Electrochemical ammonia synthesis using proton-conducting ceramics

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U.S. DoE, NASA, FuelCell Energy, and Colorado School of Mines have invested in proton-conducting ceramics

- **ARPA-E REBELS**: Proton-conducting ceramic fuel cells (5 years)
- **ARPA-E REFUEL**: NH$_3$ synthesis with protonic ceramics (3.5 yrs)
- **EERE HTWS**: Proton-conducting ceramic electrolyzers (2 yrs)
- **FE NETL**: CO$_2$-to-fuels through electrochemical catalysis (2 yrs)
- **NASA NSTRF**: Making fuel on Mars with protonic ceramics (2 yrs)
Proton-conducting ceramics are an emerging material with broad energy applications.

Protonic-ceramic electrochemical cell for “green” ammonia synthesis.
The CSM FuelCell Energy team explores electrochemical NH₃ synthesis from many perspectives

- Experimental efforts on electrochemical ammonia synthesis
  - Neal P. Sullivan, Liangzhu Zhu, Chuancheng Duan, Ryan O’Hayre, Max Pisciotta, Long Le, Carolina Herradon Hernandez, Michelle Butler, Colorado School of Mines

- Catalyst characterization
  - Chris Cadigan, Canan Karakaya, Robert J. Kee, Colorado School of Mines

- Techno-economic analysis of electrochemical ammonia synthesis
  - Fred Jahnke and Hossein Ghezel-Ayagh, FuelCell Energy
The proton-conducting ceramic electrochemical cell is the heart of our ammonia-synthesis approach

- Perovskite ceramic membrane
  - $\text{BaCe}_{0.4}\text{Zr}_{0.4}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-d}$ (BCZYYb)
- Composite metal – ceramic fuel electrode
  - Porous Ni - BCZYYb
  - Forms mechanical support for MEA
- Porous steam electrode
  - $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.2}\text{O}_{3-\delta}$ (BCFZY)
  - Triple-conducting electrode (H$^+$, O$^{2-}$, e$^-$)
  - Splits H$_2$O into H$^+$ and O$_2$
- Operating conditions
  - $\sim 600$ °C at atmospheric pressure
  - Need to increase pressure and lower temperature for NH$_3$ synthesis
FuelCell Energy has successfully scaled up proton-conducting ceramics, targeting 1-kW$_e$ stack.

World's largest proton-conducting ceramic cells

Target stack
A patent-pending catalyst developed by StarFire Energy reacts N₂, H₂ and H⁺ to form NH₃

- “Ru-B2CA” catalyst
  - Ruthenium catalyst
  - Ba₂CaAl₂O₆ support

![Graph showing NH₃ production rate vs. temperature at different pressures.](image)

NH₃ Production Rate (mmol NH₃ g⁻¹ hr⁻¹)

- 20 bar
- 15 bar
- 10 bar
- 5 bar

Temperature (°C)

150 350 550 750
Colorado School of Mines has invested in a pressurized electrochemical test stand

Effect of pressure on electrochemical NH$_3$-synthesis rate

- NH$_3$ synthesis rate (moles/cm$^2$ s x 10$^8$)
- Operating pressure (bar$_g$)

Cell packaging

- Assembly fixtures
- Fuel gases
- Male manifold
- Seal (2x)
- NH$_3$ cell
- Female manifold
- Current collection
- Electrolysis gases
- Assembly fixture

Pressure vessel

- Access ports
- Cylinder head
- Cylinder collar
- Thermal wells (1.4 kW)
- Hot-zone MgO housing
- NH$_3$ cell assembly
- Linear-actuator compression
- Load cell
- Cooling jacket outlet

NH$_3$ synthesis rate

- Operating pressure

Data points:

- 0 bar$_g$: 0 moles/cm$^2$ s x 10$^8$
- 1 bar$_g$: 1 moles/cm$^2$ s x 10$^8$
- 2 bar$_g$: 2 moles/cm$^2$ s x 10$^8$
- 3 bar$_g$: 3 moles/cm$^2$ s x 10$^8$
- 4 bar$_g$: 4 moles/cm$^2$ s x 10$^8$
- 5 bar$_g$: 5 moles/cm$^2$ s x 10$^8$
- 6 bar$_g$: 6 moles/cm$^2$ s x 10$^8$
We have had the most success when decoupling the hydrogen production from the ammonia catalysis.

**Coupled approach**
Electrolysis and catalysis at 600 °C
A bit hot for NH$_3$ synthesis

**Decoupled approach**
Electrolysis at 600 °C
NH$_3$ catalysis at ~ 450 °C
The protonic-ceramic / B2CA combination shows encouraging longer-term, “reversible” operation.

**Reversible cell:**

NH₃-synthesis = energy storage;

NH₃ fuel cell = electricity generation

**NH₃-fueled protonic-ceramic fuel cell for electricity generation**
Techno-economic analysis at FuelCell Energy finds pressures need to reach 60 bar to be cost-competitive.

**Diagram:**
- **N_2** feed
- **H_2O** recycle
- **NH_3** condensation
- **Pure NH_3 product**
- **Recycle:** NH_3 / H_2 / N_2
- **Haber Bosch NH_3-synthesis reactor**
- **Protonic-ceramic H_2O electrolysis cell for H_2 generation**
- **Inerts**

**Equations:**
- N_2 + H_2O → NH_3 + H_2 / N_2
- Recycle: NH_3 / H_2 / N_2
- Protonic-ceramic H_2O electrolysis cell for H_2 generation
Cost drivers are electric power to drive water splitting, and pure nitrogen feedstock.

Sensitivity analysis at 60 bar operation:

- Current Density: ±50%
- Reactor Temp: ±4%
- Electricity: ±20%
- Maintenance: ±50%
- Capital Cost: ±20%
- N₂ Cost: -50% / +30%
- ROI: ±50%

Power:
- 64%
  - 5¢ / kWh

N₂:
- 19%
  - 16¢ / kg N₂

Capital:
- 14%

Maintenance:
- 3%

Projected production costs = $557 / ton NH₃
We have built a kW-capacity pressurized test stand to explore stack performance at elevated pressure.
The CSM-FCE team is making encouraging progress towards cost-competitive green ammonia production

• Proton-conducting ceramics
  – Efficient H\textsubscript{2} production
  – Scalable devices

• Ru – B2CA catalyst
  – Good performance at modest pressures

• Techno-economic analysis
  – Encouraging cost projections

• Going forward
  – Drive H\textsubscript{2}O-electrolysis temperature down to NH\textsubscript{3}-catalysis condition
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