Solar High-Temperature Water Splitting Cycle with Quantum Boost

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San Diego, California

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PD027

Overview

Timeline

- Start date: 09/01/2007
- End date: 8/31/2014
- Percent complete: 45%

Budget

- Total project funding
  - DOE share: $4M
  - Contractor share: $1M
- Funding recvd. in FY10: $500k
- Funding for FY11:

  $892k - planned

  $150k - rec'd to-date

Barriers

U. High-Temperature Thermochemical Technology

V. High-Temperature Robust Materials

W. Concentrated Solar Energy Capital Cost

X. Coupling Concentrated Solar Energy & Thermochemical Cycles

- **2017 H_2 Production Target: $3.00/kg**
- **2017 Cycle Efficiency Target: >35%**

Partners

- SAIC (Lead)

  Solar System/Receiver

- UCSD/TChemE

  Thermochemical Process

- Electrosynthesis

  Salt Electrolysis

Project Objectives

- RD&D of the Viability of a <u>New</u> & Improved Sulfur Family Thermochemical Water-Splitting Cycle (i.e., sulfur-ammonia, SA) for large-scale hydrogen production using <u>solar</u> energy

- More Specifically, Overall Project Goals are to:
    - Evaluate SA water-splitting cycles that employ photocatalytic or electrolytic hydrogen evolution steps and perform lab testing to demonstrate feasibility of the chemistry
    - Perform economic analyses of SA cycles as they evolve
    - Select a cycle that has high potential for meeting the DOE 2017 cost target of $3/kg hydrogen and efficiency goal of >35%
    - Demonstrate technical feasibility of the selected SA cycle in bench-scale, closed-loop tests
    - Demonstrate pre-commercial feasibility by testing and evaluation of a fully-integrated pilot-scale closed-cycle solar hydrogen production plant

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Past Year Project Objectives

- Perform Thermodynamic Analysis of Overall SA Cycle

- Electrolytic Hydrogen Production Advancement
  - Reduce cell voltage below 1 volt by increasing temperature/pressure, controlling pH, improving cell design
  - Investigate catalysts to reduce the over-potential and increase current density

- Begin Oxygen Production Sub-Cycle Evaluation
  - Determine if an all liquid K_2SO_4 sub-cycle is feasible

- Perform H2A economic analyses of modified SA cycles
  - Electrolytic H_2 production and K_2SO_4 oxygen production sub-cycles

- Perform Solar Concentrating System and Receiver Evaluations to Ensure Feasible, Efficient and Cost Effective Interface with the Modified SA Cycles

Impact on Program Barriers

- <u>U. High-Temperature Thermochemical Technology</u> – This project is developing a new thermochemical cycle intended to operate at lower temperatures and be more cost effective than other cycles

- <u>V. High-Temperature Robust Materials</u> – Materials able to operate in the high temperatures and caustic environment of the receivers and reactors are being developed.

- <u>W. Concentrated Solar Energy Capital Cost</u> –System costs are being reduced by optimizing the solar-chemical plant interface

- <u>X. Coupling Concentrated Solar Energy & Thermochemical Cycles</u> – The solar field and receivers are being evaluated and designed to provide appropriate amounts of energy at necessary temperature levels and with appropriate controls

Approach

- Develop an Improved Sulfur-family Thermochemical Water-Splitting Cycle with Fewer Phenomenological Hurdles
- Conduct Laboratory Evaluation of all Processes within the Cycle
- Develop Comprehensive Aspen Plus® Flowsheet(s) of the Cycle and Modifications
- Perform H2A Analysis of the Flowsheeted Cycle(s) to Compare Design and Operational Approaches
- Design a Solar Collector Field and Receivers to Complement Chemical Process and Maximize Solar/System Efficiency
- Refine Process with Improvements Suggested by Lab Testing, Solar Configuration Studies, and H2A/Aspen Plus Analyses
- Perform Bench-Scale On-Sun Testing of Individual Chemical Processes, then Integrated Pilot-Scale Testing

Milestones

Past Milestones
- Experimentally validated all reaction steps for the SA cycle
    - Photocatalytic H_2 production step
    - High-temperature step with zinc sulfate sub-cycle
    - Electrolytic H_2 production step
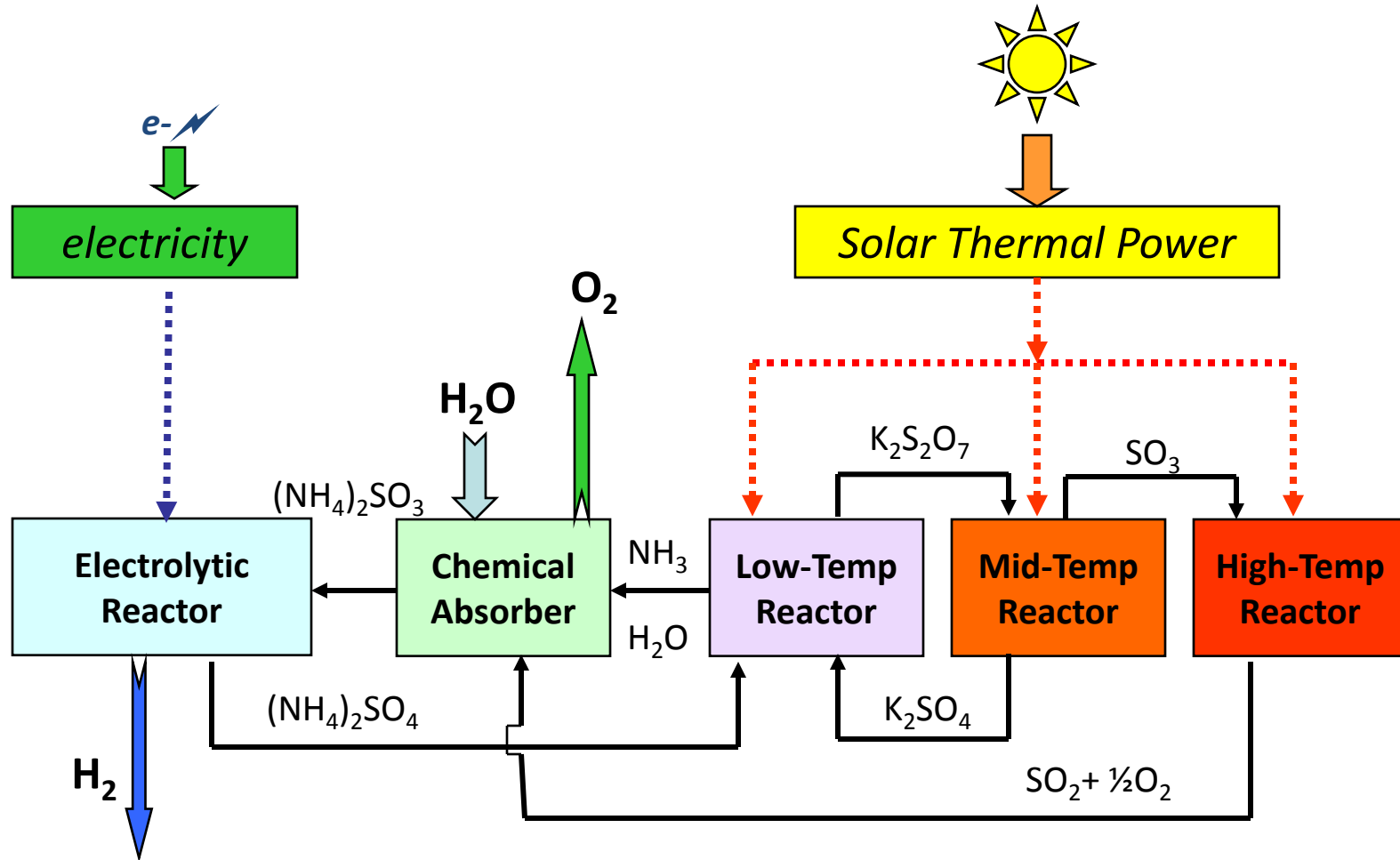- Conceptual design of solar concentrating system (central receiver) to match chemical system

Current 2011 Milestones
- Confirm thermodynamic viability of overall SA cycle - *Complete*
- Electrolytic H_2 production step optimization – *50% complete*
- All-liquid O_2 production step validation - *20% complete*
- Update solar concentrating system to match chemistry – *40% complete*

2011 Go/No-Go Decision Points
- Prove the viability of overall SA cycle, with no show stoppers
- Electrolytic cell with current efficiency >90%, voltage 0.5-0.8V, current density 3-5 kA/m^2, 500 + hour operation
- Thermodynamic and chemical plant analyses show the cycle can be closed and conversion yields for the O_2 production step are 90% + for all high temperature reactions

Electrolytic SA Process

e-

electricity

Solar Thermal Power

O_2

H_2O

$(NH_4)_2SO_3$

$K_2S_2O_7$

SO_3

Electrolytic Reactor

Chemical Absorber

NH_3

Low-Temp Reactor

Mid-Temp Reactor

High-Temp Reactor

H_2O

$(NH_4)_2SO_4$

K_2SO_4

H_2

$SO_2 + \frac{1}{2}O_2$

Thermodynamic Analyses

- Independent thermodynamic and chemical plant analyses show the cycle can be closed and indicates cycle viability

- Unoptimized flowsheet gives 32% of Second Law efficiency for production of hydrogen + export electricity
  - Electrical production could support up to 1.2 Volt electrolysis
  - Assuming 35% electrical production efficiency

- Optimized flowsheet will reduce excess electricity generation and increase hydrogen production

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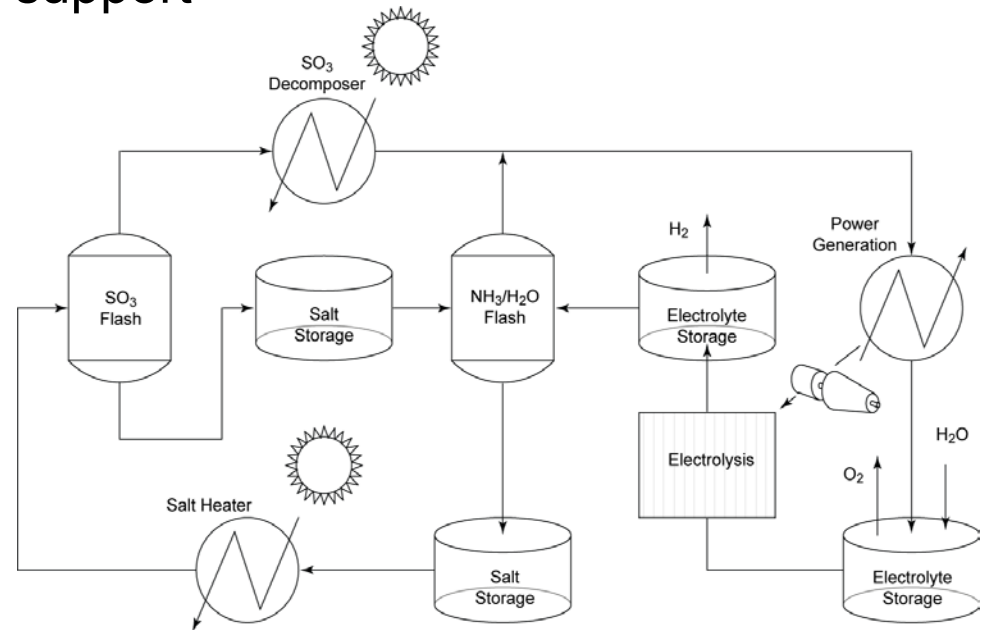
Electrolysis Progress

- New catalysts and electrode materials have been screened at 80°C. Promising materials include spinels $M_xN_{3-x}O_4$ (where M,N=Fe/Ni/Co), Pt/Co and alternate felts

- Quantitative hydrogen production with efficient sulfite oxidation has been verified with divided cells

- Undivided cell likely not possible at high temperatures as the present cathode structure becomes inefficient, with reduction of sulfite competing with hydrogen production

Voltage of electrolytic cell has been reduced at 80°C to levels similar to those previously demonstrated at 130°C

The most promising materials are being tested at higher temperatures and pressure

Initial tests on felt electrodes show 70 - 130 mV improvement @ 300 mA/cm^2 for every 10°C increase

Effect of Anode Material
**Current Density versus Cell Voltage**

- Felt A, 80oC
- Felt B, 80oC
- Electrodepsoited Pt/Co on FeltA, 80oC
- Felt A, 130oC

130°C   80°C   80°C

NRE212 MEA
Anolyte: 2 M $(NH_4)_2SO_3$
Catholyte: 0.1 M NH_4OH

Current Density (mA/cm^2) vs Cell Voltage (V)

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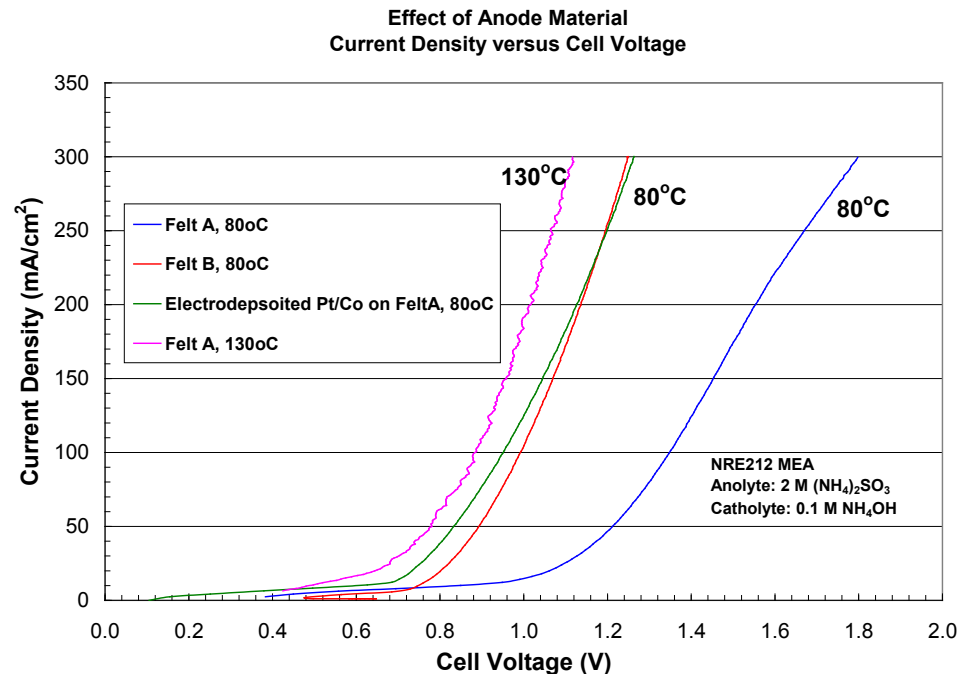
Electrolysis Progress

- High temperatures require operation at high pressures
- Pressure reactor now built, capable of 150 psi and 260°C

Anolyte
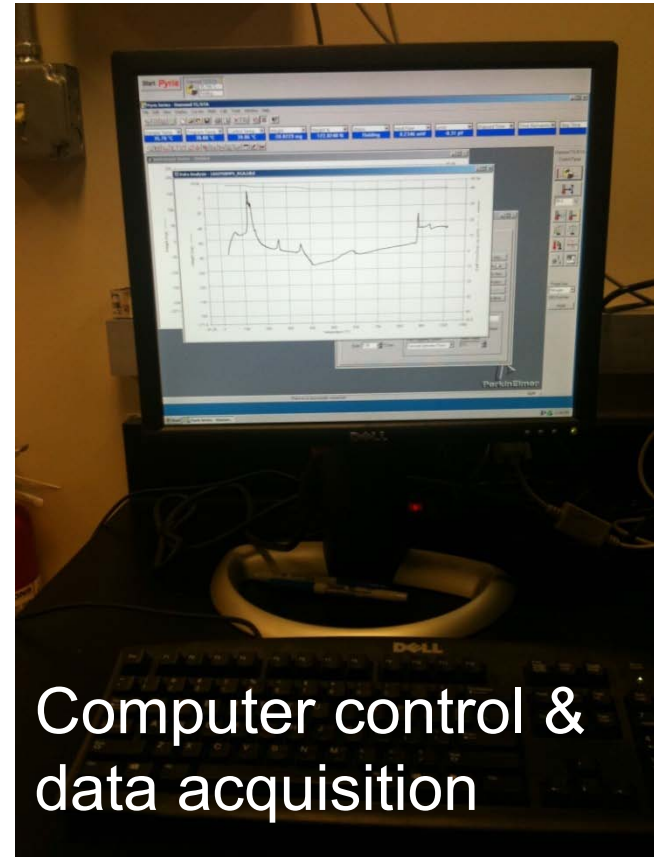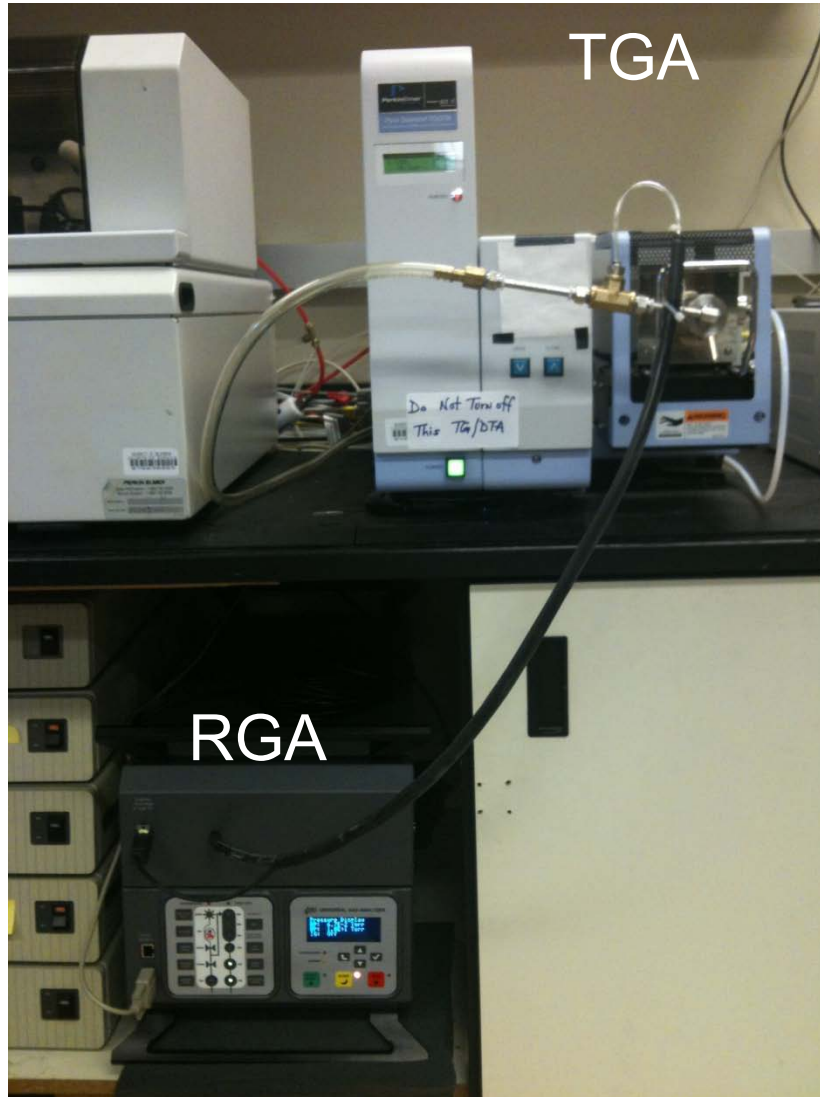
Catholyte

Cell Housing
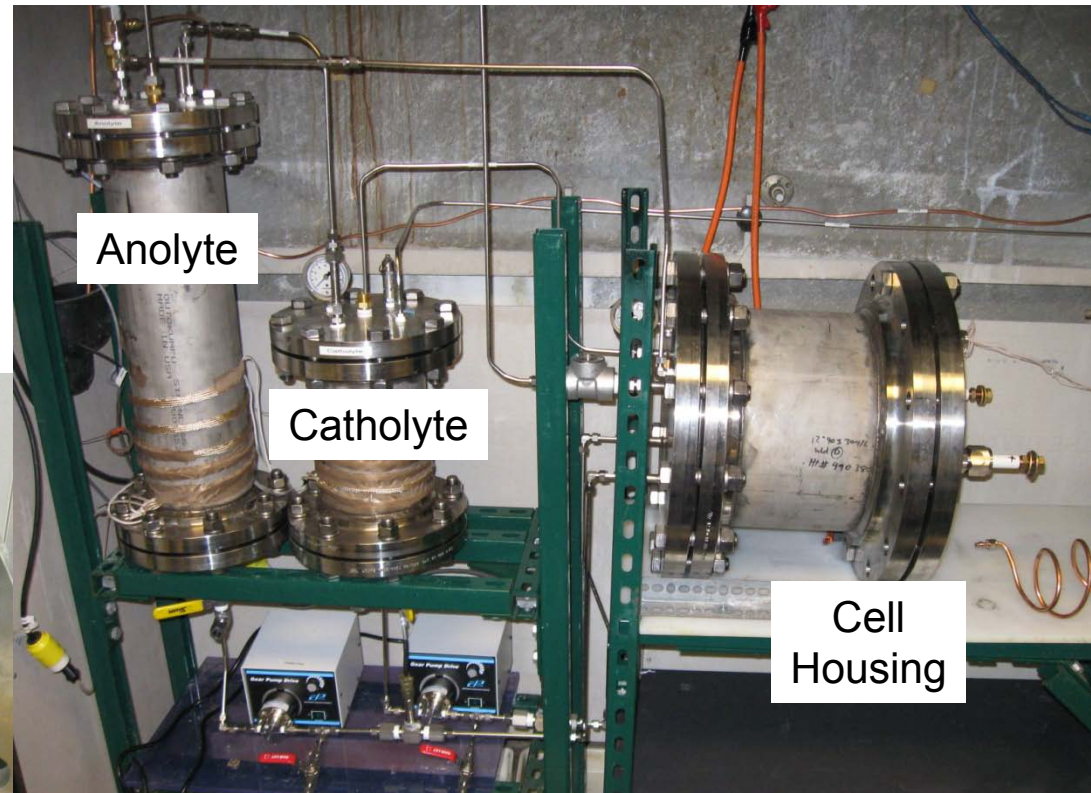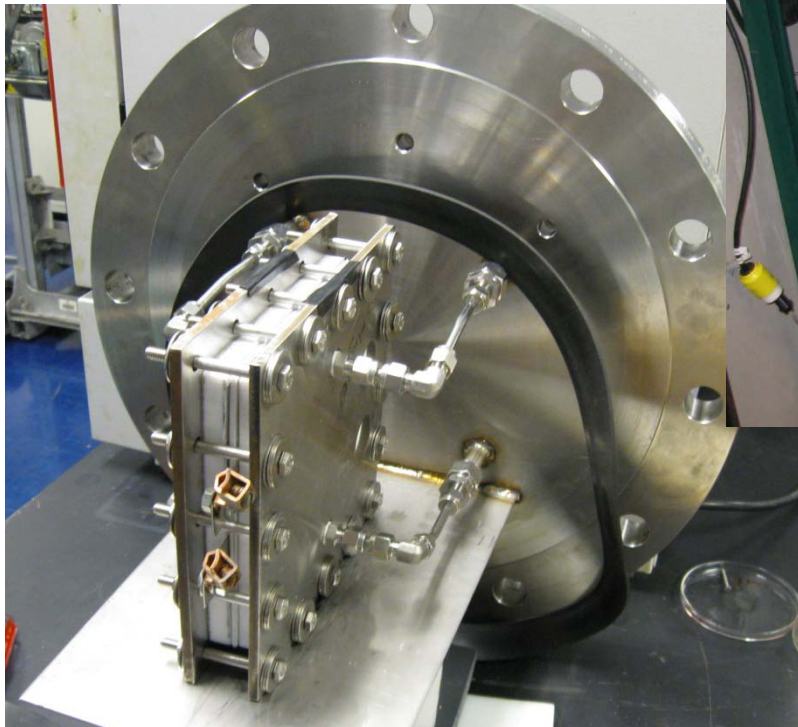
New 180 cm^2 cell designed and built, capable of ~25 L/hr H$_2$ production @54A (300 mA/cm^2)

Oxygen Generation Half-Cycle

- The All-Fluid high-temperature sub-cycle using potassium sulfate-potassium pyrosulfate appears feasible, but additional laboratory testing is needed
- Thermogravimetric (TGA) and Residual Gas Analysis (RGA) equipment is set up at UCSD and producing preliminary results
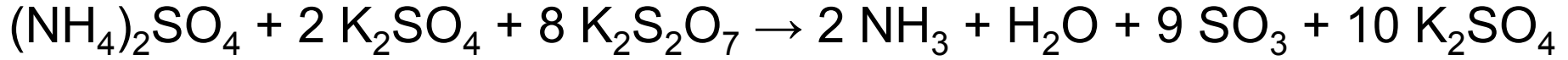

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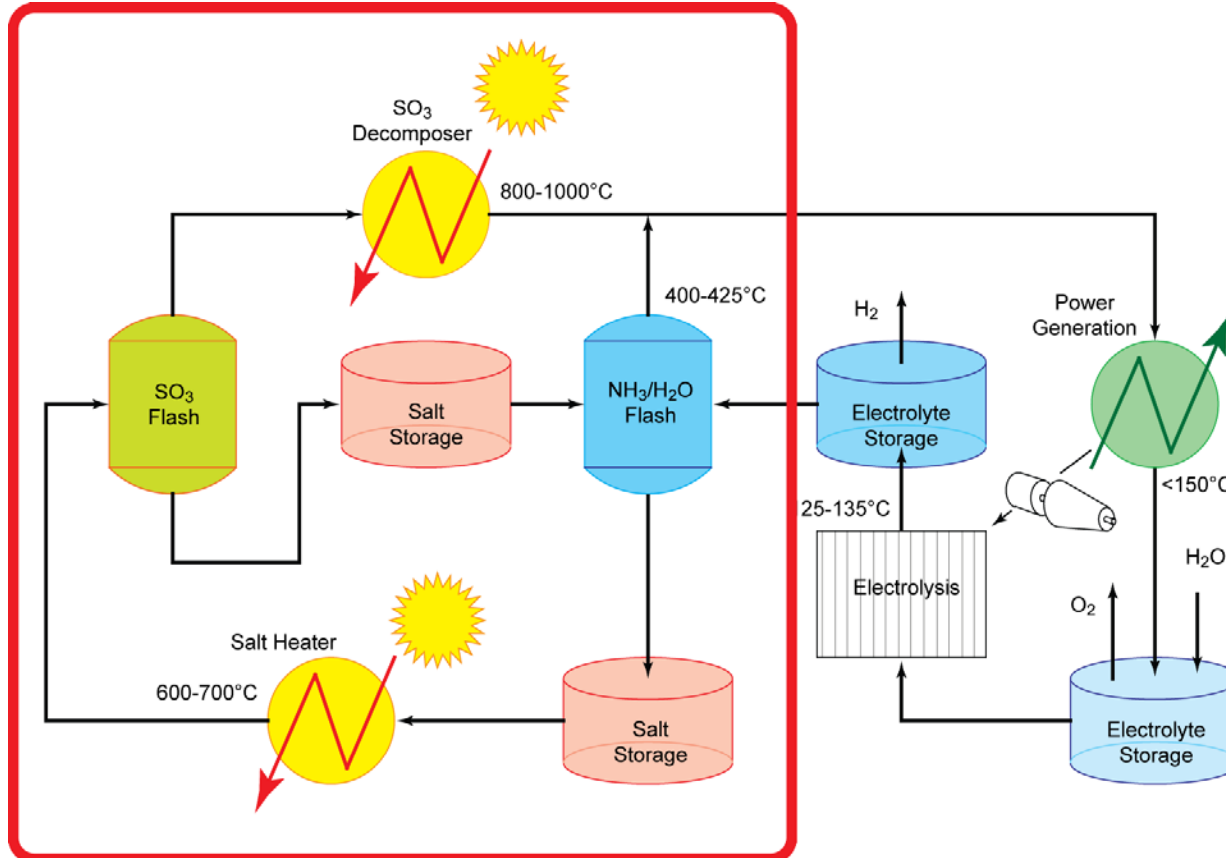
Thermogravimetric Analysis (TGA) and Residual Gas Analyzer (RGA) Set-up at UCSD
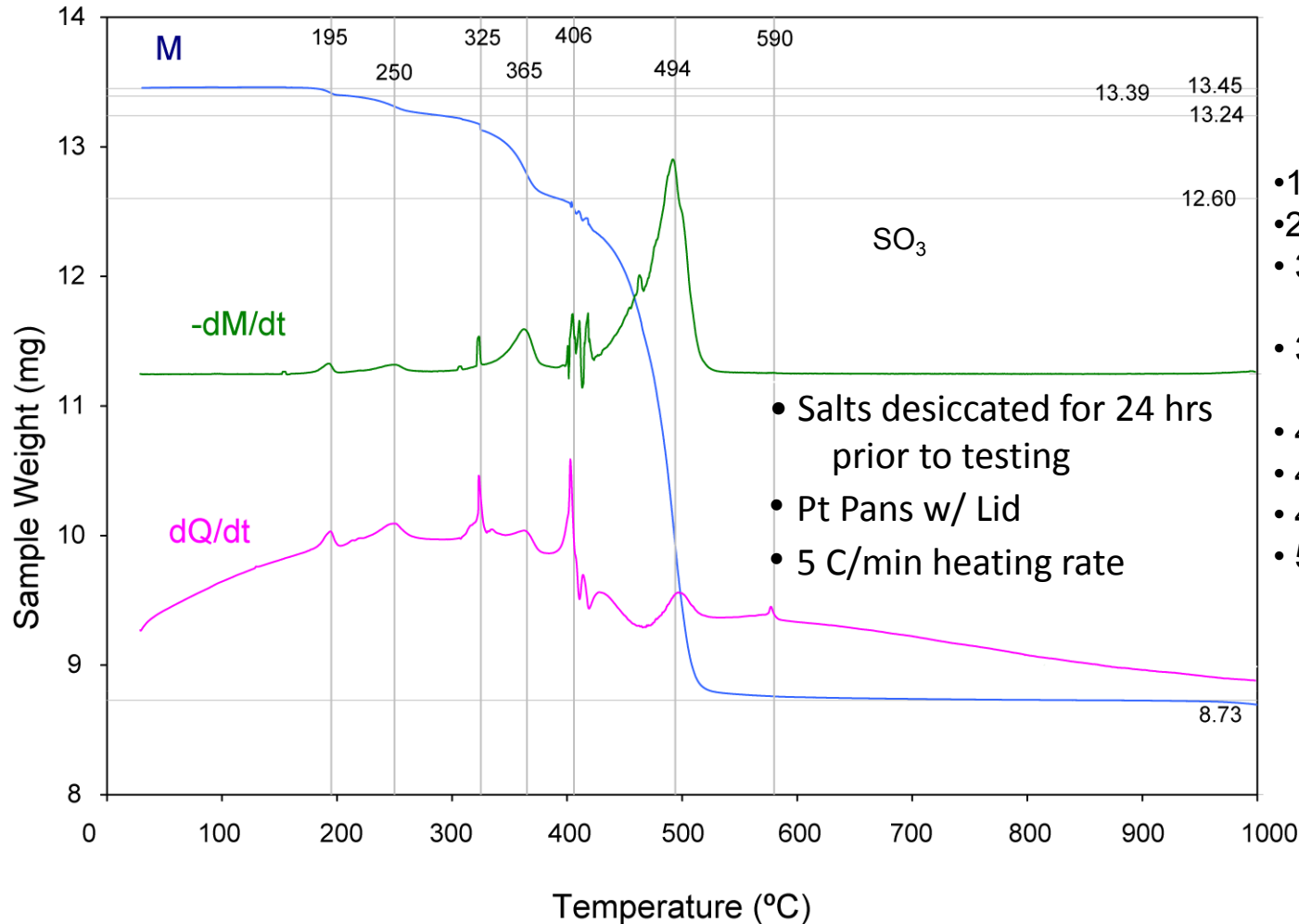
TGA

RGA

Computer control & data acquisition

TGA/DTA Analysis of:

$$(NH_4)_2SO_4 + 2\ K_2SO_4 + 8\ K_2S_2O_7 \rightarrow 2\ NH_3 + H_2O + 9\ SO_3 + 10\ K_2SO_4$$

Note: Extent of reaction is limited in process to production of one mole of SO_3

- 189ºC desorbed water
- 250ºC desorbed water
- 325ºC $K_2S_2O_7$ solid phase change
- 365ºC NH_3+H_2O gas production
- 406ºC $K_2S_2O_7$ melting
- 460ºC K_2SO_4 solidification
- 496ºC SO_3 gas production
- 590ºC K_2SO_4 solid phase change

- Salts desiccated for 24 hrs prior to testing
- Pt Pans w/ Lid
- 5 C/min heating rate

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Modeling and Economic Analysis

- ## Aspen Plus Process Analysis
  - Aspen Plus system model was developed by UCSD and is being refined based on lab results and additional data

- ## H2A Economic Analysis
  - Results were delivered to TIAX and discrepancies were adjusted to agree with other teams
    - 2015 estimated hydrogen cost: $7.74/kg
    - 2025 estimated hydrogen cost: $4.65/kg
  - The results assume no credit for excess electrical production. The process is being optimized to eliminate excess electrical production
  - Process is being optimized to improve efficiency and thus reduce cost

Solar Field Development

- Solar Field Design and Analysis
  - SAIC Heliostat field model has been extended with storage features for performing conceptual design studies
  - Molten salt storage makes 24/7 operation of the ammonia reactions feasible
  - For the H2A analysis, a solar field based on the Sandia design used by other teams has been used to ensure comparability

- Reactor/Receiver Design
  - SAIC is developing concepts for a high-temperature SO_3 decomposition reactor/receiver to allow 24/7 operation of the high-temperature system

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Molten Salt SO_3 Absorber Facilitates 24/7 Hydrogen Production

- Molten salt used to absorb SO_3 from electrolyzer product also acts as thermal storage media

- Sufficient heat is stored to generate all electrical requirements 24/7

- Hydrogen is generated "round-the-clock"

- SO_3 is stripped from salt and oxygen is generated during daylight hours

- Electrolyte storage complements salt storage

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Project Partners & Key Personnel

Science Applications International Corp. (SAIC)– Prime (Industry)
- Key Personnel: Rob Taylor, Roger Davenport
- Project management & system integration
- Solar concentrator/receiver evaluation & design
- Thermal reactor optimization & design
- Economic evaluation & hydrogen production cost estimates

University of California, San Diego (UCSD) – Sub (Academia)
- Key Personnel: Jan Talbot, Richard Herz
- Laboratory testing & thermochemical cycle development
- Chemical plant analysis

Thermochemical Engineering Solutions (TChemE) - Sub (Industry)
- Key Personnel: Lloyd Brown
- Thermochemical cycle evaluation & analysis

Electrosynthesis Company, Inc. – Subcontractor (Industry)
- Key Personnel: David Genders, Peter Symons
- Electrolytic cell development & optimization

FY11/FY12 Activities

- Complete Optimization of Electrolytic Oxidation Process
  - Test at higher temp (130^oC) & higher pressure regimes
  - Incorporate better catalysts that lower the over-potential at the anode & allow operation at high current densities
  - Maintain pH at anode and cathode to avoid formation of reduced sulfur species
  - Perform 500 hour durability test & cell design improvement
- Complete Evaluation of High-Temperature K_2SO_4 Sub-Cycle
  - Study phase equilibria of salt mixtures and identify favorable conditions for the process
  - evaluate salt mixtures to expand operational range
  - Optimization of process parameters and identification of side reactions and by-products
- Economic and Solar System Analysis
  - Continued Refinement of the Solar Field, Aspen Plus, and H2A Analyses to Incorporate Chemical Process Modifications
  - Evaluation of receiver materials, storage and control strategies

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Summary

- Independent Thermodynamic and Chemical Plant Analyses Indicate Cycle Viability and Show the Cycle Can Be Closed
- Electrolytic SA Cycle Step
  - Electrode and catalyst materials identified and the voltage of the electrolytic cell has been reduced to values at 80°C close to those previously obtained at 130°C (1.1V). Improved catalyst/electrodes do not yet achieve target voltage at 80°C therefore the high pressure high temperature reactor is still necessary. Cell design refinement and catalyst research are continuing.
- All-Liquid High-Temperature Oxygen Generation
  - Initial lab results prove the subcycle feasibility
  - Thermogravimetric (TGA) and Residual Gas Analysis (RGA) equipment operational and producing results at UCSD
  - Optimization of process and integration into viable solar concentrating system and receivers needs to be further evaluated
- Aspen Plus and H2A Continue to be Used to Optimize and Trade-off SA Cycle Configurations
- Solar Configuration Focus is Central Receiver System with Molten Salt Storage to Allow 24/7 Operation
- Next-Phase Program is to progress the SA Cycle to Bench-Scale On-Sun Tests

Technical Back-Up Slides

Efficiency

where

- First Law efficiency

  $$\eta = -(\Delta H^{o}_{f[H_2O]} + E)/Q$$

- Second Law efficiency

  $$\eta = -(\Delta G^{o}_{f[H_2O]} + E)/Q$$

- DOE working definition

  $$\eta = -\Delta H^{o}_{f[H_2O(g)]}/(Q + E/\eta_e)$$

η = Plant efficiency

$\Delta H^{o}_{f[H_2O]}$ = enthalpy of formation of water in standard state = -hhv

$\Delta H^{o}_{f[H_2O(g)]}$ = enthalpy of formation of water vapor in ideal gas state = -lhv

$\Delta G^{o}_{f[H_2O]}$ = Gibbs energy of formation of water in standard state

Q = Total heat input to cycle

E = Total electrical input to process or if negative the electrical output of the process

η_e = Efficiency by which consumed electricity is produced

Note: The First Law efficiency is the efficiency calculated from a heat balance around the total plant. The Second Law efficiency is the efficiency that, for a reversible process would be given by Carnot's Equation. The DOE working definition was designed to estimate the relative ranking of a cycle before the complete plant design was complete.

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Efficiency is a function of Electrical production efficiency, electrolysis voltage and decomposer temperature

Second Law Cycle Efficiency as a function of Electrolysis Voltage and Electricity Generation Efficiency from Recoverd Heat for 800°C Decomposer
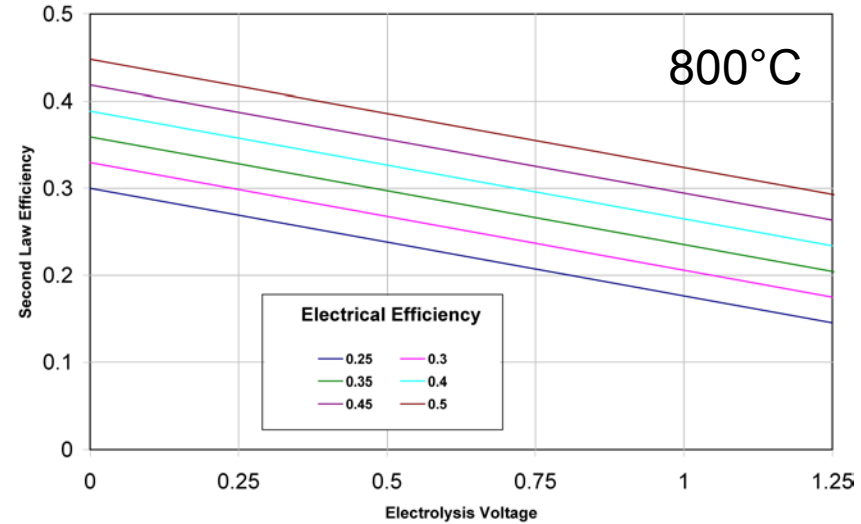
800°C

Second Law Cycle Efficiency as a function of Electrolysis Voltage and Electricity Generation Efficiency from Recoverd Heat for 900°C Decomposer
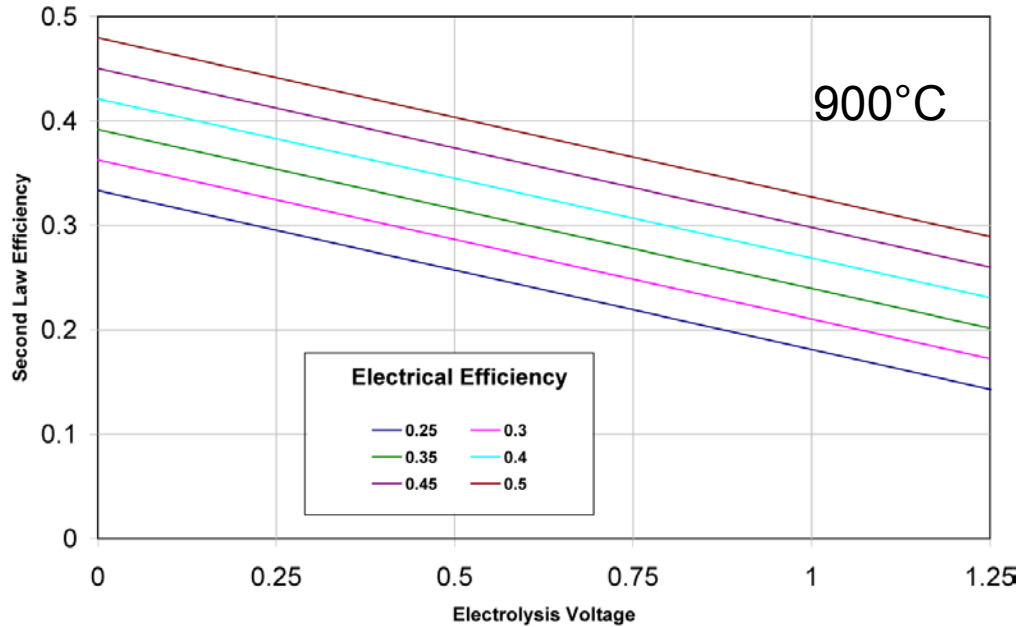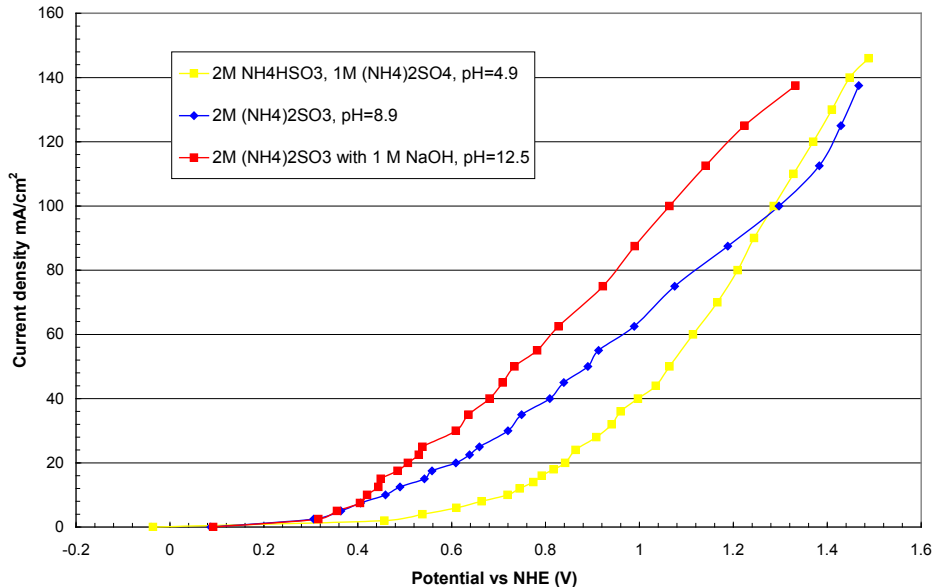
900°C

Second Law Cycle Efficiency as a function of Electrolysis Voltage and Electricity Generation Efficiency from Recoverd Heat for 1000°C Decomposer

1000°C
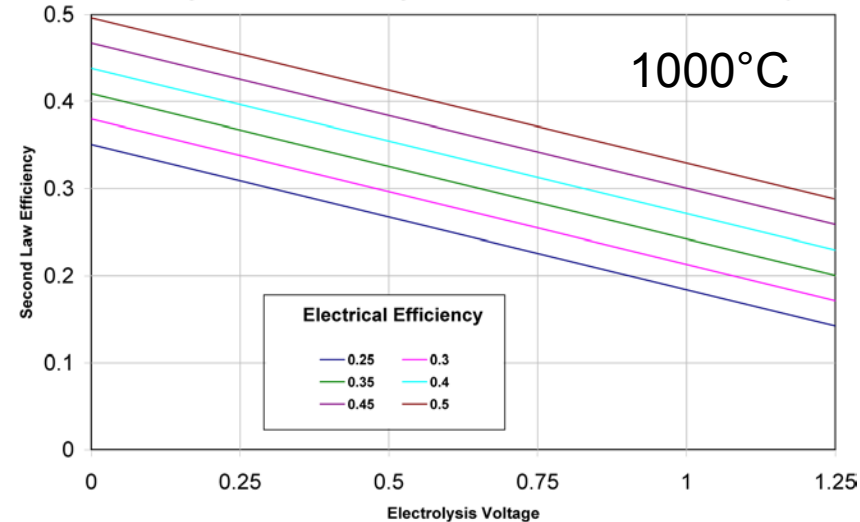
Effect of pH on Anode Overpotential/ Cell Voltage

Potential for Sulfite Oxidation on Graphite in Various Solutions.

- Oxidation is kinetically slow. Potential needed to drive current is much higher than thermodynamic potential (more than 1 V overpotential).
- Anodic oxidation of sulfite and the cathodic hydrogen evolution reaction are pH dependent.

In acidic media

- anode reaction: $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 4H^+ + 2e^-$ $E^o = 0.138$ V
- cathode reaction: $2H^+ + 2e^- \rightarrow H_2$ $E^o = 0.000$ V
- overall: $SO_2 + 2H_2O \rightarrow SO_4^{2-} + 2 H^+ + H_2$ $E^o cell = -0.138$ V

In basic media

- anode reaction: $SO_3^{2-} + 2OH^- \rightarrow SO_4^{2-} + H_2O + 2e^-$ $E^o = -0.936$ V
- cathode reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ $E^o = -0.828$ V
- overall: $SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + H_2$ $E^o cell = 0.108$ V

Salt Storage Improves Operation Flexibility

Higher temperature salt provides more electricity

Electrolyte storage Compliments salt storage

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