Electrolyzer Development for the Cu-Cl Thermochemical Cycle

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Project ID: PD013

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Overview

Time Line

- Project Start: 10/2006
- Project End: 9/2012*

Budget

- Total project funding: $2,175K
- Funding received in FY11: $540K
- Planned Funding for FY12: $375K

Barriers

- U. High Temperature Thermochemical Technology
- V. High Temperature Robust Materials
- X. Coupling Concentrated Solar Energy and Thermochemical Cycles

Partners/Collaborators

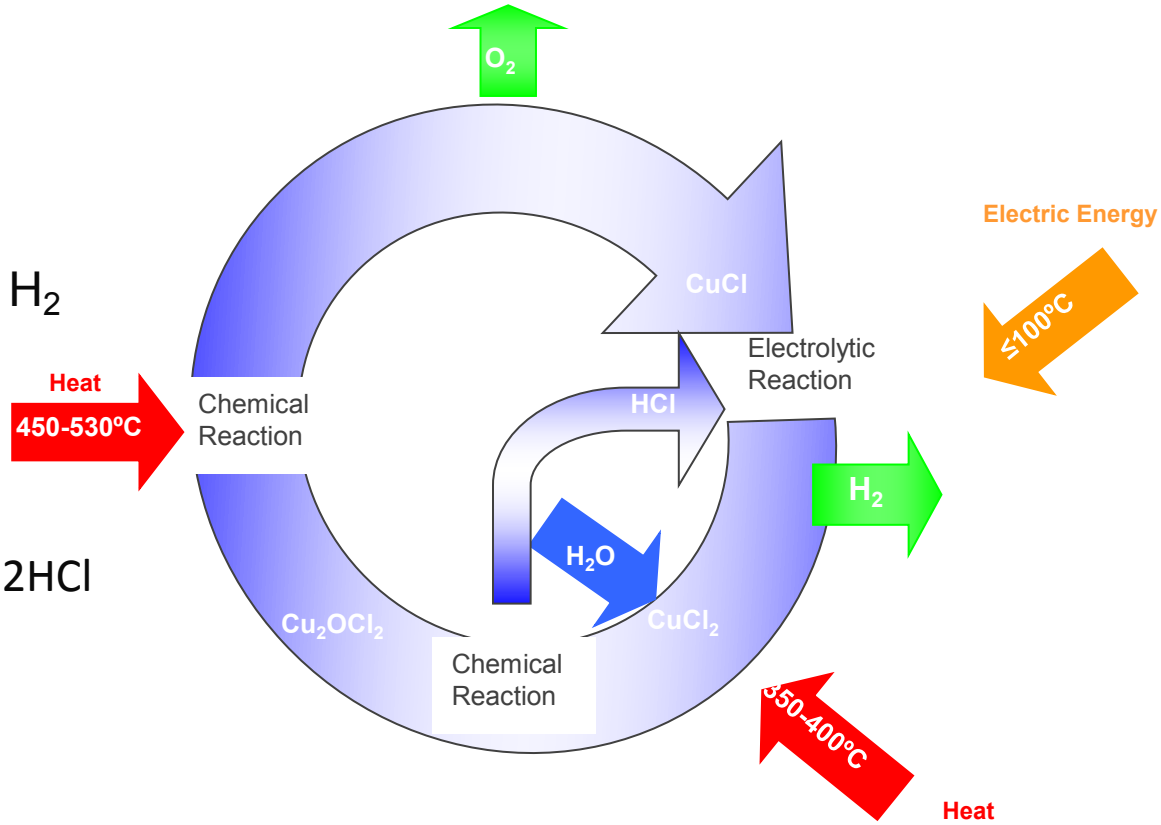
- Information exchange
  - Atomic Energy of Canada Ltd (AECL) and University of Ontario Institute of Technology (UOIT) and 5 other Canadian universities

*Project continuation and direction determined annually by DOE.

Relevance to DOE mission

- Objective: Develop a commercially viable process for producing hydrogen that meets DOE cost and efficiency targets using the Cu-Cl thermochemical cycle

- Three major reactions in cycle
  - ***Electrolysis (simplified)***
    - $2CuCl + 2HCl \Leftrightarrow 2CuCl_2 + H_2$
    - Anode: $2Cu^{+} \Leftrightarrow 2Cu^{2+} + 2e^{-}$
    - Cathode: $2H^{+} + 2e^{-} \Leftrightarrow H_2$
  - ***Hydrolysis***
    - $2CuCl_2 + H_2O \Leftrightarrow Cu_2OCl_2 + 2HCl$
  - ***Oxychloride decomposition***
    - $Cu_2OCl_2 \Leftrightarrow 2CuCl + ½O_2$



Relevance to DOE mission - Cont.

- This project is part of DOE's portfolio of projects for mid- to long-term central production of hydrogen from solar energy
  - Provides hydrogen needed to upgrade oil from the Canadian tar sands thereby contributing to energy security by reducing imports from hostile or unstable countries
  - Develops a production process for a clean infrastructure fuel
  - Verifies an integrated, solar-driven high-temperature thermochemical water-splitting cycle with targeted costs
    - 550 ^{o}C is the maximum temperature for the CuCl cycle, which is compatible with the solar power tower

- Leverages technology through international collaboration, supporting DOE's international agreements (IPHE, IEA)

Approach – Milestones

Month/Year	Milestone	Status
09/2011	Identify membrane that (1) reduces copper crossover to 10 % that of Nafion® 117; (2) is stable at 80 ^{o}C: (3) is durable for at least 24 hours; and (4) has sufficient proton conductivity	Two membranes were found: GTI - Porous polyethylene (PPE): conducts through solution in pores PSU - Nafion®-based: conducts by hopping mechanism
09/2012	Optimize electrolyzer performance to meet the current density target: 0.3 A/cm^2 at 0.7 V (H2A analysis shows optimization of electrolyzer performance is the most promising method to increase efficiency and decrease costs.)	The current density target at 0.7 V was achieved in single cells: Nafion®-based: 0.3-0.5 mA/cm^2 PPE: 0.26-0.30 A/cm^2 Work in progress to increase temperature, reduce Pt and improve durability
09/2012	Fabricate and test a full size (300 cm^2) electrolyzer	In process

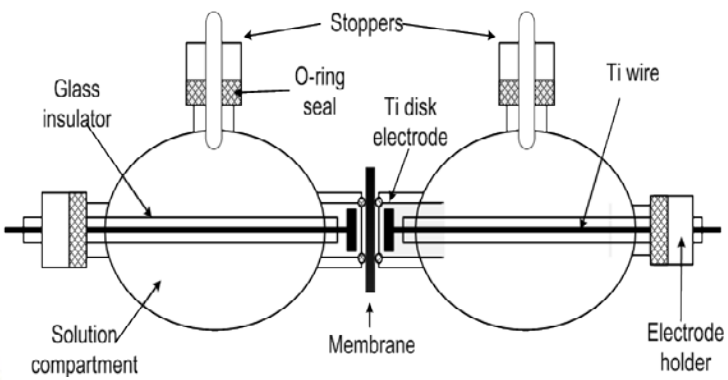
Approach for improving the CuCl electrolyzer

- Further improve membrane properties
  - Investigate coatings and/or other supports to improve the mechanical stability of PPE, a porous polyethylene membrane (1 mm thick), which is commercially available
  - Further develop pressing technique for the Nafion®-based membranes
- Investigate hardware and operating parameters that could lead to improved performance, higher cycle efficiency, lower Pt loadings and/or other catalysts to reduce costs
  - Investigate MEA design modifications
    - Use engineering expertise to modify MEA, e.g., computer painting of catalysts, fabricating different flow field patterns, controlling hydrophilic/hydrophobic properties of gas diffusion electrodes, and integrating stack and system controls
  - Investigate operating parameters such as temperature, flow rate, HCl concentration in anolyte and catholyte, % conversion of Cu(I) to Cu(II)
- Study long term durability of the electrolyzer
  - Use Electrochemical Impedance Spectroscopy (EIS) to determine degradation mechanisms

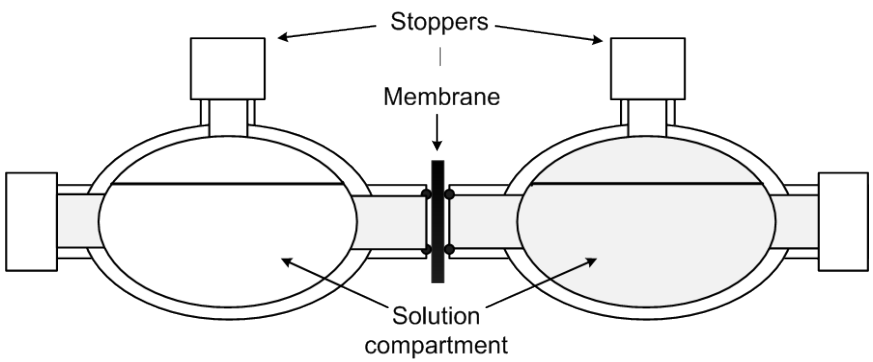
Results: Properties of Nafion® 117, Nafion®-based and PPE membranes

Property / Membrane	Conductivity (S/cm)	Permeability x 10^{-8} (cm^2/s)	Selectivity x 10^6 ($S{\cdot}s/cm^2$)	Today's Cost ($\$/m^2$)
Untreated Nafion® 117	0.083	1.8 (PSU)* 1.6 (ANL)*	4.13	550
Nafion®-based	0.057-0.076	0.15-1.92	2.5 - 39.5	> 550
Porous polyethylene (PPE)	N/A	0.094 (PSU) 0.059 (ANL)	N/A	10 Coating costs not included

Both Nafion-based and PPE membranes are suitable for the electrolysis tests.



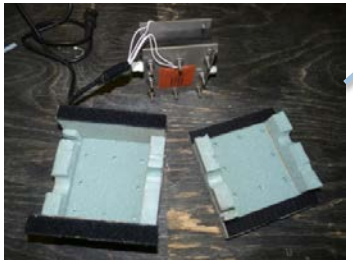
Through-plane conductivity cell



Permeability cell

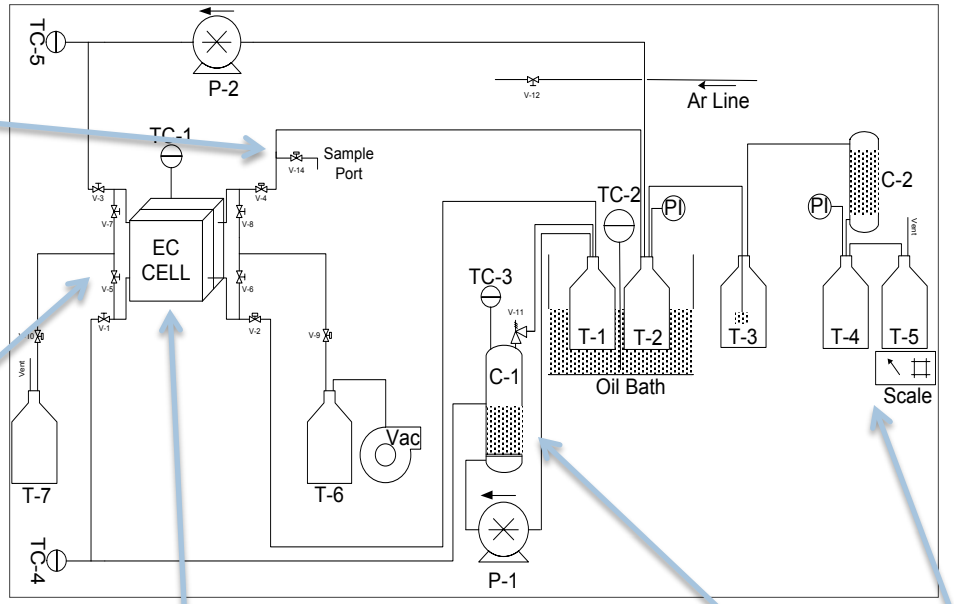
Results: New single-cell CuCl electrolyzer was developed at Penn State

Sampling port

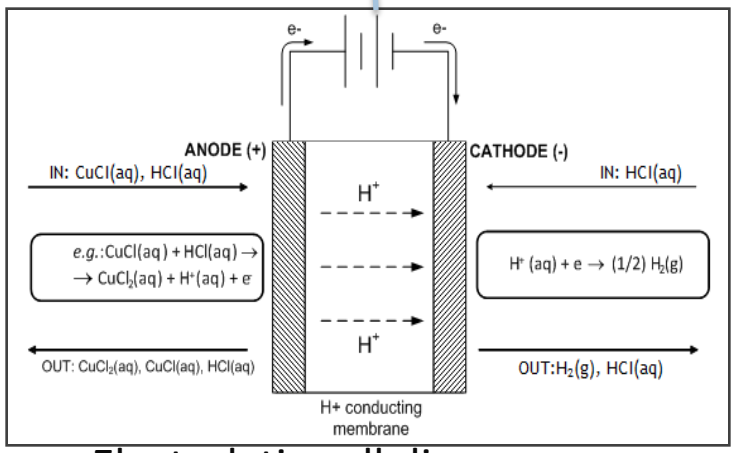


Electrolytic cell

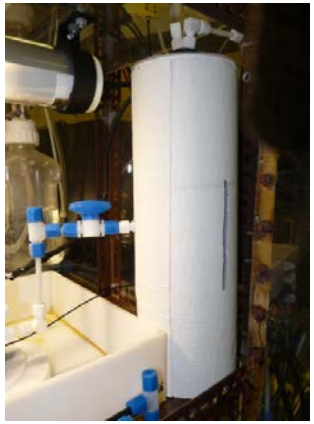
Diagram of CuCl electrolyzer



CuCl electrcolyzer



Electrolytic cell diagram

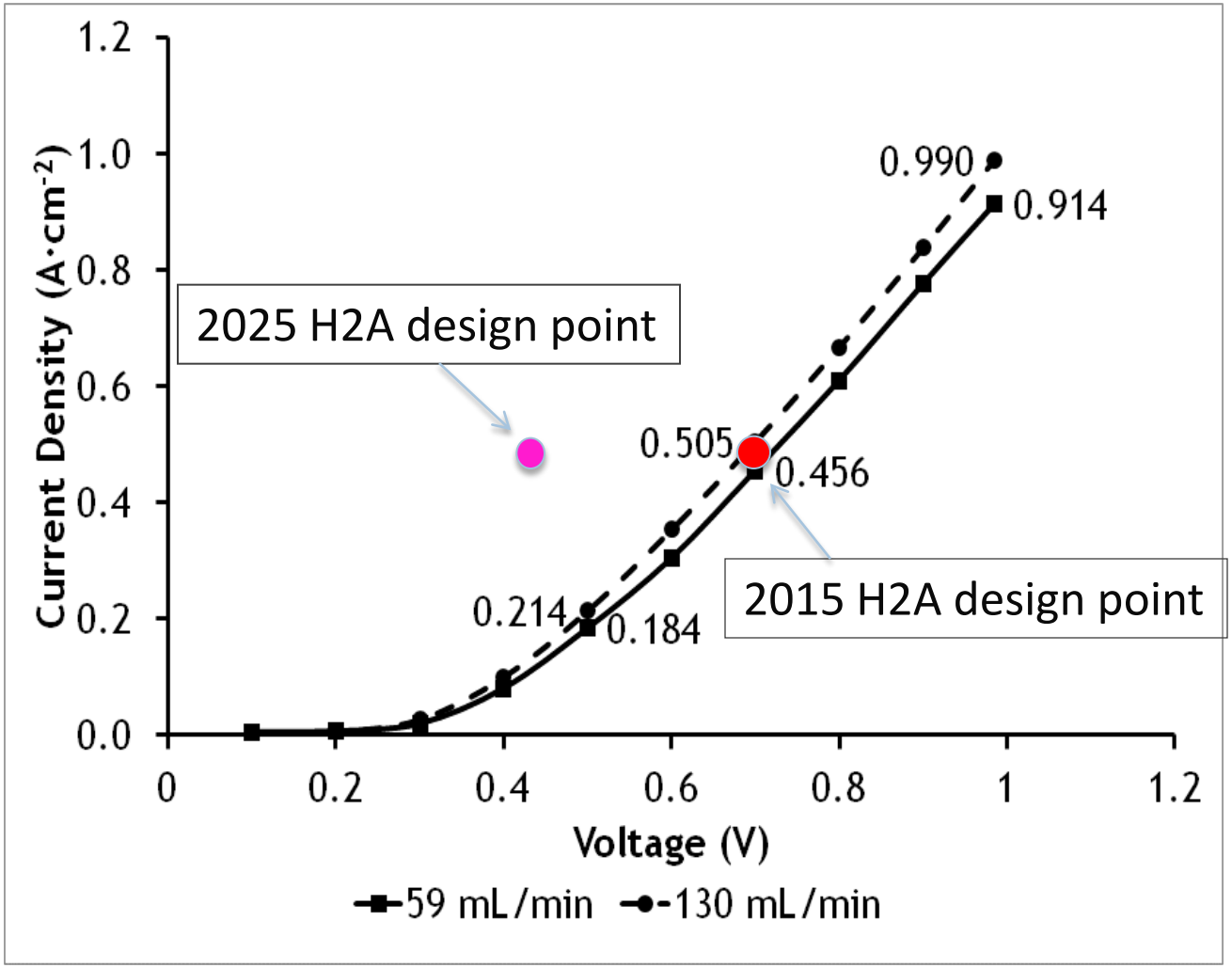


Regeneration column

H_2 measuring system

Results: Polarization curve using Nafion®-based membrane

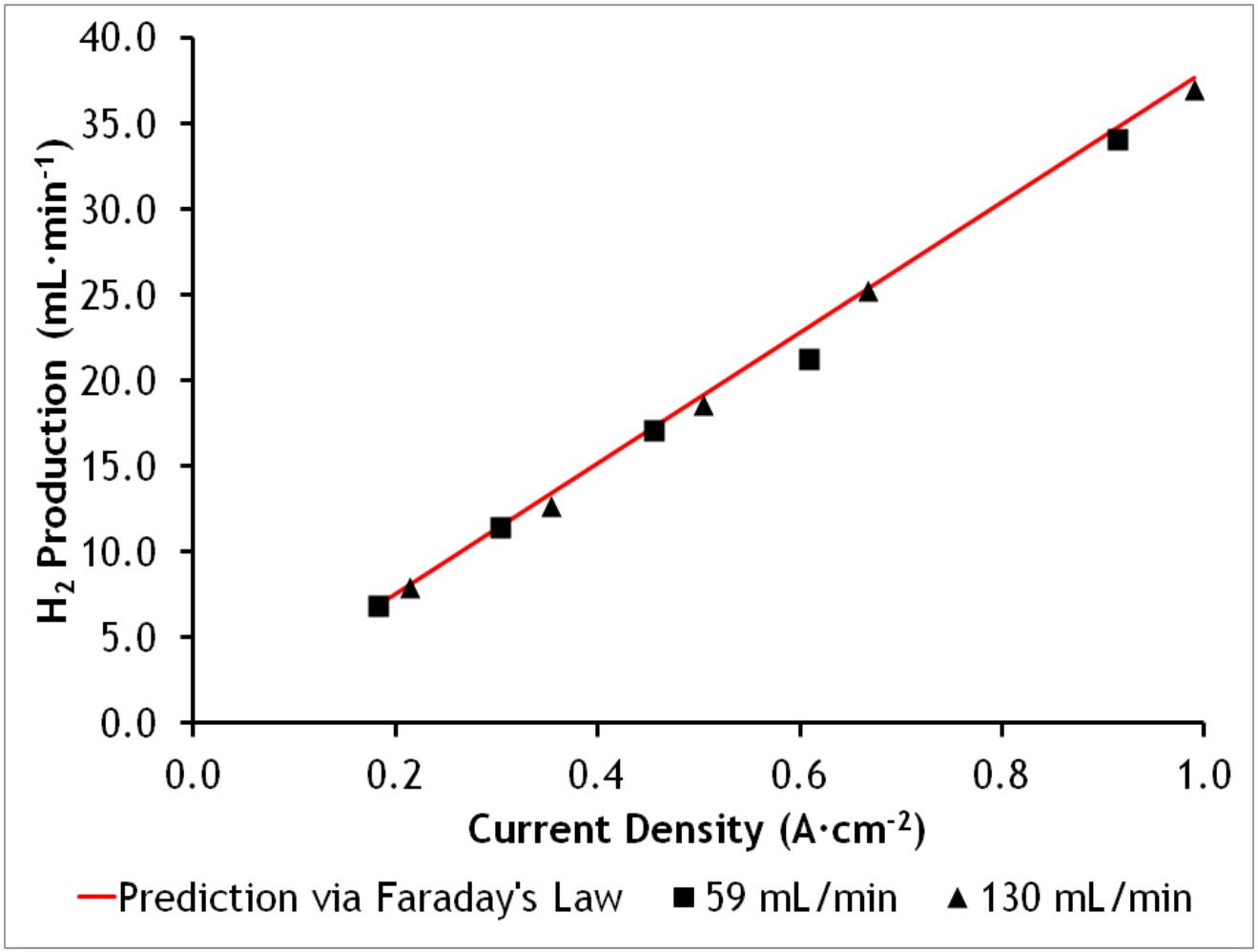
- Performance of the CuCl electrolyzer in this configuration exceeded the 2012 milestone for current density (0.30 A/cm^2).
- Stable current densities at around 0.5 A/cm^2 were obtained over 24 hours.



Conditions: 6 M HCl catholyte, 2 M CuCl + 6 M HCl anolyte, 80 °C, 1 bar, Nafion®-based membrane, Pt (0.8 mg/cm^2) electrodes impregnated into carbon cloth on both sides of the membrane, modified MEA to improve mass transfer, serpentine flow field, single diffusion layer, results are shown after 24 hours of operation.

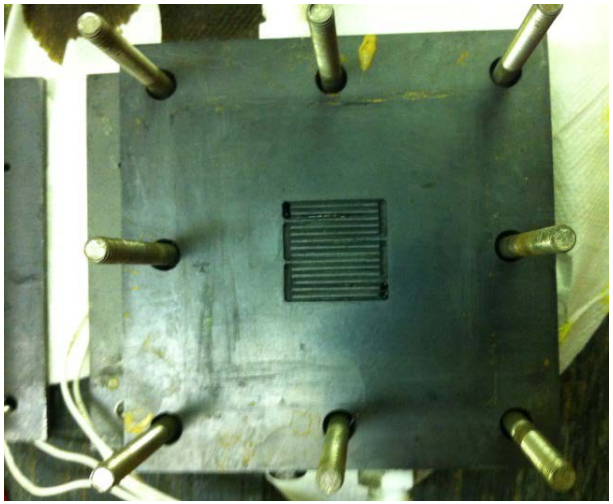
Results: Hydrogen production efficiency using Nafion®-based membrane

- Hydrogen production efficiency was 95-100 % for a period of 24 hours.
- Performance of the CuCl electrolyzer in this configuration exceeds milestone values for current density of 0.30 A/cm^2.

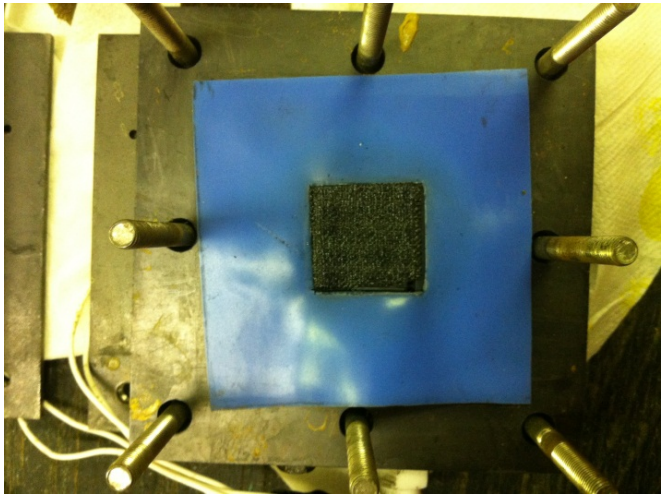


Same conditions as in previous slide

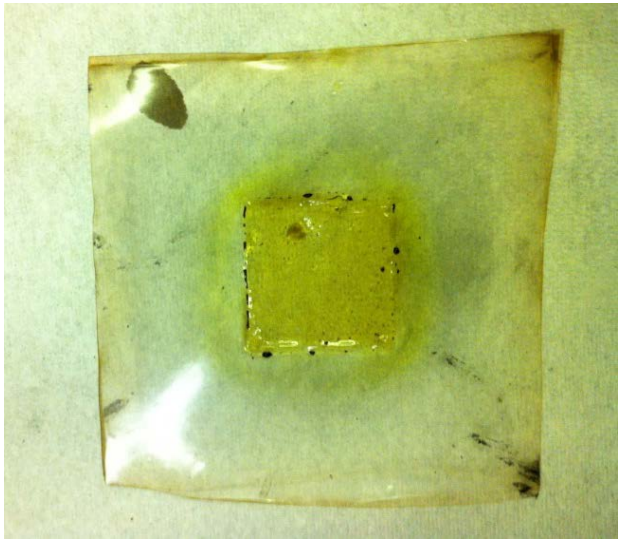
Results: No copper deposition after 24 hours using Nafion®-based membrane



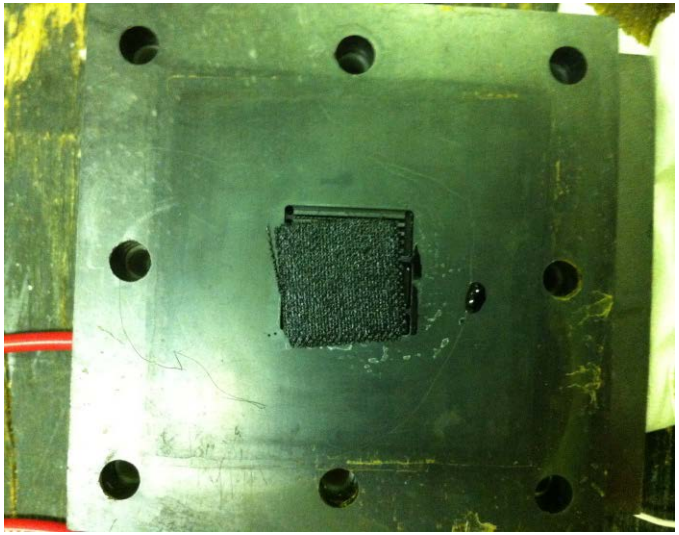
Graphite plates



Gasket and diffusion layer

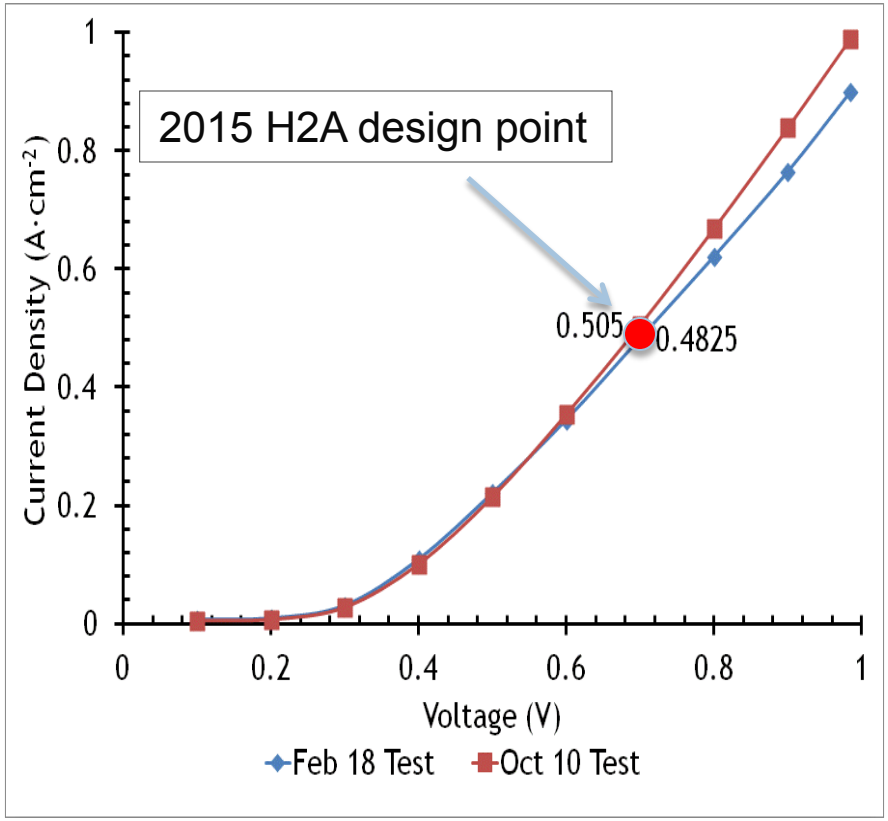


Membrane

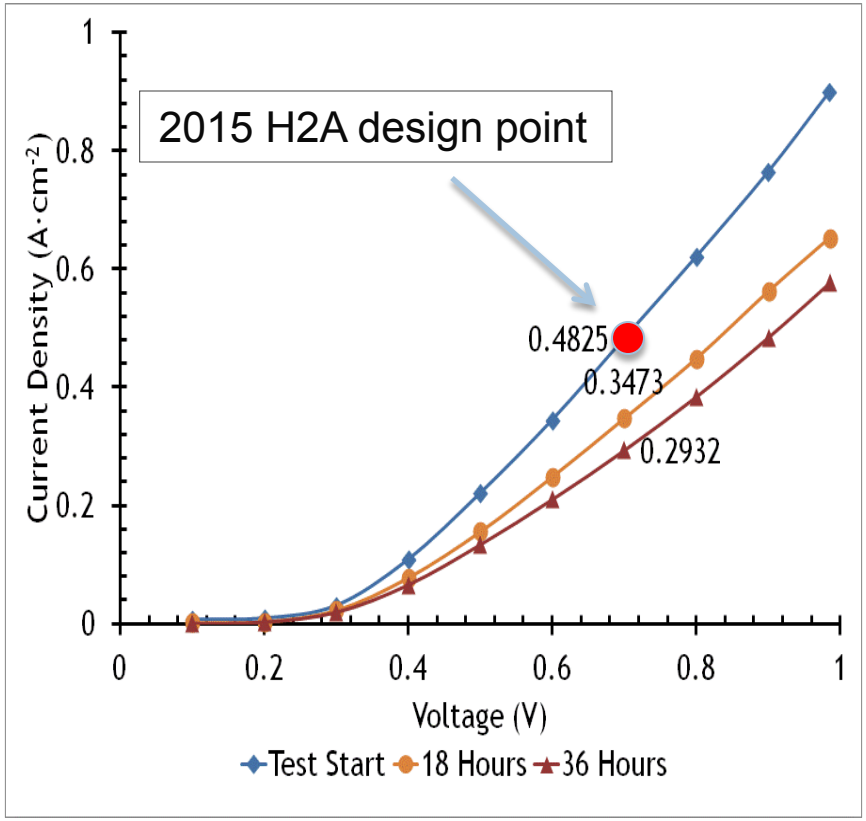


Graphite plate and diffusion layer

Results: Some polarization curves show current density decreases with time



Comparison of polarization curves using 6 M HCl (Oct. 10 Test) and 7 M HCl (February 18 Test) catholyte and anolyte. The results are almost identical.

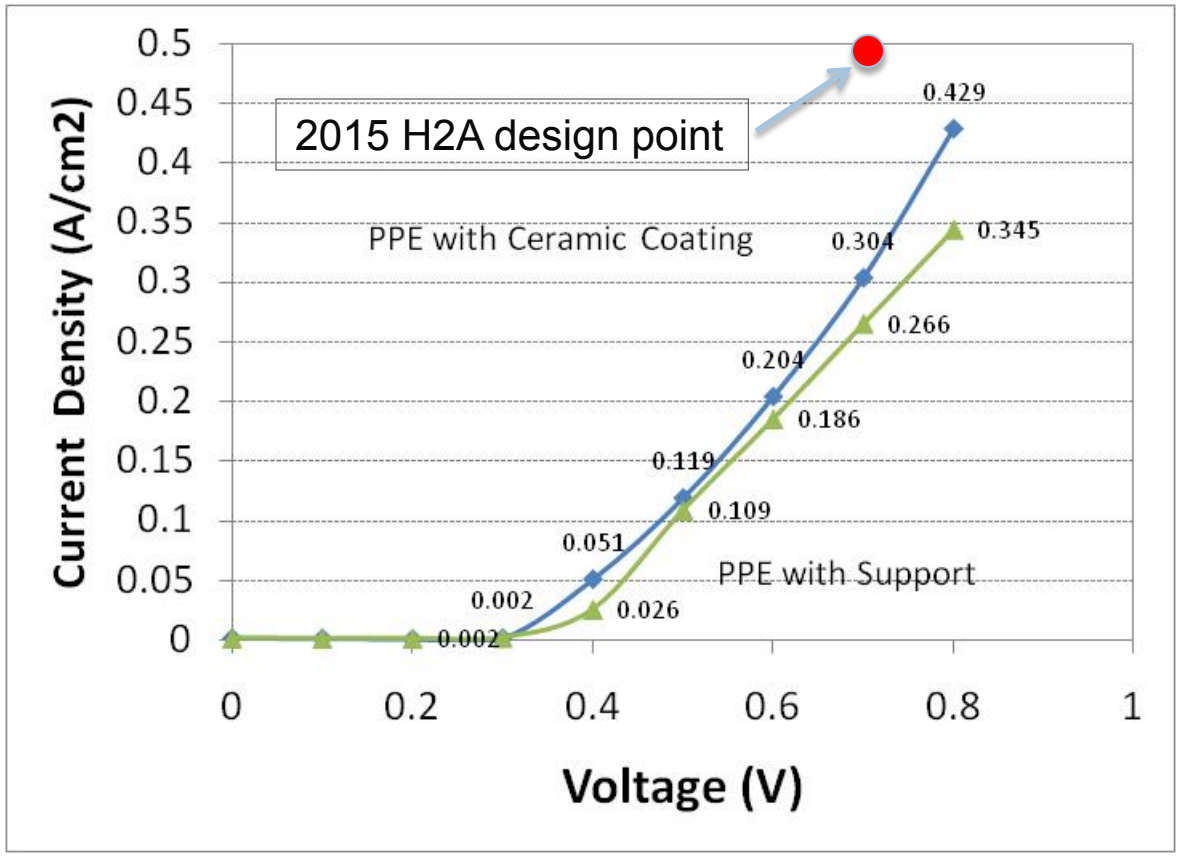


Over the course of 36 hours the current density at 0.7 V significantly decreased from 0.483 A/cm^2 to 0.293 A/cm^2.

Studies of the degradation mechanisms, using Electrochemical Impedance Spectroscopy, are needed.

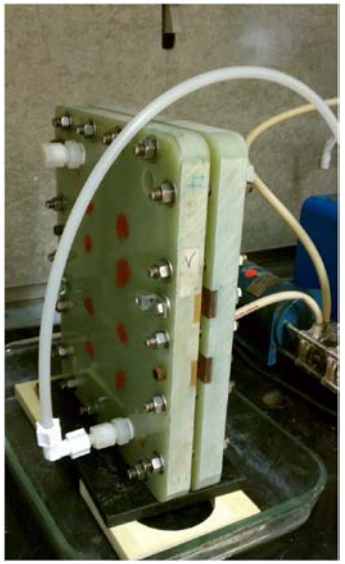
Results: Polarization curve using PPE membrane

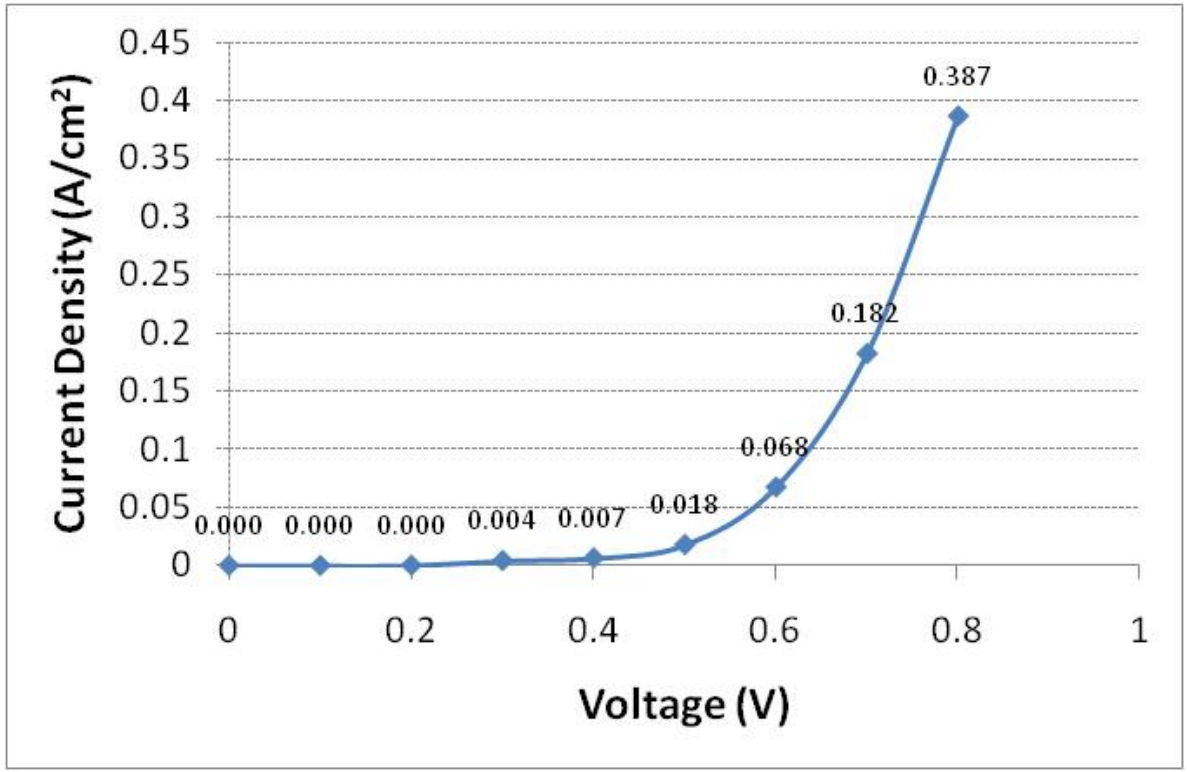
- Conditions used give current density near or at FY 2012 milestone values.
- Hydrogen production efficiency was 95-100 %.
- Current density is affected by membrane surface treatment and support structure
  - Top curve obtained with ceramic powder coating on PPE; bottom one, with a porous membrane support on PPE

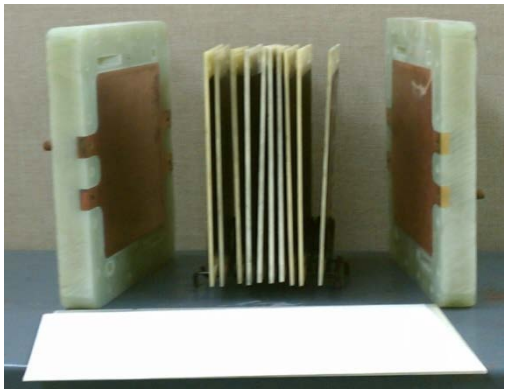


Conditions for both tests: 80 °C, 1 bar, PPE membrane with ceramic support, 2 mg/cm^2 Pt on cathode, no Pt on anode, carbon felt on both anode and cathode, water as catholyte and 1 M CuCl/10 M HCl as anolyte

Results: Initial test and electrolyzer stack design



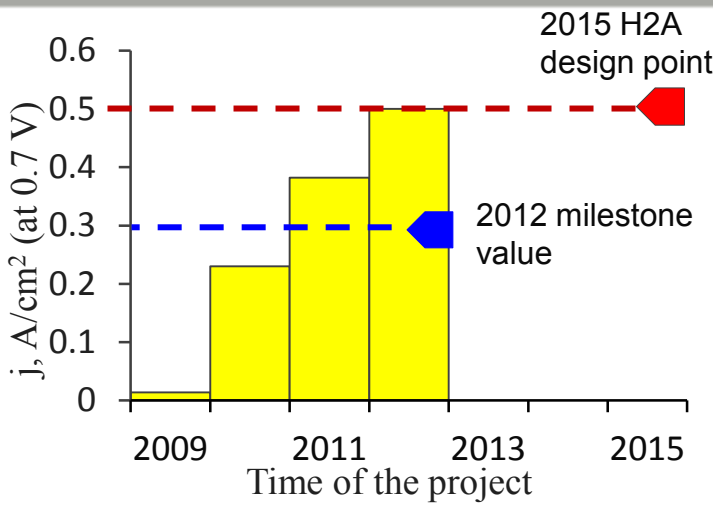




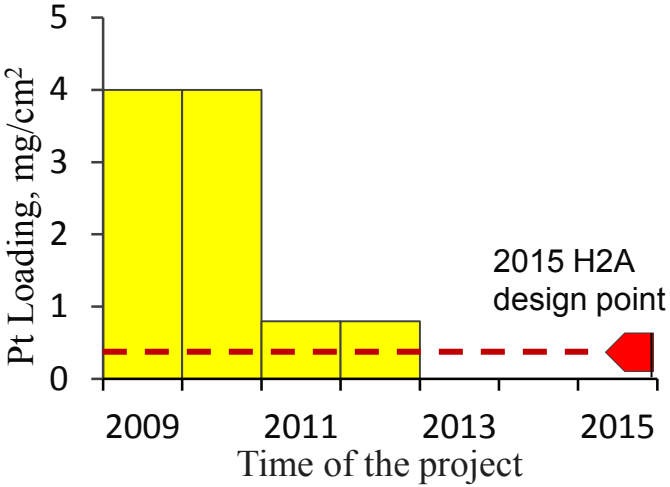
Conditions: 62 °C, 1 bar, PPE membrane with Nafion® coating, 0.5 mg/cm^2 Pt on cathode and anode, carbon felt on both anode and cathode, water as catholyte and 1 M CuCl/10 M HCl as anolyte, 1 L/min flow rate

Summary

- Two different types of membranes show promise for use in the CuCl electrolyzer
  - Porous polyethylene membrane (PPE)
    - Commercially available, inexpensive
    - Maximum current density is about 0.3 A/cm^2 (Pt loading on cathode 2 mg/cm^2)
  - Nafion®-based
    - 2015 design point of 0.5 A/cm^2 at 0.7 V obtained in many tests
    - 2012 milestone value of 0.30 A/cm^2 at 0.7 V has been exceeded
    - Pt loadings on both cathode and anode 0.8 mg/cm^2
    - No copper deposits observed in a 36 hour test with 85-100% hydrogen production efficiency
- Process feasibility demonstrated by eliminating copper deposition issue
- Developments to support cost reduction
  - Reduction in Pt loading
  - Inexpensive PPE membrane continues to show promise
- Investigation of the effect of variables in cell and MEA parameters is ongoing
  - Pt loading, hydrophobicity/hydrophilicity, membrane support (PPE), flow field design
- Full size (300 cm^2) electrolyzer fabricated and first test completed



The highest current densities reliably achieved in single cell electrolyzer under applied potential of 0.7 V in the course of the project.



The minimum Pt catalyst loadings on anode and cathode of the single cell electrolyzer applied in the course of the project

Future work

- For FY 2012
  - Continue development of the electrolyzer by improving performance of membranes, reducing Pt catalyst loading, investigating the effect of different flow field designs, flow rates, electrolyte compositions, increasing temperature
  - Initiate longer term durability tests up to 400 h
  - Study electrolyzer degradation processes using Electrochemical Impedance Spectroscopy
  - Improve our understanding of the CuCl electrolysis process by studying transport through the membrane and electrochemical kinetics at the electrode
  - Explore using other than Pt catalyst to reduce cost
  - Obtain kinetic and mechanistic information on the hydrolysis reaction using Extended X-ray Absorption Fine Structure (EXAFS) at the Advanced Photon Source
- For FY 2013 (tentative)
  - Continue longer term durability tests of a single cell and extend the test time up to 1000 h
  - Use most promising membrane in full size electrolyzer stack and test its operation using Electrochemical Impedance Spectroscopy
  - Update H2A analysis using an Aspen flow sheet with more accurate measurements of critical thermodynamic data and new data derived from the Canadian studies

Collaborations

- Argonne National Laboratory
  - Shabbir Ahmed and Magali Ferrandon
- Penn State University (PSU)
  - Richard Schatz, Soohyum Kim, Mark Fedkin and Serguei Lvov
- Gas Technology Institute (GTI)
  - Chinbay Fan and Renxuan Liu
- Orion Consulting Group
  - Dave Tatterson
- Atomic Energy of Canada Limited (AECL)
  - Sam Suppiah and Lorne Stolberg
- University of Ontario Institute of Technology (UOIT), lead for the Cu-Cl cycle development program, funded by the Ontario Research Foundation and others
  - Greg Naterer (Lead)

Some results from Canadian collaboration

- Atomic Energy of Canada Limited
  - Work has started on a small scale integrated demonstration
  - Electrolyzer performance is being optimized with respect to electrolyte composition, flow rate, Pt catalyst loading, temperature and cell design
  - Electrolyzer is being scaled up to produce 50 L H_2/h from 26 L H_2/h

- University of Ontario Institute of Technology and other Canadian universities funded by the Ontario Research Foundation
  - Work has started on integration of the electrolysis, crystallization and hydrolysis processes
  - Engineering studies for the hydrolysis reactor are near completion and include studies of the particle size, moisture content as well as the development of on-line measurement techniques for chloride ion, chlorine, soluble chloride, etc
  - Engineering studies for direct and indirect processing of molten cuprous chloride and heat recovery methods are ongoing

Technical back-up slides

Definitions of through-plane conductivity, permeability and selectivity

- **Through-plane conductivity *k* (S/cm) is calculated by**

$$k = \frac{\delta}{\Delta R * A}$$

where δ is the membrane thickness (cm), ΔR is the resistance difference between measurements with and without membrane (Ω), A is the membrane cross-section area (cm^2)

- **Permeability *K* (cm^2/s) is calculated by**

$$K = \frac{\delta * V_{sample}}{A * t_{exp}} ln \frac{C_{cu}}{C_{cu} - C_2}$$

where, V_{sample} is the sample volume, t_{exp} is time of the test, C_{cu} is the concentration of Cu^{2+} in solution, C_2 is concentration of Cu^{2+} at $t = t_{exp}$ in a chamber where pure water is at $t = 0$.

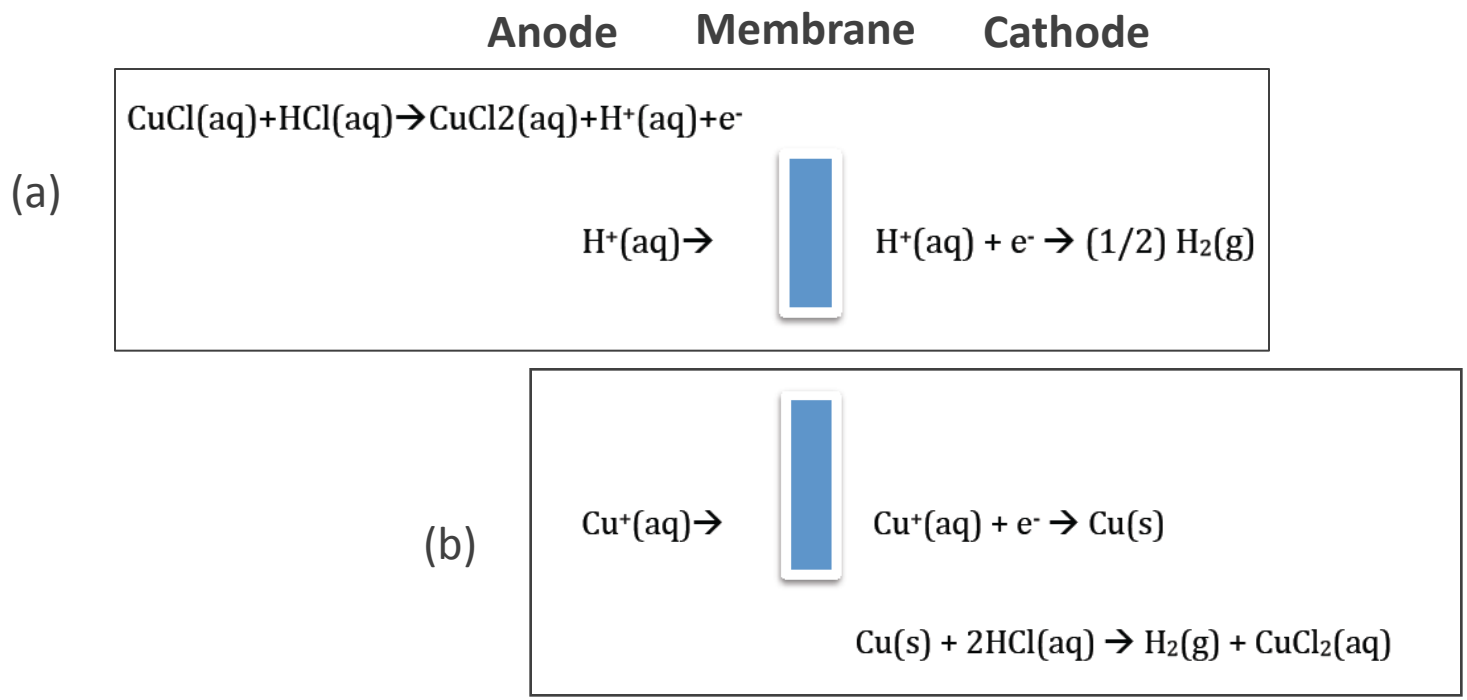
Ref.: Zhou et al. *Electrochimica Acta, 48, (2003), 2173.*

- **Selectivity (S s /cm^3) is calculated by**

$$Selectivity = \frac{Conductivity}{Permeability}$$

Ref.: Zhou et al. *Electrochimica Acta, 48, (2003), 2173.*

Possible mechanism for decreasing current density with time



- In case (a) one e^- is used to produce (1/2) mole of $H_2(g)$ and in case (b) one e^- is used to produce twice more, e.g. 1 mole, of $H_2(g)$. However, the transport of $Cu^+(aq)$ through the membrane should be three-four times slower, and this will significantly increase the membrane resistance and decrease the hydrogen production rate due to the mechanism (b). The increased membrane resistance with time will decrease the current density and will not significantly affect the hydrogen production rate.
- EIS tests and transport number measurements should be carried out to understand the current density decrease origin and mechanism.

Summary of PPE tests to explore electrolyzer performance

Test*	Current Density at 0.7 V	Current Density at 0.7 V
Flow field patterns (0.5 mg Pt/cm^2 cathode and anode, 6.25 cm^2)	0.162 A/cm^2 (Carbon Felt)	0.122 A/cm^2 (Flow Channel)
Support membrane (Carbon felt as flow field and 2 mg Pt/cm^2 on cathode, 6.25 cm^2)	0.304 mA/cm^2 (Ceramic Coating)	0.266 mA/cm^2 (Complex Membrane)
Different Pt loadings (Carbon felt as flow field, PEE with Nafion® coating)	0.191 A/cm^2 (2 mg Pt/cm^2 on cathode 0.5 mg Pt/cm^2 on anode, 6.25 cm^2 cell)	0.182 A/cm^2 (0.5 mg Pt/cm^2 cathode and anode, 300 cm^2 cell)

*In each comparison test, only one feature was changed.

Economics and some details of the process design from H2A revision in 2011

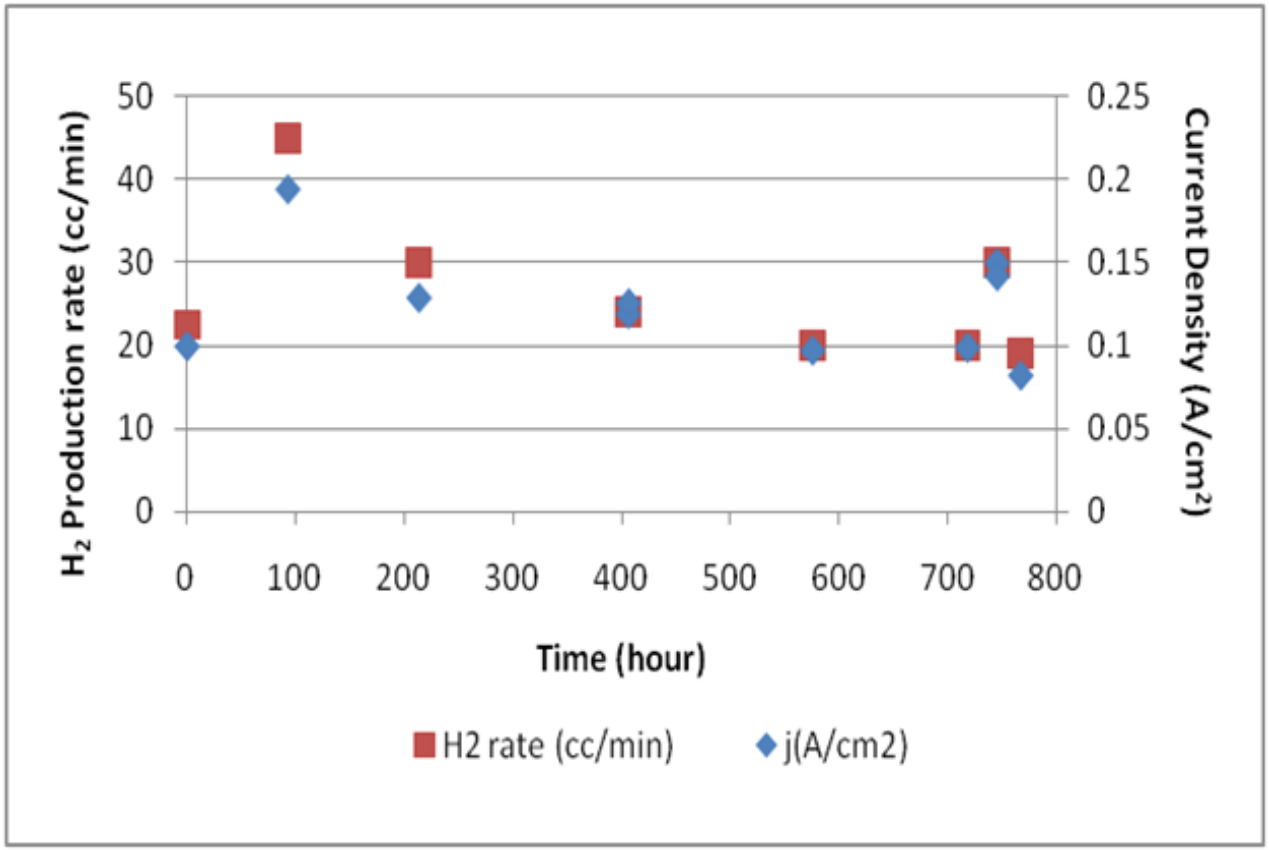
- H2A analysis was completed in August 2011. The current estimate for 2025 case is $4.44/kg H2. This assumes overnight operation with heat storage provided by the molten salt bath of the power tower. It also assumes the overall operating factor is 75%, which is determined by the solar plant, not the chemical plant.
- The solar plant investment is $353MM while the chemical plant investment is $89MM. The electrolyzer cost is about 1/3 of the chemical plant cost.
- Improvement in the electrolyzer provides the biggest bang for the buck. Increasing the kinetics of the electrolysis process (current densities) reduces the size of the electrolyzer and lowering the cell voltage reduces electrical work.
- Efficiency: The overall efficiency of the chemical plant is 34% (LHV).
- H2A electrolyzer design points: for 2015: 0.5 A/cm^2 at 0.7 V and for 2025: 0.5 A/cm^2 at 0.5 V
- Other design points: for 2015: 0.3 mg/cm^2 Pt and $95/$m^2$ for Nafion® and for 2025: 0.2 mg/cm^2 Pd and $58/$m^2$ for Nafion®

800-hour test with PPE membrane in 31 cm^2 electrolyzer

The single cell electrolyzer operated for a period of 800 h at 0.7 V.

The current density was 0.1 – 0.15 A/cm^2 and hydrogen production efficiency was 95 %.

Hydrogen production rate and current density were stable.



Conditions: 85°C, 1 bar, PPE membrane with a porous support, 2 mg/cm^2 Pt on GDL at cathode, carbon cloth on anode without Pt, water as catholyte and 1 M CuCl/10 M HCl as anolyte.