Thermochemical Systems
Overview

Presented by:

Bob Evans

National Renewable Energy Laboratory

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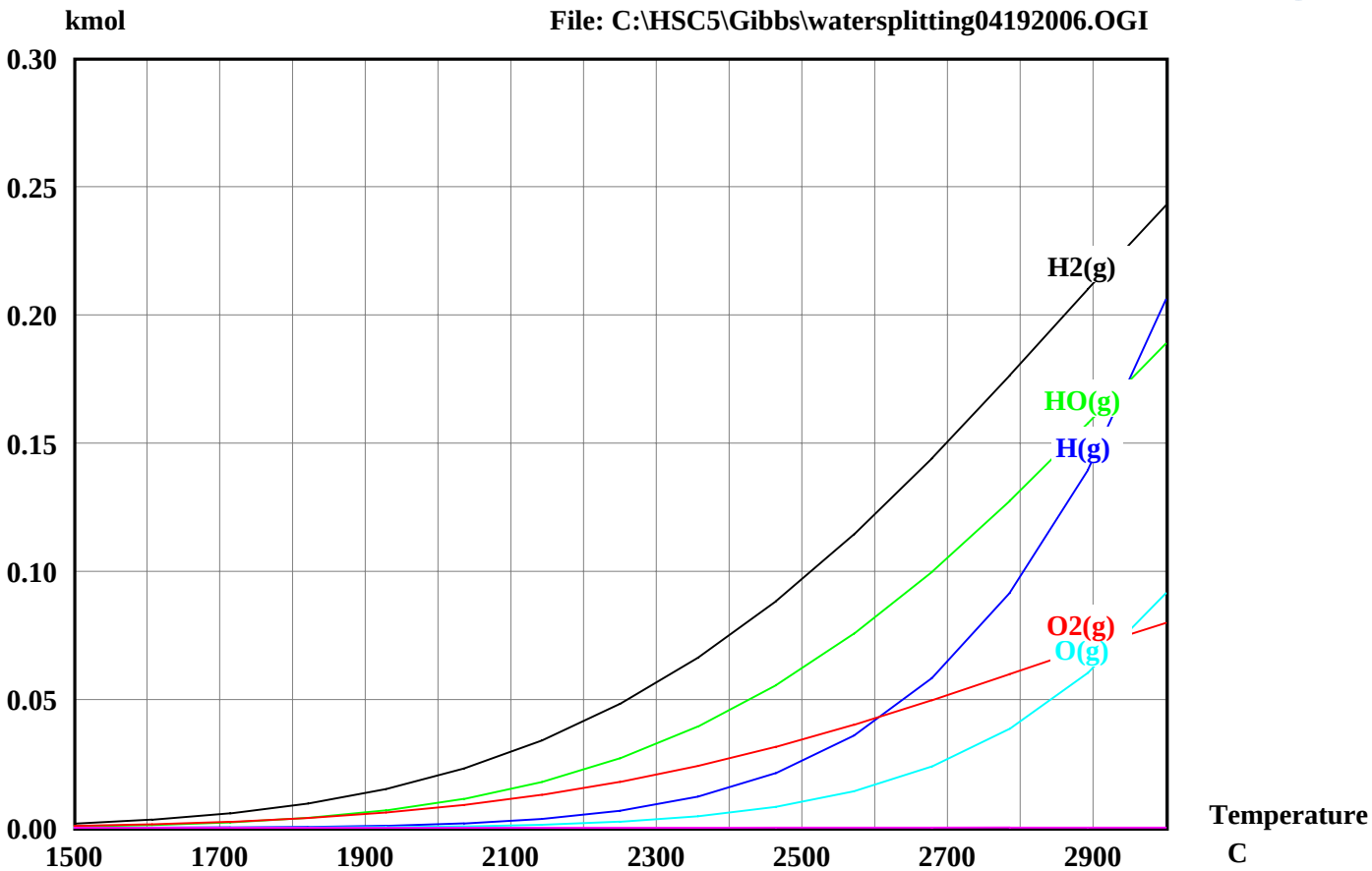
Overview

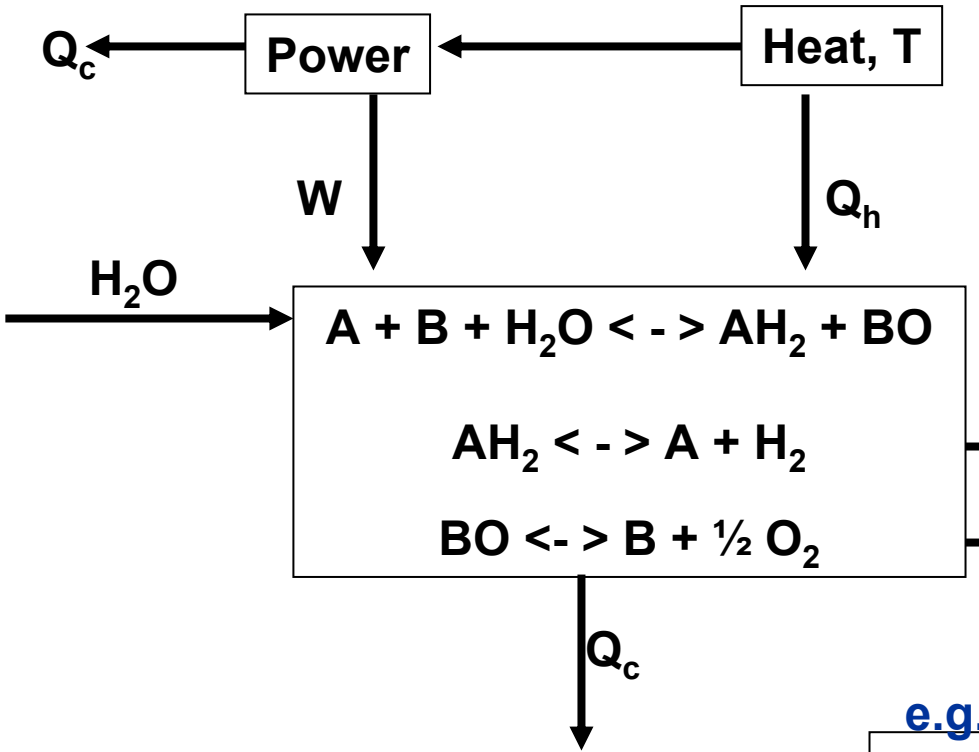
- Thermochemical Cycles Background
- Criteria and Approaches
- The NHI TC Priority Areas
  - Sulfur-Iodine Integrated Lab Experiment
  - Hybrid Sulfur Electrolyzer Development
  - Alternative Cycles
  - Enabling Science and Technology
- FY07 Plans

Direct Thermal Water Splitting



Two Problems: High Temperature and Recombination

Example of 3 Step Thermochemical Cycle



$$Eff = \frac{-\Delta H^o(H_2O)}{Q_h + \frac{W}{\eta_r}}$$

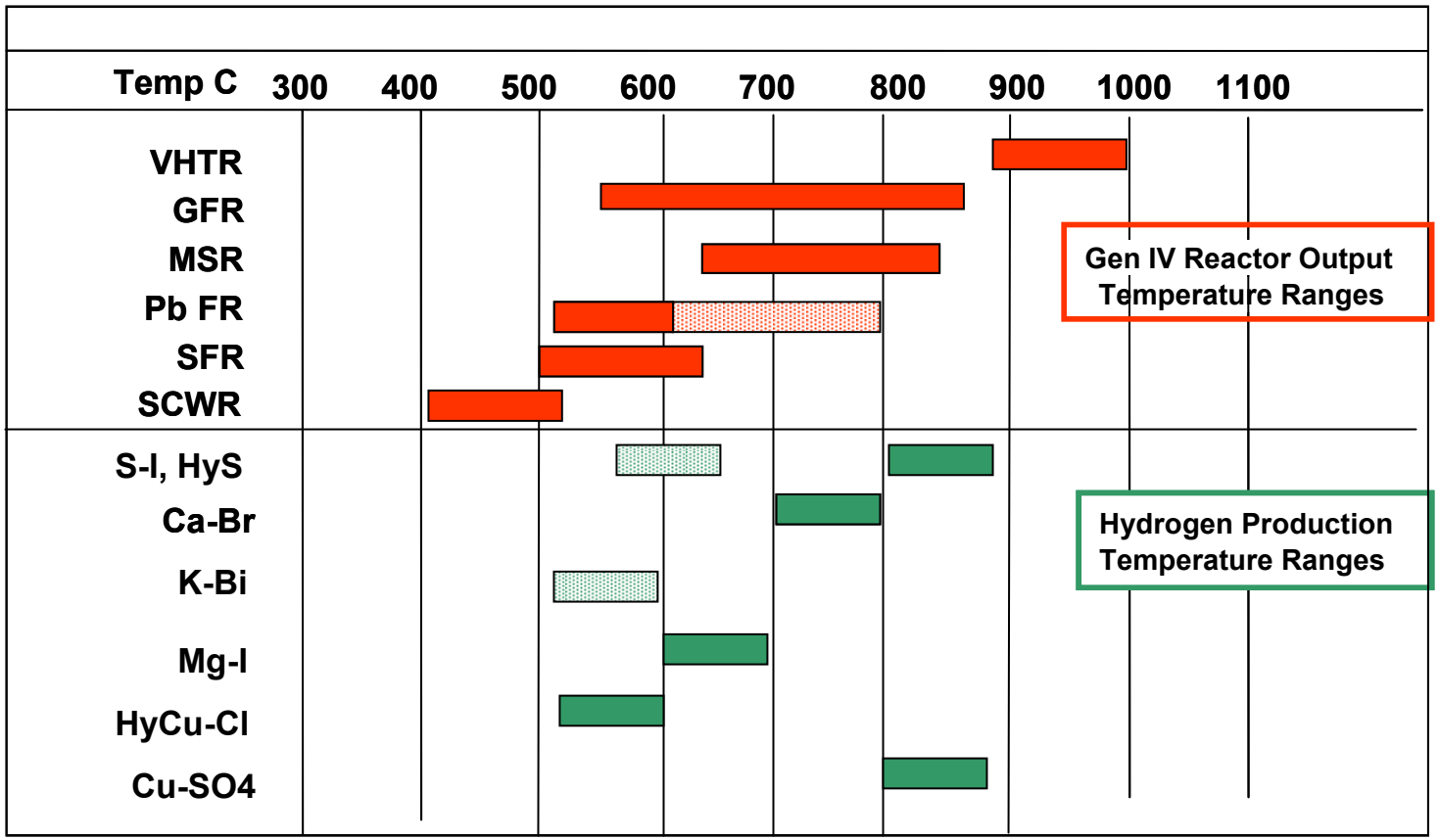
e.g. of 2 step cycle:

$X + H_2O <- > XO + H_2$

$XO <- > X + ½ O_2$

Generation IV Energy Conversion

- Electrical generation - ***Gen IV Energy Conversion Program***
- Hydrogen production - ***Nuclear Hydrogen Initiative (NHI)***

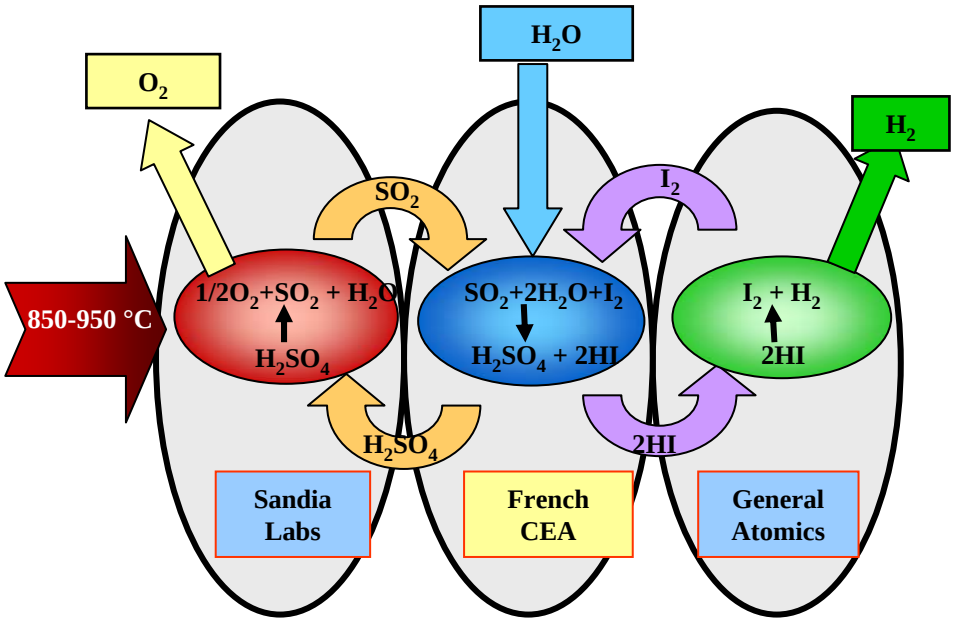


1969 Ispra Meeting Criteria

- Thermal efficiency
- Conversion of chemical reactions
- Side reactions
- Toxicity
- Availability and cost of materials
- Separation
- Corrosion
- Materials handling
- Maximum process temperature
- Heat transfer

Sulfur Thermochemical Cycles

TC cycles require high temperatures, extensive thermal management, and high temperature, corrosion resistant materials

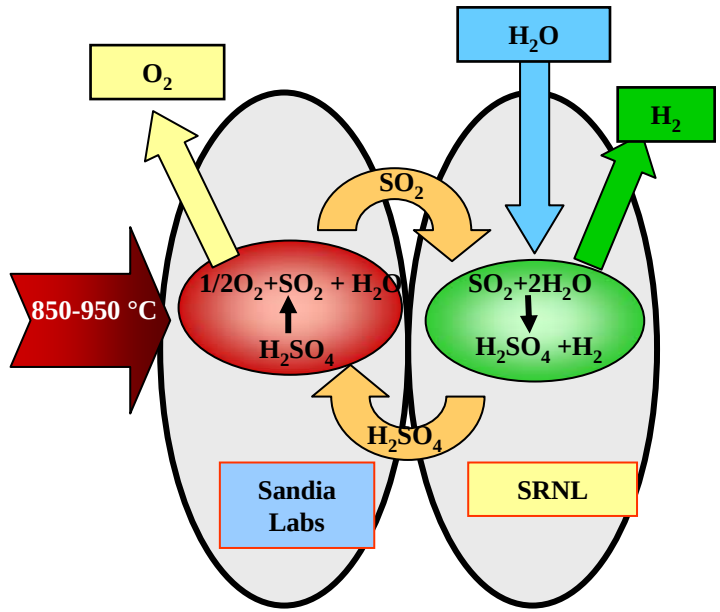


Sulfur Iodine

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

(2) $2HI \rightarrow I_2 + H_2$

(3) $2H_2O + SO_2 + I_2 \rightarrow H_2SO_4 + 2HI$



Hybrid-Sulfur

(1) $H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2$

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

Section 1: Bunsen Reaction Section

- Thermal management in reaction column (S formation)
- Recycle volumes from HI section
- Thermo-physical data uncertain (HI/I2/H2O -VLE)
- Materials – corrosion
- Process Complexity
- Water management

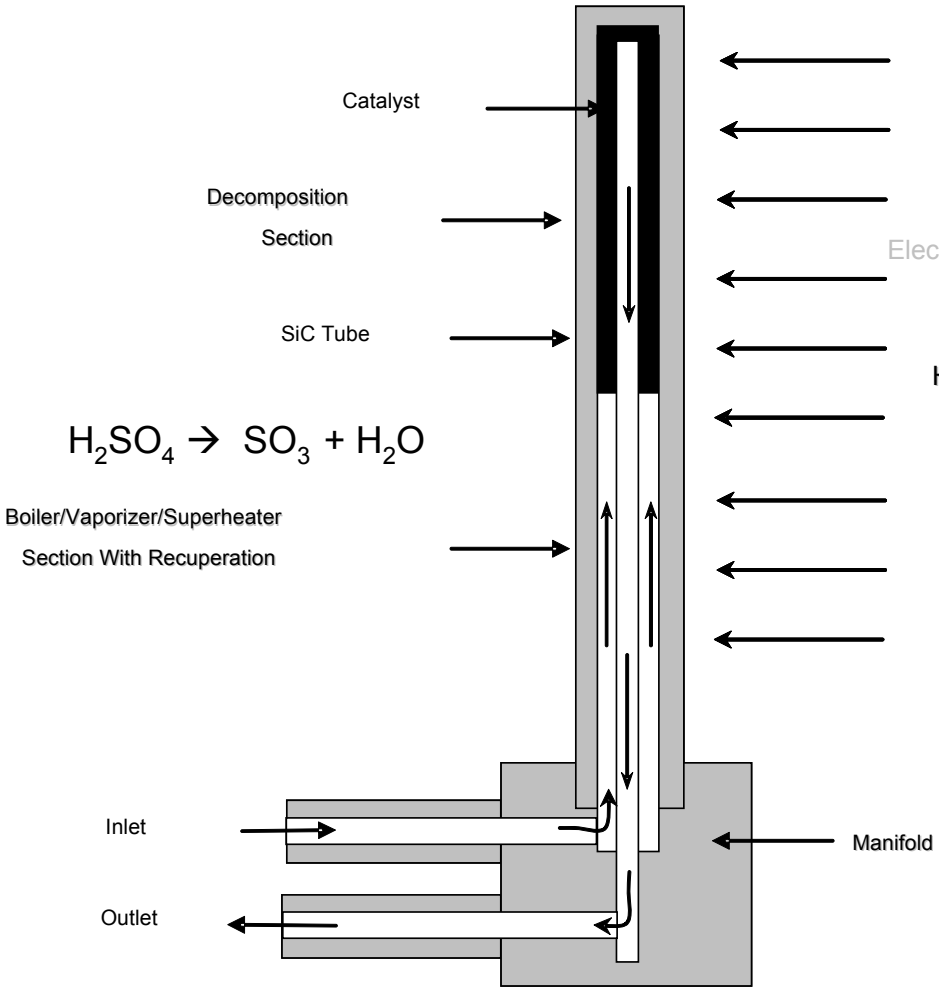
$$A + B + H_2O <-> AH_2 + BO$$

$$I_2 + SO_2 + 2\,H_2O <-> 2\,HI + H_2SO_4$$

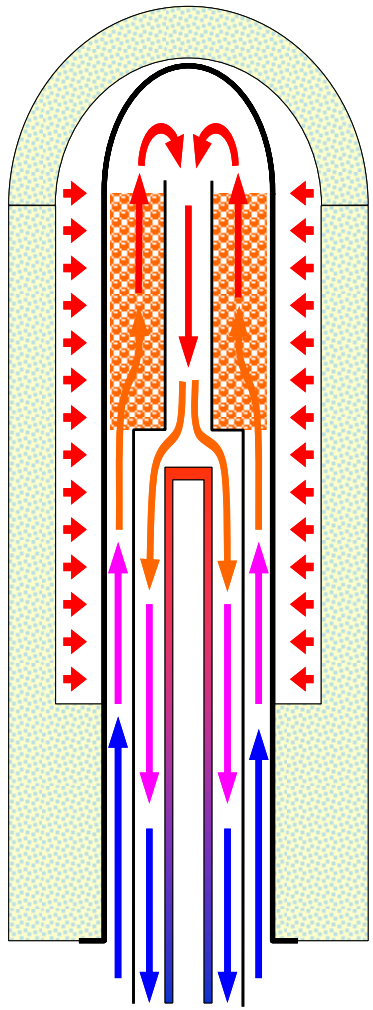
$$9\,I_2 + SO_2 + 16\,H_2O <-> [2\,HI + 10H_2O + 8I_2] + [4\,H_2O + H_2SO_4]$$

Commissariat à l'énergie atomique (CEA)

Section 2: SiC Based H2SO4 Decomposer

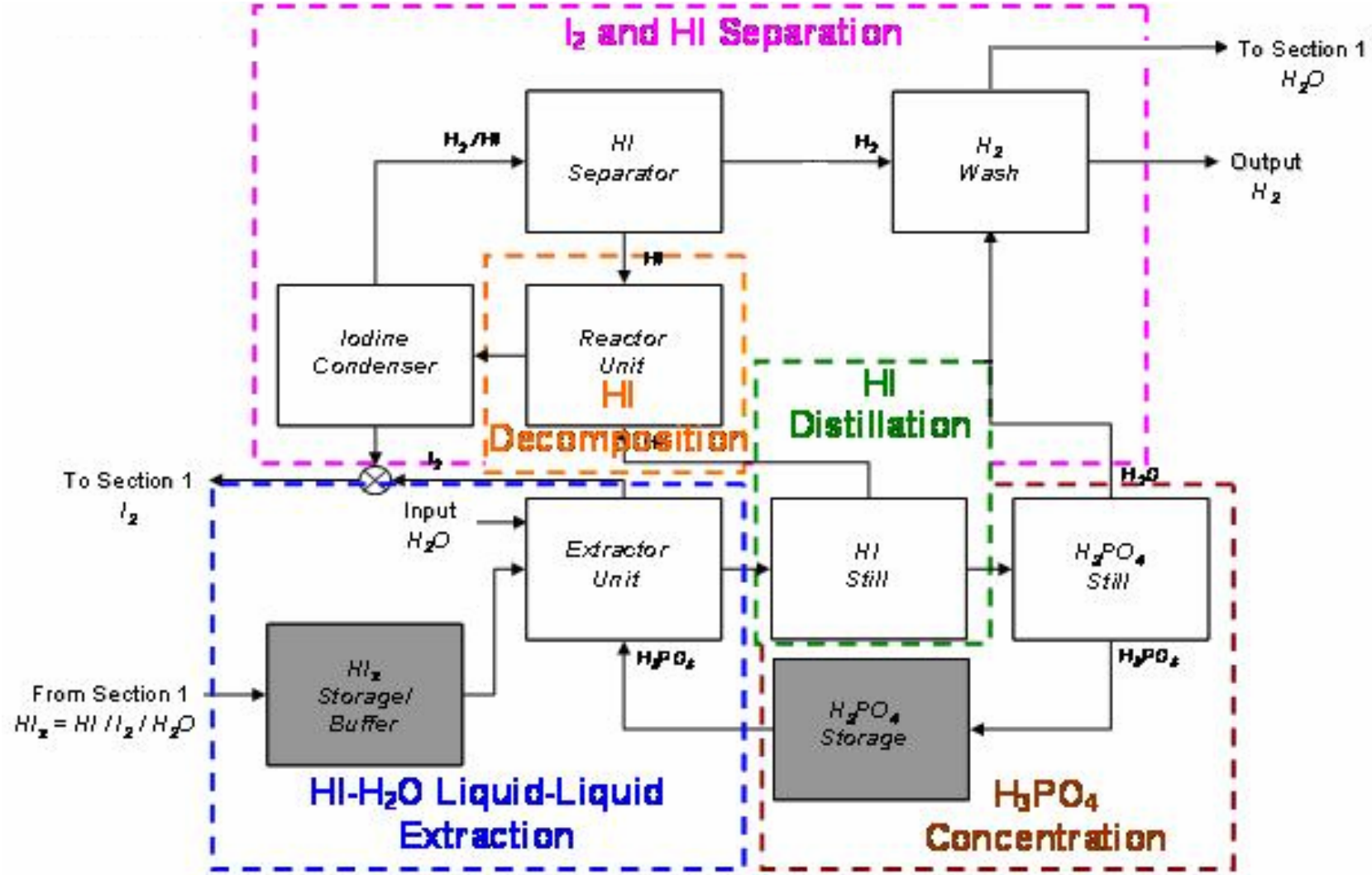


$SO_3 \rightarrow SO_2 + ½\ 0_2$



Sandia National Lab

Section 3: 2HI → H2 + I2



General Atomic

SRNL Electrolyzer Development

Half-cell Reactions:

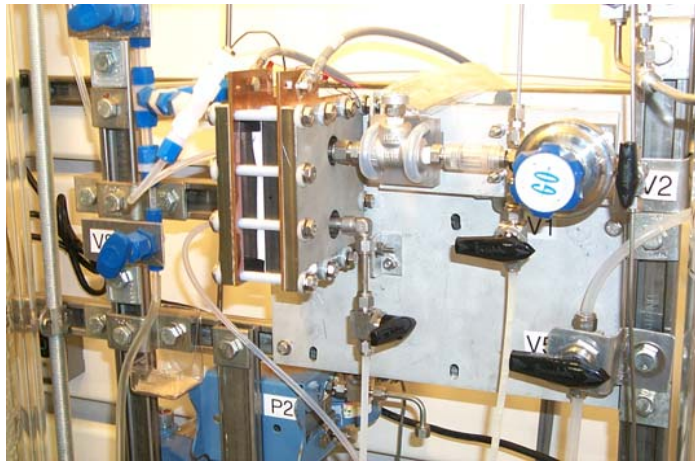
Anode: SO_2 (aq) + 2 H_2O (aq) → H_2SO_4 (aq) + 2 H^+ + 2 e^-

Cathode: 2 H^+ + 2 e^- → H_2 (g)

Major Challenges:

- Minimize power requirements
- Develop high performance membrane w/o SO2 crossover
- Materials and operating conditions for long-life
- Scale-up and potential for low-cost

SRNL, (USC NERI)



SO2-depolarized electrolyzer

SDE Test facility in FY05

Alternative cycles:
Identify and evaluate promising cycles

- Sources of cycles:
  - "High Efficiency Generation of Hydrogen Fuels Using Solar Thermochemical Splitting of Water…:
    - » GA-A24972 by B. McQuillan, et al.
  - Literature evaluations by university partners
- Evaluate using a consistent 3-stage methodology
  - Screening criteria
  - Efficiency for stoichiometric reactions
  - Efficiency for equilibrium conditions and/or flowsheet

Alternative Cycles Lab Work

- Hybrid Ca-Br – Argonne National Lab - 45%
  - **$CaBr_2 + H_2O(g) = CaO + 2HBr$ 750 C**
  - $CaO + Br_2 = CaBr_2 + ½O_2$ (g) 550 C
  - $2HBr(g) = H_2 + Br_2$ (g) 25 C
- K-Bi – Penn State University
  - $0.3\ K_3Bi + H_2O(g) = KOH(l) + H_2$ (g) + 0.3 Bi 575 C
  - **$KOH(l) + 0.3\ Bi = .5\ O_2$ (g) + $0.5H_2$ (g) + $0.3\ K_3Bi$ 575 C**
- Mg-I – University of South Carolina - 45%
  - $6MgO + I_2$ (s) = $Mg(IO_3)_2$ (s) + $5MgI_2$ (aq) 150 C
  - $Mg(IO_3)_2$ (s) = $MgO + I_2$ (g) 600 C
  - $5MgI_2 + 5H_2O(g) = 5MgO + 10\ HI(g)$ 400 C
  - **$10\ HI\ (g) = 5H_2(g) + 5I_2(g)$ 500 C**
- Hybrid Cu-Cl – ANL - 42%
  - $2Cu + 2HCl(g) \rightarrow 2CuCl\ (l) + H_2(g)$ 450 C
  - $4CuCl \rightarrow 2CuCl_2 + 2Cu$ 25 C
  - **$2CuCl_2(s) + H_2O(g) \rightarrow CuO•CuCl_2\ (s) + 2HCl(g)$ 400 C**
  - $CuO•CuCl_2$ (s) $\rightarrow 2CuCl(l) + ½O_2(g)$ 550 C
- Hybrid Cl - Clemson University - 34%
  - **Cl2(g) + H2O (g) = 2HCl (g) + ½O2 (g) 850 C**
  - 2HCl (g) = H2(g) + Cl2(g) 75 C
- Cu-SO_4 Tulane University - 52%
  - **CuO + SO2 (g) + H2O = Cu SO4 + H2 (g) 25 C**
  - CuSO4 = CuO + SO2 (g) + ½O2 (g) 850 C

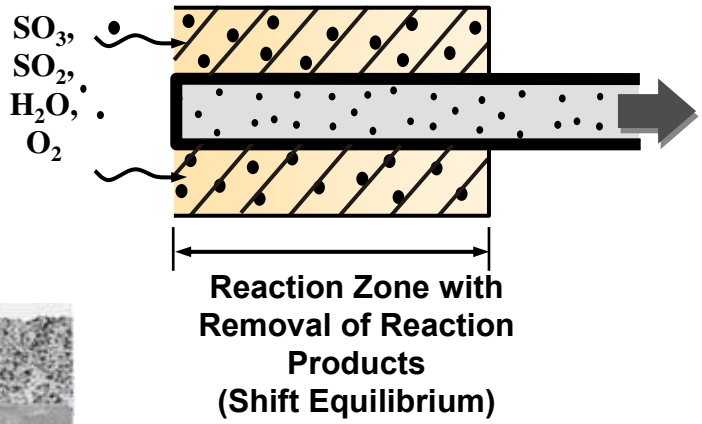
Key Enabling Technical Areas

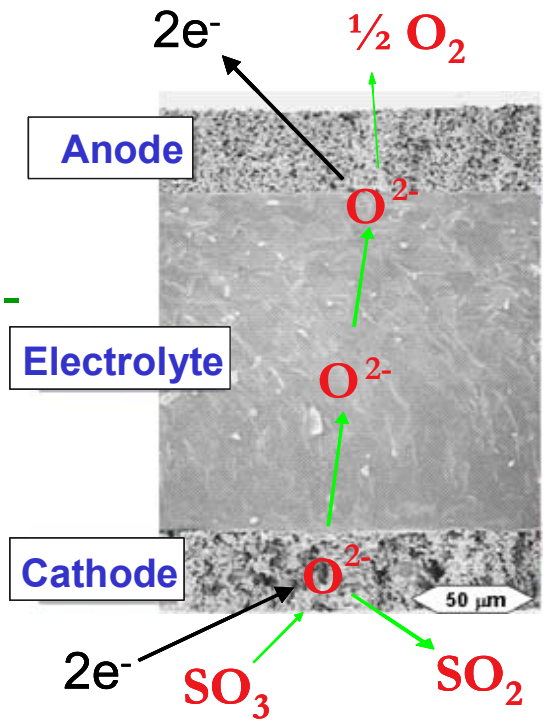
	Membranes	Catalysts	Process Analytical Chemistry*	Modeling
Efficiency	●	●		●
Conversion	●	●		●
Side rxtns	●		●	●
Toxicity			●	●
Durability		●	●	
Separation	●			●
Temp	●	●		●

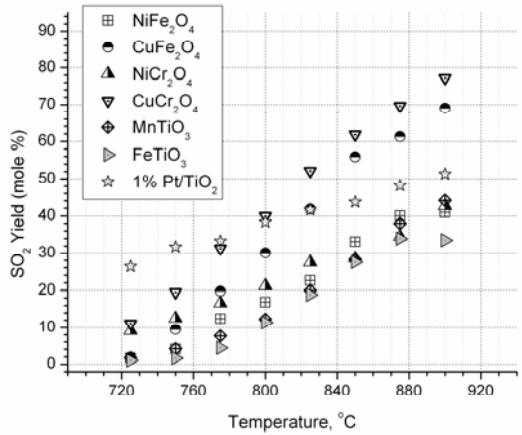
***Enables a Data Driven Approach**

Supporting Technology Activities

- Membranes – high temperature inorganic membranes for acid decomposition (ORNL)
- SO_3 decomposition - electrolysis (ANL)
- Membranes for water separation (INL)
- Acid decomposition - catalysts (INL)







FY07 Thermochemical Systems Overview

- *FY07 Technical Objectives*
  - *S-I ILS NHI skids up and running*
  - *HyS electrolysis 100 hr single cell run*
  - *Alternative cycle viability determined to balance portfolio*
  - *Role of catalysis and membranes defined*
- *Key Technical Issues*
  - *Reliability/Durability:*
    - *Corrosion, Contamination*
  - *Efficiency:*
    - *Water Management, Product Separation*
    - *Lower Temperature Operation*
  - *Deployment Options:*
    - *Identify low temperature systems*