Low Temperature Electrolytic Hydrogen Production

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Overview

Timeline
• July 1, 2004
• December 31, 2005
• 60%

Budget
• Total project funding
  – DOE Share: $244,693
  – Contractor share: $0
• Funding received in
  FY04: $244,693
• Funding for FY05: $0

Barriers
• Barriers addressed
  – Energy Efficiency
  – System Cost
  – Robust Materials

Partners
• Savannah River National Laboratory: William Summers
• Argonne National Laboratory: Richard Doctor
• Idaho National Laboratory: Michael Simpson
Objectives

Assist DOE in developing highly efficient, cost affective thermochemical cycles for $\text{H}_2$ production. Our focus is on the electrochemical step used in a variety of thermochemical cycles (e.g., hybrid sulfur, modified Ca-Br).
Approach

• Develop a gas phase proton exchange membrane (PEM) electrolyzer to convert HBr to Br$_2$ and SO$_2$ to H$_2$SO$_4$

• Quantify the relationships among design and operating parameters.

Our unique gas-phase process has significantly lower mass-transfer resistance that will provide:

– Higher current densities (i.e., lower electrolyzer cost)
– Better thermal management (i.e., higher efficiencies)
– Lower voltages (i.e., higher efficiencies)
– Lower reactant crossover (i.e., reduce poisoning providing longer life)
– Better control of product purity (i.e., higher efficiencies)
– Lower catalyst loadings (i.e., lower electrolyzer cost)
Key Measurements

• Voltage → Electrical Energy and Efficiency
• Current Density → Electrolyzer Size
  \( (i.e., \text{capital costs}) \)
• Outlet Concentration → Separation Cost and Efficiency
• Voltage Drift → Replacement Costs
Operating Parameters

- Current
- Temperature
- Pressure
- Anode feed flow rate
- Anode feed composition
- Acidity of cathode feed
Design Parameters

• Catalyst type and loading
  → Electrolyzer Costs
  → Voltage
  → Poisoning

• Membrane type and thickness
  → Voltage
  → Poisoning
  → Water Management
Ca-Br-Fe Cycle (UT-3)
Modified Ca-Br Cycle

O₂ → \( \text{CaBr}_2 \) → Electrolysis → HBr → \( \text{CaO} \) → Heat → \( \text{H}_2 \) → \( \text{H}_2\text{O} \) → O₂

Decomposition

760° C

Heat
Anhydrous HBr Electrolysis
Using a PEM Reactor

Anode:
\[2\text{HBr}(g) \rightarrow \text{Br}_2 (g) + 2 \text{H}^+(aq) + 2 \text{e}^-\]

Cathode:
\[2\text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2(g)\]

Overall:
\[2\text{HBr}(g) \rightarrow \text{H}_2(g) + \text{Br}_2(g)\]

Anode Side Reaction:
\[2 \text{H}_2\text{O} \rightarrow 4 \text{H}^+ + \text{O}_2 + 4\text{e}^-\]
Electrochemical Conversion of Halides
(T=80°C; P=1.0 atm; RuO$_2$ catalyst)

Graph showing the relationship between voltage and current density for liquid-phase HCl reaction (Uhde Process) and gas-phase HCl and HBr reactions.
Sulfur Iodine (S-I) Process
Hybrid Sulfur (HyS) Process

1. Decomposition of $\text{H}_2\text{SO}_4$ at $850^\circ \text{C}$
2. Electrolysis of $\text{H}_2\text{SO}_4$
3. Formation of $\text{H}_2$ and $\text{SO}_2$
4. Re-formation of $\text{H}_2\text{SO}_4$

Reactions:

- $\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{SO}_2 + \text{H}_2 + \text{Water}$
- $850^\circ \text{C}$

Diagram:

- $\text{O}_2$ to $\text{SO}_2$
- $\text{H}_2\text{SO}_4$ to $\text{H}_2$ and $\text{SO}_2$
- Electrolysis of $\text{H}_2\text{SO}_4$
- $\text{H}_2$ back to $\text{H}_2\text{SO}_4$
Anhydrous SO₂ Electro-Oxidation
Using a PEM Reactor

**Anode:**

\[
\text{SO}_2(g) + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + 2 \text{H}^+(aq) + 2 \text{e}^-
\]

**Cathode:**

\[
2\text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2(g)
\]

**Overall:**

\[
\text{SO}_2(g) + 2\text{H}_2\text{O} \rightarrow \text{H}_2(g) + \text{H}_2\text{SO}_4
\]

**Poisoning Reaction:**

\[
\text{SO}_2 \rightarrow \text{S} + \text{O}_2 + 2\text{e}^-
\]
Low Temperature Electrolysis

![Graph showing electrolysis data]

- **Liquid-phase HCl Reaction (Uhde Process)**
- **Gas-phase HCl**
- **Gas-phase HBr**
- **Westinghouse SO₂ oxidation data**
  - 1 atm; 50°C [1]
  - 5-20 atm; 80°C [1]
- **Westinghouse projection**
  - 1 atm; 80°C

Oxidation of \( \text{SO}_2 \) to \( \text{H}_2\text{SO}_4 \)

Westinghouse Data [1]
1 atm; 50 °C;
Catalyst Loading: 7 mg-Pt/cm\(^2\)

Our Data
1 atm; 80 °C; 5% conversion, dry SO\(_2\)
Catalyst Loading: 0.65 mg-Pt/cm\(^2\)

Westinghouse Projections [1]
Pressure 5-20 atm; 80 °C

Oxidation of $\text{SO}_2$ to $\text{H}_2\text{SO}_4$

($T=80^\circ\text{C}; \ P=1.0 \ \text{atm}$)

**Current Density, kA/m²**

- Voltage, V

- 5% Conversion (Dry SO₂)
- 20% Conversion (Dry SO₂)

- 13 wt% $\text{H}_2\text{SO}_4$
- 46 wt% $\text{H}_2\text{SO}_4$
Conclusions for Gas-Phase HBr Oxidation

• Electrochemical conversion of HBr to Br₂ and H₂ in a PEM reactor is very promising. (20 kA/m² @ < 2.0V)

Future Work

• Measure performance as a function of temperature and pressure

• Develop mathematical models that can predict cell performance. These models could be fed into process flowsheet models being developed by Argonne National Laboratory.
Conclusions for Gas-Phase SO$_2$ Oxidation

- Electrochemical conversion of SO$_2$ to H$_2$SO$_4$ and H$_2$ in a PEM reactor is encouraging (e.g., 4 kA/m$^2$ @ 0.9V).

Future Work

- Measure performance as a function of temperature and pressure
- Develop mathematical models that can predict cell performance. Feed these models into process flowsheet models being developed by Savannah River National Laboratory.
Technical Presentations
(speaker underlined)


• J. W. Weidner, P. Sivasubramanian, and F. Freire, “Electrochemical Conversion of Anhydrous HBr to Br2 for Hydrogen Production,” The Electrochemical Society, Honolulu, HI, October, 2004. Please list any publications and presentations that have resulted from work on this project.
Hydrogen Safety

We produce hydrogen via our electrochemical reactor. However, the concentrations are low and the vented in a hood. The risk of a hydrogen explosion or very low.