SRNL-STI-2019-00115

Savannah River National Laboratory™

OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

Hybrid Electrical/Thermal Hydrogen Production Process Integrated with a Molten Salt Reactor Nuclear Power Plant

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Project ID# H2026

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Overview

Timeline

Start: July 1, 2018

End: June 30, 2020

Barriers

A. Hydrogen Levelized Cost
B. System Energy Efficiency
C. Total Capital Investment

Budget

Total Center Funding:

DOE Share:	$ 525,000
DOE Share Expended: *(as of 1/1/19)*	$ 259,000
Cost Share:	$ 525,000

Partners

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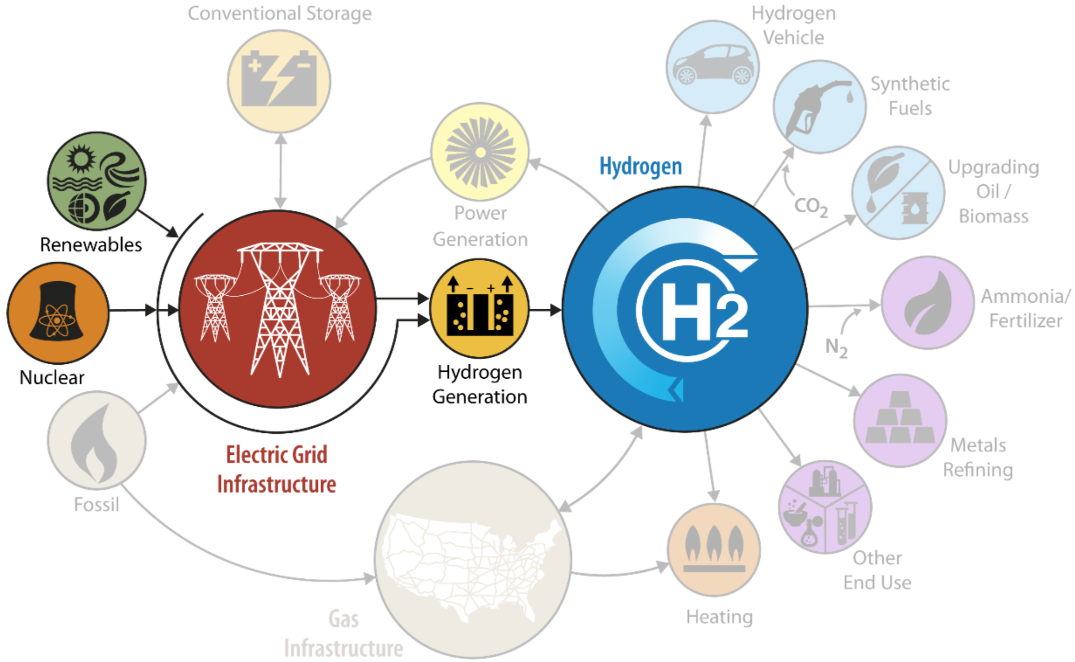
Southern Company

INL Idaho National Laboratory

Sandia National Laboratories

TERRESTRIAL ENERGY USA

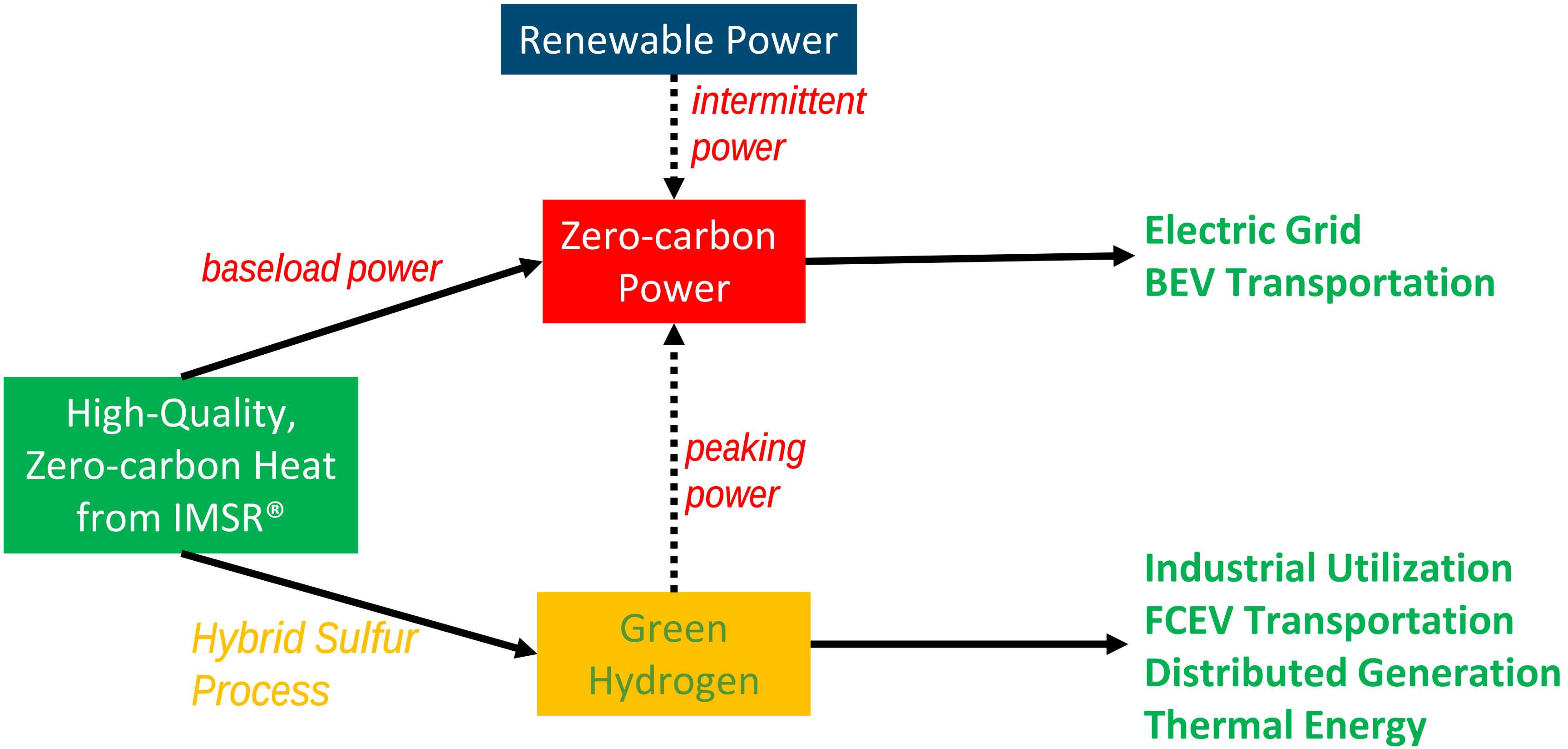
Relevance to H2@Scale



- **The Hybrid Sulfur (HyS) Hydrogen Generation process has the potential to produce hydrogen gas using both thermal and electrical energy at a cost of <$2/kg.**
- **HyS can utilize thermal energy from a Integral Molten Salt Reactor (IMSR®) along with renewable electrical energy from either wind or solar generation to efficiently produce hydrogen.**
- **The HyS process, being a two step process, can act as a buffer and store thermal energy chemically as liquid SO_2, to be used to generate hydrogen as required to minimize generation and storage costs.**

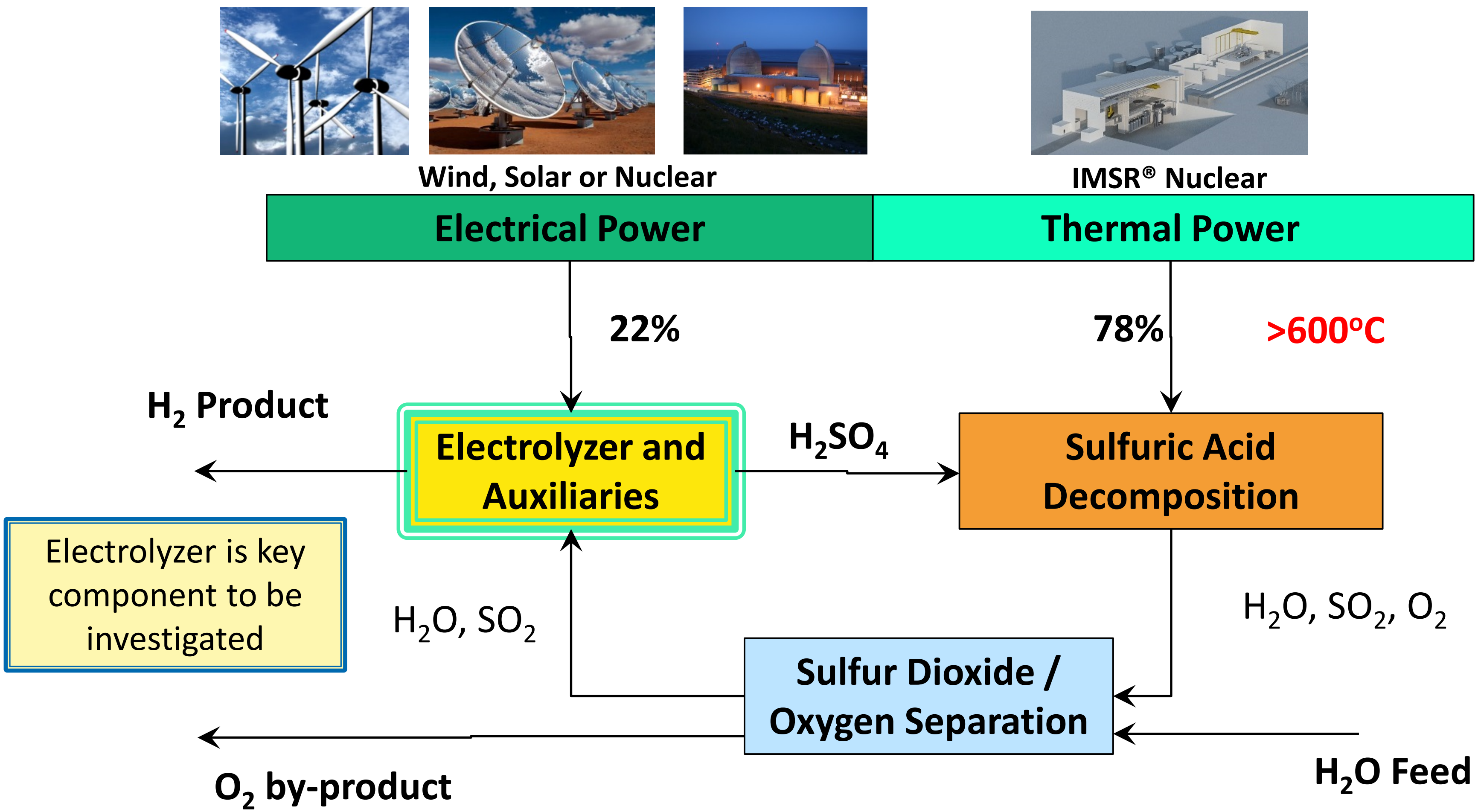
Advanced Nuclear Power + Hydrogen = Economy–wide Energy Decarbonization

Southern Company



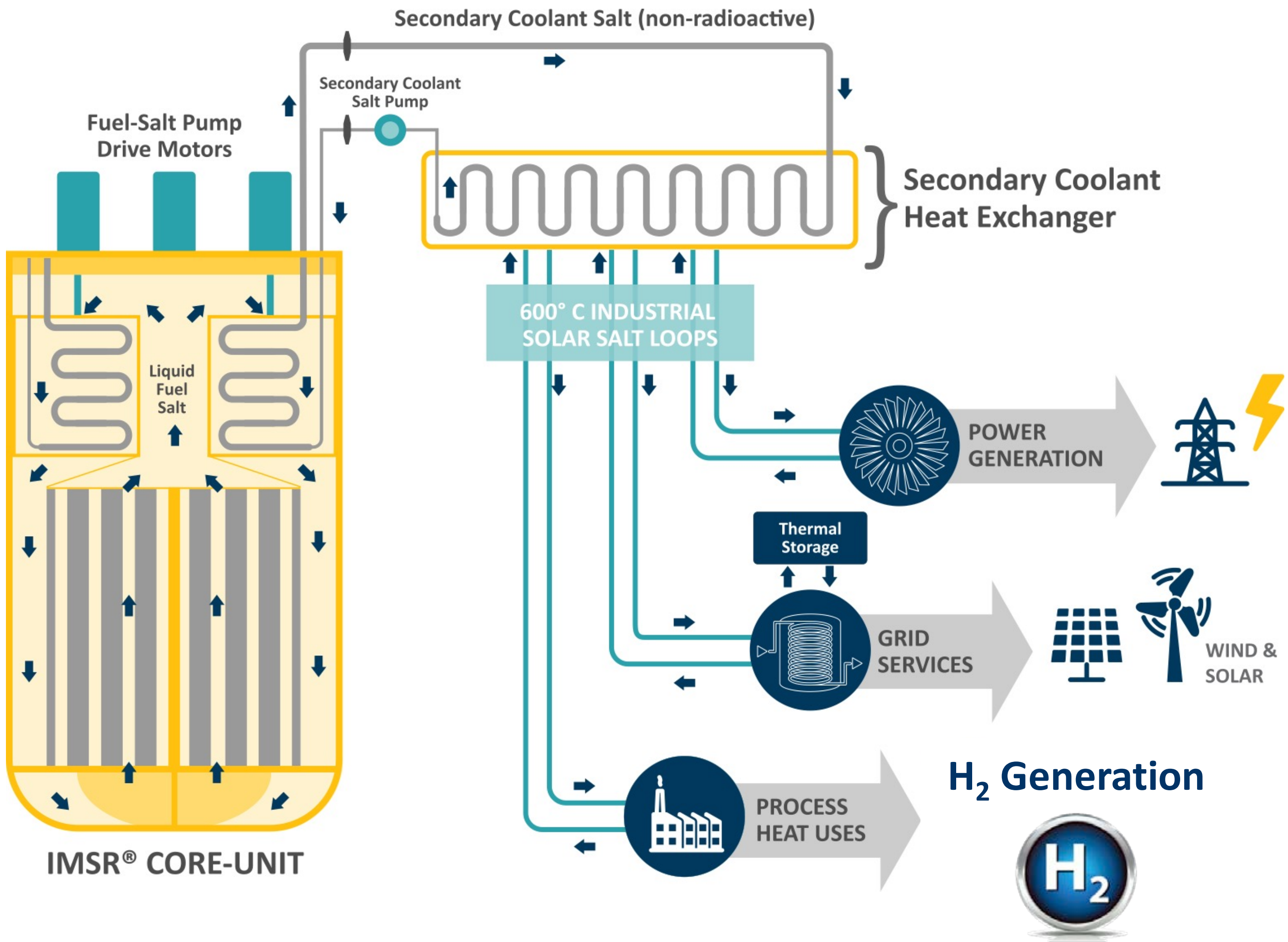
IMSR® Implementation of HyS

- **HyS is “hybrid” cycle requiring electrical and thermal energy input**
- **Optimization of the system requires trade-offs between the various components**



Integration of Hydrogen Generation with an Integral Molten Salt Reactor IMSR®

TERRESTRIAL ENERGY USA



HyS Chemistry

- **Hybrid Sulfur (HyS) is a two-step thermo-chemical cycle based on sulfur oxidation/reduction**
- **Key reaction step is electro-chemical water splitting using an SO_2 depolarized electrolyzer (SDE).**
- **All fluid processing minimizes entropic losses due to phase changes**

HyS Process

$H_2SO_4 \rightarrow H_2O + SO_2 + {}^1/_2\, O_2$	**Thermochemical:** 600-900°C
$SO_2 + 2\, H_2O \leftrightarrow H_2SO_4 + H_2$	**Electrochemical:** 0.17 v_{th} 80-140°C
$H_2O \rightarrow H_2 + {}^1/_2\, O_2$	**Net Reaction**

vs. Low Temperature Electrochemical

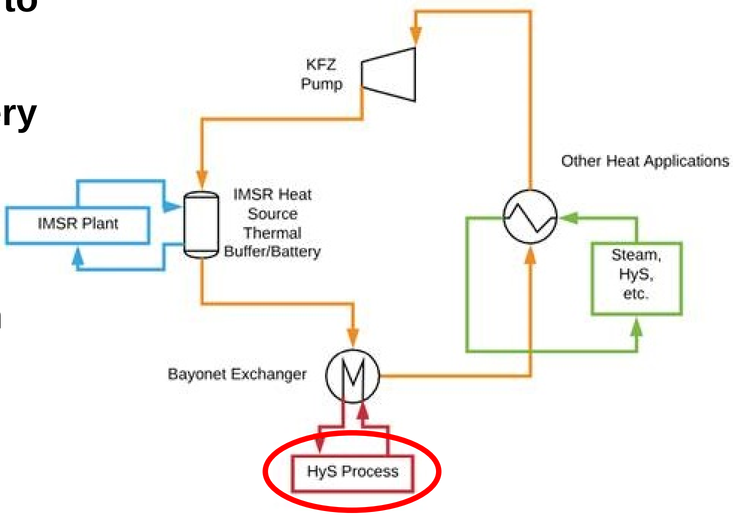
$H_2O \rightarrow H_2 + {}^1/_2\, O_2$	**Electrochemical:** 1.23 v_{th}

Approach

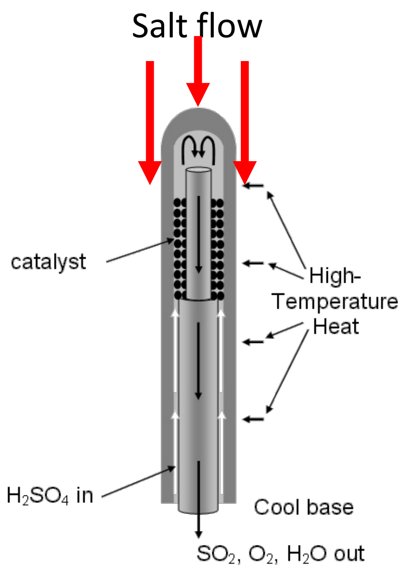
- **System Analysis**
  - Develop a plausible path to hydrogen production cost less than \$2/kgH_2 based on the process design and cost estimation.
  - Develop a conceptual plant design for MSR-HyS
  - Develop a techno-economic analysis of H_2 production via MSR-HyS
- **MEA Development**
  - Develop an SDAPP membrane composition showing better ion conductivity than Nafion®112 in 6 M sulfuric acid.
  - Develop electro-catalyst that show a 20mV performance improvement over Pt/C in 3.5M sulfuric acid solution containing dissolved sulfur dioxide or sodium sulfite
  - Demonstrate performance of at least 100mV lower cell voltage than Nafion® of an MEA using higher temperature membranes and improved catalysts.

System Analysis – Nuclear Thermal Heat Transfer

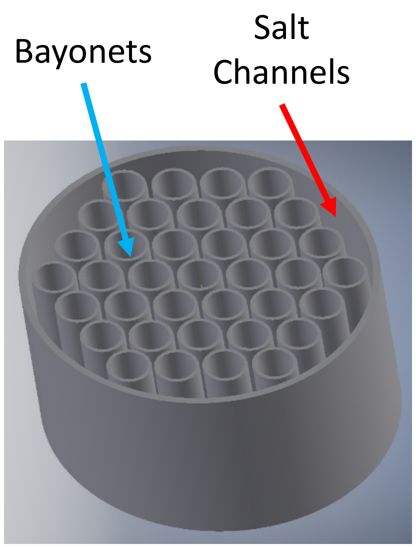
1. **Design thermal hydraulic heat delivery system in IMSR®/HyS to establish circulation pump design specifications.**
2. **Develop RELAP5-3D module to assess thermal energy delivery system from TEUSA Integral Molten Salt Reactor (IMSR®) to HyS process**
3. **The RELAP5 series of codes has been developed at Idaho National Laboratory; RELAP5-3D is the latest code version in the series including more than 25 working fluids including water, gases, liquid metals, refrigerants, and molten salts**

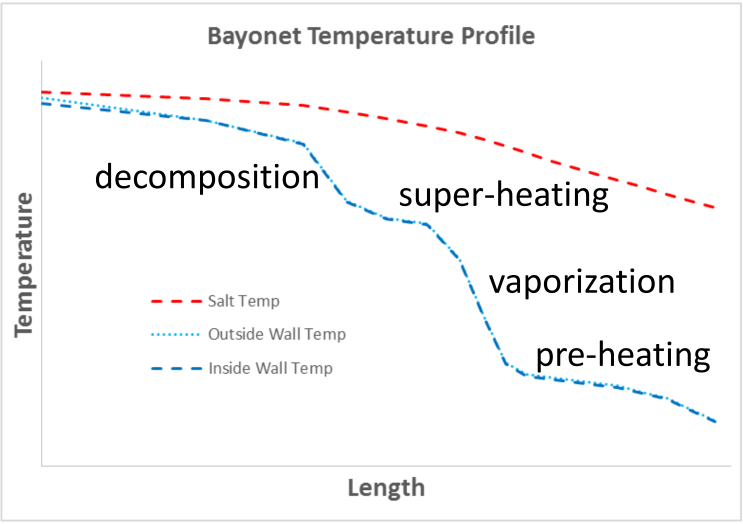


Single Bayonet



Bayonet Array





System Analysis – HyS Process

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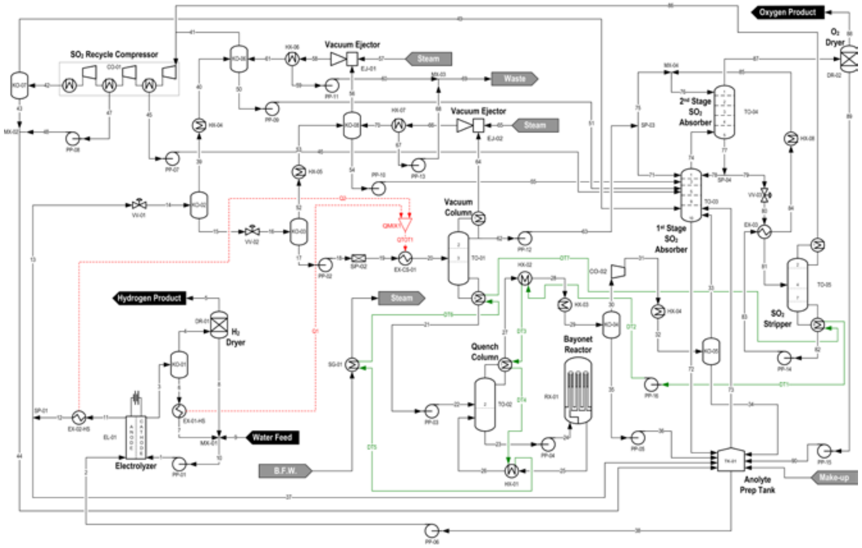
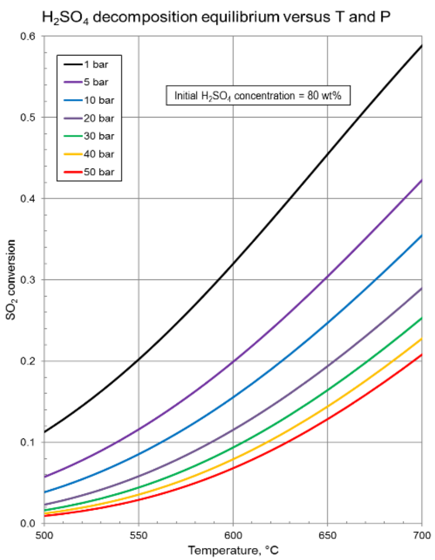
Investigate feasibility of lower acid decomposition temperature

- **675°C acid decomposition HyS flowsheet achieved 40% HHV efficiency**
- **Molten salt reactor outlet temperature ≤ 650°C flow sheet developed**
  - Acid decomposition temperature < 650°C
    - Lower per pass acid conversion
    - Higher acid recycle
  - Heat consumed by acid decomposition likely higher

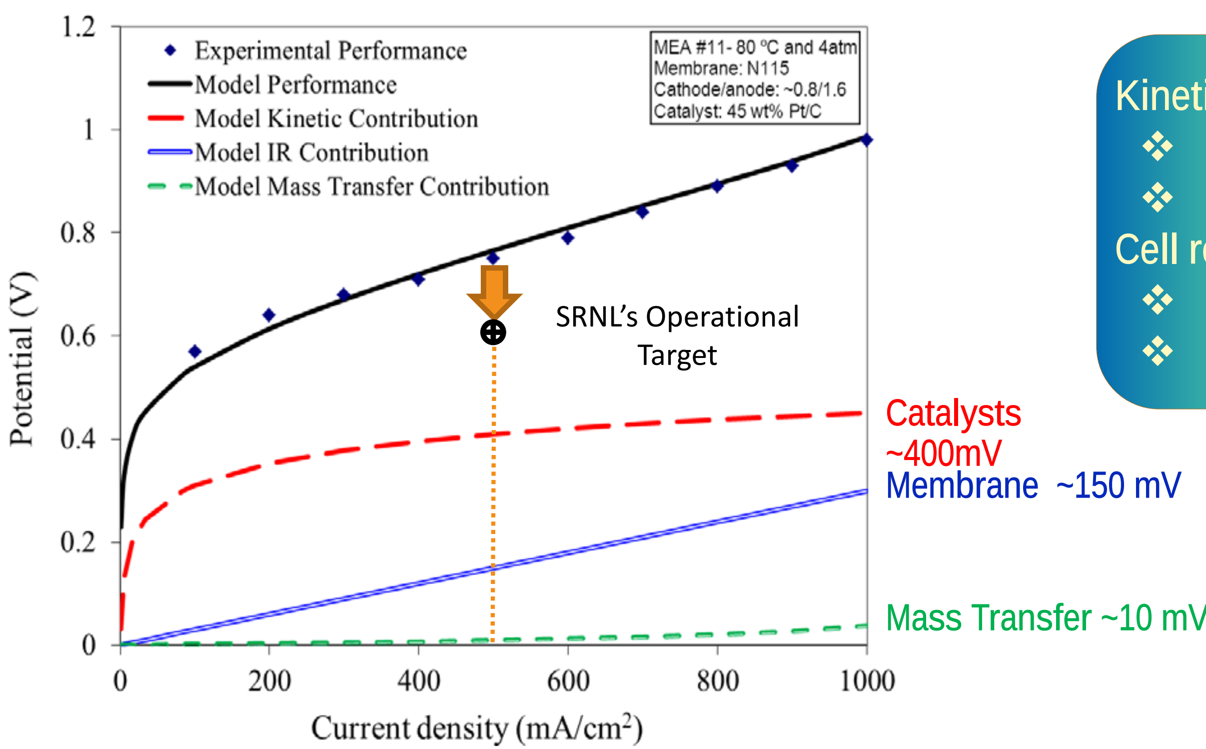


- **Recent improvements in electrolyzer technology should overcome effects of lower decomposition temperature**
  - **SDE temperature ≥ 140°C**
    - Lower cell power requirement due to reduced anodic overpotential
    - Better heat integration with acid decomposition
- **Energy efficiency > 40% HHV basis expected**



Electrochemical Cell Performance Targets

- New high temperature membranes having minimal SO_2 permeability and durability in SO_2/SO_3 environment required.
- New catalysts and supports resulting in 600mV potential at 500mA/cm2 required
- Membrane electrode Assembly (MEA) required having >10% degradation in potential after 700 hrs. operation.



Kinetics (catalyst)
- ↑ Operating temperature
- ↑ Intrinsic higher activity

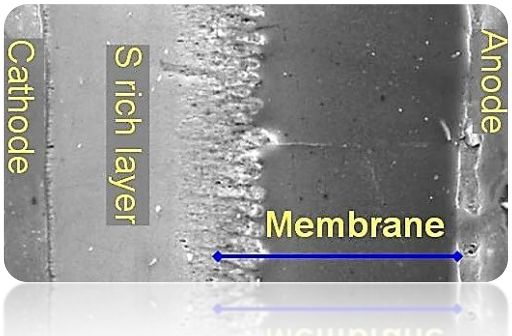
Cell resistance (membrane)
- ↑ Operating temperature
- ↑ ionic conductivity

Electrochemical Cell Component Development

Membrane

- Improve ionic conductivity and stability at high acid concentrations and temperatures
- Prevent sulfur formation at the cathode
  - Limit or eliminate formation H_2S and SO_2 reactants*
- Utilize membranes with low SO_2 permeability

$$2H_2S + SO_2 \rightarrow {}^{3}/_{8}S_8 + 2H_2O$$



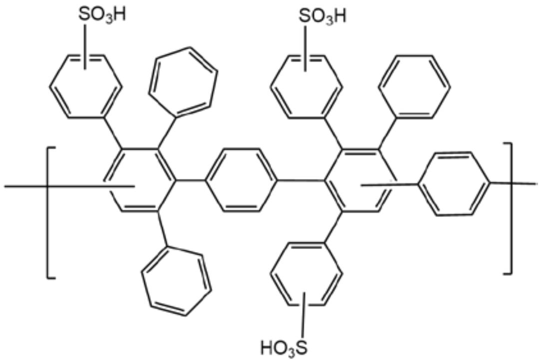
*Steimke JL, Steeper TJ, Herman DT; Savannah River Nuclear Solutions, LLC, assignee. "Method to prevent sulfur accumulation in membrane electrode assembly." US patent No. 8,709,229 B2. April 29, 2014.

Electro-catalyst

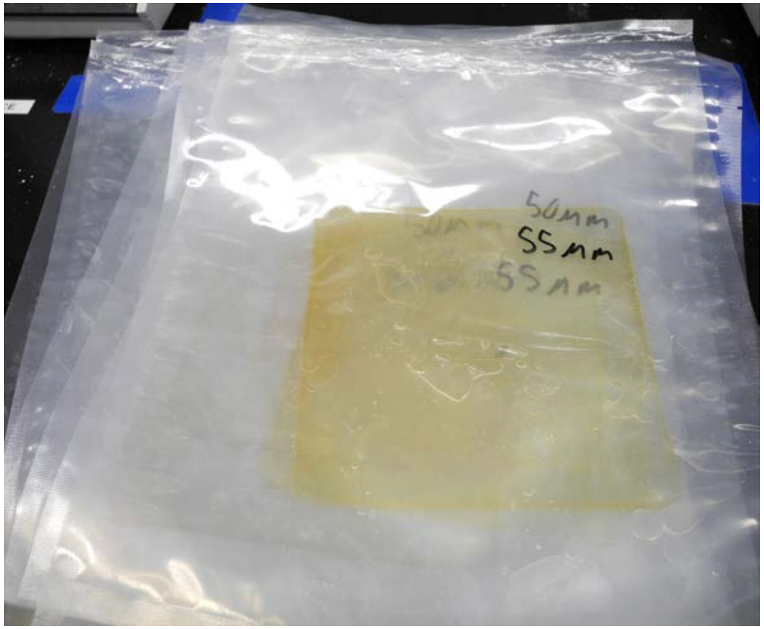
- Maximize reaction kinetics of the anode towards the sulfur dioxide oxidation
  - Minimize use of PGM
  - Minimize size of electrolyzer
- Maximize catalyst stability
- Minimize cathode reactivity towards SO_2 through catalyst selection

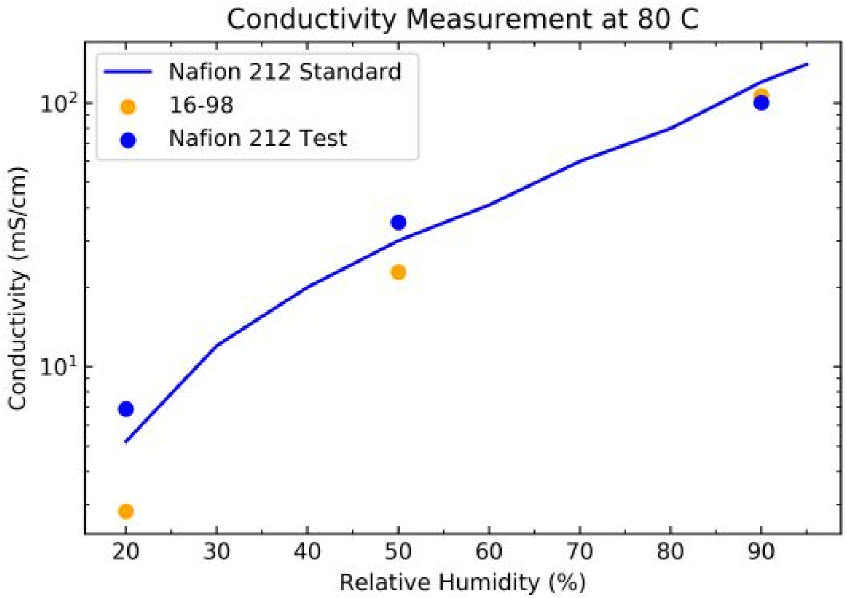
Sandia SPP Membrane

- Measured IEC 3.0 meq/g
- Water uptake 81%
- Conductivity similar to Nafion212
- Cast six films and shipped to SRNL for testing
- Preparing alternate acid content films to optimize MEA performance

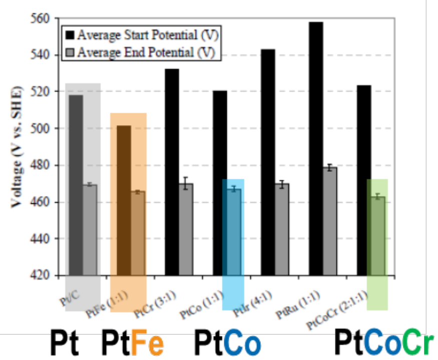


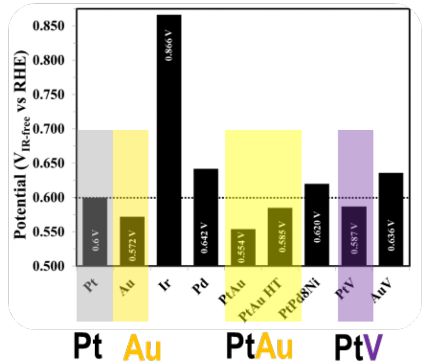
sulfonated poly(phenylene)



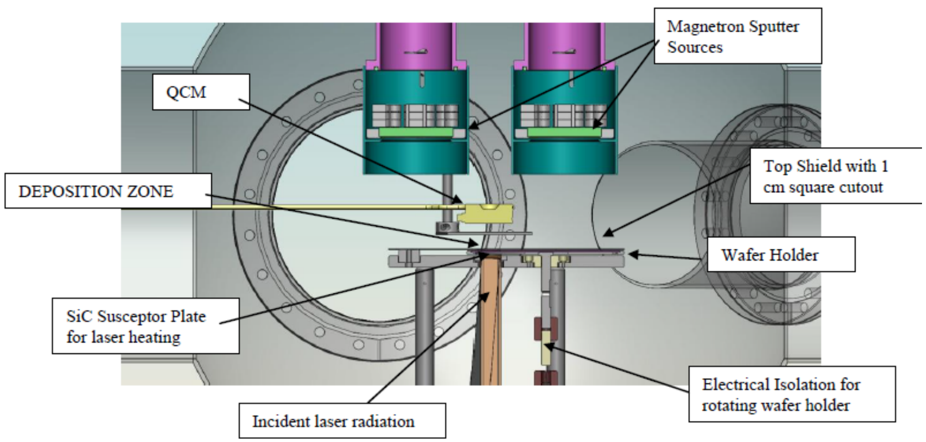


High-Throughput Catalyst Development

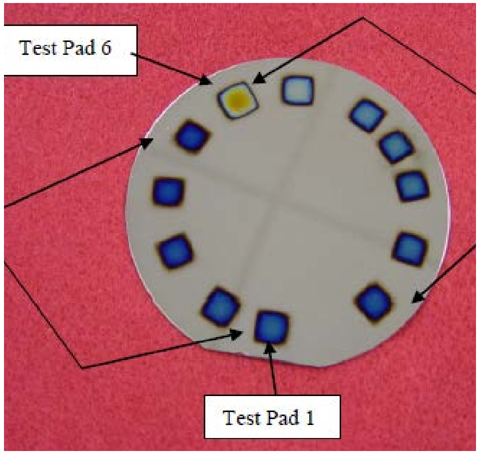




- Au, PtAu, and PtV performed better than Pt for SO_2 oxidation on individually sputtered samples[1]
- Other transition metals enhanced reactivity of Pt[1]
- Need to investigate full range of compositions for PtAuM (M = transition metal)
- Combinatorial methodology needed to span wide compositional space



Multi-magnetron shutter system for fabrication of combinatorial catalyst compositions



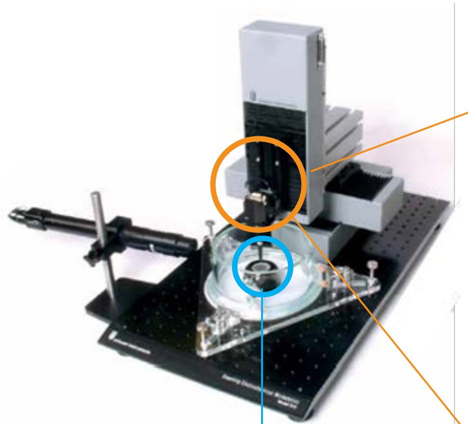
Substrate and catalyst patch each having a uniform but varying composition

- Synthesize many different compositions on one test pad
- Map composition by EDS or XPS; crystal orientations from XRD
- Measure activity of thin films in model solutions; correlate to composition

Rapid catalyst optimization

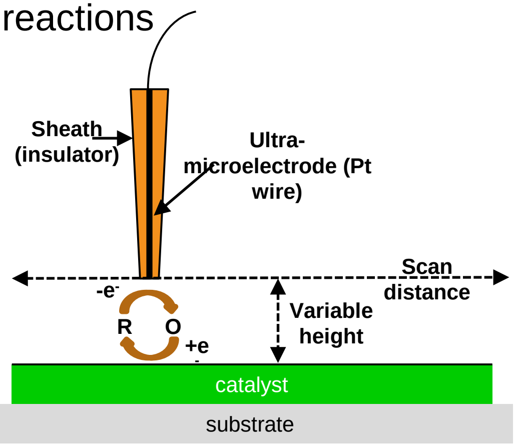
1. Colon-Mercado, H.; Elvington, M.; Hobbs, D. *CLOSE-OUT REPORT FOR HYS ELECTROLYZER COMPONENT DEVELOPMENT WORK AT SAVANNAH RIVER NATIONAL LABORATORY*; SRNL-STI-2010-00019, SRS: 2010.

High-Throughput Electrochemical Analysis

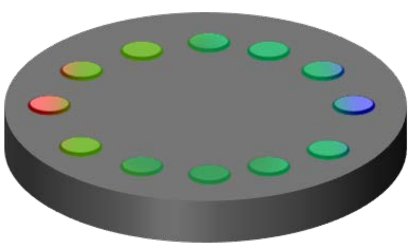


Uniscan Instruments Model 370 Scanning Electrochemical Workstation

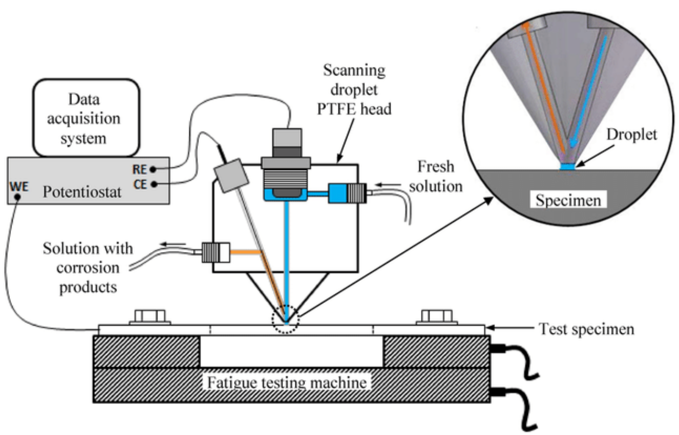
SECM ultramicroelectrode probe for reversible redox reactions



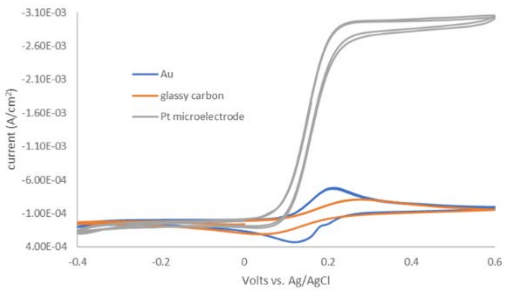
Sample



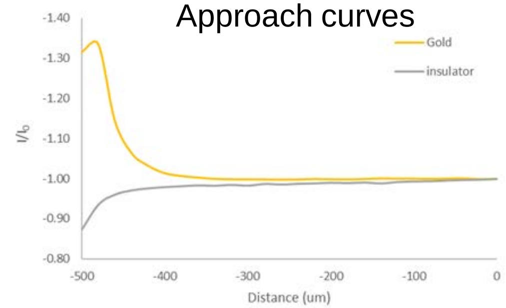
Scanning droplet system (SDS) probe for irreversible redox reactions



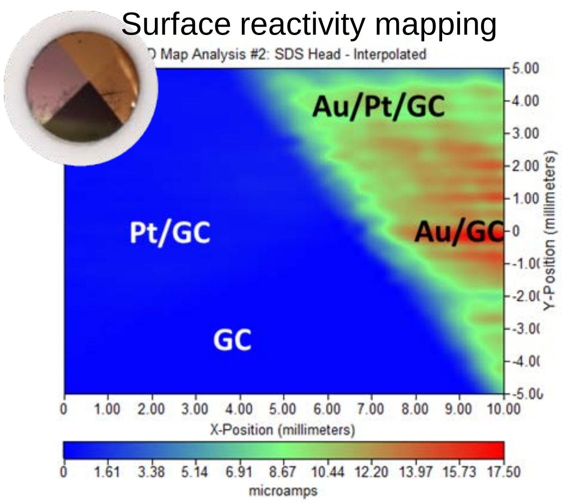
Cyclic voltammetry



Approach curves

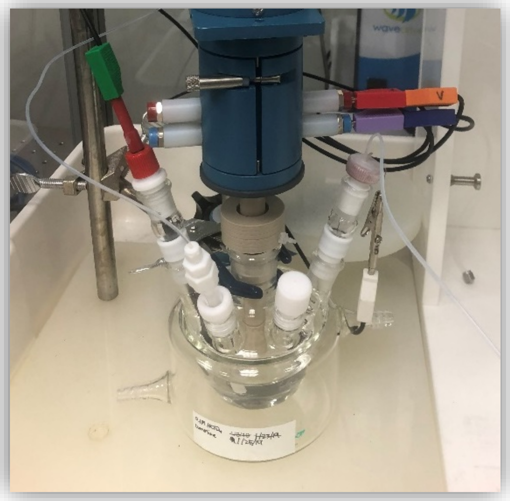


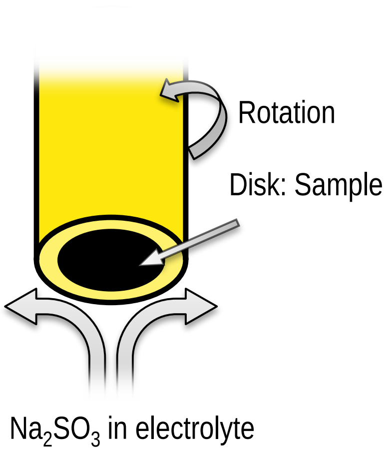
Surface reactivity mapping



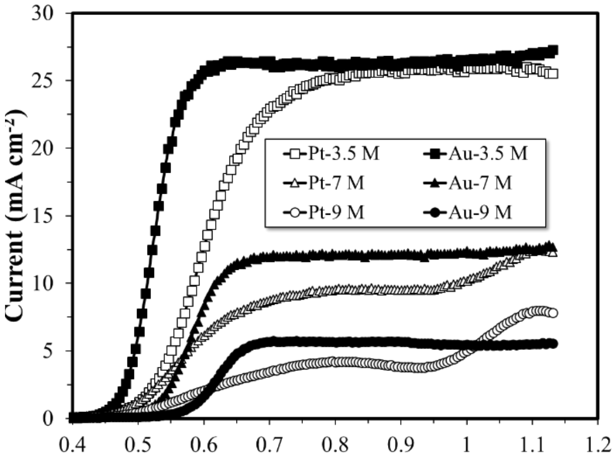
Quickly scan many different metal compositions to find ideal catalyst for SO_2 oxidation

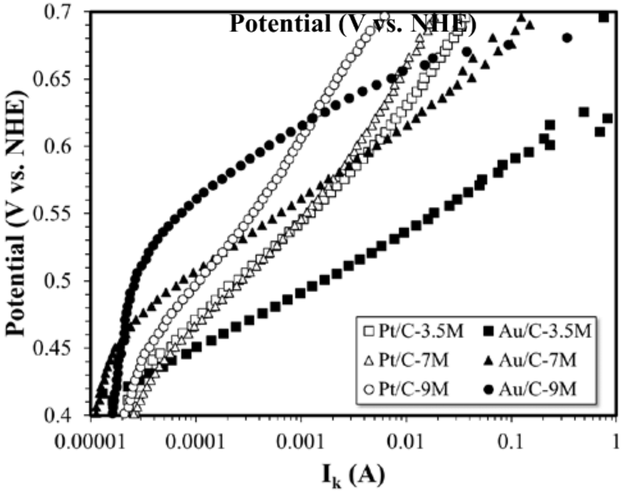
Ex-situ Catalyst Evaluation: Rotating Disk Electrode





Rotating disk electrode with Na_2SO_3 dissolved in sulfuric acid was used to evaluate the catalyst performance



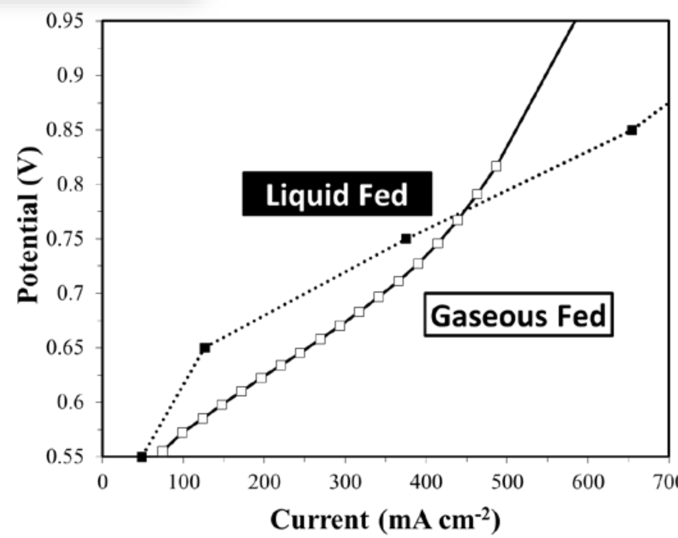


Results:

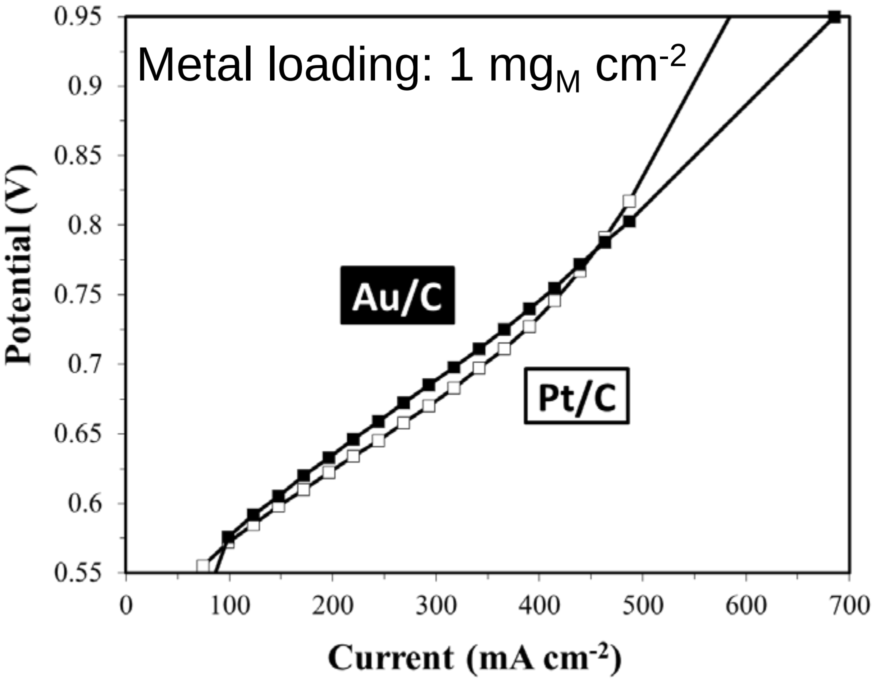
- Diffusion currents decrease as the acid concentration increases
- Kinetic currents decrease as the acid concentration increases
- Kinetic currents for Au/C are much higher than Pt/C at low acid concentrations
- Au/C kinetics are more affected by the acid concentration

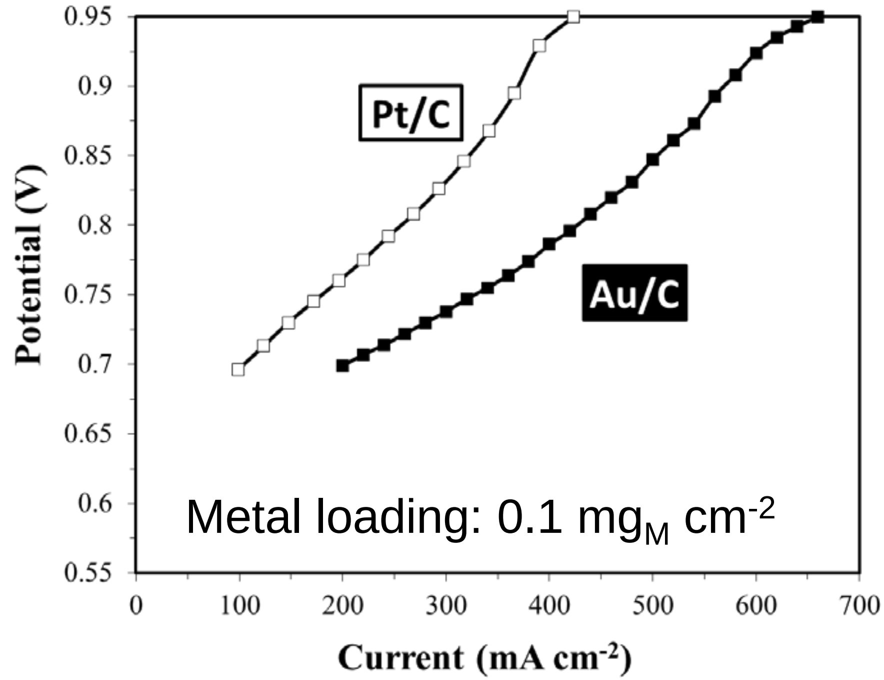
In-situ Catalyst Evaluation: Gaseous Feed Test Facility

- Electrolyte cell was modified to allow gaseous reactant flow to the anode
- Allows rapid screening of MEAs while simplifying laboratory testing
- System performance was validated against the liquid fed cell under comparable conditions.
- Gaseous fed system shows better performance at low to medium current densities



In-situ Catalyst Evaluation





- Traditional catalyst loadings (~1 mg$_M$ cm^{-2}) used in the anode shows no difference in electrolyzer performance between Au and Pt indicating performance is limited due to mass transport and conductivity limitations.
- Effect of catalyst type can be observed at low metal loadings (~0.1 mg$_M$ cm^{-2}) where similar behavior is observed as in rotating disk electrode measurements with electrolyzer performance of Au significantly superior to Pt.

Proposed Future Work

System Design and Analysis

IMSR/HS Integration

An IMSR® HX design study will be completed with SRNL conducting a flowsheet analyses of IMSR® HX and HyS mass and energy. INL will model heat transfer from the IMSR ® HX to the HyS. Based on the modeled scenarios.

IMSR/HS Process Design

A process design study will be conducted for advanced MEAs will be in an Aspen® flowsheet analyses to develop a conceptual design of the MSR-HyS plant. SRNL will provide a conceptual design for the HyS process using the available heat, including design of electrolyzer, decomposition reactor, SO_2/O_2 separation, and heat recovery/integration. INL will provide a conceptual design for heat recovery process meeting a +/-30% capital cost and +/-10% operating and maintenance cost.

IMSR/HyS Economic Analysis and Hydrogen Production Cost Estimate

SRNL will use that cost and the process design to estimate hydrogen production cost using DOE H2A tool. INL will estimate the cost of the MSR process heat. The INL will include materials costs, maintenance, and energy used.

Sulfur Depolarized Electrolyzer Development

High Temp Membrane Development

SNL will conduct a systematic investigation of the optimal ion content in sulfonated poly(phenylene) membranes.

Electrocatalyst Development

SRNL will perform a systematic optimization of the Pt-Au-M (M: V, Co, Fe, etc.) electro-catalyst compositions for the SO_2 oxidation reaction.

High Temp MEA Evaluation and Analysis

SRNL will perform rapid screening of MEA using advanced membranes and electrocatalysts, utilizing the upgraded Gaseous feed MEA test facility.

Any proposed future work is subject to change based on funding levels.

Summary

IMSR® best choice for high turn-down electrical power generation efficiency

- Thermal energy can be used most effectively through hybrid thermo-chemical/electro-chemical process.
- HyS process utilizes 78% thermal energy and 22% electrical energy with ability to store SO_2 or H_2SO_4 indefinitely as required.
- Efficient utilization of <650°C IMSR® thermal output needs to be integrated into HyS process.

Electro-chemical step key to efficient SO_2 oxidation

- Potential high temperature membrane with minimal SO_2 permeation identified as SPP which needs to be optimized for SO_2/SO_3 environment.
- Potential $Pt_xAu_yV_z$ alloy catalyst identified to greatly reduce required cell potential.
- Upgraded gaseous MEA test facility will validate operational endurance of SPP/ $Pt_xAu_yV_z$ MEA.