Low Temperature Electrolytic Hydrogen Production

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This presentation does not contain any proprietary or confidential information

Project ID #PDP56

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 Natioinal Laboratory: Richard Doctor
- Idaho National Laboratory: Michael Simpson

Objectives

Assist DOE in developing highly efficient, cost affective thermochemical cycles for 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_2SO_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.*, capital costs)
- Outlet Concentration → Separation Cost and Efficiency
- Voltage Drift → Replacement Costs

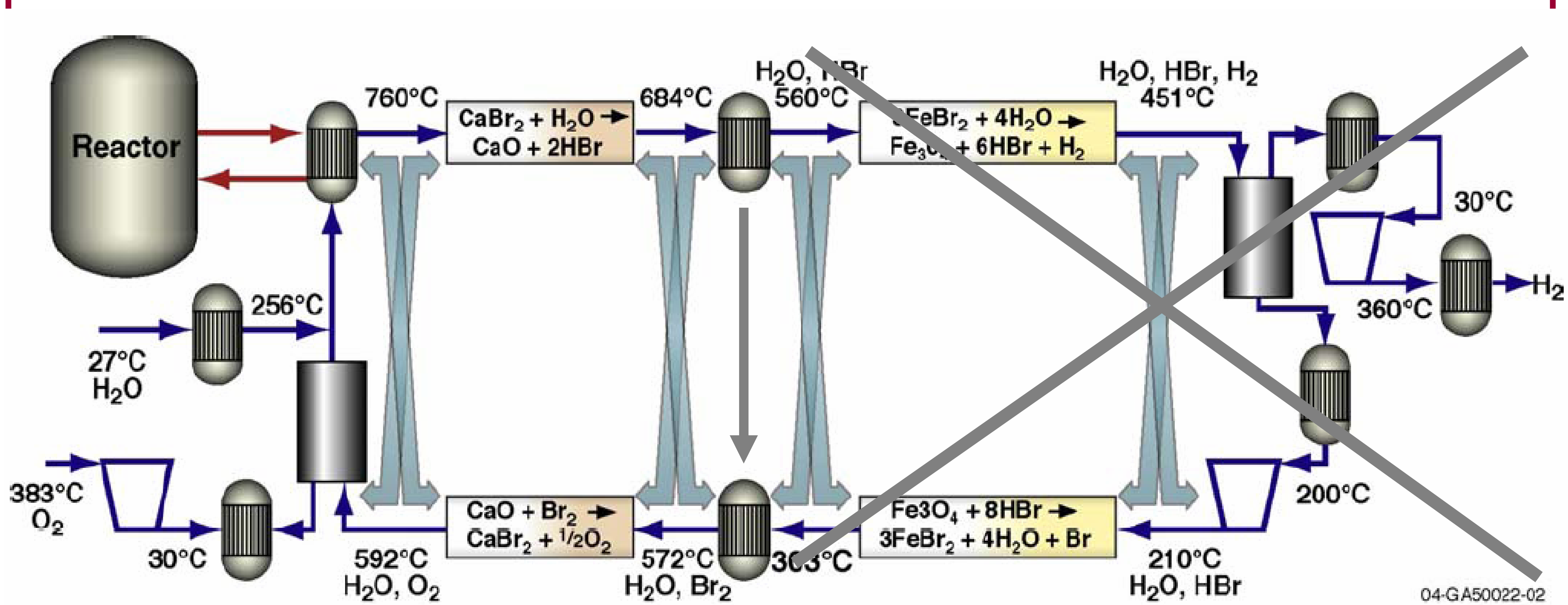
Operating Parameters

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

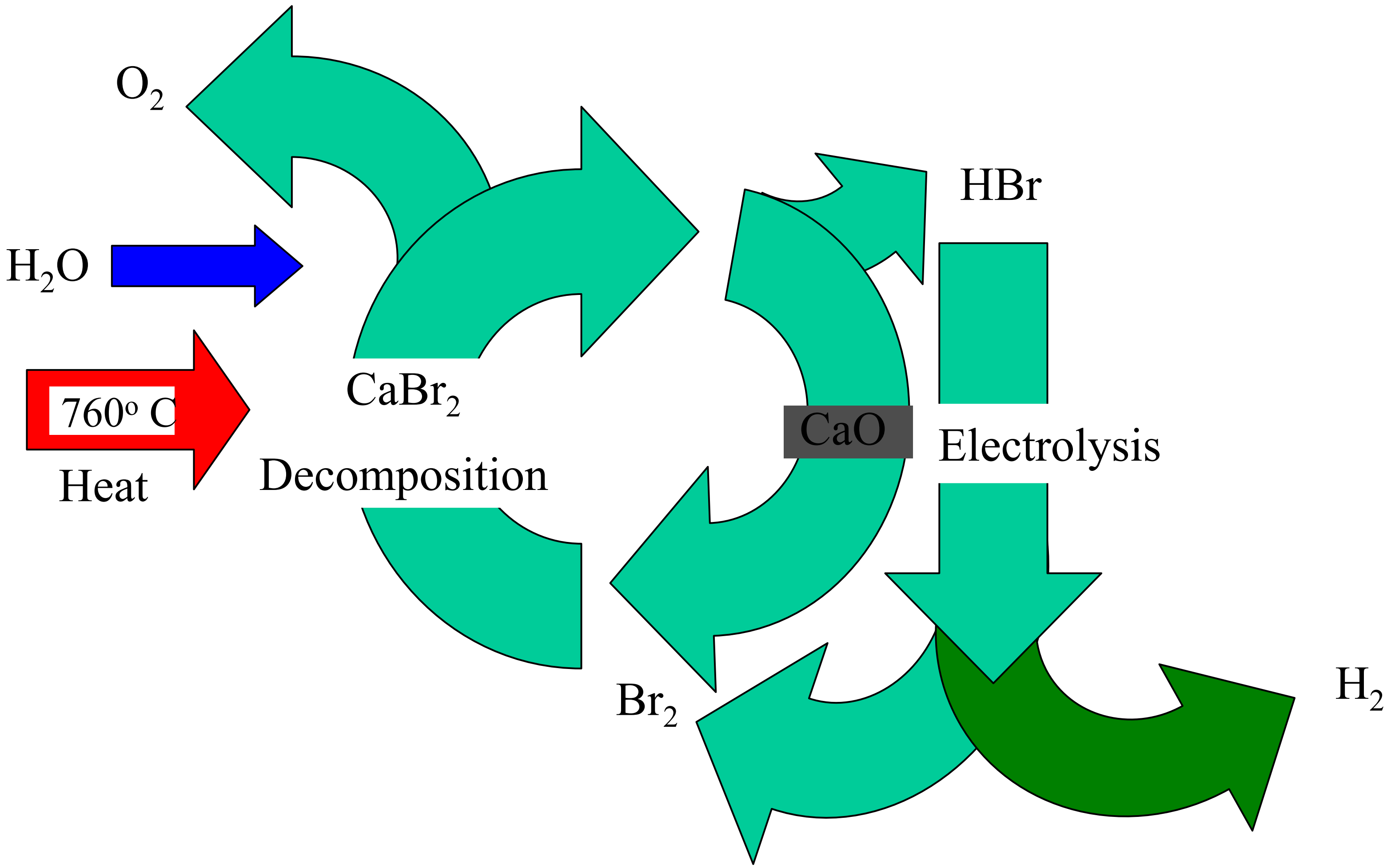
Design Parameters

- Catalyst type and loading
  - → Electrolyzer Costs
  - → Voltage
  - → Poisoning
- Membrane type and thickness
  - → Voltage
  - → Poisoning
  - → Water Management

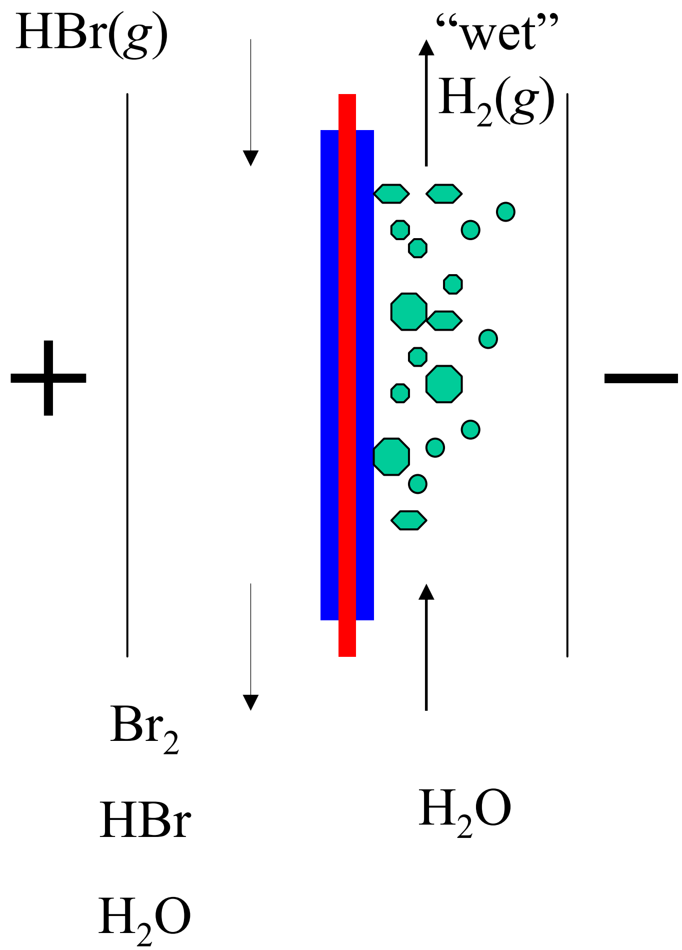
Ca-Br-Fe Cycle (UT-3)



Modified Ca-Br Cycle



Anhydrous HBr Electrolysis Using a PEM Reactor



Anode:

$$2HBr(g) \rightarrow Br_2\ (g) + 2\ H^+(aq) + 2\ e^-$$

Cathode:

$$2H^+(aq) + 2\ e^- \rightarrow H_2(g)$$

Overall:

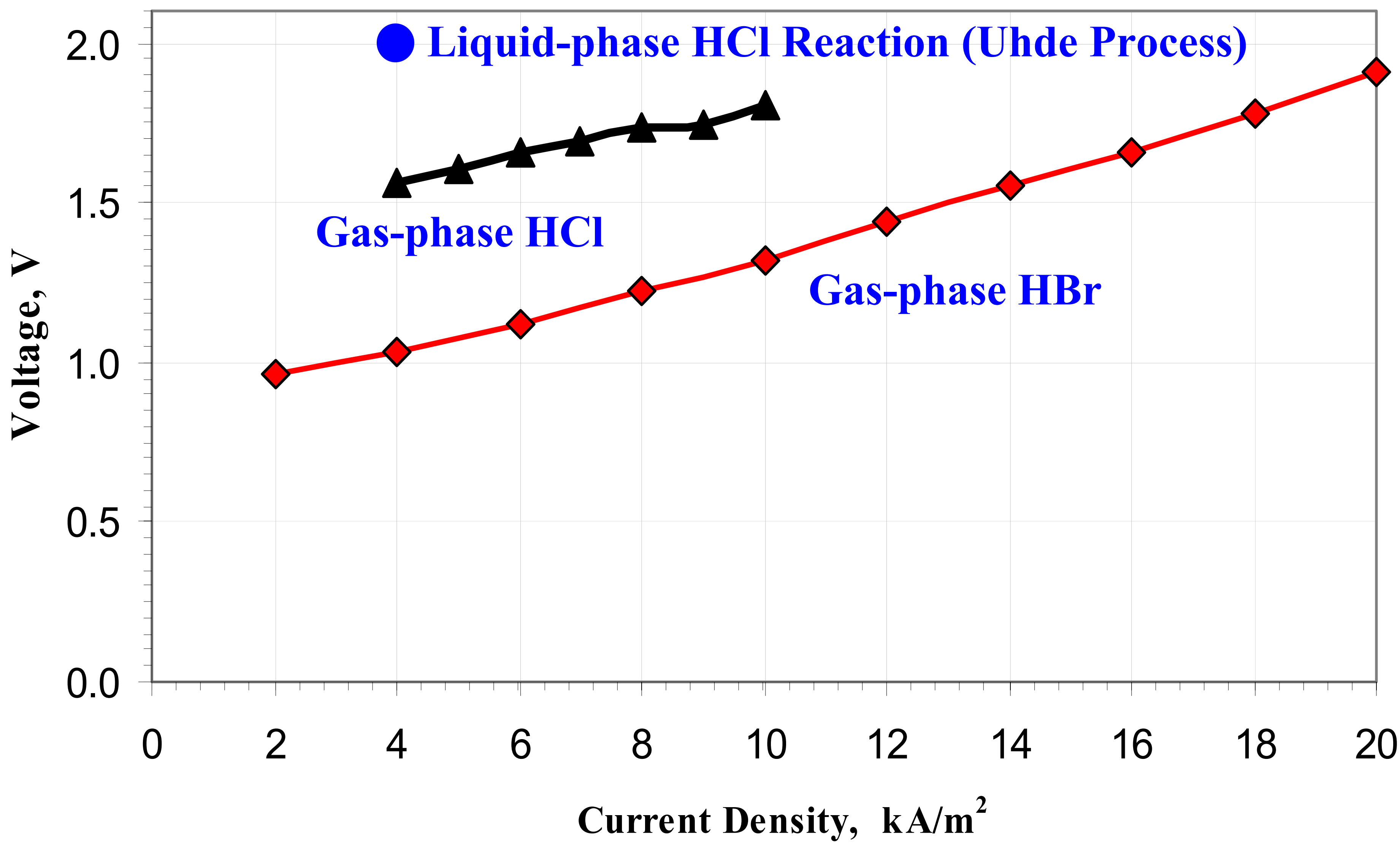
$$2HBr(g) \rightarrow H_2(g) + Br_2(g)$$

Anode Side Reaction:

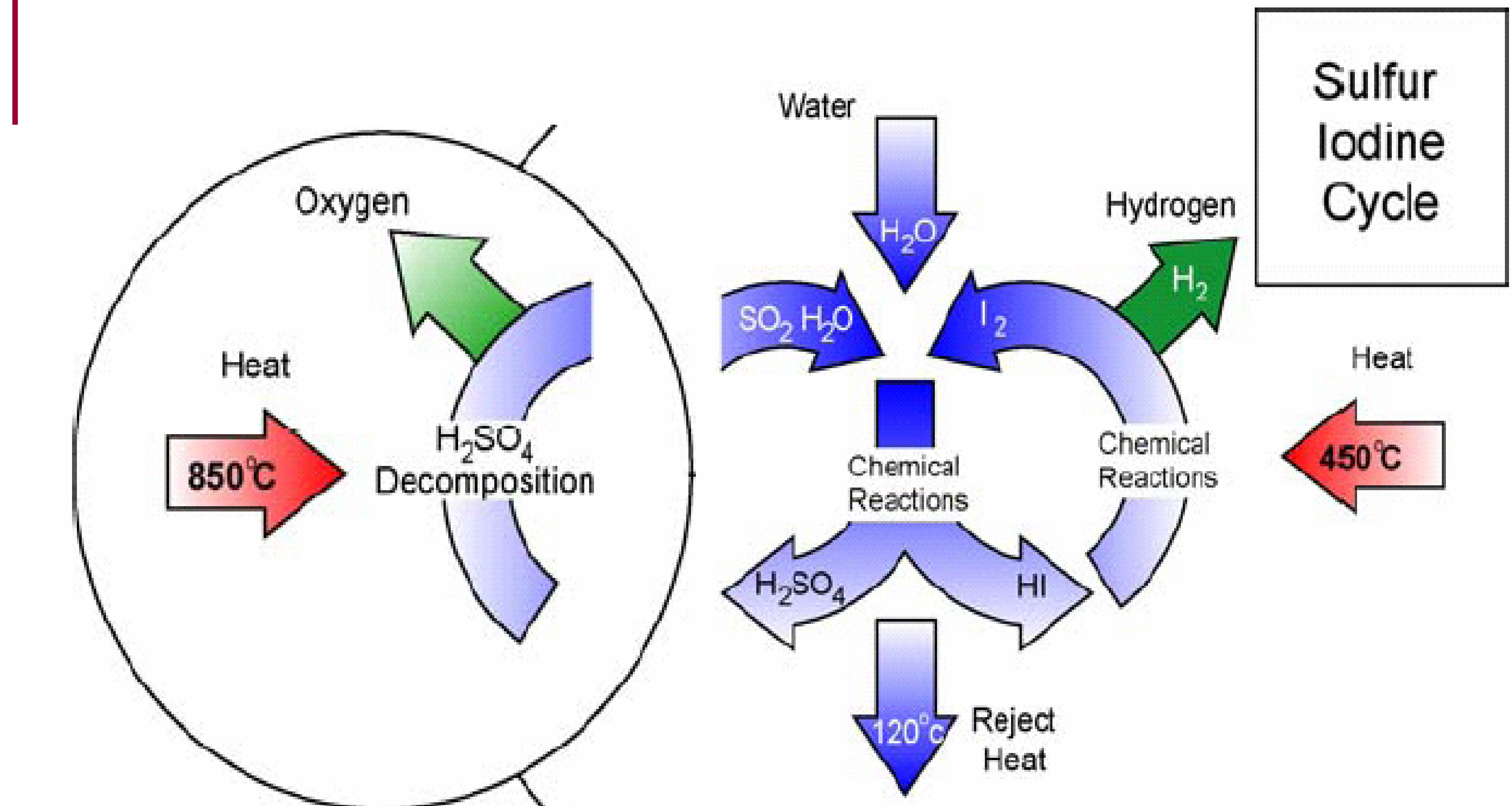
$$2\ H_2O \rightarrow 4\ H^+ + O_2 + 4e^-$$

Electrochemical Conversion of Halides

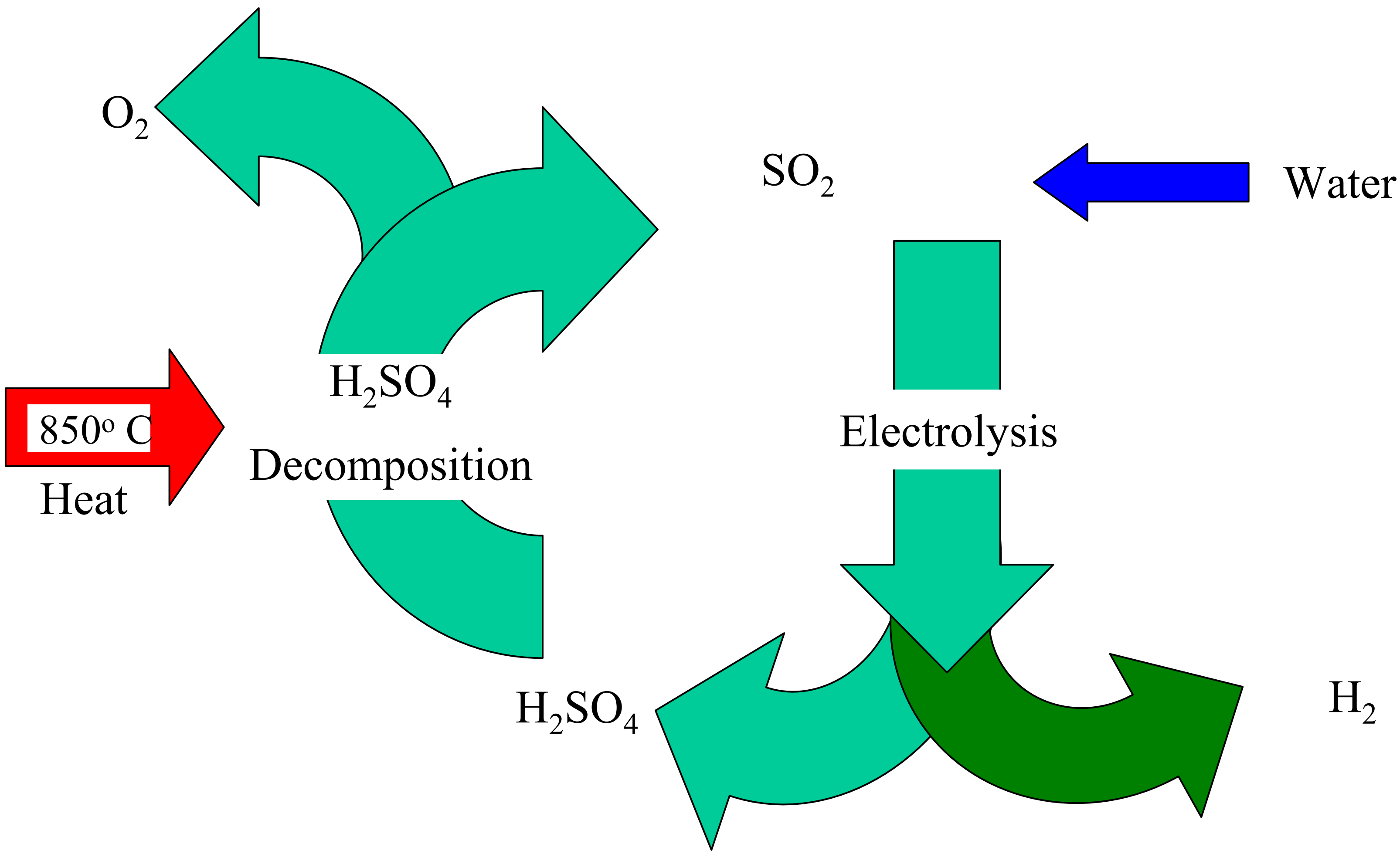
(T=80°C; P=1.0 atm; RuO_2 catalyst)



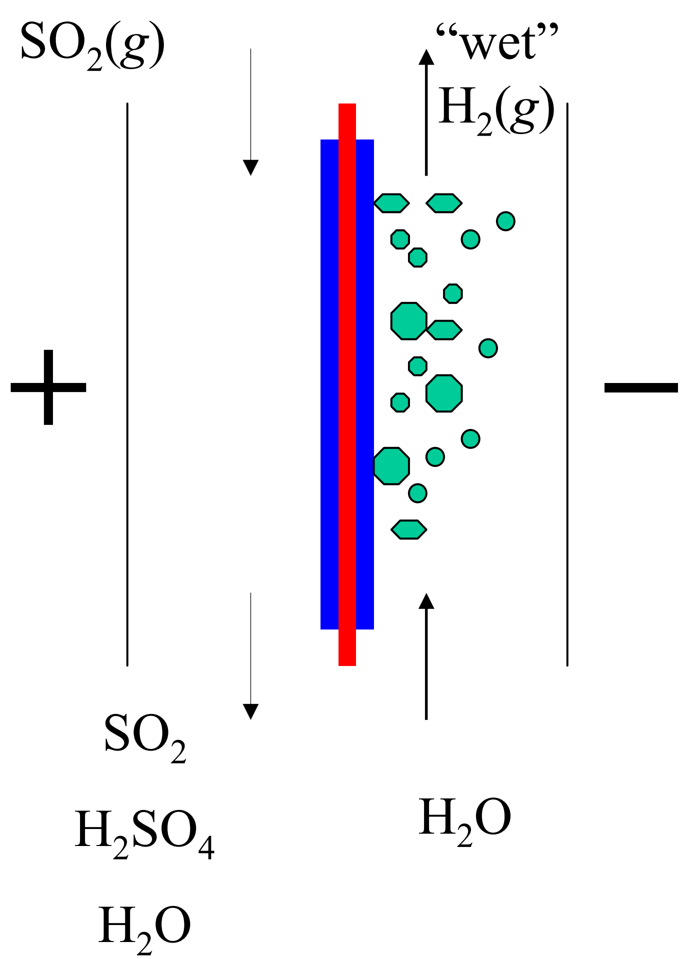
Sulfur Iodine (S-I) Process



Hybrid Sulfur (HyS) Process



Anhydrous SO_2 Electro-Oxidation Using a PEM Reactor



Anode:

$$SO_2(g) + 2H_2O \rightarrow H_2SO_4 + 2\ H^+(aq) + 2\ e^-$$

Cathode:

$$2H^+(aq) + 2\ e^- \rightarrow H_2(g)$$

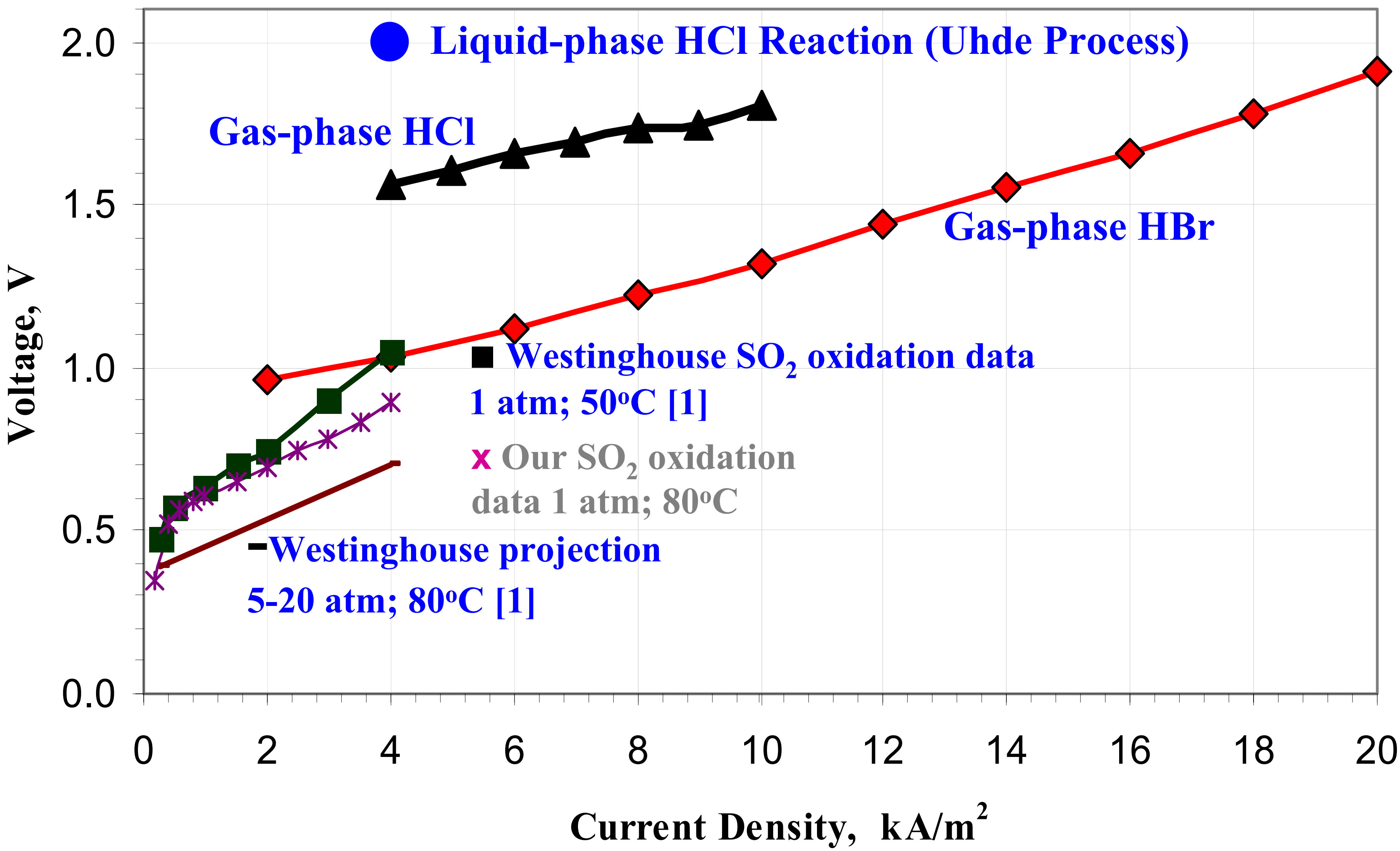
Overall:

$$SO_2(g) + 2H_2O \rightarrow H_2(g) + H_2SO_4$$

Poisoning Reaction:

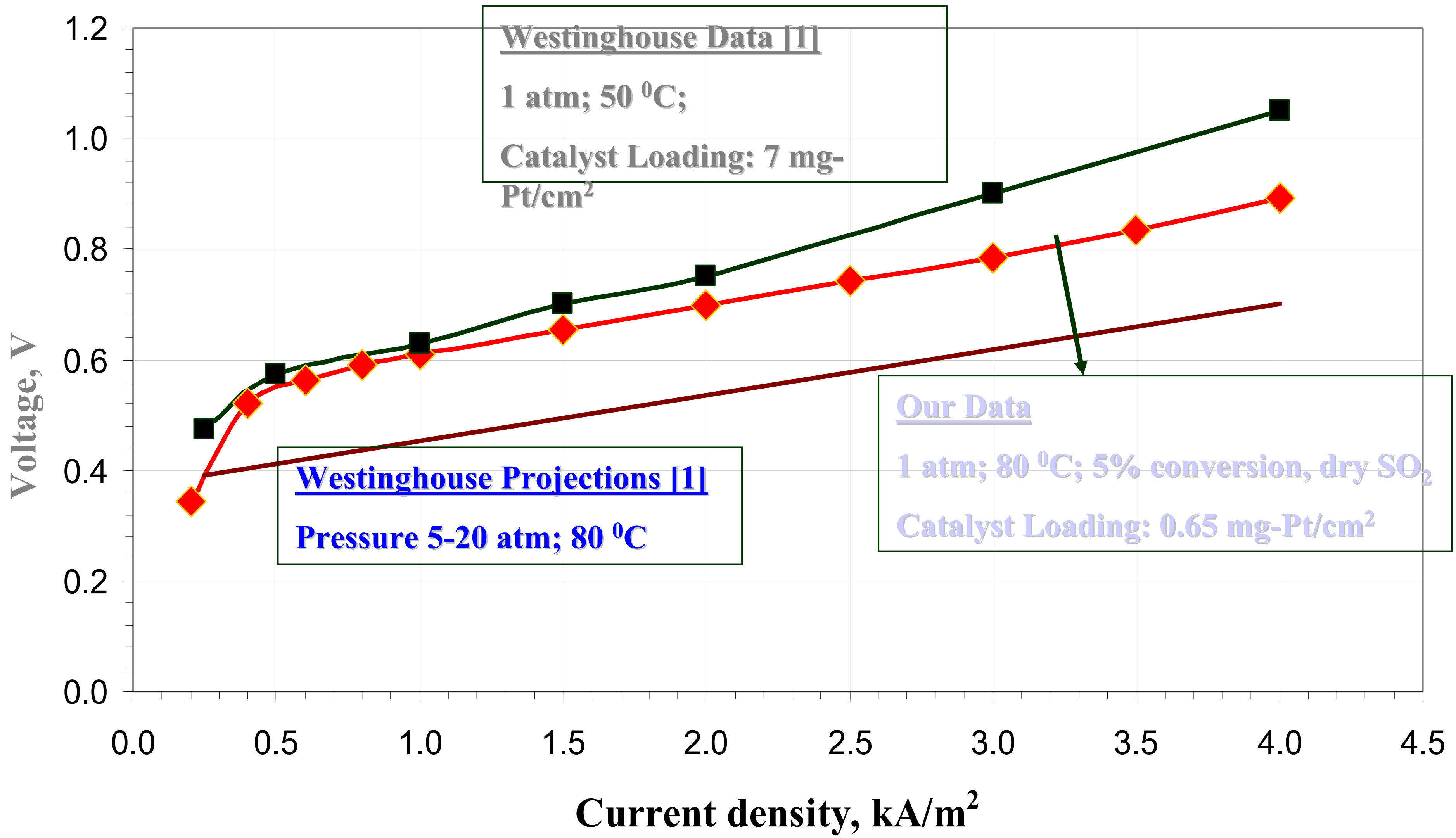
$$SO_2 \rightarrow S + O_2 + 2e^-$$

Low Temperature Electrolysis



[1] P.W. Lu *et. al., J. Appl. Electrochem.*, 347 (1981).

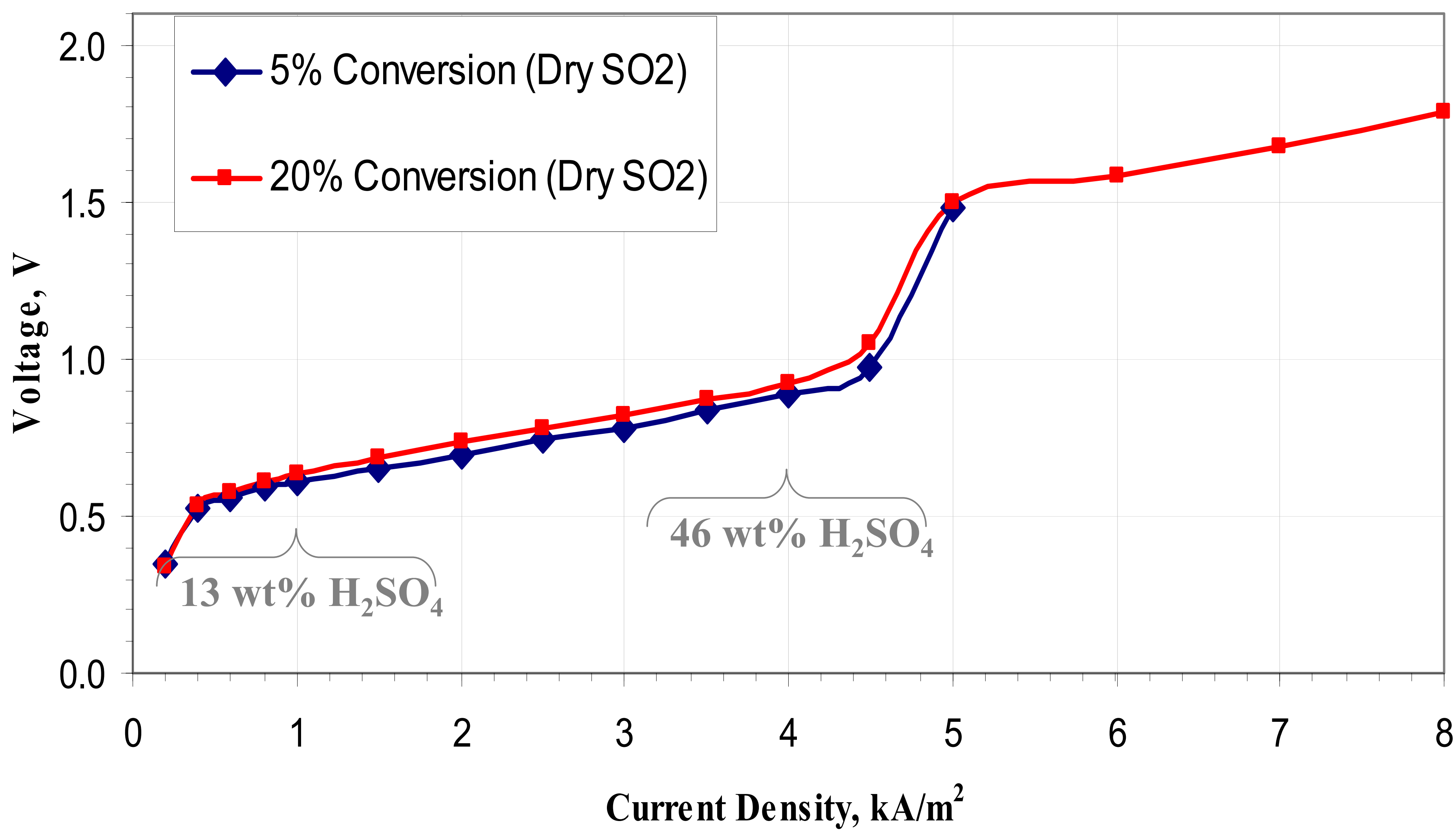
Oxidation of SO_2 to H_2SO_4



[1] P.W. Lu *et. al., J. Appl. Electrochem.,* 347 (1981).

Oxidation of SO_2 to H_2SO_4

(T=80°C; P=1.0 atm)



Conclusions for Gas-Phase HBr Oxidation

- Electrochemical conversion of HBr to Br_2 and H_2 in a PEM reactor is very promising . (20 kA/m^2 @ < 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_2SO_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, R. Ramasamy, C.E. Holland and F. Freire, "Electrochemical Generation of Hydrogen via Thermochemical Cycles," The American Institute of Chemical Engineerings, Atlanta, GA, April, 2005.
- 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.