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: 9/2013*

Budget
- $2M 2007-2012
- $375 K for FY13

Technical Barriers
- S. High-Temperature Robust Materials
- T. Coupling Concentrated Solar Energy and Thermochemical Cycles
- W. Materials and Catalysts Development
- X. Chemical Reactor Development and Capital Costs

Partners/Collaborators
- Atomic Energy of Canada Ltd (AECL)
- University of Ontario Institute of Technology (UOIT), lead, for other Canadian universities

*Project continuation and direction determined annually by DOE
Relevance to DOE mission

**DOE mission**: The hydrogen threshold cost ($2-$4/gge dispensed) is a key driver of Hydrogen Production R&D.

- The CuCl cycle is an integrated, solar-driven thermochemical water splitting cycle for producing hydrogen and its R&D is focused on meeting DOE’s cost and efficiency targets.
- The CuCl cycle couples with the solar power tower, which is near commercialization and provides heat near the 550°C required for the highest temperature reaction.
- DOE also supports international agreements such as the IPHE and the IEA and leverage technology through international collaboration.
  - The CuCl cycle is under development in Canada as one possible method to produce the hydrogen needed to upgrade oil from the tar sands using heat from nuclear power plants and waste heat from cement plants.
Approach dictated by results from process design

- Preliminary process design and economics identifies the major cost and energy usage driver as the electrolyzer in the CuCl cycle

- R&D is focused on maximizing performance of the electrolyzer to meet targets in model so that production costs are within range of DOE guidelines
  - **Voltage**: 0.7V (2015) and 0.5V (2025) at current density of 500 mA/cm²
    - Reductions in voltage increase efficiency, increases in current density lower H₂ production costs
  - **Catalyst loading**: 0.3 mg/cm² Pt (2015), 0.2 Pd mg/cm² (2025)
  - **Cu(I) to Cu(II) conversion**: 75% at 118C and 24 bar
  - **Membrane cost**: $98/m² for 2015 and $58/m²

- Other issues impacting electrolyzer performance that are being addressed
  - Cu crossover, membrane and catalyst durability, lifetime
Approach includes both fundamental and pre-engineering studies

<table>
<thead>
<tr>
<th>Where</th>
<th>Size, cm²</th>
<th>Membrane</th>
<th>Test Types and Pt loading on anode and cathode</th>
<th>Temperature, C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSU</td>
<td>5</td>
<td>Hot pressed Nafion® 117</td>
<td>Temperature effects, lifetime tests, membrane durability, EIS and SEM studies to determine degradation mechanisms, Pt loading*</td>
<td>30, 80, 100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*0.8 mg/cm² Pt on both anode and cathode is current loading</td>
<td></td>
</tr>
<tr>
<td>GTI</td>
<td>300*</td>
<td>CG2N and Nafion® 112</td>
<td>Flow rate, holding force, shunt currents, modifications to CG2 One and two-cell stacks, 0.5 mg/cm² Pt on both anode and cathode*</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>*For consistency with the single cell 300 cm² test</td>
<td></td>
</tr>
<tr>
<td>GTI</td>
<td>6.45</td>
<td>Supported CG2N</td>
<td>Elimination of Pt on anode 0.5 mg/cm² Pt on both anode and cathode and only on cathode</td>
<td>80</td>
</tr>
</tbody>
</table>

*The CuCl electrolyzer is significantly different from the conventional water electrolyzer and scale up will be more difficult; Flow rate tests show mass transfer limitations and shunt currents are important because both anolyte and catholyte are conductive.
<table>
<thead>
<tr>
<th>Month/year</th>
<th>Milestone</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>09/2012</td>
<td>Operate a 5 cm² electrolyzer with 95 % current efficiency for 168 h cumulative at 300 mA/cm² at 0.7 V</td>
<td>Completed</td>
</tr>
<tr>
<td>09/2012</td>
<td>Fabricate and test a full size 300 cm² electrolyzer</td>
<td>Completed</td>
</tr>
<tr>
<td>05/2013</td>
<td>Design, build and test an electrolyzer that operates at 100 °C and 1.5 bar to achieve higher current density at 0.7 V</td>
<td>Completed</td>
</tr>
<tr>
<td>08/2013</td>
<td>Run single-cell electrolyzer at 0.7 V and 0.5 A/cm² while using a total of 50 % less platinum than the current 0.8 mg/cm² Pt loading for each electrode</td>
<td>In progress</td>
</tr>
<tr>
<td>08/2013</td>
<td>Operate a 10-cell full-size stack at 0.7 V and 200 mA/cm² for 100 h and 60 °C</td>
<td>In progress</td>
</tr>
</tbody>
</table>
Schematic of a generic electrolyzer

Overall reaction: \( 2\text{CuCl} + 2\text{HCl} \Leftrightarrow 2\text{CuCl}_2 + \text{H}_2 \)
Pennsylvania State University

Serguei Lvov*, Derek Hall, Richard Schatz, Sanchit Khurana

*Contact person
Accomplishment: Current density at or above milestone target in 168 h, 5 cm² electrolyzer test

- Current passed through the cell producing H₂ for 168 hours with a minimum current density of 0.3 A/cm² at 0.7 V; hydrogen production efficiency was 95-100% for the 168 hours of operation.

- Solutions were in contact with the membrane for more than 400 hours.

- Electrochemical impedance spectroscopy (EIS) was used to characterize electrolyzer processes and degradation mechanisms.

- EIS measurements indicate the decrease in current density is due to increased internal ohmic resistance, which suggests membrane degradation.

Membrane: Single Pressed Nafion® 117, Electrode area 5 cm², Catalyst on each electrode 20% Pt on XC-72R 4 mg·cm⁻², Catalyst loading 0.8 mg·cm⁻² Pt.

Accomplishment: Electrochemical impedance spectroscopy (EIS) determines dominant resistances in 5 cm² cells

- EIS data taken from the 168-hour test showed that as the applied potential was increased, ohmic resistance was the largest source of impedance.
- Better understanding of the dominant resistances at operating conditions allow us to focus on those areas which offer the most potential for improving performance.
- Scanning electron microscopy of the electrode surface will also be used to identify possible degradation mechanisms.

Temperature 80 °C, Pressure 1 bar, AC potential range 10 mV rms, DC potential 0.22 (OCP), 0.4 and 0.6 V
Frequency range 30,000 to 0.1 Hz
Accomplishment: Current density dependence on T measured

- For every 20°C increase in the operating temperature of the 5cm² electrolyzer, the current density increased from 15 to 25% at an applied potential of 0.7 V.
- These results indicate that further increases in operating temperature will result in either higher current densities at 0.7V or a decrease in applied potential for the same current density.

Membrane: Single Pressed Nafion® 117, Catalyst on each electrode: 20% Pt on XC-72R 4 mg·cm⁻², Catalyst loading: 0.8 mg·cm⁻², Pressure: 1-1.3 bar, Anolyte: 2 M CuCl in 7 M HCl, Catholyte: 7 MHCl, Flow rate: 230 mL/min.
Accomplishments: EIS measurements quantify how ohmic resistance decreases with temperature

- The ohmic resistance, the value of the real impedance at high frequencies when the imaginary impedance is zero, decreases with increasing temperature.
- The decrease in ohmic resistance explained a significant portion of the improved performance when temperature was increased.
- The ohmic resistance is mainly due to the membrane resistivity.

**Temperature 30-100 °C, Pressure 1-1.3 bar, AC potential range 10 mV rms, DC potential 0.24, 0.4 and 0.6 V, Frequency range 30,000 to 0.1 Hz**
Gas Technology Institute

Chinbay Fan* and Renxuan Liu

*Contact person
Milestone-2012: Single cell 300 cm$^2$ electrolyzer tested
Milestone-2013: Fabricate and test 10-cell stack

Issues:
1. Sealing of the cells within the stack
2. Evenly distributing the anolyte/catholyte through all the cells in the stack so that each cell has the same mass flow
3. Improving electric contact within each cell
4. Minimizing shunt current within the stack
Accomplishment: 300 cm$^2$ cell fabricated and tested at 60$^\circ$C—operated above H2A design target for 2015 (500 mA/cm$^2$ at 0.7V)

Membrane  Nafion® 112, Catalyst 0.5 mg/cm$^2$ Pt on cathode and anode, Flow channel design serpentine channels, anode Pt faces membrane, Anolyte 1M CuCl/7M HCl, Catholyte 7M HCl, Temperature 60$^\circ$C, Pressure 1 bar, Flow rate 120 mL/min, IR: 160.8 mΩ·cm$^2$
Next step: Fabrication of 2-cell 300 cm$^2$ stack

Current collector
Graphite plate
Electrode

$\text{Cu}^+ - e^- \rightarrow \text{Cu}^{2+}$

$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$
Accomplishment: Performance of 2-cell 300 cm$^2$ stack with Nafion®112 exceeds 300mA/cm$^2$ milestone target at 0.7V

- Full size 2-cell stack performance at 0.7V operated at milestone target
- Conversion of Cu(I)$\rightarrow$Cu(II) is 65% at 0.7V, close to mass transfer limit
  - A larger flow rate would boost current density for the two cell stack
  - A larger capacity pump has been ordered and is being installed

Membrane  Nafion® 112, Catalyst 0.5 mg/cm$^2$ Pt on cathode and anode, Flow channel design serpentine channels, anode Pt faces membrane, Anolyte 1M CuCl/7M HCl, Catholyte 7M HCl, Temperature 60°C, Pressure 1 bar, Flow rate 210 mL/min
Accomplishment: Performance of 2-cell, 300cm² stack with CG2N membrane is stable

- CG2 costs significantly less than Nafion® and is preferred for that reason
  - Current density with the CG2 membrane is stable for the five tests but conversion is 36%
    - Possible reasons are that CG2 is more sensitive to flow rate and is slightly more hydrophobic than Nafion®

Membrane modified CG2, Catalyst 0.5 mg/cm² Pt on cathode and anode, Flow channel design serpentine channels, anode Pt faces membrane, Anolyte 1M CuCl/7MHCl, Catholyte 7M HCl, Temperature 60°C, Pressure 1 bar, Flow rate 210 mL/min
Accomplishment: Preliminary tests with 1 in² cell show it may be possible to eliminate Pt at the anode

<table>
<thead>
<tr>
<th>Pt Catalyst</th>
<th>Membrane</th>
<th>Current density at 0.7V(mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Cathode</td>
<td>Nafion®112</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

- The elimination of catalyst on anode side does not significantly affect performance in these tests
- Small differences in current density are attributable to possible differences in MEA preparation
Summary and conclusions

- 5cm² electrolyzer run successfully for 168 h at milestone value of 300 mA/cm² at 0.7V
  - Degradation in current density was observed as the initial value of 500 mA/cm² gradually decreased to ~300 mA/cm²; EIS studies suggest membrane degradation
- Current densities increased with increasing operating temperature

- One cell 300 cm² electrolyzer with CG2 ran at >500 mA/cm² at 0.7V

- Two-cell stack 300 cm² electrolyzer was tested with both Nafion® and CG2
  - Nafion®: Operated at >300 mA/cm² at 0.7V and 65% conversion of Cu(I) to Cu(II)
  - CG2: Operated at 200 mA/cm² at 0.7V, achieved only 36% conversion
    - CG2 is sensitive to flow rate and a larger capacity pump is needed (now being installed)
    - CG2 is slightly hydrophobic while Nafion is hydrophilic

- Preliminary tests indicate it may be possible to eliminate Pt catalyst from anode
  - Atomic Energy of Canada Limited reports that their electrolyzer operates consistently without Pt at the anode
Planned work for 2013

- **PSU**
  - Implement new catalyst application procedure to reduce Pt loading
  - Identify potential replacements for the Pt catalyst
  - Use EIS and other techniques to determine reasons for current density decline in lifetime tests

- **PSU and GTI**
  - Continue with tests to determine effects of eliminating Pt from the anode
  - Research new electrolyzer flow field designs to reduce mass transfer and interfacial resistances to improve performance
  - Investigate methods and procedures to improve performance and lifetime

- **GTI**
  - Improve CG2’s mechanical stability
  - Increase number of cells in the 300 cm² electrolyzer and study effect of flow rate to improve conversion of Cu(I) to Cu(II)
  - Investigate the possibility of catalyst degradation
Future work

- Operate electrolyzer at 120°C and 20 bar to increase current density at 0.7V (PSU)
- Test newly developed membranes characterized by high conductivity, low Cu permeability, high mechanical/thermal stability, and low cost (PSU)
- Continue studies to reduce Pt usage (PSU and GTI)
- Optimize flow field designs to improve mass transfer (PSU and GTI)
- Continue lifetime tests, identify mechanisms for performance degradation and develop methods to reduce the effects of these mechanisms (PSU and GTI)
- Continue modification studies of CG2 (GTI)
- Measure the solubility of CuCl₂, CuCl and their mixtures in highly concentrated (up to 10 mol/L) HCl solutions over a wide range of temperatures up to 100°C and develop thermodynamic model (PSU)
  - Needed to understand how the spent anolyte will be handled prior to introduction into the subsequent hydrolysis reactor
- Continue development work on the hydrolysis reactor (as funds permit)
Collaborations

- Argonne National Laboratory
  - Shabbir Ahmed and Magali Ferrandon
- Penn State University (PSU)
  - Richard Schatz, Soohyum Kim, Mark Fedkin
- Orion Consulting Group
  - Dave Tatterson
- Consortium of researchers at Atomic Energy of Canada Limited (Sam Suppiah, Lead) and six Canadian universities with University of Ontario Institute of Technology (UOIT) as lead
Activities at AECL and the Canadian universities

- Completed 1000 h lifetime test for the electrolyzer
- Overall objective of the work in the universities is to develop an integrated system
- Identification and testing of corrosion-resistant materials for use as reactors
- Development of new membrane and electrode materials
- Identification of other sources of waste heat that could be used as process heat by co-locating the thermochemical cycle plant near other heat-producing chemical process plants
- Other R&D activities
  - Solubility of CuCl and CuCl₂ in HCl solution
  - Molten salt reactor design
  - Simulations of conceptual integration in hydrolysis and electrolysis steps using Aspen software
  - Crystallization- scale up binary system CuCl₂ and water, ternary system experiments CuCl₂, HCl and water
Technical back up slides
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

- 3 major reactions in cycle
  - **Electrolysis (simplified)**
    - $2\text{CuCl} + 2\text{HCl} \rightleftharpoons 2\text{CuCl}_2 + \text{H}_2$
    - Anode: $2\text{Cu}^+ \rightleftharpoons 2\text{Cu}^{2+} + 2\text{e}^-$
    - Cathode: $2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{H}_2$

  - **Hydrolysis**
    - $2\text{CuCl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2\text{OCl}_2 + 2\text{HCl}$

  - **Oxychloride decomposition**
    - $\text{Cu}_2\text{OCl}_2 \rightleftharpoons 2\text{CuCl} + \frac{1}{2}\text{O}_2$
Results: Penn State’s single-cell CuCl electrolyzer

Diagram of CuCl electrolyzer

Electrolytic cell diagram

CuCl electrolyzer

H₂ measuring system

Regeneration column
SEM/EDS evidence for the elimination of Cu deposits

- Previous thermodynamic calculations have shown the formation of copper at the cathode should be thermodynamically unfavorable at high concentrations of HCl(aq).

- These calculations took into account the important complex speciation for CuCl(aq) and CuCl$_2$(aq) in an aqueous phase and non-ideality of the solution components in the highly concentrated HCl (aq) solutions which depends on both the total concentration and temperature.

- The results of SEM and EDS analyses of the electrolyzer cathode surface showed no signs of copper deposition as well.
## Results from TIA*X study

<table>
<thead>
<tr>
<th>Case</th>
<th>Capital Investment, $MM, Solar/Chemical</th>
<th>Cell EMF, V</th>
<th>Electrical Cost, $/kw</th>
<th>$/kg of H2</th>
<th>Sensitivity Range, $/kg</th>
<th>Efficiency, % (LHV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 Solar Fields 2015</td>
<td>421/106</td>
<td>0.7</td>
<td>0.068</td>
<td>6.02</td>
<td>4.80-7.11</td>
<td>30</td>
</tr>
<tr>
<td>2 Solar Fields 2025</td>
<td>353/89</td>
<td>0.50</td>
<td>0.048</td>
<td>4.43</td>
<td>3.53-5.37</td>
<td>34</td>
</tr>
<tr>
<td>1 Solar Field 2025</td>
<td>290/89</td>
<td>0.50</td>
<td>0.048</td>
<td>4.00</td>
<td>3.25-4.81</td>
<td>34</td>
</tr>
</tbody>
</table>

Efficiency = Kg of H2 Produced * LHV

(External Heat + Electrochemical work + Shaft work)

*www.hydrogen.energy.gov/pdfs/progress07/ii_f_1_perret.pdf · PDF file
Results of electrolyzer lifetime tests at AECL

- AECL latest electrolyzer test results show stable performance for about 1000 hours
  - Operating conditions are significantly different compared to those used in the US
  - AECL’s results of temperature studies similar to those in the US