Progress in the Electrochemical Synthesis of Ammonia

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Catalysis Today (2016)

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Ammonia fixation in nature

$$N_2 + 8H^+ + 8e^- + 16ATP \rightarrow 2NH_3 +$$
$$H_2 + 16ADP + 16(PO_3^-)$$

244 kJ/mol NH_3

4.0 kWh/kg

Haber-Bosch

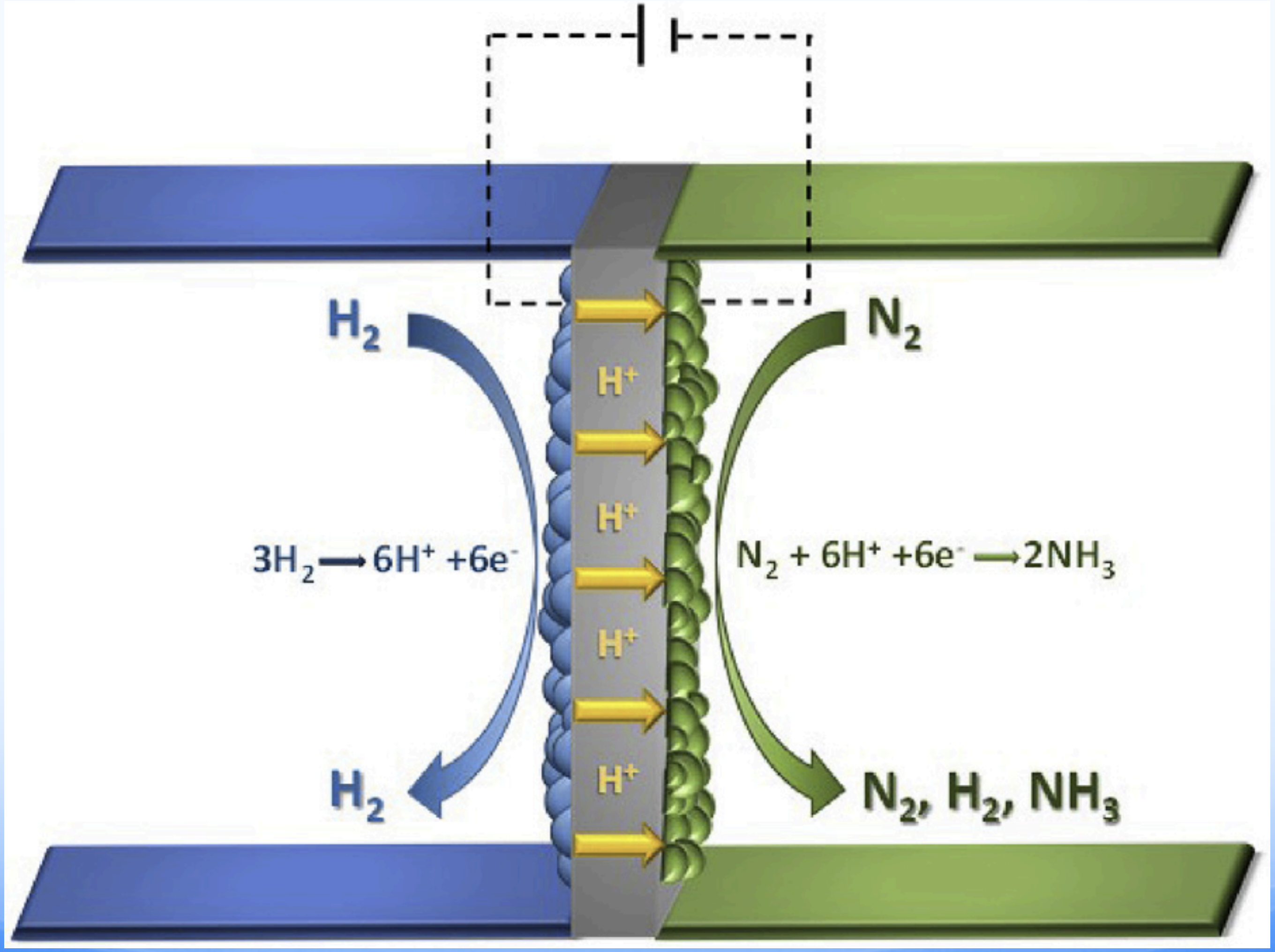
$$N_2 + 3H_2 \rightarrow 2NH_3$$

Solid State Ammonia Synthesis

$$\text{Anode: } 3H_2 \rightarrow 6H^+ + 6e^-$$

$$\text{Cathode: } N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$$

Basic Solid State Ammonia Synthesis, SSAS



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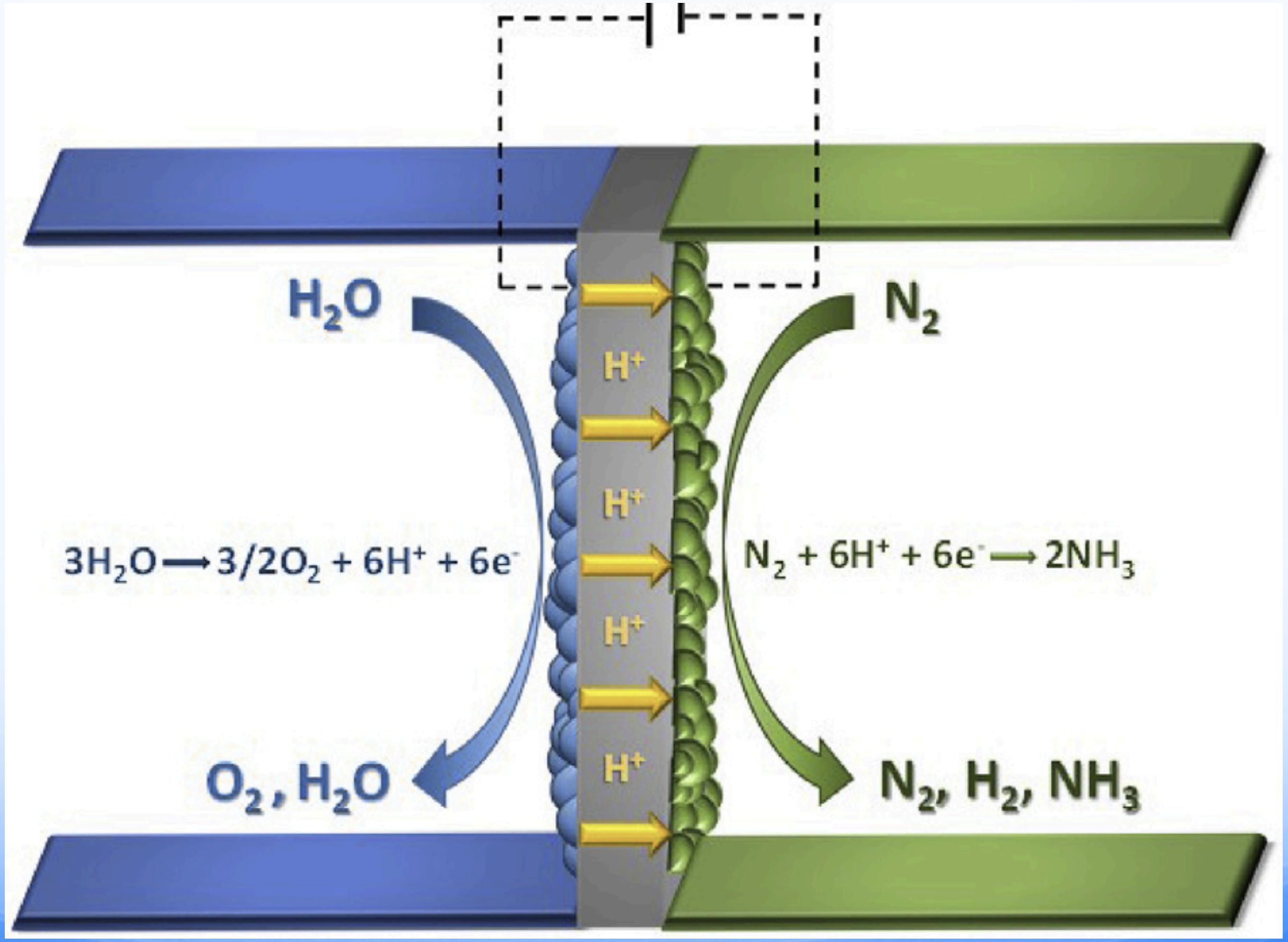
SSAS coupled with Steam Electrolysis



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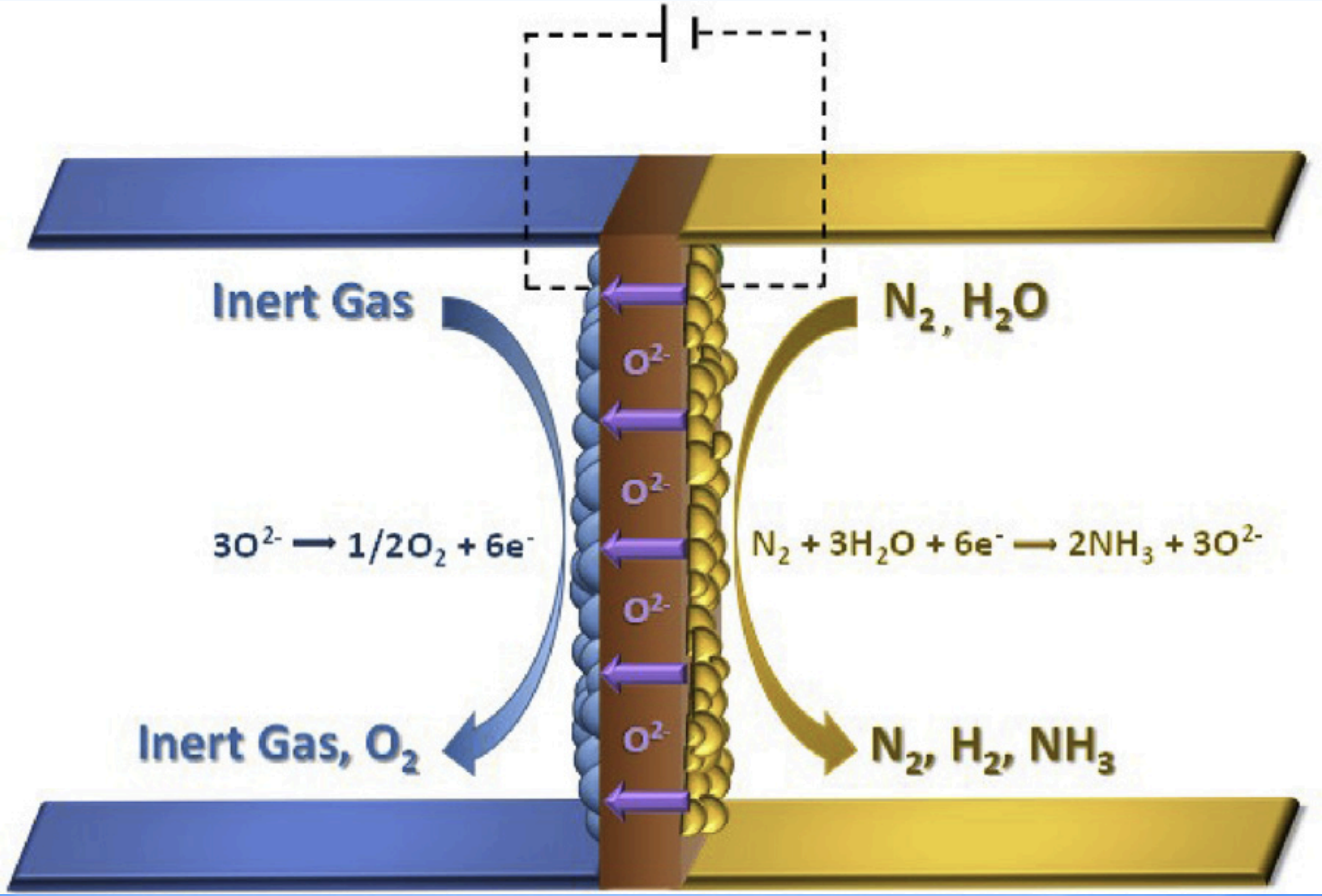
SSAS using ceramic oxygen ion conductors



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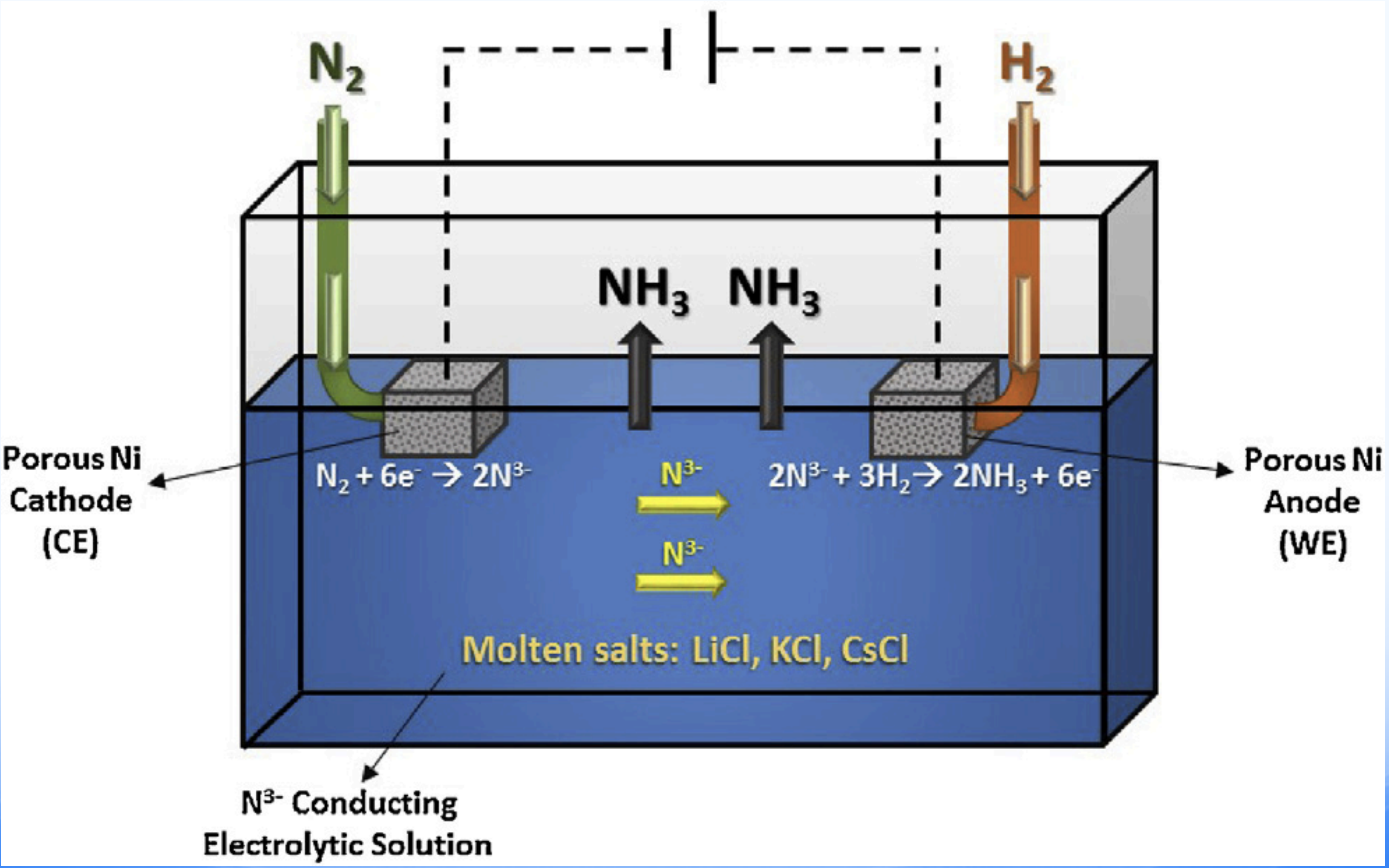
Intermediate Temp SSAS
(100C < T < 500C)



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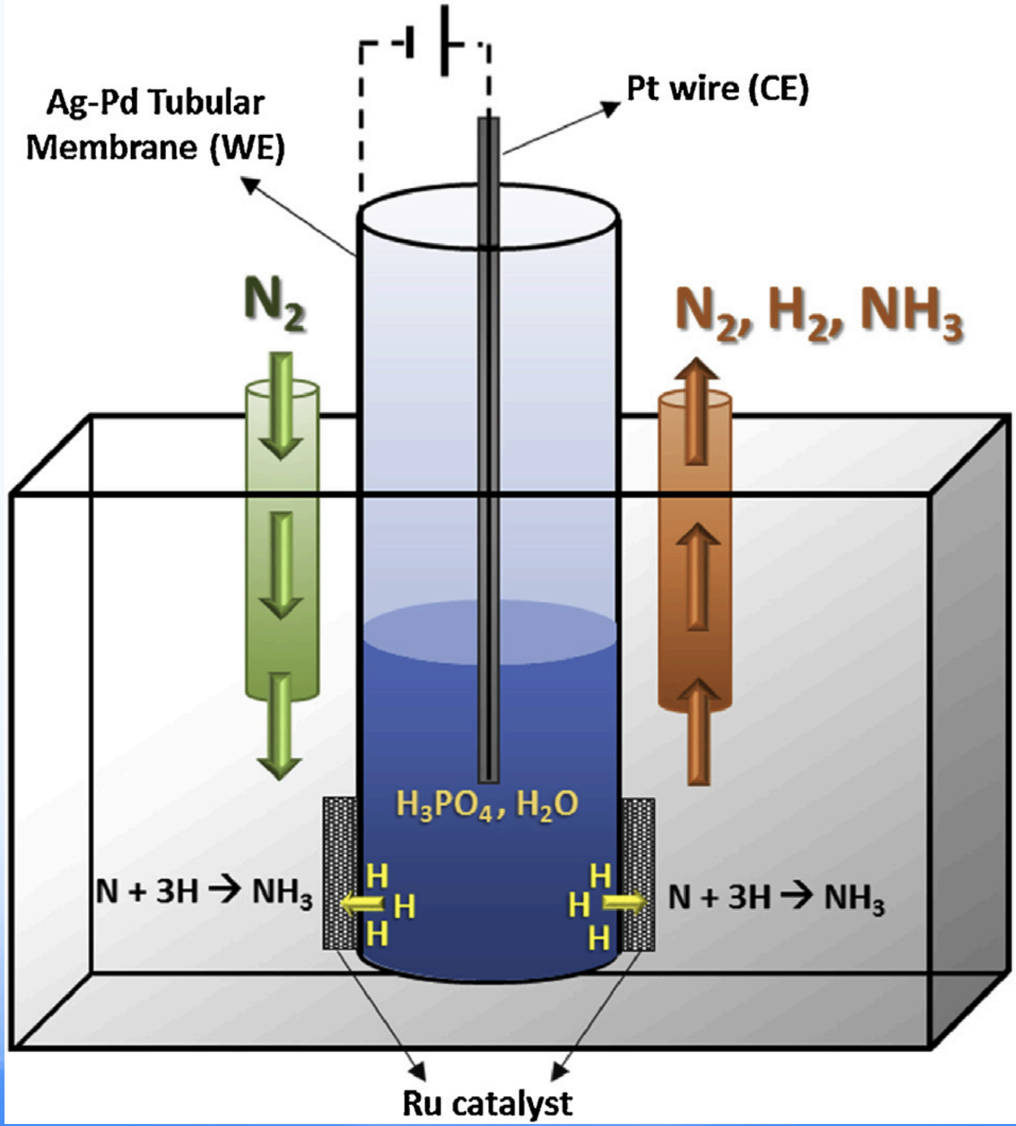
Direct Low Temp SSAS
(100C < T < 500C)



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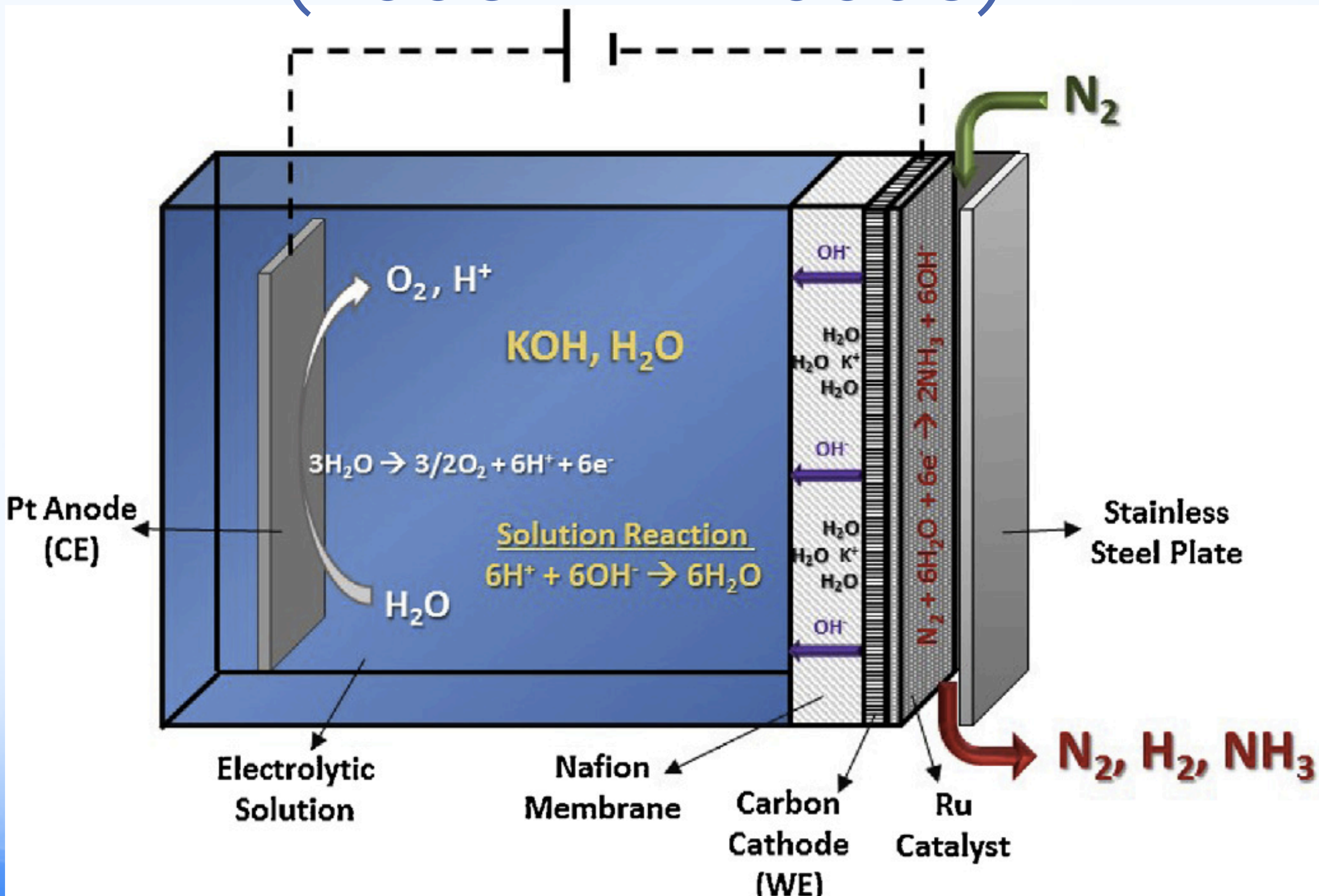
Low Temp Membrane SSAS
(100C < T < 500C)



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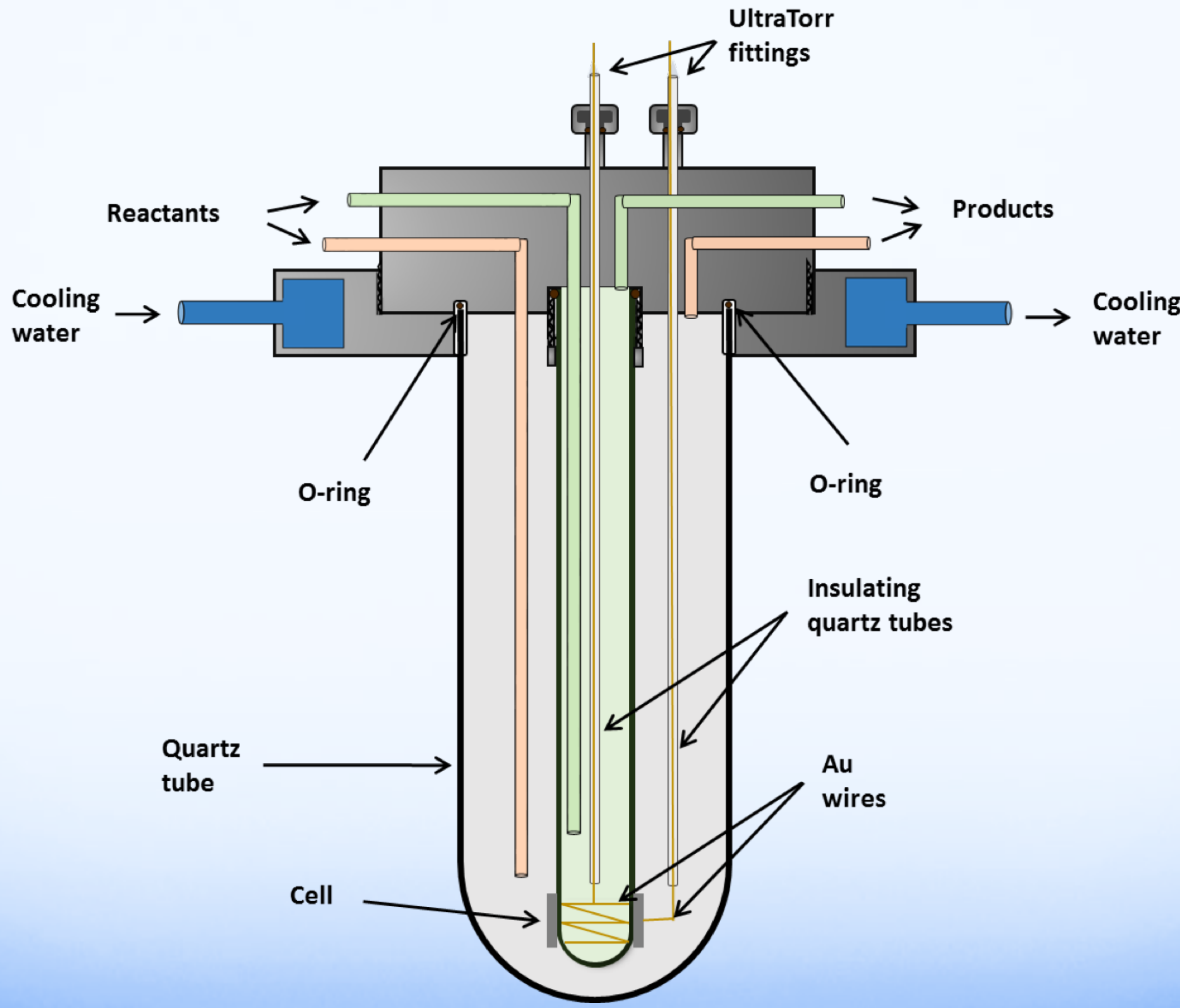
CERTH SSAS Reactor



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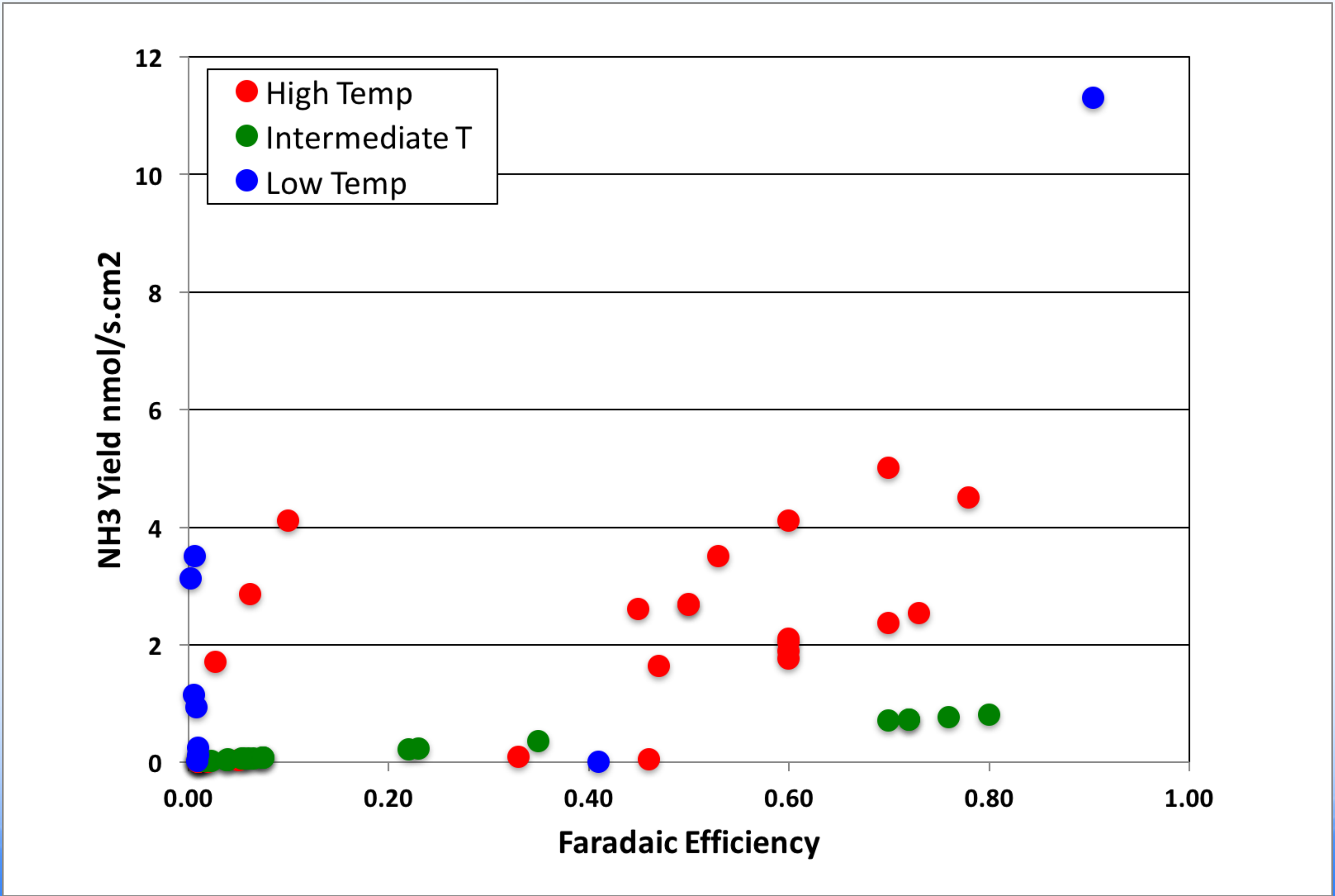
Cumulative SSAS results



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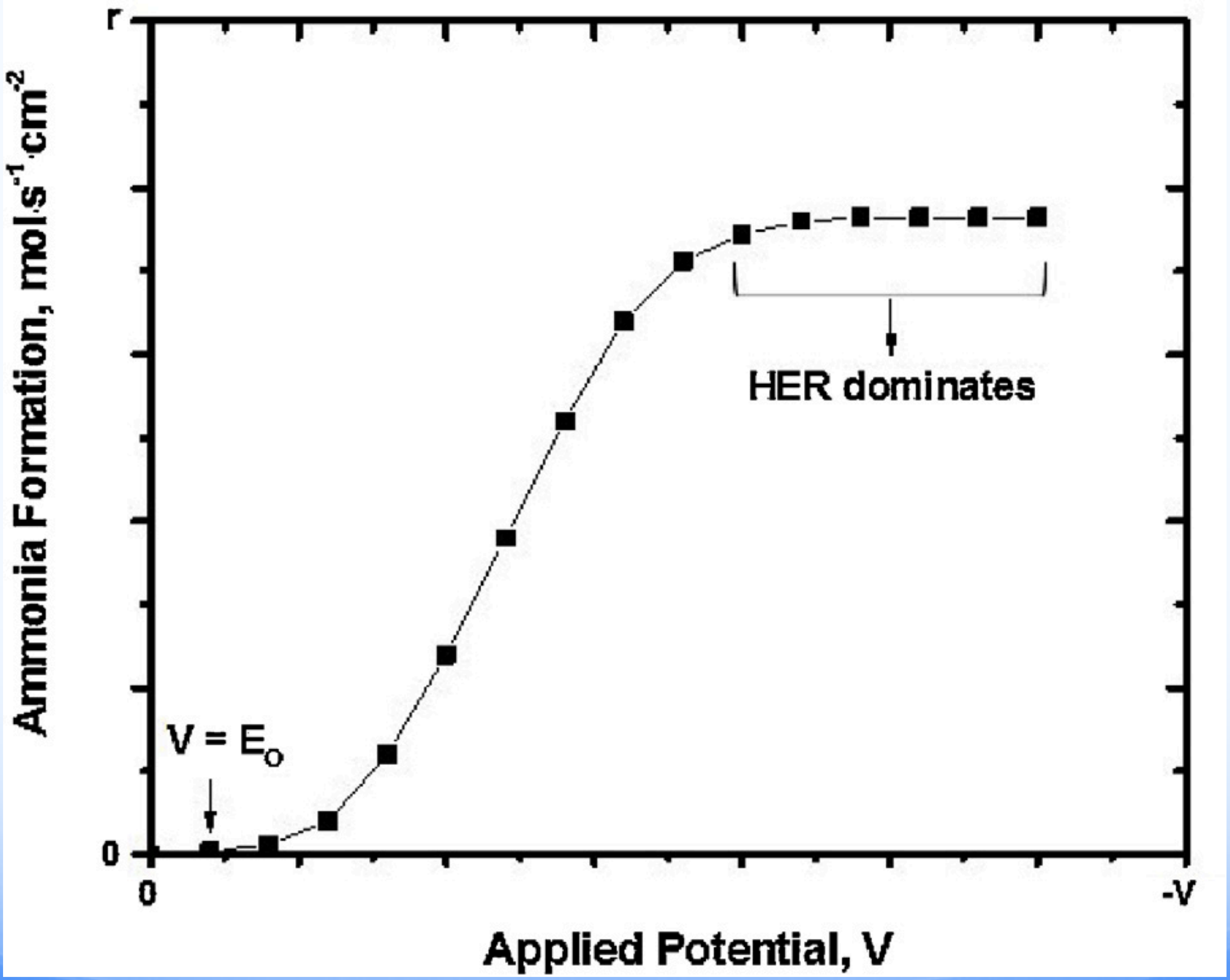
The Underlying Challenge



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Giddey Commercial Benchmark*

$>1\ \mu mol\ NH_3/s.cm^2$ at >50% FE (.145 mA/cm2)

(0.25 – 0.50 mA/cm2 : $J(NH_3) = A/3F \times \eta_{FE}$

1×10^{-6} mol/s.cm² x 17 g NH_3/mol x 10^5 cm²/m² x 3600 s/h x 8,760 hr/year

50 t/m².yr

200×10^6 tonne = 4×10^6 m²

**Giddey, et al., Review of electrochemical ammonia production technologies and materials, Intl. J. Hydrogen Energy (2013)*

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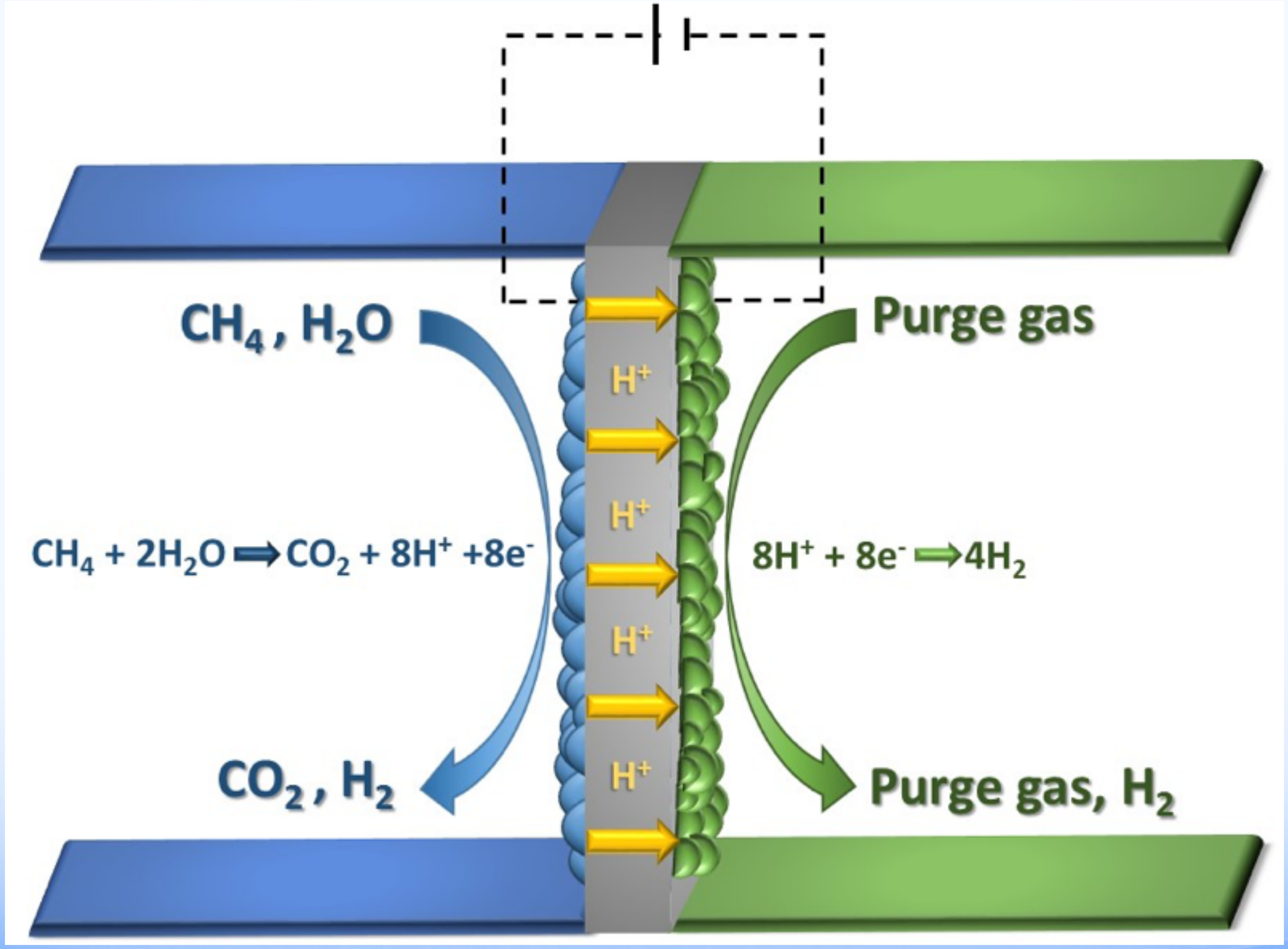
Critical Assessment

- Single-step SSAS is feasible, just not commercially viable at this time
- Challenge: effective N_2 dissociation and NH_3 synthesis catalysts needed
- Decoupled H_2 production with Haber-Bosch?

Decoupled H_2 Production



Hydrogen Separation Membranes (2010)

	Dense Polymer	Microporous Ceramic	Dense Ceramic	Porous Carbon	Dense Metallic
Temperature Range	<100°C	200°–600°C	600°–900°C	500°–900°C	300°–600°C
H_2 Selectivity	Low	Moderate	Very high	Low	Very high
H_2 Flux	Low	High	Moderate	Moderate	High
Known Poisoning Issues	HCl, SO_x, CO_2		H_2S	Strong vapors, organics	H_2S, HCl, CO
Example Materials	Polymers	Silica, alumina, zirconia, titania, zeolites	$SrCeO_{3-\delta}$, $BaCeO_{3-\delta}$	Carbon	Palladium alloys, Pd–Cu, Pd–Au
Transport Mechanism	Solution/diffusion	Molecular sieving	Solution/diffusion	Surface diffusion, molecular sieving	Solution/diffusion

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Protonic Ceramic Membranes under Asymmetric Steam Atmosphere

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[2]Solid State Energy,
[3]Colorado School of Mines,
Golden Colorado

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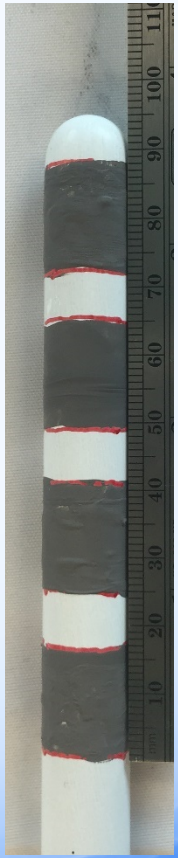
Solid State Energy Group, LLC

COLORADO SCHOOL OF MINES
EARTH ENERGY ENVIRONMENT

Ni-BZCY Symmetric Cell by Solid State Reactive Sintering

- $BaZr_{0.8}Ce_{0.1}Y_{0.1}O_{2.9}$ **(BZCY81) and** $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{2.9}$ **(BZCY72)**
- **Mix precursor oxides, (**ZrO_2**,** CeO_2**,** Y_2O_3**) and** $BaSO_4$ **with 60 Wt.% NiO in a water based slurry**
- **Slip cast tubular support**
- **Ultrasonically spray coat electrolyte precursor mixture (w/o NiO).**
- **Apply outer electrode (same slurry used for the support)**
- **Co-fire producing a fully dense two phase ceramic by SSRS.**



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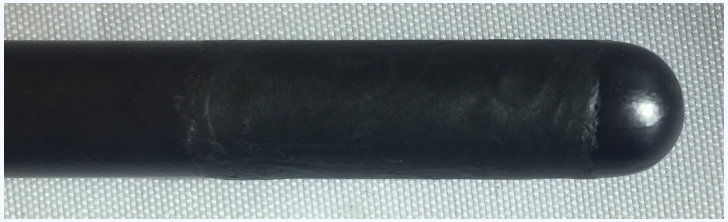
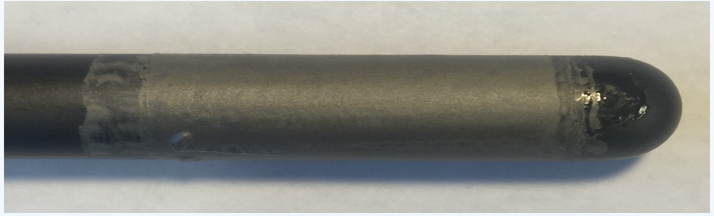
Co-fired H_2 Membrane Tubes
10 mm OD x 20 cm long COE

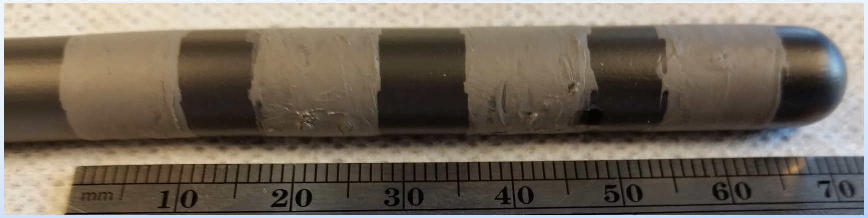


Fired tube with single electrode before being reduced



Fired tube with single electrode after being reduced in 4% H_2 96% Argon

Fired tube with multiple electrodes after being reduced in 4% H_2 96% Argon



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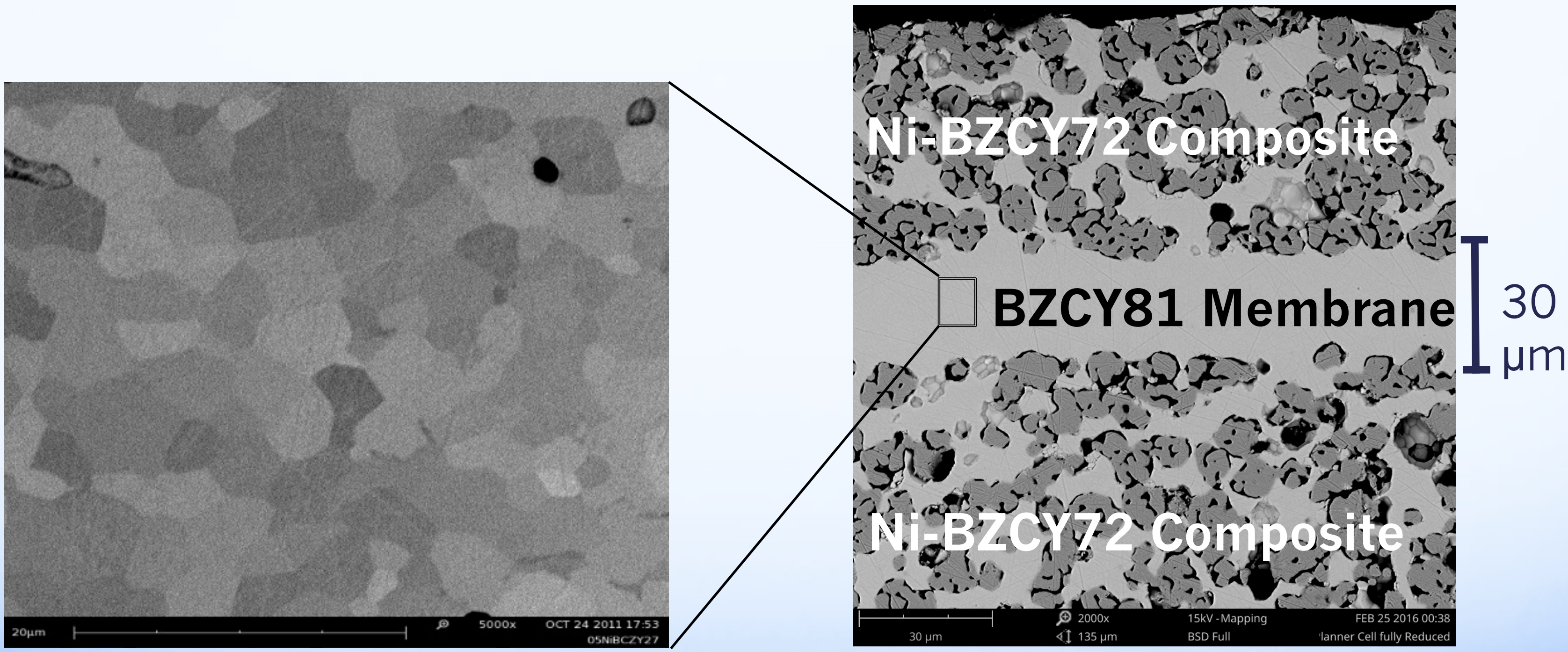
Dense membrane microstructure of BZCY81 between Ni-BZCY72 electrode composite



3-5 µm grains

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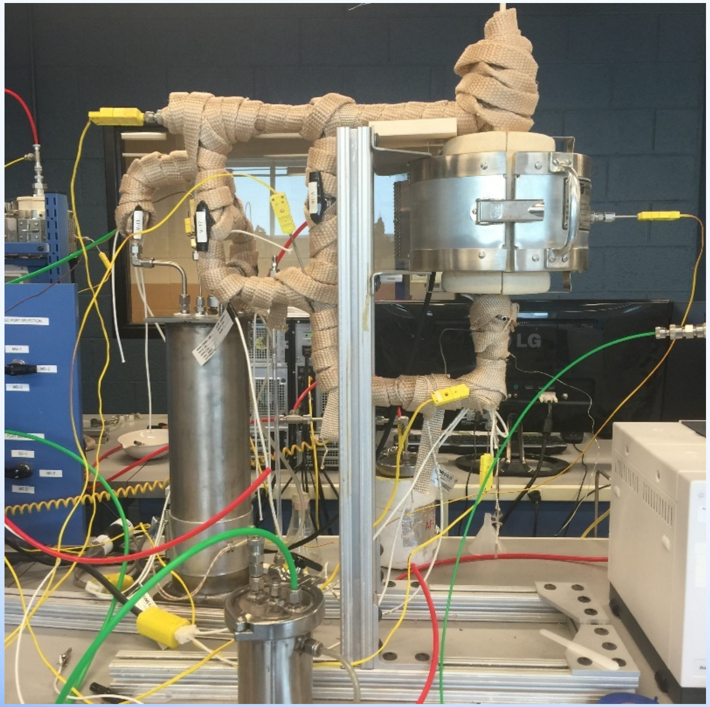
Courtesy: Anthony Manerbino

H2 Flux Measurements by Stoichiometric Titration



- 2 ATS clam-shell furnaces
- Alicat Scientific MFC's
- 2 Agilent 34410A DMM's
- Agilent E3466A DC power supply
- LabVIEW program for system integration
- O_2 Lambda Sensor
- Cirrus 2 MS and Agilent Micro GC for leak monitoring

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Principle of Stoichiometric Titration

ST uses a simple titration technique to determine the amount of oxygen needed to react with hydrogen to create a large pO_2 change between the reference gas and the product gas at the stoichiometric point also called the ***Lambda Transition.*** This is done using a closed end tubular 10YSZ oxygen lambda sensor with Pt electrodes.

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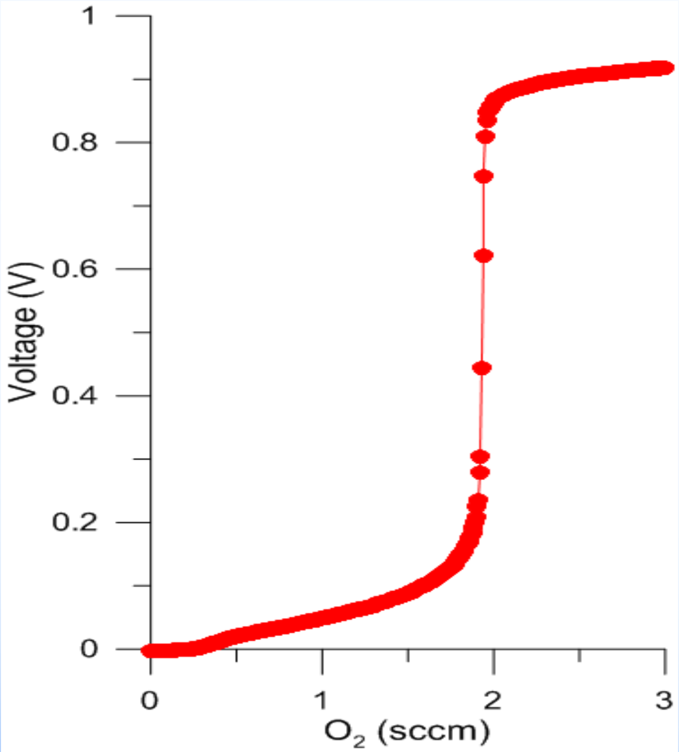
Lambda Transition at Stoichiometric Point.



- **Calibration conditions**
  - **Lambda sensor at 725 ºC,**
  - **Reference gas 4% H_2 balance Ar.**
  - **Flow rate 100 NmL/min**

- **The stoichiometric point occurs by titrating in oxygen until all hydrogen in the reference gas is consumed.**

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$$

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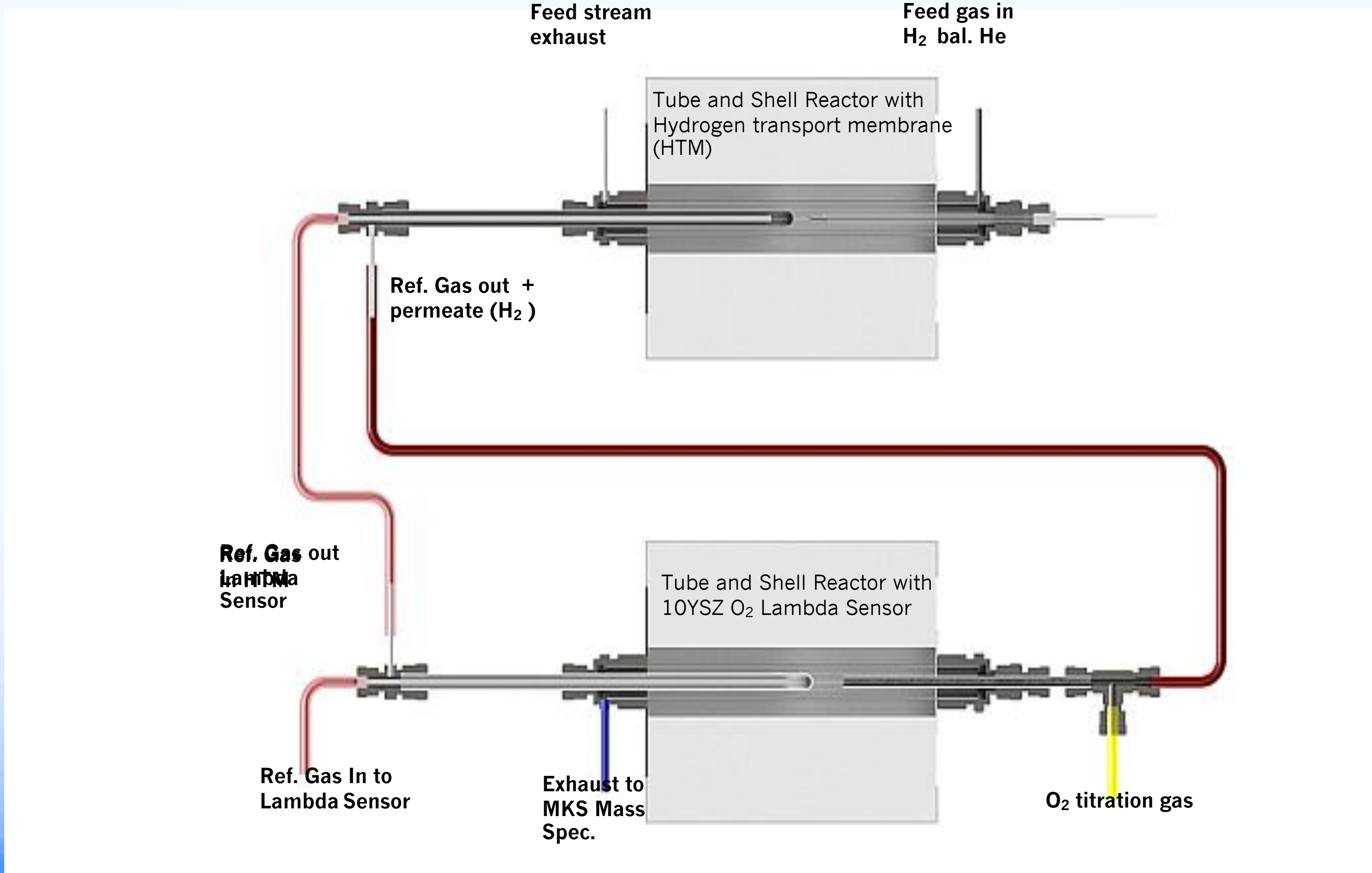
ST Apparatus



Outer Electrode and Current Collector

- Nickel fabric is placed under Nickel wire for good contact at the electrode

- A voltage sense wire is used at each electrode tested for accurate IV measurements.

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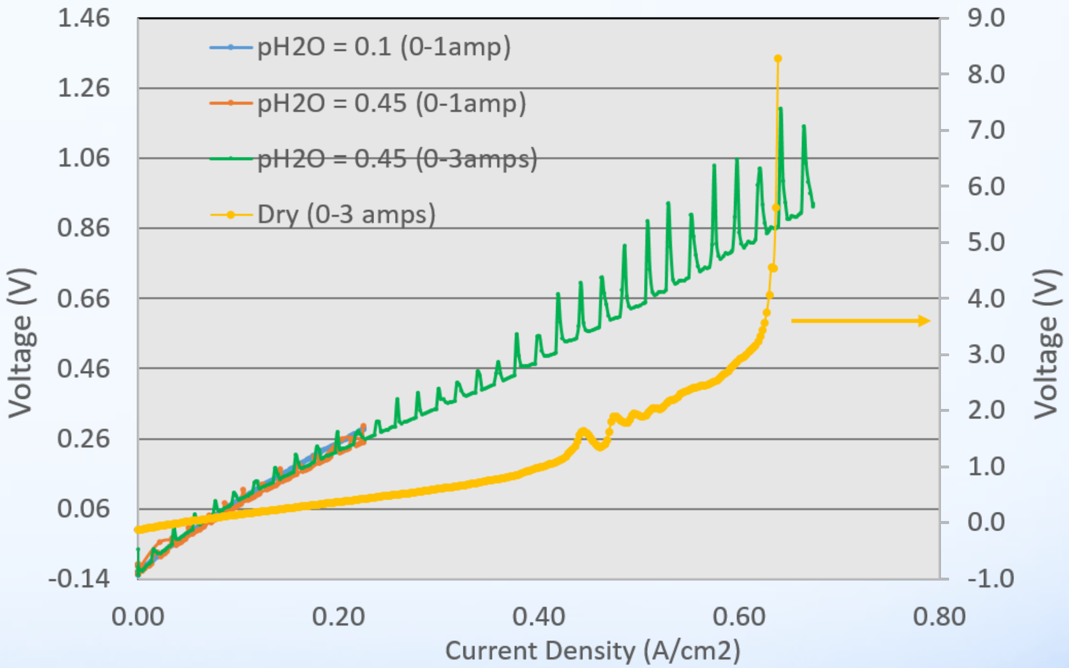
Membrane IV Polarization

- **The linearity of 10% and 45% steam is attributed to high protonic conductivity**
- **Dry conditions gives rise to electronic conductivity at higher current densities.**



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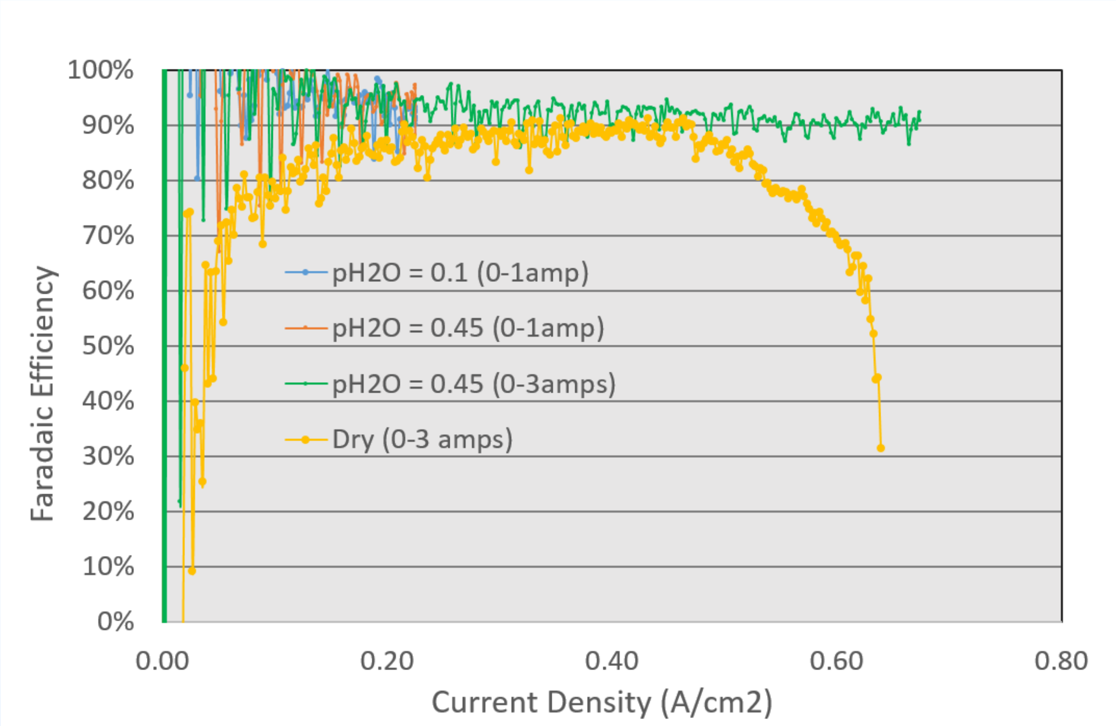
High Faradaic Efficiency

- 90% FE when membrane is hydrated
- Dry condition showed as high as 90% but saw polarization effects at low and high current densities
- Membrane performance was highly repeatability when hydrated



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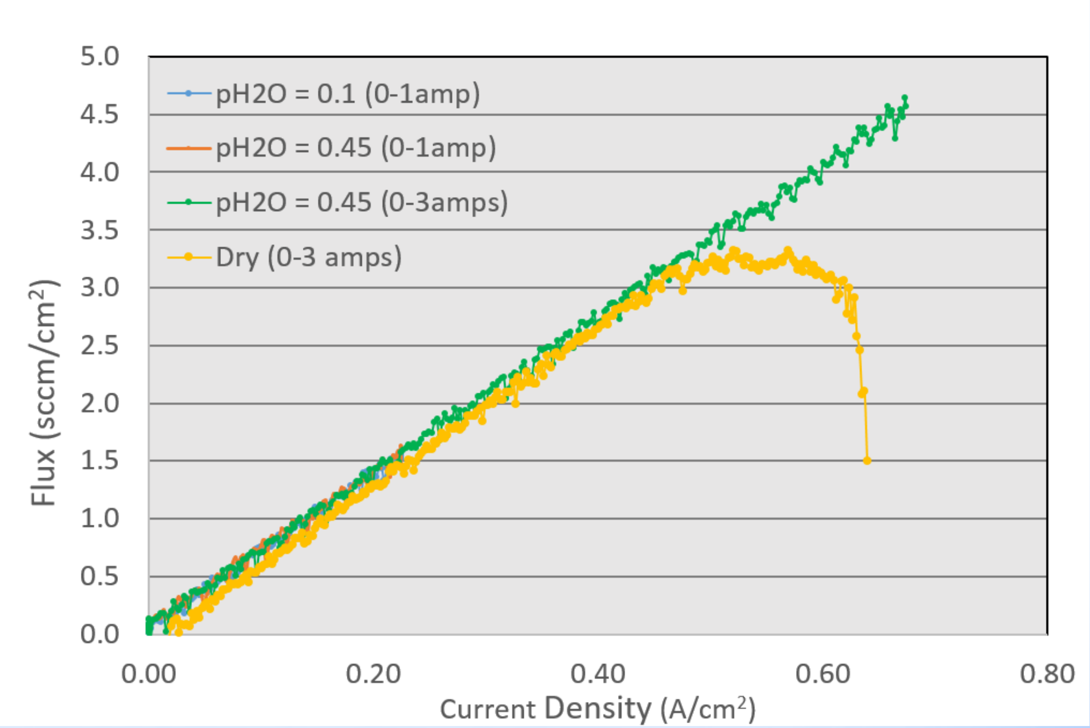
H_2 Flux Measurement

- A maximum flux of 3.3 mL/min/cm² under dry conditions was achieved before a polarization a effect is seen.

- With steam present in the system a very high flux, 4.6 mL/min/cm² can be attained at modest current densities.



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Summary

Distributed H_2 Production?

- **\$5/kg distributed H_2 (filling-station scale) in sight**
- **Protonic membrane reactors (PMR) fuel flexible**
- **Centralized production of H_2 for vehicles not viable**
- **SSAS in PMR is feasible but not practical (even with perfect N_2 catalysts) \$5/kg H2 → \$0.60 NH_3**

Summary

Centralized vs. Distributed NH_3 Production

- **Commodity ammonia cost $0.60 to $1.00/kg**
- **Ammonia is easy to distributed (pipeline and tanker)**
- **Infrastructure and technology is mature**
- **Small-scale NH_3 production feasible, but not commercially viable**

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