity for at least 1000 hours. This target was not achieved. The longest period of sustained 10^{-2} proton conductivity was 100 hours.

Target 3 – Mechanical strength (at 300°C) comparable to that of a commercial proton exchange-based electrolyzer membrane. Because the PEE configuration evolved (in response to project findings) from a membrane to a ceramic-like thin disk, this target is no longer applicable. The thin disk C-PEE has demonstrated adequate mechanical strength at 300°C.

Target 4 – As measured in an MEA operating at 300°C, an electrical current efficiency of $\geq 65\%$ for ammonia formation at current density of $\geq 0.25 \text{ amps/cm}^2$ (A/cm^2), ammonia production energy efficiency of $\geq 65\%$, and $\leq 0.3\%$ performance degradation per 1000 hours of operation. Using an MEA comprising a C-PEE sandwiched between a platinum anode and RuO_x/rGO cathode, ammonia synthesis (at 300°C and ambient pressure) was demonstrated at a rate of 1×10^{-10} moles per second per square centimeter of electrode active area ($\text{mol-s}^{-1}\text{-cm}^{-2}$), current density of 2 milliamps/cm² (mA/cm^2), and current efficiency of 2%. Although not determined, production energy efficiency was likely not above 5%. The observed synthesis rate, current density, current efficiency, and energy efficiency are all below target values (for commercial viability) of $4 \times 10^{-7} \text{ mol-s}^{-1}\text{-cm}^{-2}$, 250 mA/cm^2 , 65%, and 65%, respectively. However, the values are likely indicative of the need for improved MEA and (possibly) electrode fabrication techniques rather than poor PEE or cathode catalyst performance. Reasons for this likelihood are:

- PEE conductivity at 300°C was measured at 0.015 S/cm, 50% higher than the 0.01-S/cm target (for commercial viability). This means that the PEE is capable of proton transport at the volume needed to achieve a commercially relevant ammonia synthesis rate.
- In cathode catalyst screening tests at room temperature in liquid electrolyte (0.1 M H_2SO_4), the RuO_x/rGO catalyst yields an ammonia synthesis rate of $1.7 \times 10^{-10} \text{ mol-s}^{-1}\text{-cm}^{-2}$ at a current density of 2.4 mA/cm^2 and current efficiency of 2.0%. This means that the catalyst is able to facilitate dissociation of the extremely stable N_2

molecule (in which the two nitrogen atoms are held together by a triple bond) at room temperature. Because catalytic reaction rates typically double with every 10°C increase in temperature, the (theoretical) rate of N₂ dissociation at 300°C would be roughly 268 million times higher than at 20°C, which—assuming availability of protons at the cathode—would translate to a much higher ammonia synthesis rate than observed. Because protons are being generated at the anode and transported through the C-PEE (as indicated by the high measured proton conductivity), the low synthesis rate indicates that these protons are not moving from the PEE to the cathode surface for reaction with partially dissociated (high-reactivity) nitrogen molecules.

- The observed low current density and current efficiency are indicative of 1) ohmic losses resulting from inadequate contact between anode, PEE, and cathode, often a result of nonoptimal integration/bonding during MEA fabrication and 2) inadequate proton and electron transport pathways in the MEA, often a result of nonoptimal ratios of catalyst, proton-conducting “ionomer” (CUP), and binder in the catalyst ink.

Bottom-Line Takeaway – Key project outcomes are a partially optimized 300°C-capable PEE and high-activity electrocatalyst for ambient-pressure ammonia production, both of which demonstrated high potential for commercial deployment. An improved MEA fabrication method that enables more intimate/near-seamless anode–PEE–cathode integration would more fully leverage the proton-conducting and catalytic capabilities of the C-PEE and RuO_x/rGO cathode catalyst, respectively, thereby yielding an MEA capable of supporting the higher current density needed for ammonia synthesis at a commercially viable rate and efficiency.

MEMBERSHIP AND FINANCIAL INFORMATION

This project is being sponsored by the North Dakota Industrial Commission (NDIC), DOE, UND Chemistry, NDSU, and Proton OnSite. Table 2 shows the proposed budget of \$3,164,010 for this project and the expenses to date.

Table 2. Project Cost

Funding Source	Funding Source Total	Expenses to Date
DOE	\$2,497,983	\$2,493,524
NDIC	\$437,000	\$436,214
UND Chemistry	\$69,027	\$69,027
NDSU	\$120,000	\$120,000
Proton OnSite	\$40,000	\$40,000
Total	\$3,164,010	\$3,158,765

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