Low-Pressure Electrolytic Ammonia (LPEA) Production via Polymer–Inorganic Composite (PIC) Membrane

EERC

Critical Challenges. **Practical Solutions.**

12 November 2019

LPEA Project Partners

PROTON
THE LEADER IN ON SITE GAS GENERATION.

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NDSU MECHANICAL ENGINEERING

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PROGRAM
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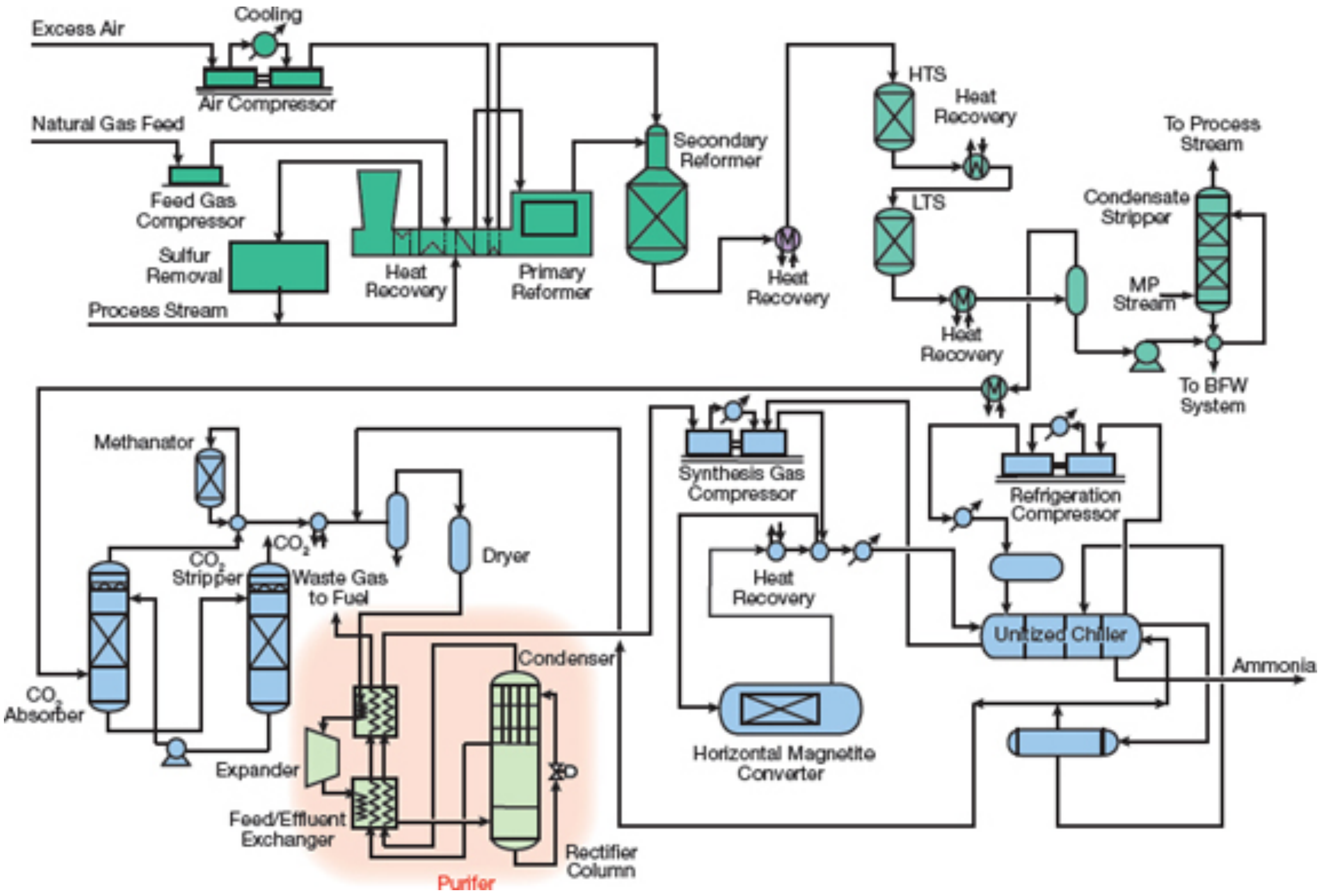
LPEA versus Haber Bosch (HB)

- HB processes need expensive high pressure (2000–3000 psi)
  - High cost of high pressure means large (1000–4000-tons/day) plants to achieve economy of scale
  - Large centralized plants mean storage/transportation costs
- Electricity as driver eliminates need for high pressure, enabling:
  - Economically viable ammonia production at smaller distributed plants in response to local/regional demand
  - Accommodation of intermittent operation, allowing use of renewable and/or lower-cost off-peak electricity



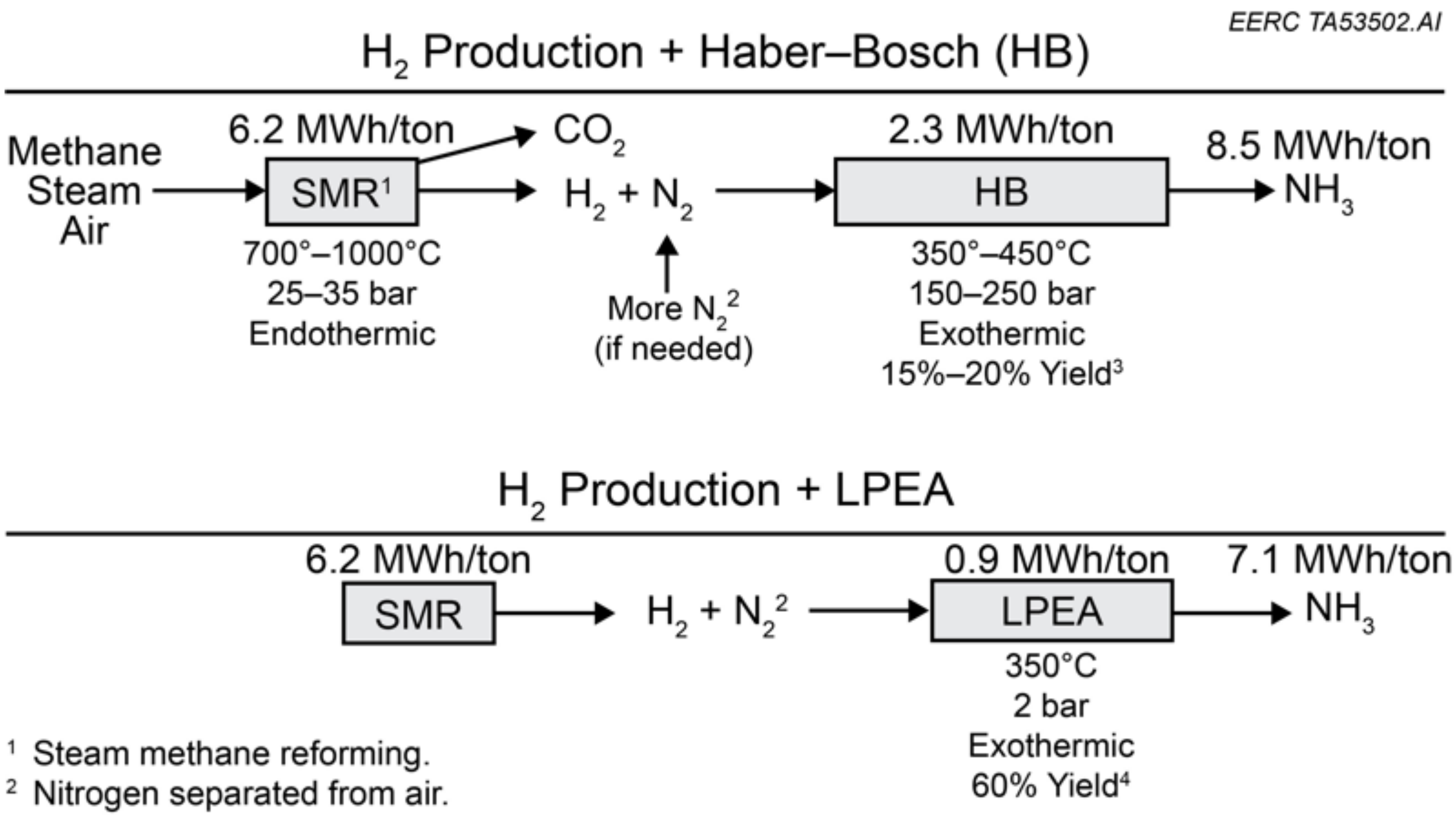
LPEA Project Goals

Demonstrate 16% LPEA energy input reduction versus state-of-the-art (2018) HB processes:
8.5 to 7.1 MWh/ton NH_3

Demonstrate LPEA reduced capital/operating cost and turn down/on/off flexibility

Key to achieving goals is high-temperature (≥300°C) high-proton-conductivity gas-impermeable polymer–inorganic composite (PIC) proton exchange membrane

Also need cathode catalyst with high activity/specificity for nitrogen reduction



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H_2 Production + Haber–Bosch (HB)

Methane
Steam
Air

6.2 MWh/ton
SMR[1]
700°–1000°C
25–35 bar
Endothermic

CO_2

$H_2 + N_2$

More N_2[2]
(if needed)

2.3 MWh/ton
HB
350°–450°C
150–250 bar
Exothermic
15%–20% Yield[3]

8.5 MWh/ton
NH_3

H_2 Production + LPEA

6.2 MWh/ton
SMR

$H_2 + N_2$[2]

0.9 MWh/ton
LPEA
350°C
2 bar
Exothermic
60% Yield[4]

7.1 MWh/ton
NH_3

[1] Steam methane reforming.
[2] Nitrogen separated from air.
[3] Single-pass yield based on hydrogen conversion.
[4] Targeted single-pass yield based on current efficiency of 65% at current density of 0.25 A/cm^2.

HB-based ammonia production versus LPEA – energy consumption comparison

Process/Pathway	**MWh/ton NH_3**
SMR + HB – Theoretical minimum	5.6[1]
SMR + HB – State of the art, 2018	8.5[2]
SMR – State of the art (high-purity H_2 production only)	6.2[3,4]
LPEA – Project target (ammonia synthesis from H_2 and N_2)	0.8*
N_2 separation from air + NH_3 product condensation, compression	0.1
SMR + N_2 separation + LPEA + NH_3 condensation, compression	7.1

* Based on achieving polymer–inorganic composite membrane performance targets and LPEA process operating at NH_3 production energy efficiency of 65%.

Key economics consideration – When LPEA is integrated with steam methane reforming (SMR) infrastructure, electricity represents about 13% (0.9 MWh/7.1 MWh) of total ammonia production energy input, with remaining 87% provided by natural gas.

1) Noelker, K.; Ruether, J. 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. Half Year Results Presentation. Available at Incitec Pivot Limited, 2018. 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.; Rostrup-Nielsen, T. Large-Scale Hydrogen Production. Paper based on keynote lecture presented at 6th World Congress of Chemical Engineering, Melbourne, Australia, 2001.

DYNO
Dyno Nobel

Waggaman – Economics

Long-term production is fully contracted or committed

Under long-term agreements with strong counterparties

Contract Profile

1/3 to Trammo via pipeline, rail, truck and barge

10 year contract

Primarily for US agriculture and industrial chemicals

1/3 to Cornerstone via onsite pipeline

25 year contract

Primarily for specialty chemical applications

1/3 notionally to Dyno Nobel

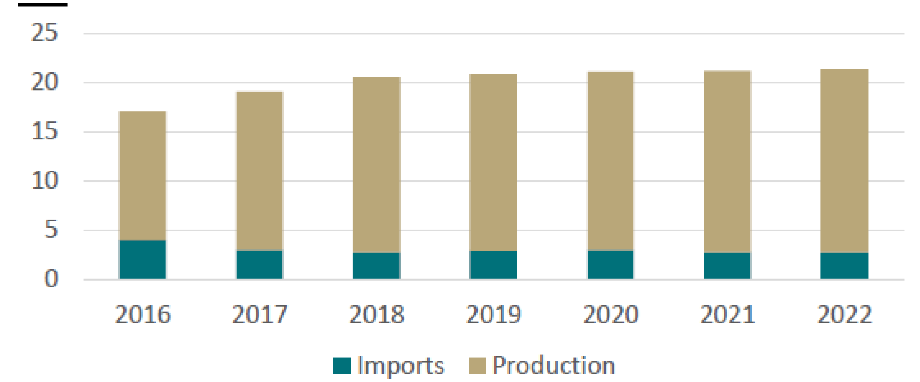
Louisiana, Missouri plant through pipeline

Cheyenne, Wyoming plant through 3rd party arrangements

In aggregate, product sold at slight (~5%) discount to Tampa CFR

North America Ammonia Industry Profile[1]

Million MT; Calendar Years



Name plate production capacity	~800,000mt of ammonia
Natural gas requirement	~32mmbtu per mt = 8.5 MWh/ton
Natural gas pricing index	Henry Hub
Natural gas delivery fee	~US$0.15 per mmbtu
Gas hedging	Floor and Cap prices of US$3.27 to US$4.52/mmbtu[2] FY18: ~5.9% FY19: ~0.4%
Fixed conversion cost	~US$47.00/mt based on name plate production
Offtake arrangements	~1/3 notionally to Dyno Nobel ~2/3 sold to counterparties In aggregate, product transferred at slight (~5%) discount to Tampa CFR
Asset value	Sum of total cash spend and capitalised interest to date Cash Spend: US$814.7m Capitalised interest: US$86.1m
Tax depreciation	Accelerated depreciation over 6 years as estimated below[3] FY16: ~5% FY18: ~23% FY20: ~11% FY17: ~38% FY19: ~14% FY21: ~9%
Accounting depreciation	Average asset life estimated ~35 years

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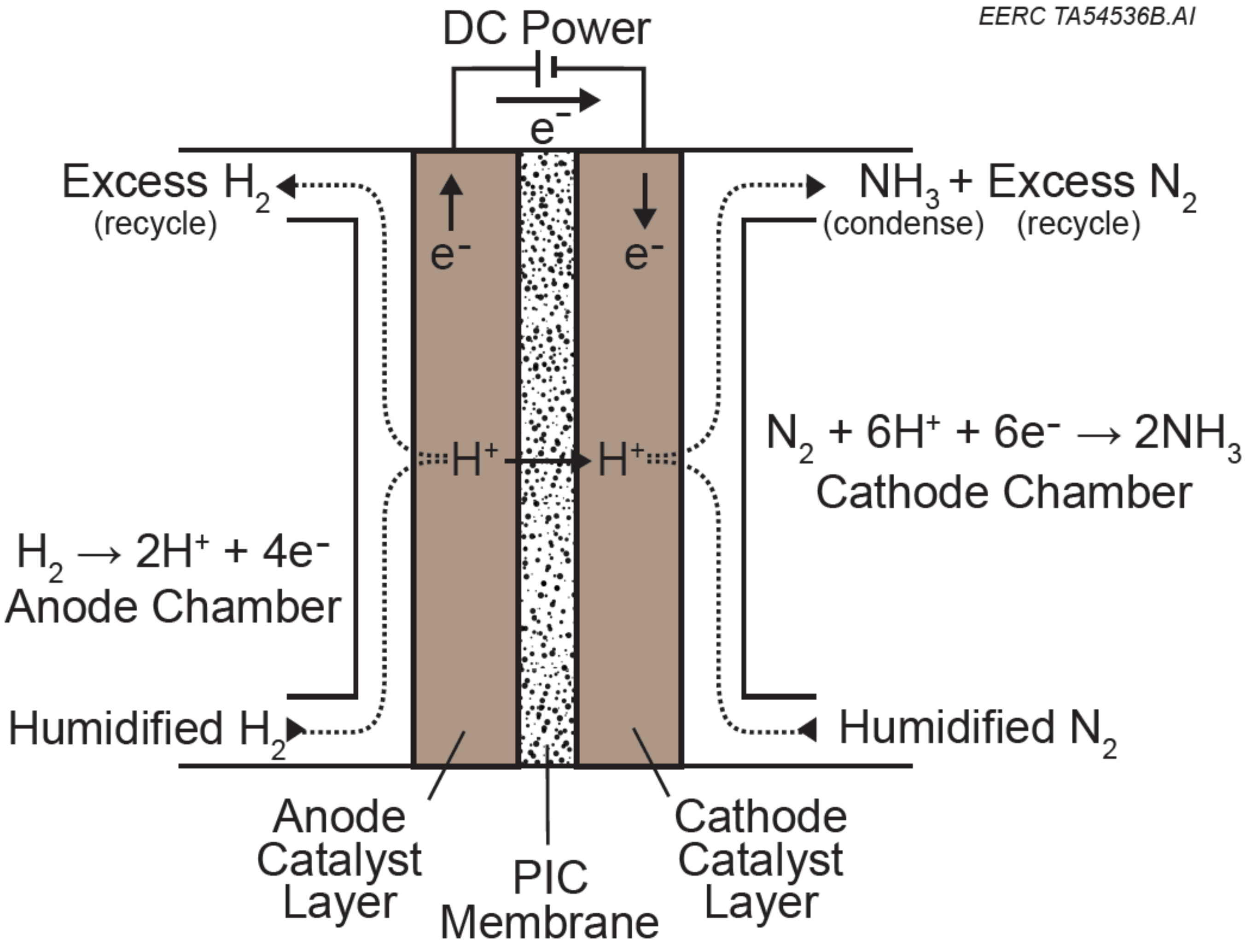
1. Source: CRU as of November 2017; North America comprises US and Canada
2. Percent of expected natural gas requirement per financial year based on nameplate production
3. Estimated financial year tax depreciation rates based on current asset allocation; subject to change

Electrolytic ammonia synthesis via PIC membrane



- Low-cost inorganic proton conductor (IPC) particles are composited in high-temperature polymer polybenzimidazole (PBI) matrix to yield 300°C-capable PIC membrane

- Compositing PBI with stable high-temp proton conductor (versus PBI “doping”) maintains PBI thermal stability and mechanical properties, translating to high stability and strength of PIC membrane

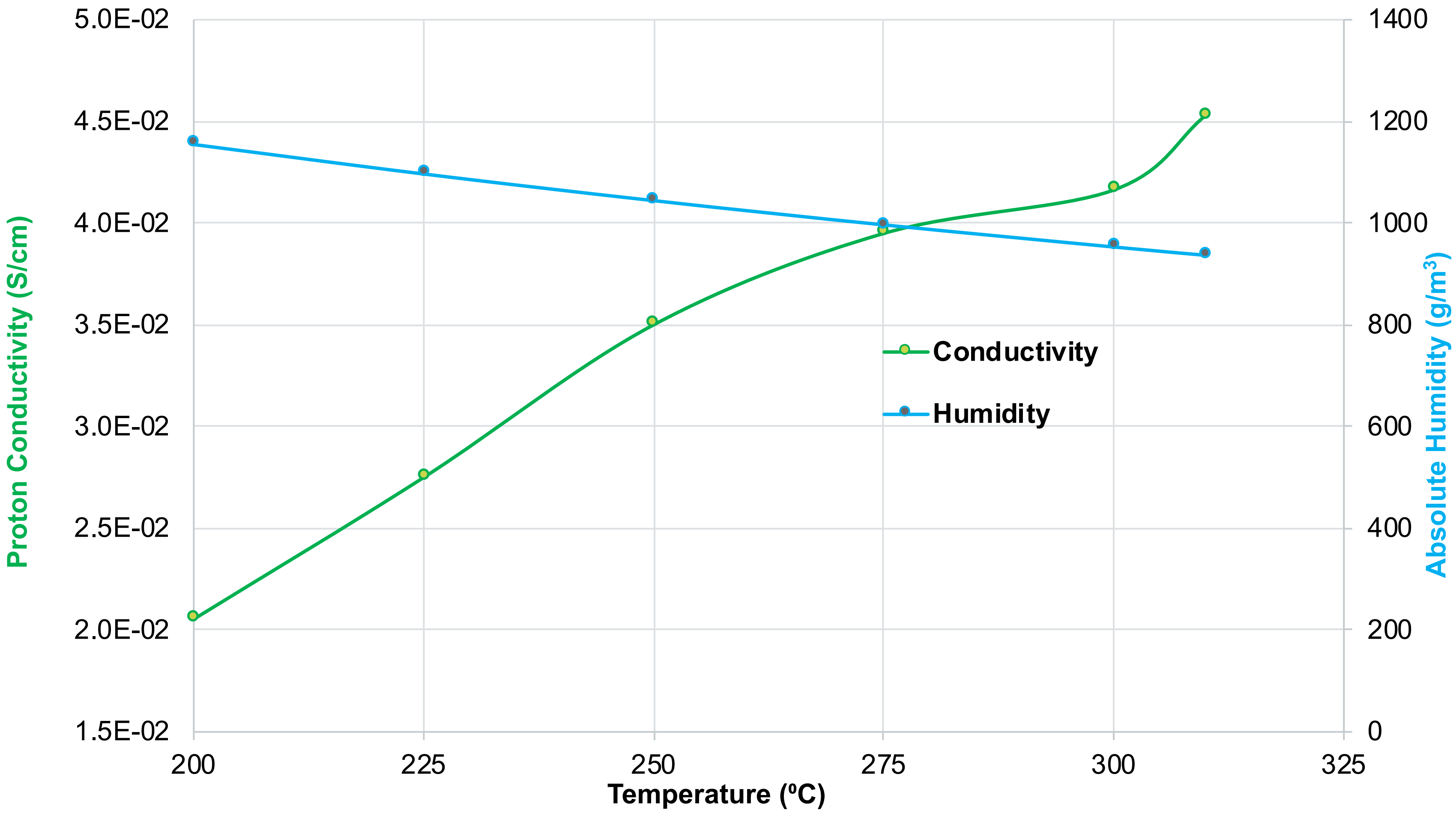
- Resulting PIC membrane is (ideally) gas-tight with high-proton-conductivity at ≥300°C operating temperature, required for commercially relevant NH_3 production rate

PIC proton exchange membrane performance targets

- Proton conductivity of ≥10^{-2} Siemens/centimeter at 300°C
- Gas permeability of <2% at 300°C
- Ability to sustain 10^{-2} Siemens/centimeter proton conductivity for at least 1000 hours
- As measured in membrane–electrode assembly (MEA) at minimum temperature of 300°C:
  - Current efficiency of ≥65% for ammonia formation at current density of ≥0.25 amps/centimeter^2*
  - Ammonia production efficiency of ≥65%*

*** U.S Department of Energy-specified performance target**

Pressed-disk PIC membrane initial performance validation via impedance testing



PIC Membrane

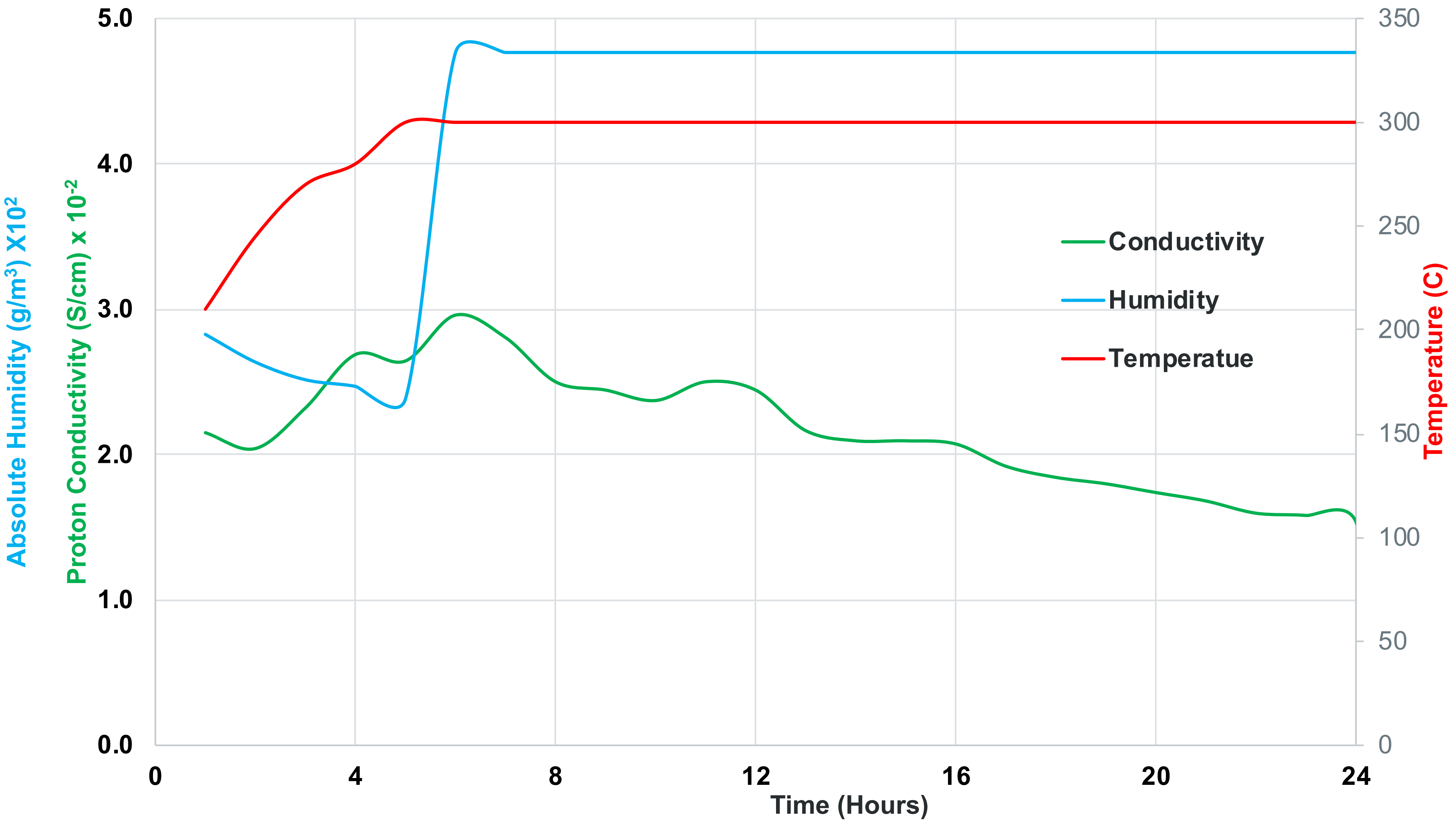
- 800-µm thickness
- 94% IPC
- 6% PBI

Test Conditions

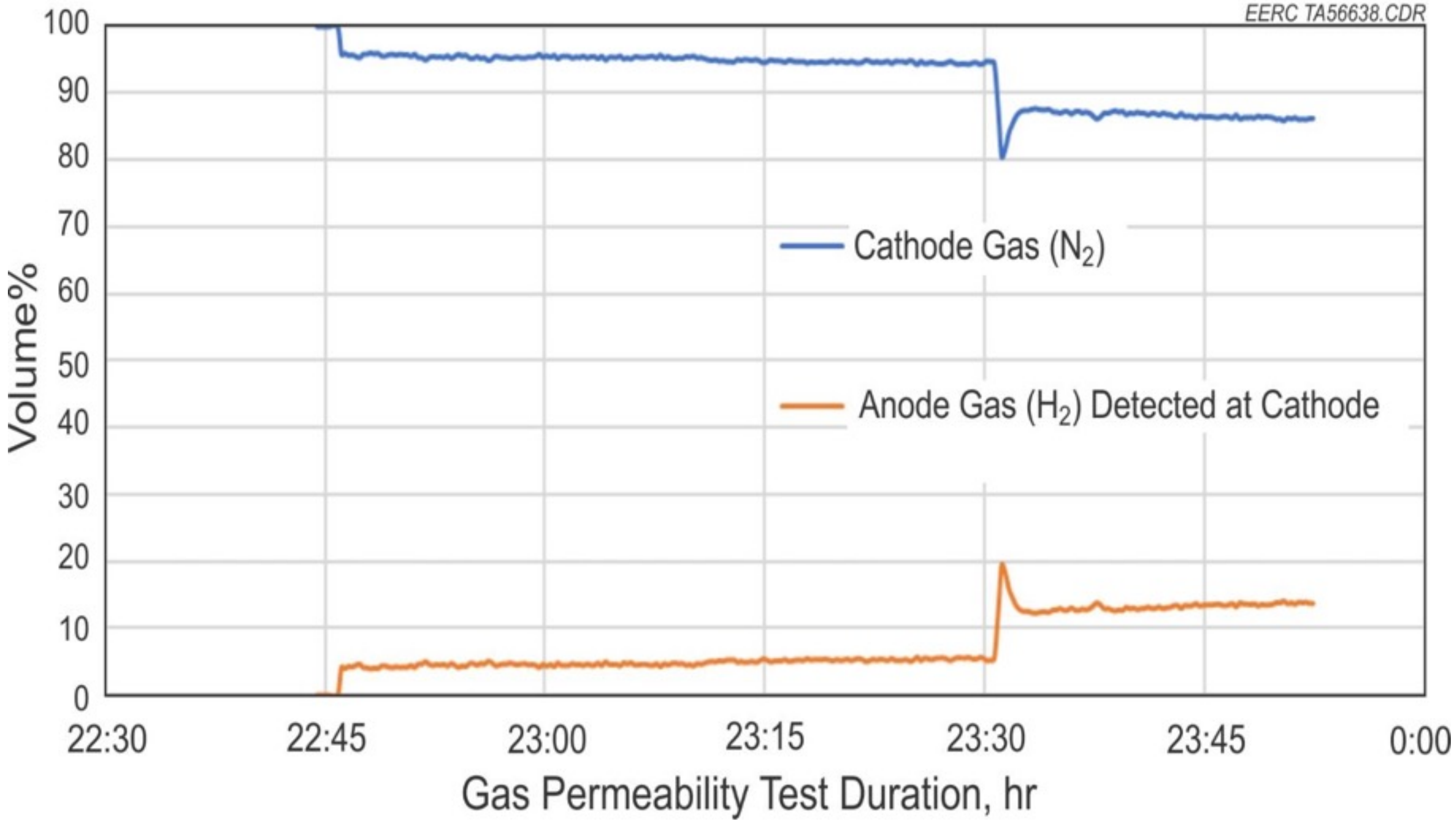
- 100 sccm hydrogen flow over anode
- 100 sccm nitrogen flow over cathode
- Humidity supplied as steam to both anode and cathode

Humidification required to achieve high proton conductivity at 300°C

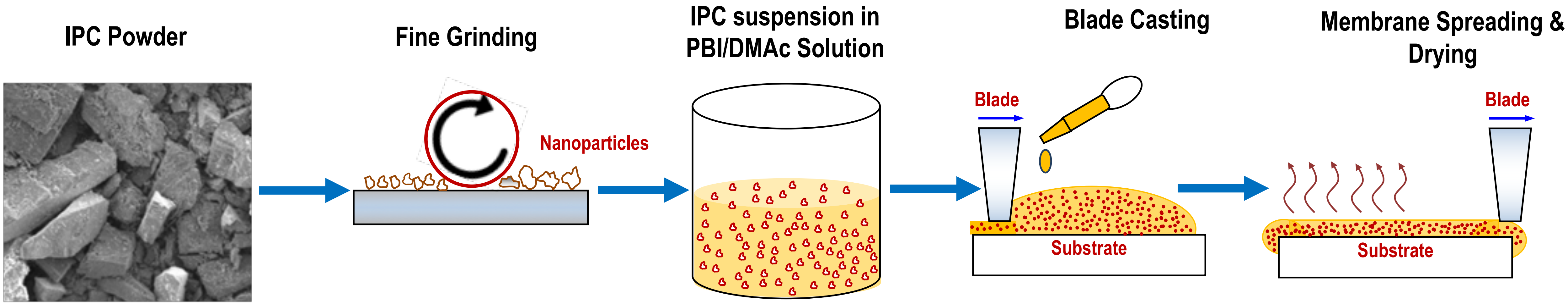
Pressed-disk PIC membrane – 24-hour impedance testing



Gas permeability (H_2 cross-over) measured during proton conductivity testing of pressed-disk PIC membrane at 300°C, 475 g/m^3 absolute humidity



Cast film PIC membrane fabrication – early-stage



IPC Powder

Fine Grinding

IPC suspension in PBI/DMAc Solution

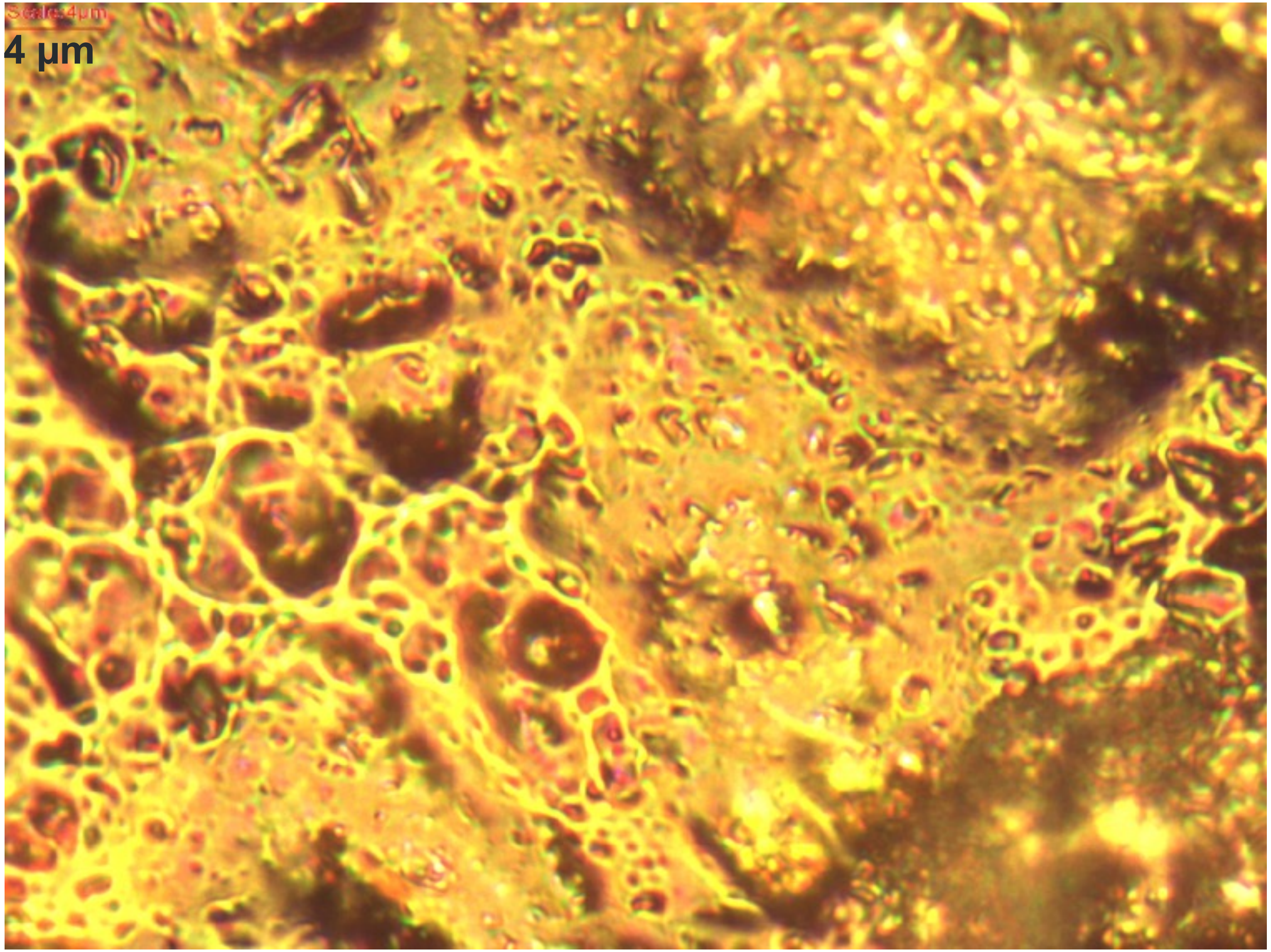
Blade Casting

Membrane Spreading & Drying

Commercial PBI film (left) and early-stage lab-fabricated PBI film (middle), 54% IPC–46% PBI film (right)

Commercial film appears more compacted/dense than early-stage lab-fabricated films

Optical image of early-stage 67% IPC–33% PBI cast film membrane

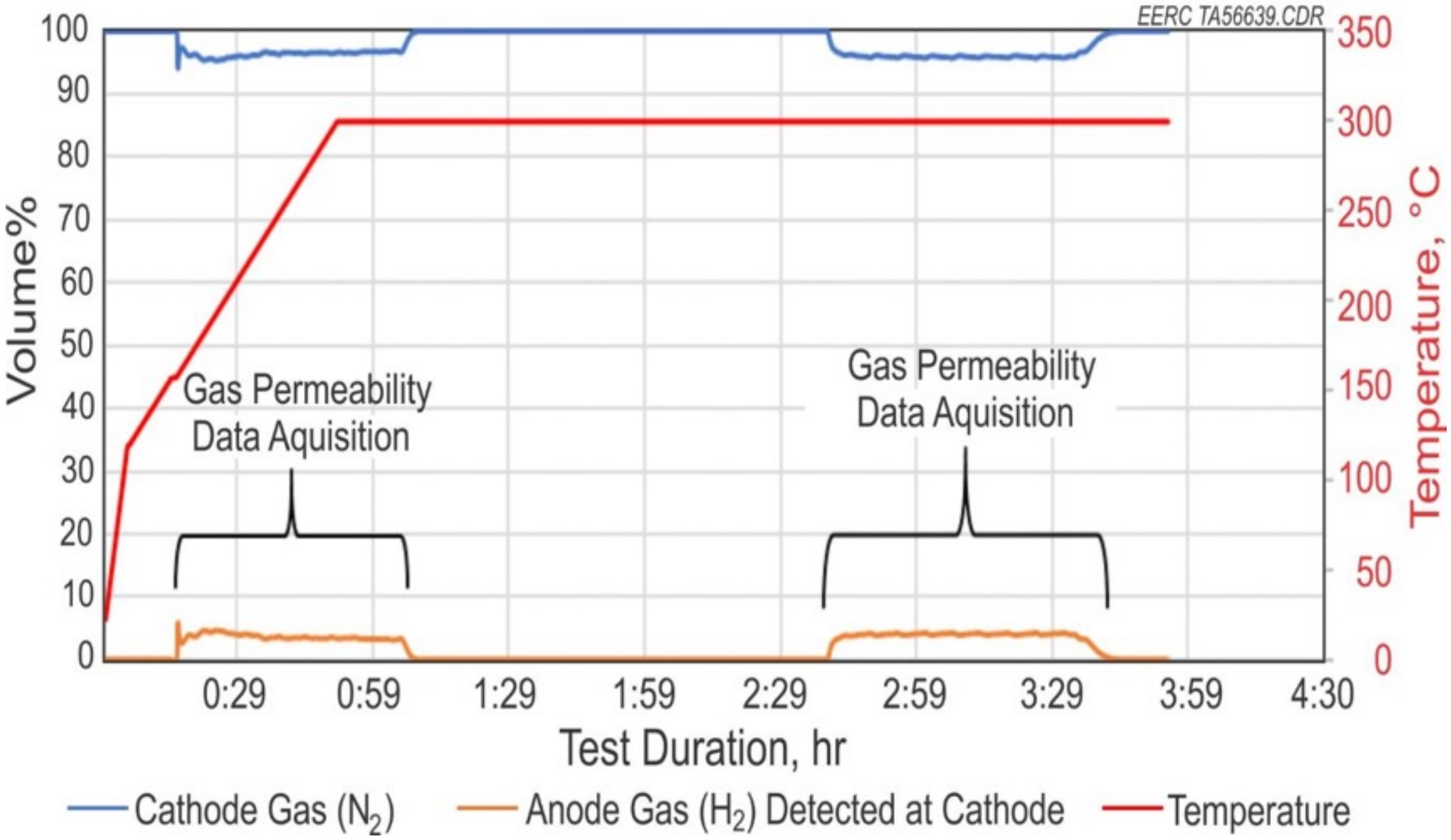


IPC particles initially ground to 5–15 µm; now using 0.5–1.5-µm particles

Blade/drawdown bar-induced liquid film spreading results in bumpy surface, uneven drying/solvent evaporation, particle aggregation

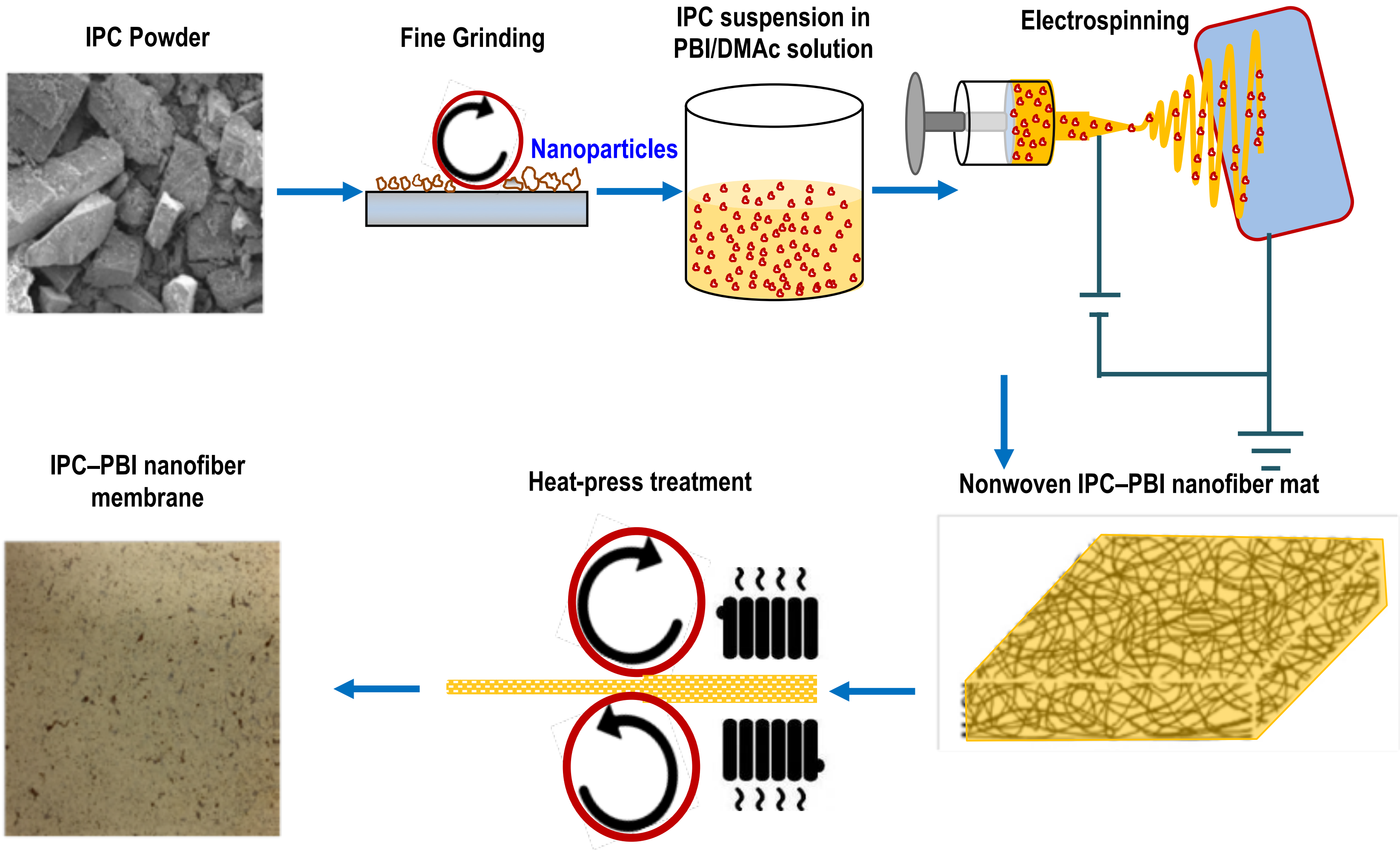
Working on quality improvement via optimization of polymer concentration, layer thickness, blade spreading speed, heating temperature and duration, temperature–time profile

H_2 cross-over measured for 67% IPC–33% PBI cast film membrane (with proton conductivity of $0.2*10^{-2}$ S/cm) at 300°C, 330 g/m^3 absolute humidity



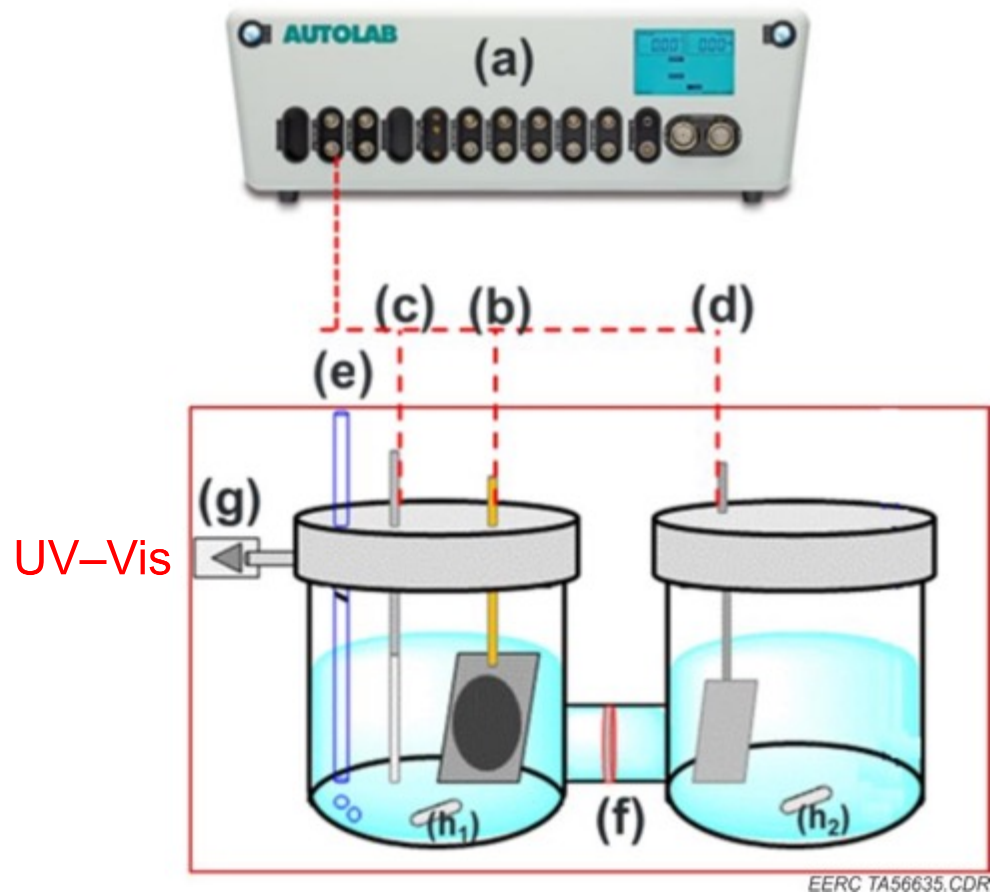
Commercial PBI film exhibited zero H_2 cross-over for over 24 hours at 300°C, 330 g/m^3 absolute humidity

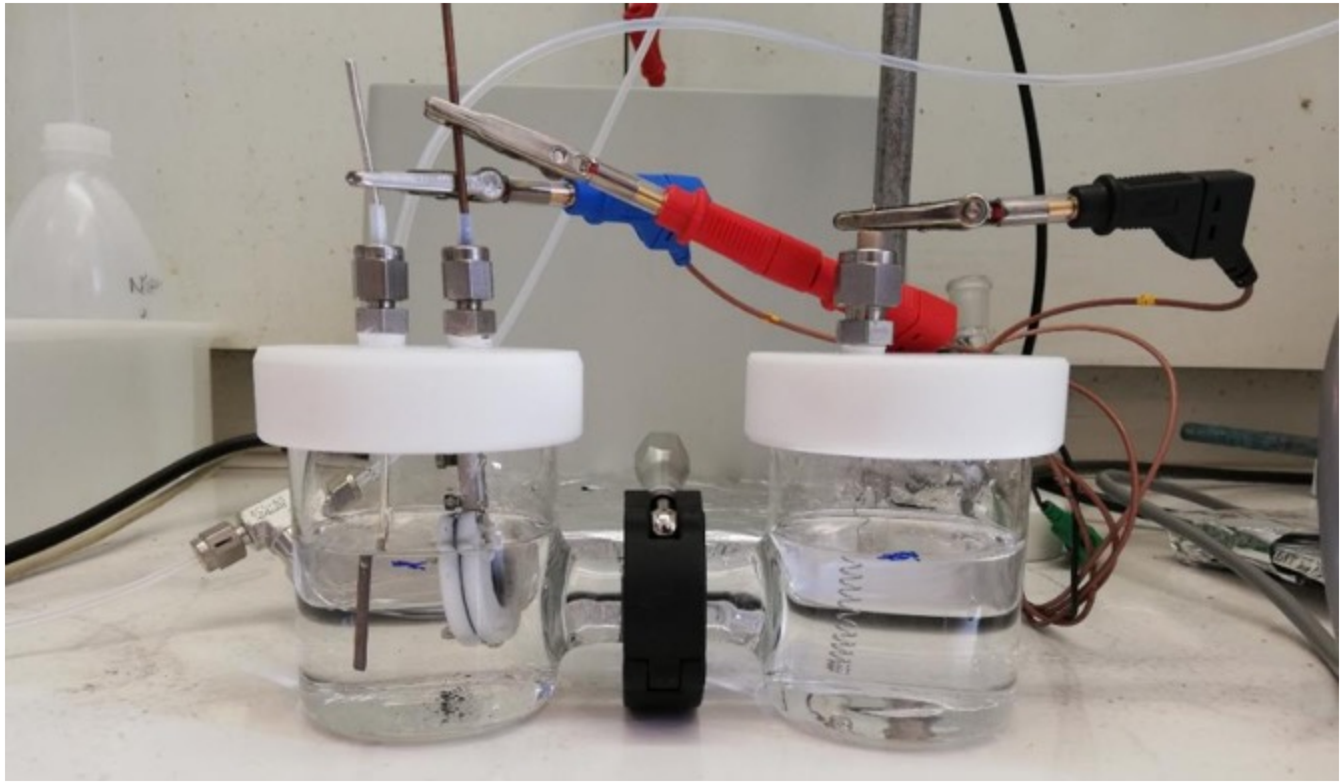
IPC–PBI matted (versus aligned) nanofiber PIC membrane fabrication – early-stage



Depending on nanofiber IPC loading achievable and resulting membrane performance, may investigate nanofiber alignment to increase proton conductivity

Catalyst screening to identify serviceable (versus highly optimized) cathode catalyst





a) potentiostat, b) working electrode (candidate cathode catalyst), c) reference electrode (Ag/AgCl), d) counter/anode electrode (Pt wire/cage), e) N_2 inlet, f) Nafion membrane, g) following test, cathode solution undergoes UV–Vis spectrophotometry analysis for ammonia quantitation, h) magnetic stirrer.

Cathode catalyst screening objective –
Identify catalyst with 50% faradaic efficiency for NH_3 synthesis at room temp

Candidate Catalysts

- Single-atom-iron on nitrogen-doped carbon
- Single-atom-ruthenium on nitrogen-doped carbon
- Ruthenium nanoparticles on reduced graphene oxide
- Bismuth nanocrystals
- Gold and nickel nanoparticles on nitrogen-doped carbon
- Zirconium nitride
- Niobium nitride
- Chromium nitride

How about your catalyst?

By 14 June 2021….

- Optimize PIC membrane based on
  - Performance and durability at 300°C
  - Compatibility with Nel Hydrogen MEA fabrication technique and equipment
- Identify serviceable cathode catalyst that meets all Nel form factor requirements for MEA fabrication
- Deploy Nel-fabricated MEAs in multi-cell LPEA system
  - Optimize system performance
  - Conduct long-term performance and durability testing of PIC membrane and other system components
- Evaluate techno-economic viability of PIC membrane-based LPEA process

ACKNOWLEDGMENT

Disclaimer

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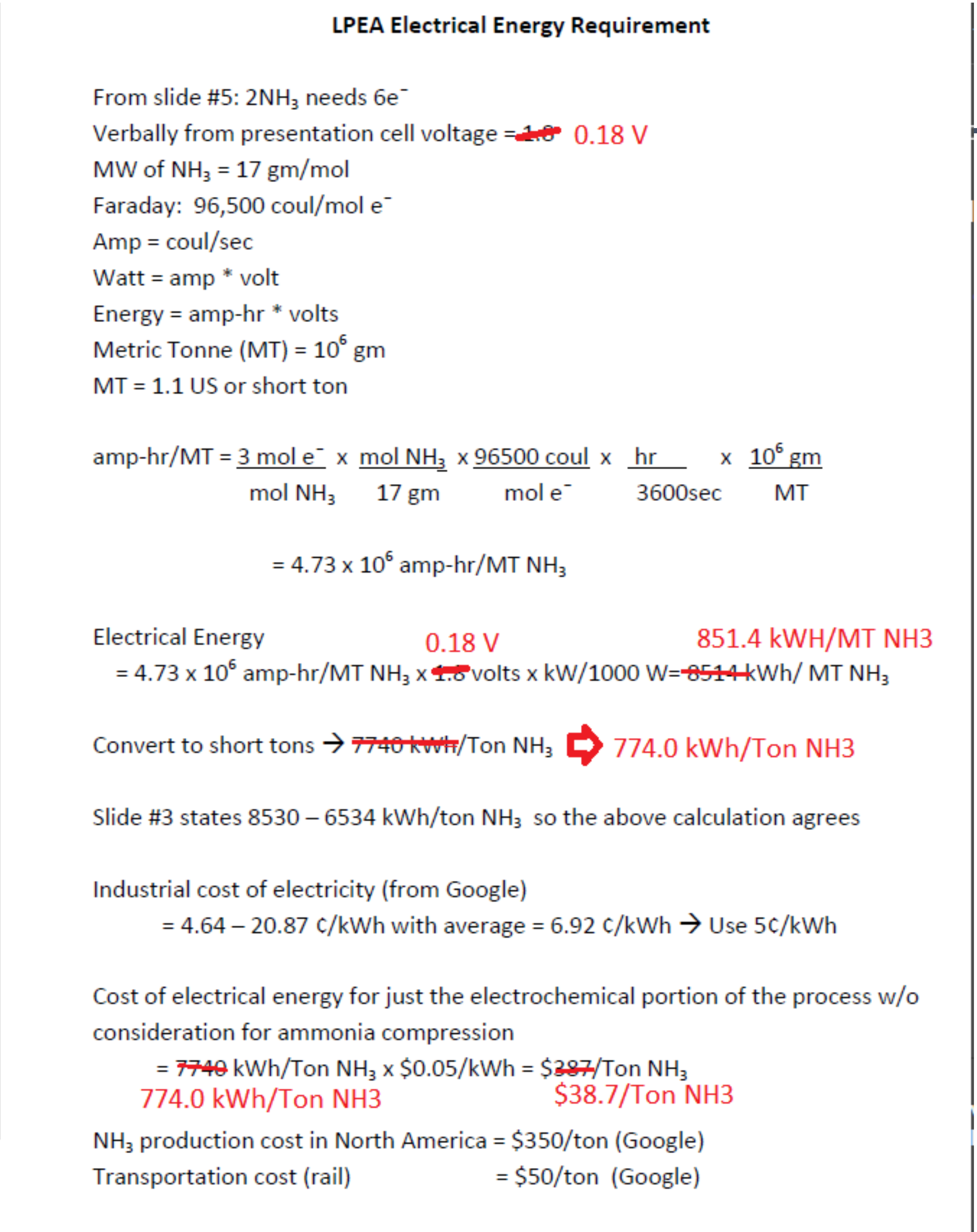

LPEA Electrical Energy Requirement

From slide #5: $2NH_3$ needs $6e^-$

Verbally from presentation cell voltage = ~~1.8~~ 0.18 V

MW of NH_3 = 17 gm/mol

Faraday: 96,500 coul/mol e^-

Amp = coul/sec

Watt = amp * volt

Energy = amp-hr * volts

Metric Tonne (MT) = 10^6 gm

MT = 1.1 US or short ton

$$\text{amp-hr/MT} = \frac{3\text{ mol }e^-}{\text{mol }NH_3} \times \frac{\text{mol }NH_3}{17\text{ gm}} \times \frac{96500\text{ coul}}{\text{mol }e^-} \times \frac{\text{hr}}{3600\text{sec}} \times \frac{10^6\text{ gm}}{\text{MT}}$$

$$= 4.73 \times 10^6\text{ amp-hr/MT }NH_3$$

Electrical Energy

0.18 V 851.4 kWH/MT NH3

= 4.73 x 10^6 amp-hr/MT NH_3 x ~~1.8~~ volts x kW/1000 W= ~~8514~~ kWh/ MT NH_3

Convert to short tons → ~~7740 kWh~~/Ton NH_3 ⇨ 774.0 kWh/Ton NH3

Slide #3 states 8530 – 6534 kWh/ton NH_3 so the above calculation agrees

Industrial cost of electricity (from Google)

= 4.64 – 20.87 ¢/kWh with average = 6.92 ¢/kWh → Use 5¢/kWh

Cost of electrical energy for just the electrochemical portion of the process w/o consideration for ammonia compression

= ~~7740~~ kWh/Ton NH_3 x \$0.05/kWh = \$~~387~~/Ton NH_3

774.0 kWh/Ton NH3 \$38.7/Ton NH3

NH_3 production cost in North America = \$350/ton (Google)

Transportation cost (rail) = \$50/ton (Google)