High-Temperature Electrolysis

Richard Doctor, Diana Matonis, Robert Lyczkowski
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9-10 November 2004

Argonne National Laboratory

A U.S. Department of Energy
Office of Science Laboratory
Operated by The University of Chicago
Evaluation of Cycles for Hydrogen Production

Heat 1050K

Thermochemical Cycles
- S-I
- UT-3
- Cu-Cl

Electrolysis

Hybrid Systems
- S-I
- Ca-Br
- Cu-Cl

High T Steam Electrolysis
High-Temperature Electrolysis for Hydrogen Production - Materials

- Drivers for High-temperature electrolysis:
  - Oxygen is the charge carrier, rather than hydrogen – this requires high temperatures, but no use of strategic metals
  - Low-footprint for this system, it is adaptable to many scales
  - Highest efficiency for electrolysis
Higher temperatures for steam electrolysis are one contributor to reduced power demands.
High-Temperature Electrolysis for Hydrogen Production - Materials

- (1) coordinate with the experimental work at INEEL that will demonstrate the improvements in performance for a high-temperature steam electrolysis system operating at up to 1,000 K and assure that the data required to conduct a detailed process design study are linked into an ASPEN-based process design
- (2) consider the issues affecting the long-term performance of electrolyzer cells in this service
- (3) consider the requirements for producing and handling reagent-grade water that will be employed for these cells, starting from a base of available non-potable water at the production facility site
High-Temperature Electrolysis for Hydrogen Production - Materials

- (4) examine the technological features as they link to process economics, surveying what would be needed to achieve commercial viability using these technologies, particularly the appropriate scale of operations
- (5) perform life-cycle emissions evaluations to quantify the reductions that can be achieved by using these technologies.
OBJECTIVES – High Temperature Electrolysis

• Optimize Hydrogen Production
  - Choice of process
  - Optimize materials and operating conditions

• Optimize Overall Plant System
  - Integrate selected process into balance of plant
  - Heat Recuperation from product streams
    - Perform a energy/pinch analysis
  - Perform an overall efficiency analysis of plant.

• Cooperative program with INEEL
Linkage of steam-electrolysis to a solar energy system will improve scalability and economics

Hirsch and Steinfeld, Paul Scheer Institute in

*Hydrogen Energy* 29, 2004 47-59

Demonstrates very encouraging progress that could be directly applied to steam electrolysis
Multiple paths for linking steam electrolysis to renewable energy are being pursued

Hirsch and Steinfeld, Paul Scheer Institute
Hydrogen Energy 29, 2004 47-59
Computational Fluid Dynamics

Electrochemistry Model

Thermodynamics
- Standard Reduction Overpotential
  
  \[ E = E_0 + \frac{RT}{2F} \ln \frac{P_{\text{H}_2} P_{\text{O}_2}^{1/2}}{P_{\text{H}_2\text{O}}} \]

Kinetics
- Activation Overpotential
- Butler-Volmer

Mass Transport
- Concentration Overpotential

Energy
- Heat Effects
- Ohmic Losses
- Limiting Current Density
  - Diffusion (Ficks, S-M, DGM)

System Integration

Balance of Plant

Material Selection
- Geometry

Characterization
- Current Distribution

Electrode Design
SOFC/SOEC Modeling Overpotential

\[
E = E_o + \frac{RT}{2F} \ln \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} + \eta_C + \eta_a + \eta_r
\]

Reversible Cell Voltage

Overpotential:

Fuel Cell Mode

Electrolysis

- Fuel Cell Mode

- Electrolysis

- Activation Polarisation Dominated

- Ohmic Resistance Dominated

- Mass Transfer Dominated

Conditions:

- \( T = 800 \text{ C}; T_{dp, i} = 27.4 \text{ C} \)
- \( Q_{A_t} = 140 \text{ sccm} \)
- \( Q_{H_2} = 40 \text{ sccm} \)
Button and Stack SOFC/SOEC Experiment

Porous Cathode, Nickel-Zirconia cermet

\[ 2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow 2 \text{H}_2 + 2 \text{O}_2 \]

Gastight Electrolyte, Yttria-Stabilized Zirconia

\[ 2 \text{O}_2 \rightarrow \text{O}_2 + 4 \text{e}^- \]

Porous Anode, Strontium-doped Lanthanum Manganite

\[ \text{H}_2\text{O} + \text{H}_2 \rightarrow \]

Next Nickel-Zirconia Cermet Cathode

\[ \text{H}_2\text{O} \downarrow \]

Interconnection

\[ \leftarrow \text{O}_2 \]

\[ \text{H}_2 \uparrow \]

\[ \text{H}_2 \uparrow \]

\[ \downarrow \text{H}_2\text{O} \]

Available Commercial CFD Codes

• Code Selection
  ✓ Femlab
  ✓ Star-CD
  ✓ Fluent

  ➢ Calculations based on current
  ➢ Current density establishes rate of oxygen transport through electrolyte

• STARCD
  • 350 Node Linux Parallel Cluster at ANL
V-I Characteristics

\[ E = E_{\text{rev}} + \frac{(r_1 + r_2T)}{A} I + (s_1 + s_2T + s_3T^2) \log_{10} \left( \frac{t_1 + t_2/T + t_3/T^2}{A} \right) I + 1 \]

- \( E \) operating cell voltage
- \( E_{\text{rev}} \) reversible cell voltage
- \( R \) ohmic resistance of electrolyte
- \( s, t \) coeff for overvoltage on electrodes

Ohmic Losses

• Area Specific Resistance (ASR)
  • ASR = thickness/conductivity(ó)

• Voltage Loss due to Ohmic resistance
  • V = i * ASR

• Electrolyte offers considerable resistance
  • ó(YSZ) = 0.3685 + 0.002838 exp(10300/T)

• Electrodes offer relatively small resistance and are given in literature.
  • Many treat as constants
    • Anode: 0.0014 Ù-cm
    • Cathode: 0.0186 Ù-cm
  • Interfacial Resistances: ~0.1 Ù-cm
Butler –Volmer Approximation $\alpha=0.5$ most assume for fuel cells

- Electrode charge-transfer overpotential
- Combined for both electrodes
- Three adjustable parameters for calibration

\[ V_{B-V} = \left( \frac{R \cdot T}{\alpha \cdot F} \right) \cdot \sinh^{-1} \left( \frac{i}{2 \cdot i_0} \right) \]

\[ i_0 = P_{\text{exp}} \cdot \exp \left( -\frac{E_{\text{act}}}{R \cdot T} \right) \]

$\alpha \equiv$ adjustable parameter
$i \equiv$ average cell current density
$i_0 \equiv$ exchange current density
$P_{\text{exp}} \equiv$ pre-exponential (adjustable)
$E_{\text{act}} \equiv$ activation energy (adjustable)
INEEL SUPPLIED V-I Curves

Test Conditions

<table>
<thead>
<tr>
<th>sweep</th>
<th>T_{fra} (°C)</th>
<th>T_{dp,i} (°C)</th>
<th>Q_{s,Ar}</th>
<th>Q_{s,H_2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>850</td>
<td>27</td>
<td>141</td>
<td>40.1</td>
</tr>
<tr>
<td>2</td>
<td>800</td>
<td>27</td>
<td>141</td>
<td>40.1</td>
</tr>
<tr>
<td>3</td>
<td>850</td>
<td>35.5</td>
<td>141</td>
<td>40.1</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>35.5</td>
<td>141</td>
<td>40.1</td>
</tr>
<tr>
<td>5</td>
<td>850</td>
<td>38.3</td>
<td>141</td>
<td>40.1</td>
</tr>
<tr>
<td>6</td>
<td>800</td>
<td>38.5</td>
<td>141</td>
<td>40.1</td>
</tr>
</tbody>
</table>
Cathode Concentration Overpotential

Using Fick Law of Diffusion

\[ J_A \left( \frac{gm - mol}{cm^2 s} \right) = -cD_{AB} \nabla x_A \]

\[ V = \frac{RT}{2F} \left[ \ln \left( 1 - \frac{i}{i_{H_2O}} \right) - \ln \left( 1 - \frac{i}{i_{H_2}} \right) \right] \]

\( \hat{\Omega} = \) porosity

\( \tau = \) tortuosity

\( r = \) molecular radius

\[ D_{H_2O}^{\text{eff}} = \frac{2FP_{H_2} D_{H_2}^{\text{eff}}}{RTL_a} \]

\[ D_{H_2O}^{\text{binary}} = \frac{0.001T^{1.75} \sqrt{\frac{1}{M_i} + \frac{1}{M_j}}}{P(r_i + r_j)^2} \]

Pulsed Gradient Spin Echo NMR measurements of the time-dependent diffusion coefficient, D(t).
CFD Simulations will be a very necessary elements of SOEC development
Extra components needed to

- Gases need to be circulated through the stack
- Compressors, pumps or blowers
- Electric motors to drive pumps, blowers and compressor
- Fuel cell needs to be connected to load like DC/DC converter for simple voltage regulator as used by INEEL expt.
- Cooling system, air-preheater
**Low-temperature Electrolysis – 1 kg/h \( H_2 \)**

<table>
<thead>
<tr>
<th>Item</th>
<th>Cost</th>
<th>Cost Basis</th>
<th>Power (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Housing/Forecourt dispenser (NEPA Compliant)</td>
<td>$12,000</td>
<td>0.20 $/W</td>
<td>3.50</td>
</tr>
<tr>
<td>Electric Power Transformer</td>
<td>$14,000</td>
<td>0.85 $/W</td>
<td>2.70</td>
</tr>
<tr>
<td>Water System-manifolding</td>
<td>$1,250</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Electric Power Invertor/Conditioning</td>
<td>$45,932</td>
<td>0.85 $/W</td>
<td>2.70</td>
</tr>
<tr>
<td>Electrolytic Cells ($/kW)</td>
<td>$143,199</td>
<td>2,650 $/kW</td>
<td>54.04</td>
</tr>
<tr>
<td>Hydrogen Compression (ambient - 100 psi)</td>
<td>$20,000</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Compression (100 - 5,000 psi)</td>
<td>$78,678</td>
<td>15%</td>
<td>3.60</td>
</tr>
<tr>
<td>Hydrogen dispensing (5,000 psi)</td>
<td>$17,984</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>800kW-Natural Gas Compression/Hythane (50 - 3,600 psi)</td>
<td>$29,974</td>
<td>2.09</td>
<td></td>
</tr>
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<td>800kW-Hythane dispensing (3,600 psi)</td>
<td>$11,990</td>
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</tr>
<tr>
<td>Oxygen system manifolding</td>
<td>$2,500</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>Controls/Auxillarity</td>
<td>$25,585</td>
<td>7.0%</td>
<td>0.80</td>
</tr>
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<td>Cooling fan</td>
<td>$1,250</td>
<td>1.4%</td>
<td>0.98</td>
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<tr>
<td>Profit</td>
<td>$60,657</td>
<td>15.0%</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td><strong>$465,000</strong></td>
<td><strong>Power (kW\textsubscript{electric})</strong></td>
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<td>0.20 $/W</td>
<td>-5% 2.50</td>
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<td>Water System-manifolding</td>
<td>$500</td>
<td></td>
<td>0.10 0.00</td>
</tr>
<tr>
<td>Steam system</td>
<td>$8,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electric Power Invertor/Conditioning</td>
<td>$30,820</td>
<td>0.85 $/W</td>
<td>-5% 1.81</td>
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<tr>
<td>Electrolytic Cells ($/kW)</td>
<td>$123,282</td>
<td>$3,400 $/kW</td>
<td>93% 36.26</td>
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H₂ (kW-HHV/kg) = 33.721

Power (kW \(_{\text{electric}}\)) = 51.02

Power (kW \(_{Q@1050K}\)) = 10.66
## Capital Cost Comparison

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## Power use comparison

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Cross-Cutting Research Directions

- **Membranes and Separation**
  - Ceramic membranes used for the separation of oxygen from air must simultaneously achieve high-flux oxygen transport and equally large electronic transport, and, at the same time, must survive the extreme conditions of the membrane reactor
    - high temperatures
    - reactive environments
    - highly reducing conditions on one surface of the membrane

- **Characterization and measurement techniques**
  - Advanced Photon Source
  - Electron Microscopy

- **Theory, modeling and simulation**
  - Diffusion Models
  - Continued Interdisciplinary Effort
**Issues with High-Temperature Electrolysis**

- Desirable for product hydrogen to be produced at high pressures
  - Robust cell design necessary
- Electrical energy intensive
  - High ohmic losses due to thick electrolyte
    - High strength design needed
  - High overpotential on oxygen electrode
  - High overpotential and degradation of steam/hydrogen electrode
  - High thermodynamic potential to overcome
Conclusions – High Temperature Electrolysis

- Capital Costs appear competitive
- Physical plant footprint will be larger
- Premium *(Electric)* Power demands are much lower
- Premium heat demands now needed