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Savannah River National Laboratory™

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

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**Project ID# h2026**

*This presentation does not contain any proprietary, confidential or otherwise restricted information*

# Overview

## Timeline

**Start: ~June 1, 2018**

**End: ~ May 31, 2020**

**Project has yet to start. Start date in negotiation.**

## Budget

**Total Center Funding:**

DOE Share: $ 525,000

Cost Share: $ 525,000

## Barriers

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

## Partners

SRNL Savannah River National Laboratory

Southern Company

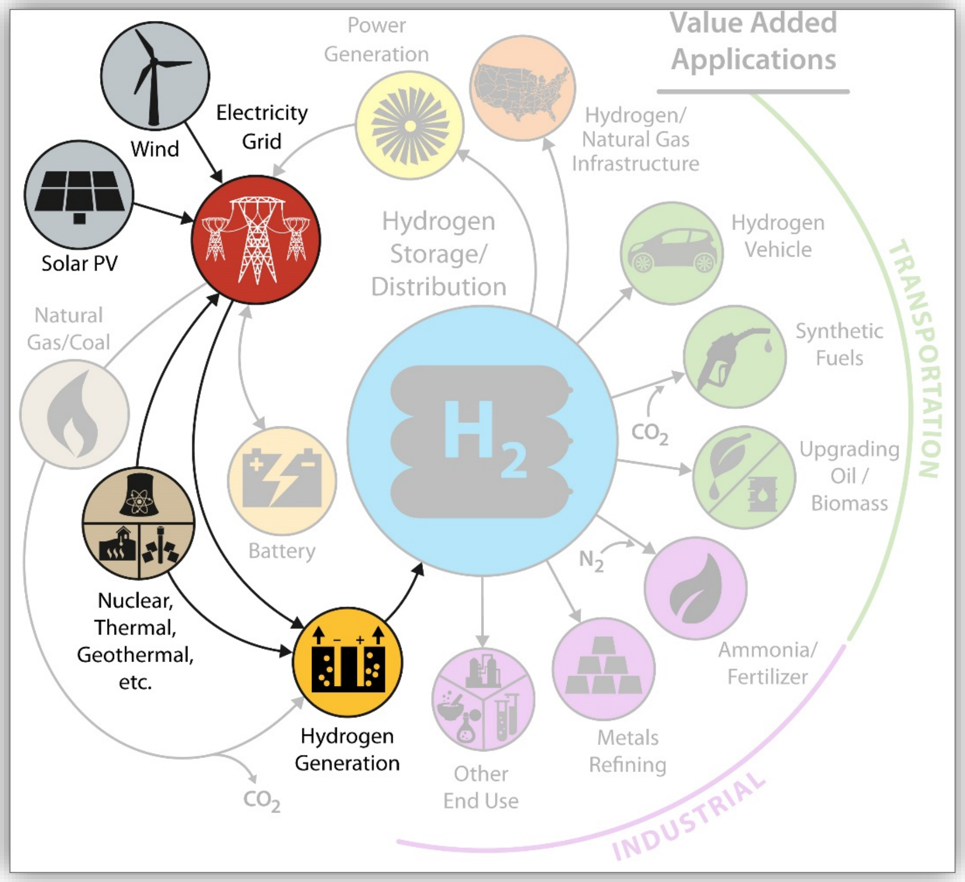
Idaho National Laboratory

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 molten salt reactor (MSR) 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.**



# Objectives

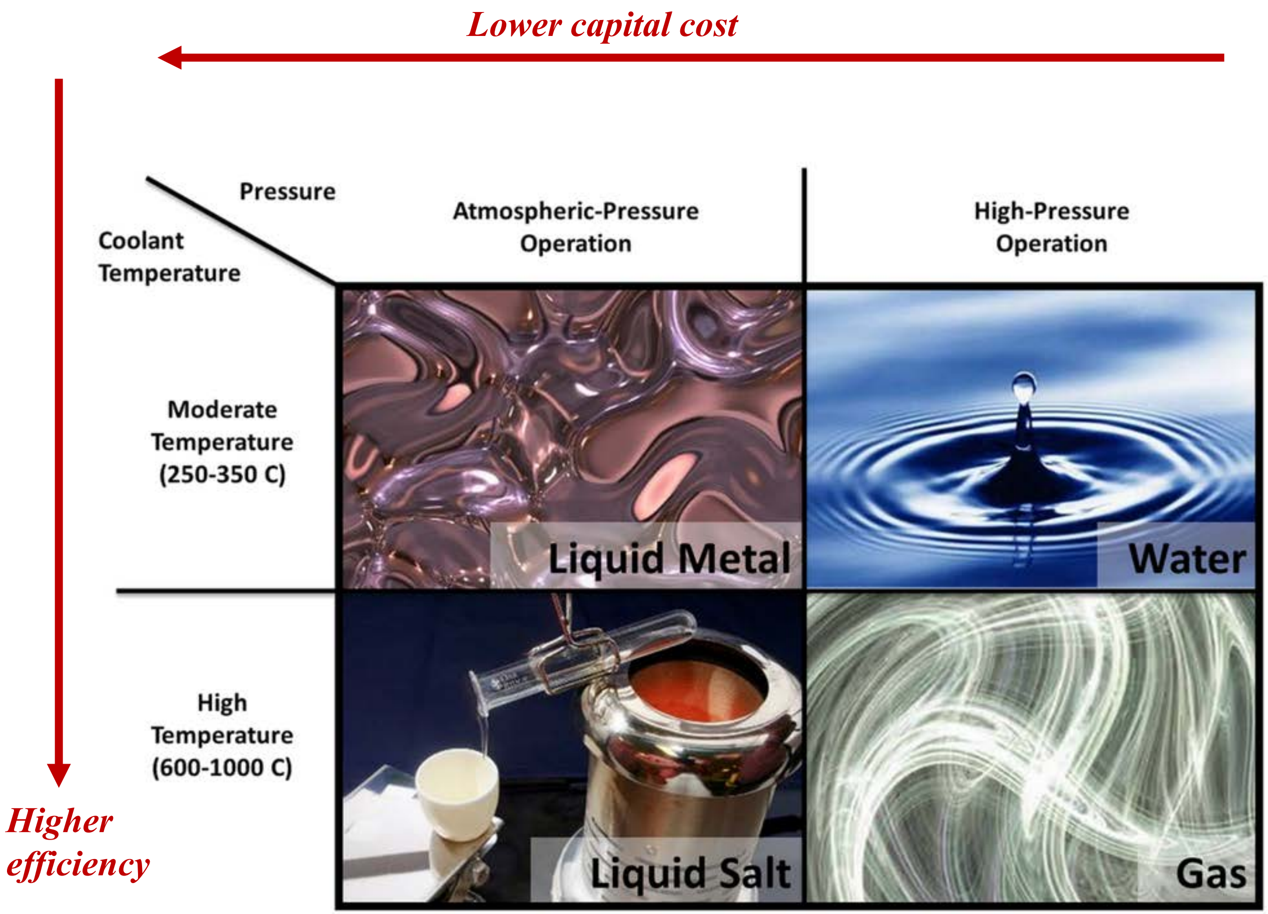
**This program will:**

- **System Analysis**
  - Develop a plausible path to hydrogen production cost less than \$2/kg$H_2$ 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.

# Fuel/Coolant Selection

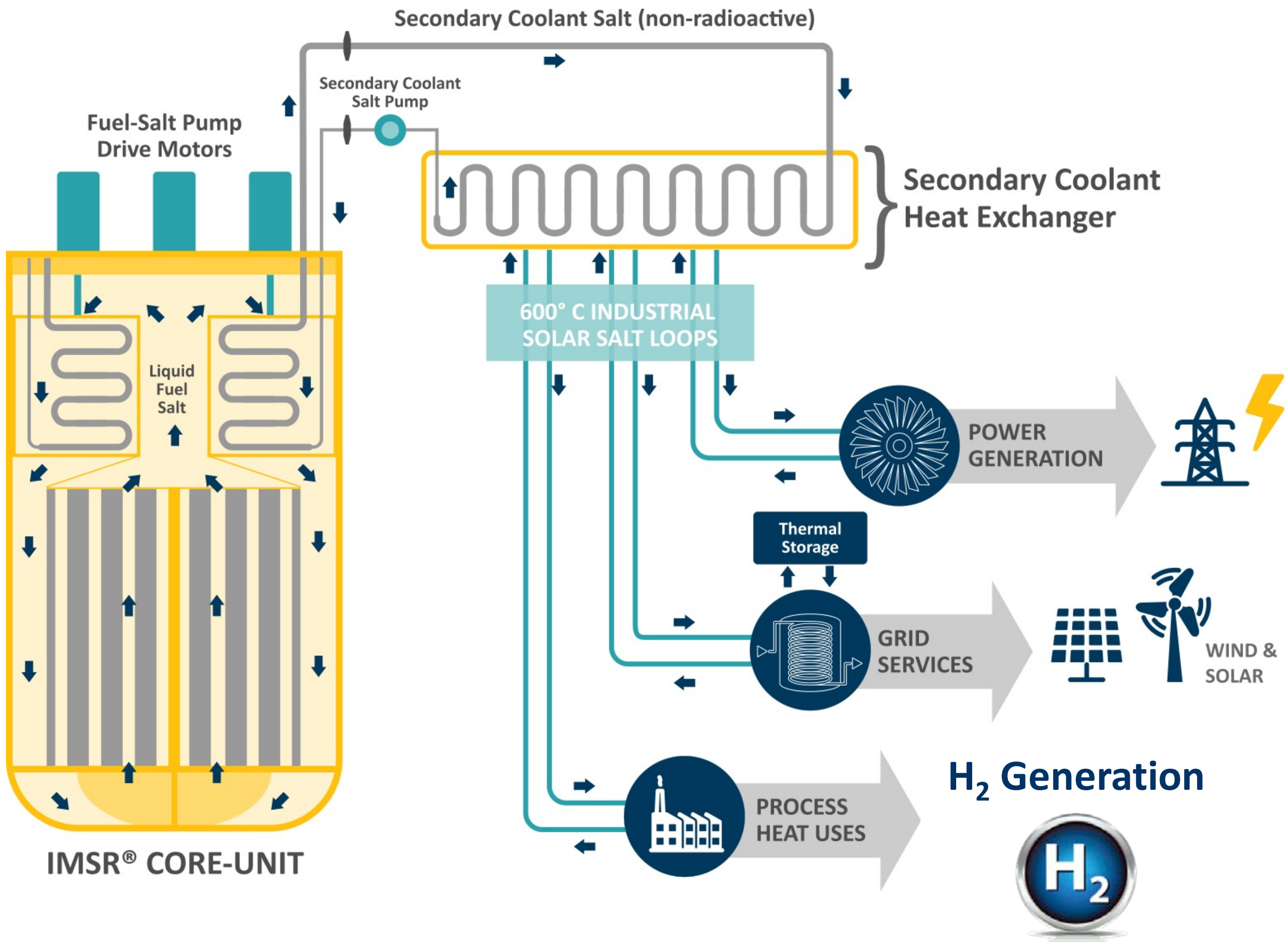
Southern Company

Molten salt cooled reactors show highest thermal efficiency with lower capital cost



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

TERRESTRIAL ENERGY USA



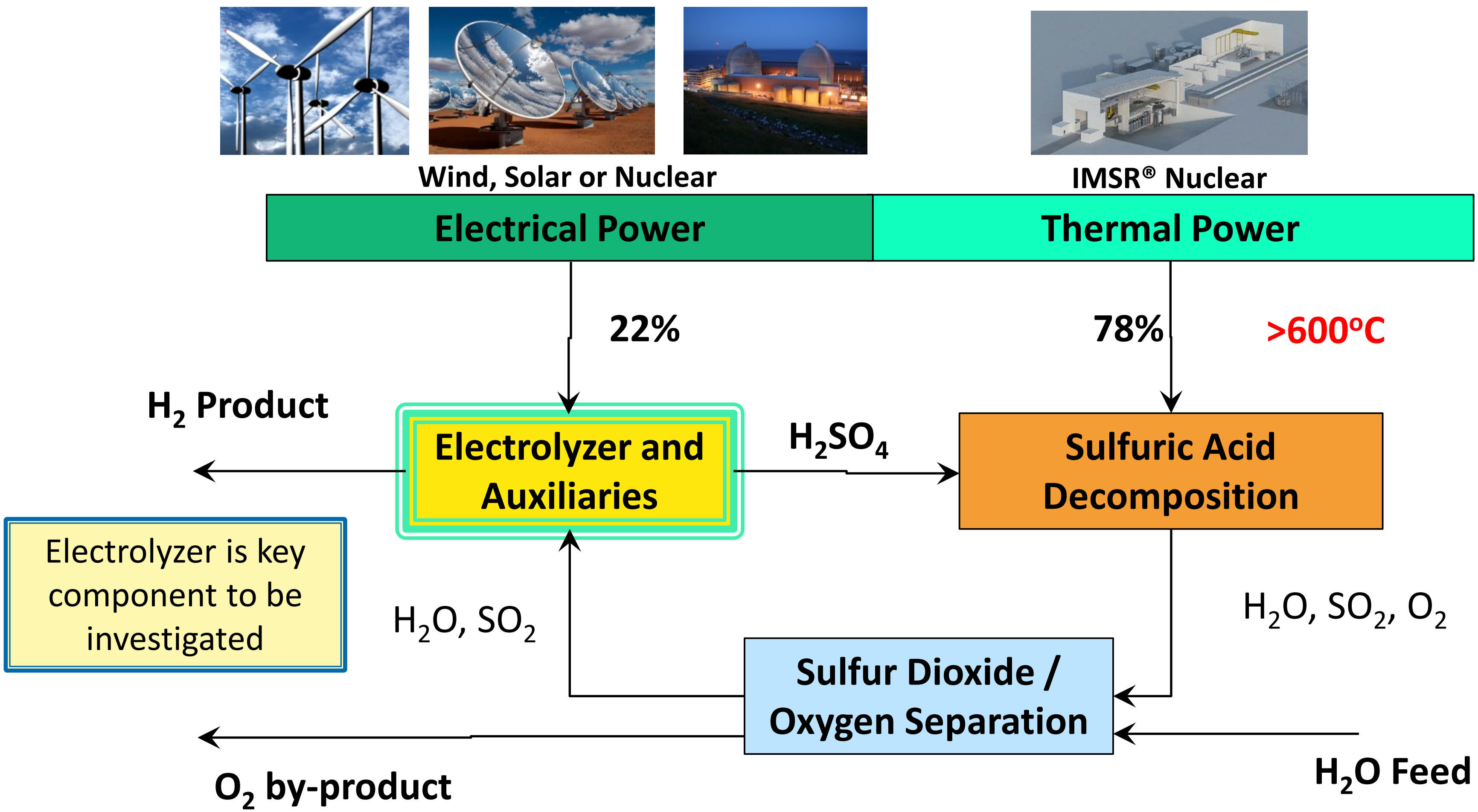
# HyS Chemistry

- **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**

| | |
|---|---|
| $H_2SO_4 \rightarrow H_2O + SO_2 + {}^1/_2\, O_2$ | **Thermochemical:** 600-900$^oC$ |
| $SO_2 + 2\, H_2O \leftrightarrow H_2SO_4 + H_2$ | **Electrochemical:**<br>0.17 $v_{th}$ (~0.5$v_{pr}$) 80-140$^oC$ |
| $H_2O \rightarrow H_2 + {}^1/_2\, O_2$ | **Net Reaction** |

# MSR Implementation of HyS

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

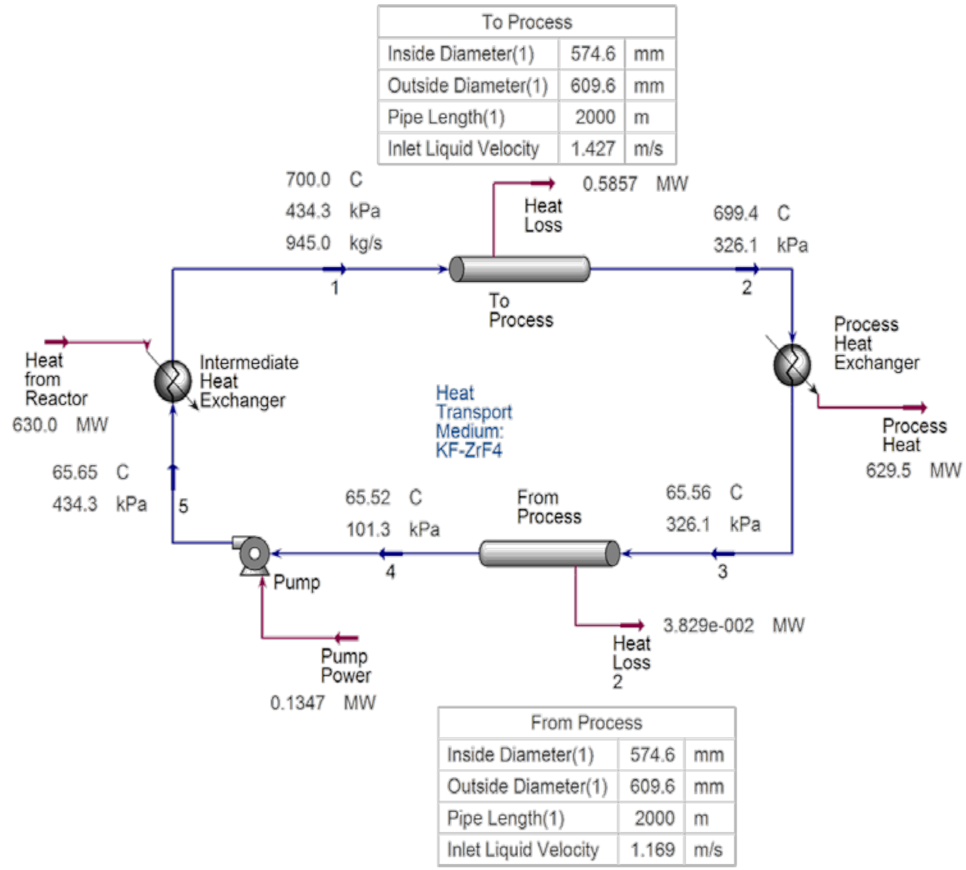


# System Analysis – Nuclear Thermal Heat Transfer

Idaho National Laboratory

1. **Design thermal hydraulic heat delivery system in HYSYS to establish pipe and circulation pump design specifications**
2. **Develop RELAP5-3D module to assess thermal energy delivery system from TEUSA Molten Salt Reactors 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**

RELAP5-3D

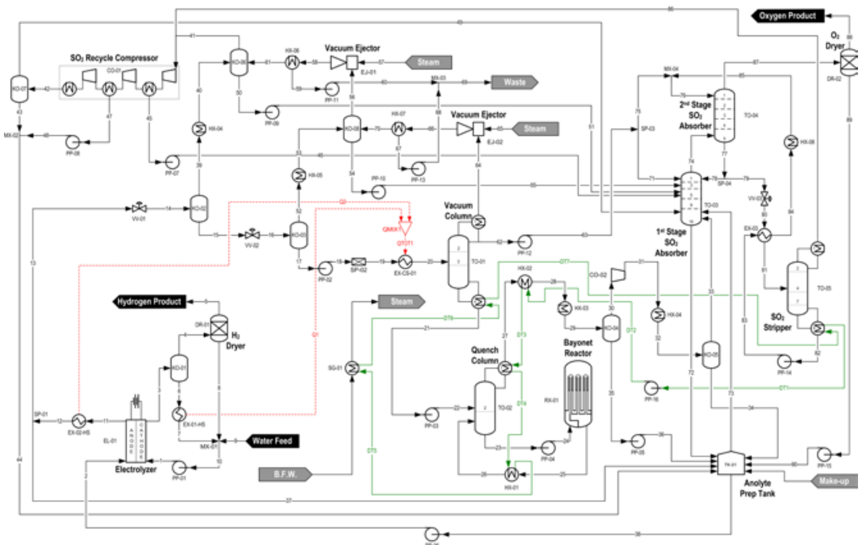



**HYSYS Model: Molten Salt Heat Delivery Loop**

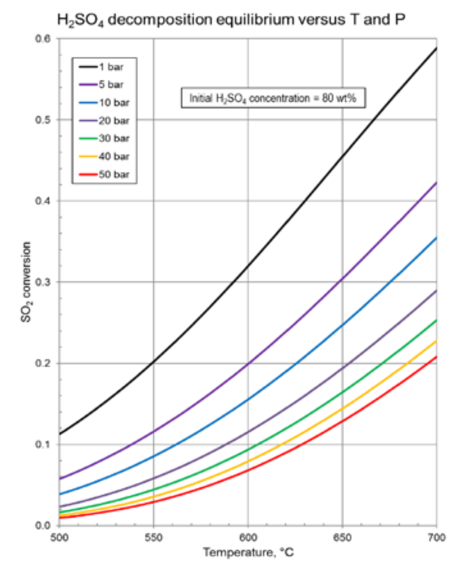
# System Analysis – HyS Process

**Investigate feasibility of lower acid decomposition temperature**

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

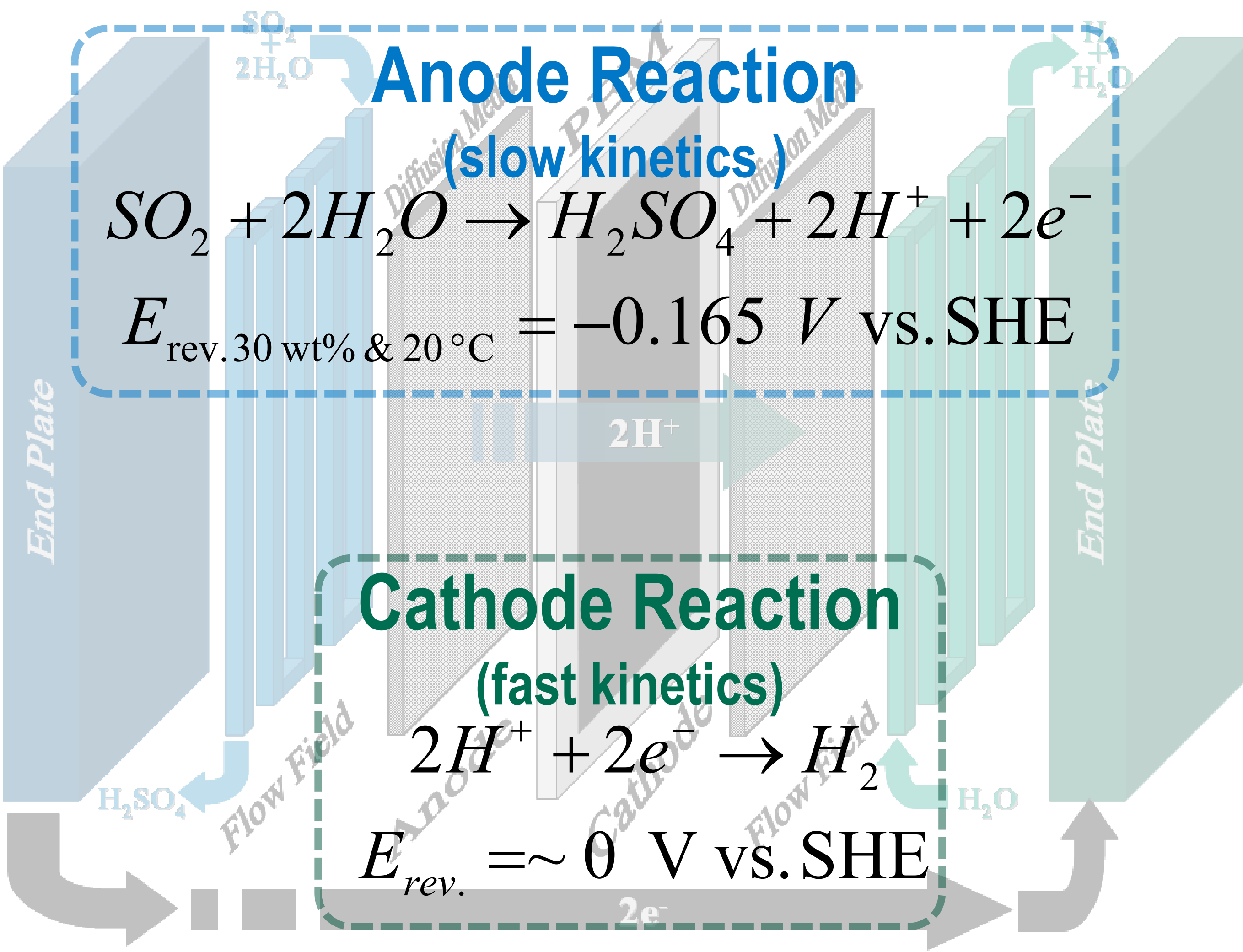



- **Recent improvements in electrolyzer technology should overcome effects of lower decomposition temperature**
  - **SDE temperature ≥ 140°C**
    - Lower cell power requirement due to reduced anodic overpotential
    - Better heat integration with acid decomposition
- **Energy efficiency > 40% HHV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




* Gorensek. "Hybrid sulfur cycle flowsheets for hydrogen production using high-temperature gas-cooled reactors." Int J Hydrogen Energy. 2011, 36, 12725−41.

# Electro-Chemical Cell Operation




## Anode Reaction

(slow kinetics )

$$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H^+ + 2e^-$$

$$E_{\mathrm{rev.\,30\,wt\%\,\&\,20\,^\circ C}} = -0.165\ V\ \mathrm{vs.\,SHE}$$

## Cathode Reaction

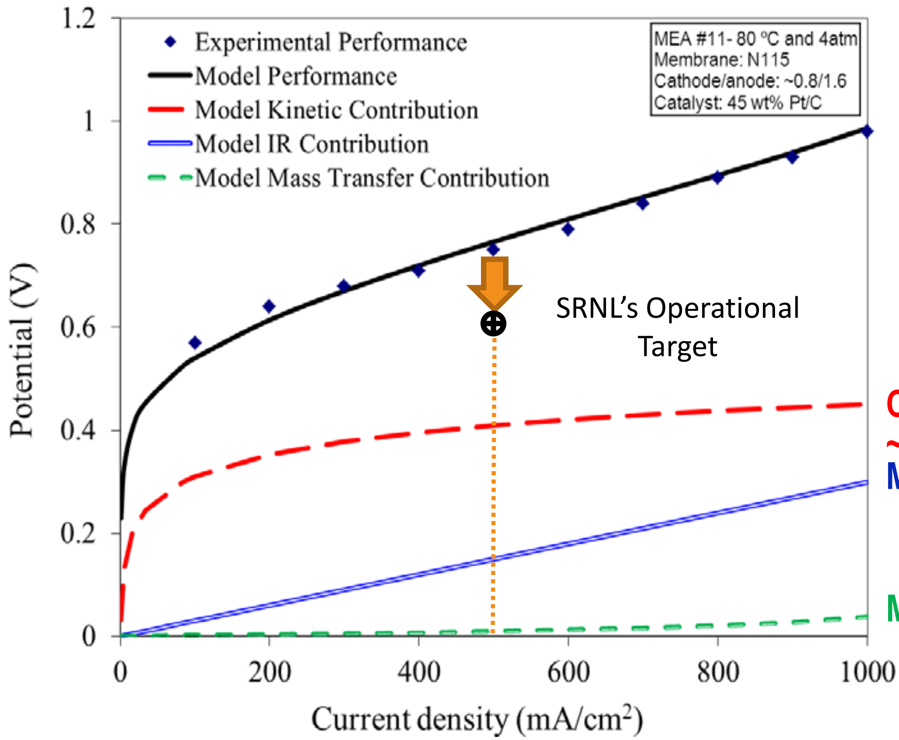
(fast kinetics)

$$2H^+ + 2e^- \rightarrow H_2$$

$$E_{rev.} = \sim 0\ \mathrm{V\ vs.\,SHE}$$

# 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.




**Catalysts ~400mV**

**Membrane ~150 mV**

**Mass Transfer ~10 mV**

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

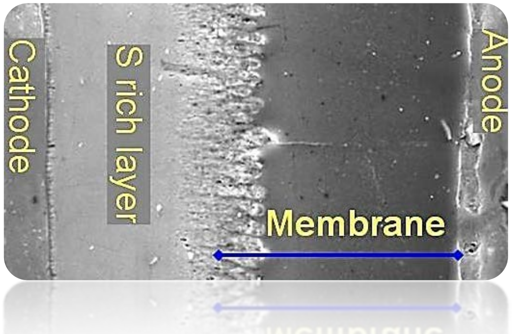
**Cell resistance (membrane)**
- ↑ Operating temperature
- ↑ ionic conductivity

# 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

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



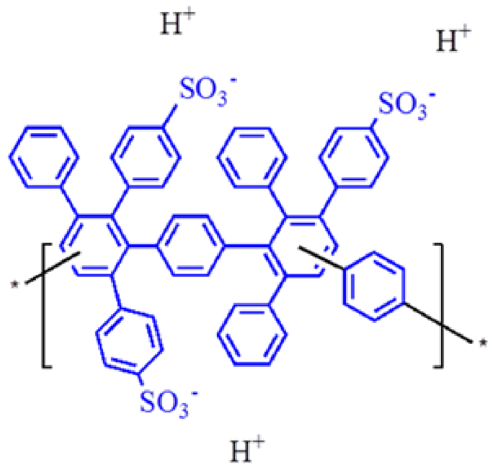

**Steimke JL, Steeper TJ, Herman DT; Savannah River Nuclear Solutions, LLC, assignee. "Method to prevent sulfur accumulation in membrane electrode assembly." US patent No. 8,709,229 B2. April 29, 2014.*

## Electro-catalyst

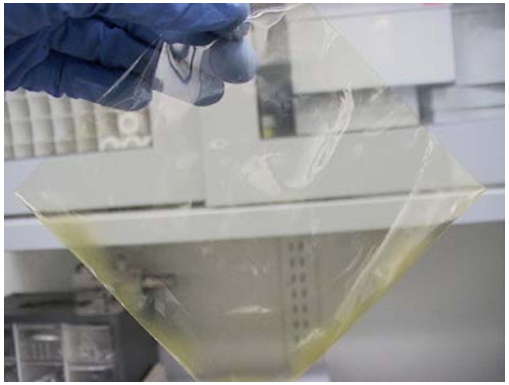
- Maximize reaction kinetics of the anode towards the sulfur dioxide oxidation
  - Minimize use of PGM
  - Minimize size of electrolyzer
- Maximize catalyst stability
- Minimize cathode reactivity towards $SO_2$ through catalyst selection

# High Temperature Membrane Development

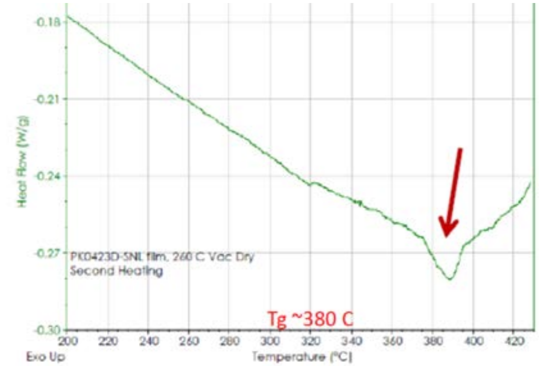
Sandia National Laboratories



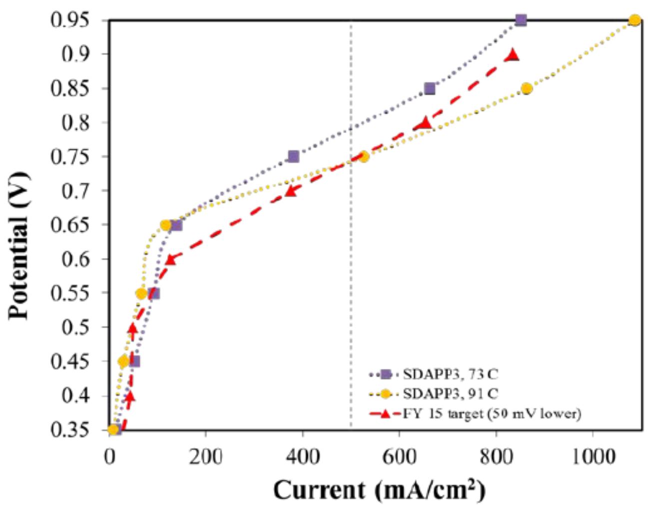

**S**ulfonated **D**iels **A**lder **P**oly(**p**henylene)
SDAPP



SDAPP membrane as manufactured




DSC of SDAPP showing $T_g$ = >350°C

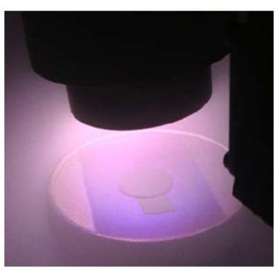



- SDAPP high thermal/chemical stability
- High $T_g$, near 400°C, good candidate for high temperature studies.
- Preliminary studies in 2016 looked at one sample SDAPP and found it met current/potential targets at 91°C.
- Need to find optimal sulfonate anion content required for HyS application.

# Electro-Catalyst Development

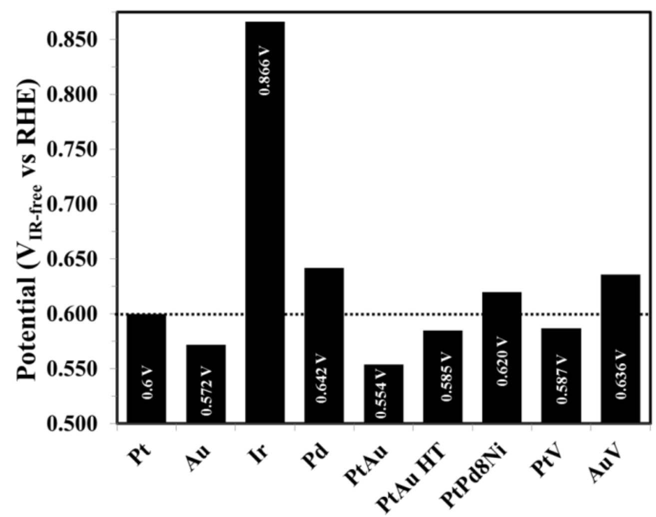
- Previous electrocatalyst developments required individually sputtered compositions, and evaluation in electrochemical cell
- Au, $Pt_{0.5}Au_{0.5}$ and $Pt_{0.5}V_{0.5}$ compositions have been identified as superior to Pt alone
- Full compositional range of $Pt_xAu_yV_z$ (for x+y+z=1) needs to be investigated to identify optimum catalytic activity
- Additional transition metal compositions (i.e. $Pt_xAu_yTm_z$) need to be investigated to identify potential alternate ternary compositions of interest.
- A combinatorial methodology needs to be identified to cover this large compositional space.

Catalyst Screening PVD-3 source PVD



PVD Catalyst on Substrate

Test Cell



# High Throughput Combinatorial Catalyst Development

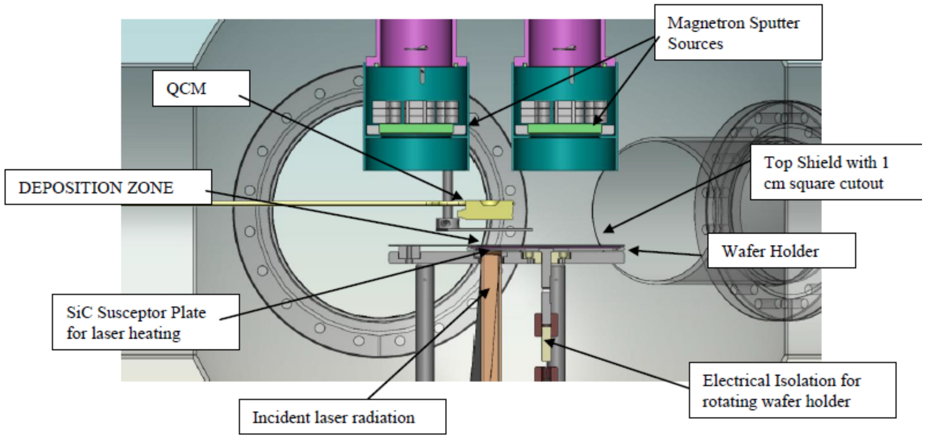
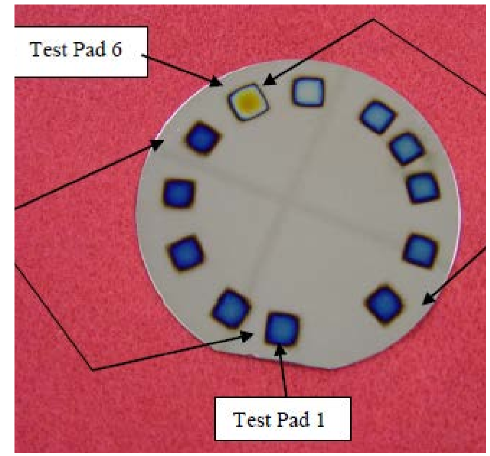



Diagram of multi-magnetron shutter system for fabrication of combinatorial catalyst compositions




Substrate and catalyst patch each having a uniform but varying composition

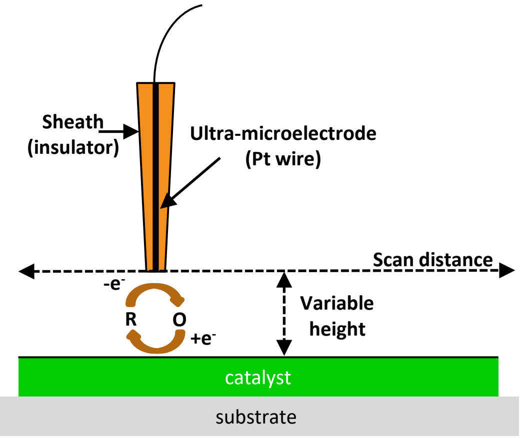
**Pt/Au/V Combinatorial Matrix**

| | | | Sample 1 | | | Sample 2 | | | Sample 3 |
|---|---|---|---|---|---|---|---|---|---|
| Pad # | Pt/Au | Pt | Au | V | Pt | Au | V | Pt | Au |
| 1 | 0.000 | 0.00 | 1.00 | 0.00 | 0.00 | 0.90 | 0.10 | 0.00 | 0.80 |
| 2 | 0.111 | 0.10 | 0.90 | 0.00 | 0.09 | 0.81 | 0.10 | 0.08 | 0.72 |
| 3 | 0.250 | 0.20 | 0.80 | 0.00 | 0.18 | 0.72 | 0.10 | 0.16 | 0.64 |
| 4 | 0.429 | 0.30 | 0.70 | 0.00 | 0.27 | 0.63 | 0.10 | 0.24 | 0.56 |
| 5 | 0.667 | 0.40 | 0.60 | 0.00 | 0.36 | 0.54 | 0.10 | 0.32 | 0.48 |
| 6 | 1.000 | 0.50 | 0.50 | 0.00 | 0.45 | 0.45 | 0.10 | 0.40 | 0.40 |
| 7 | 1.500 | 0.60 | 0.40 | 0.00 | 0.54 | 0.36 | 0.10 | 0.48 | 0.32 |
| 8 | 2.333 | 0.70 | 0.30 | 0.00 | 0.63 | 0.27 | 0.10 | 0.56 | 0.24 |
| 9 | 4.000 | 0.80 | 0.20 | 0.00 | 0.72 | 0.18 | 0.10 | 0.64 | 0.16 |
| 10 | 9.000 | 0.90 | 0.10 | 0.00 | 0.81 | 0.09 | 0.10 | 0.72 | 0.08 |
| 11 | #DIV/0! | 1.00 | 0.00 | 0.00 | 0.90 | 0.00 | 0.10 | 0.80 | 0.00 |

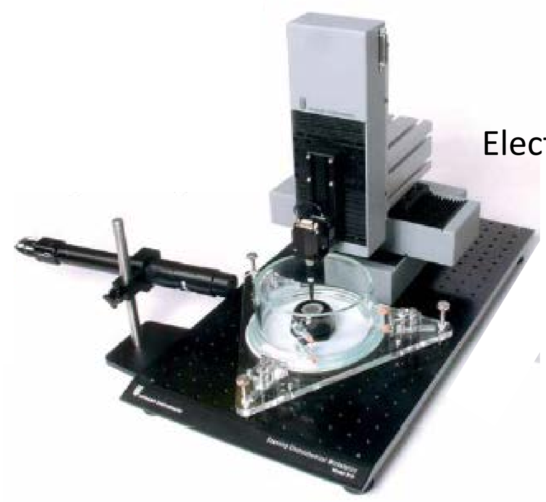
A shuttered three magnetron sputtering system has been developed for the preparation of ternary alloy catalyst patches of varying composition. Initially the Pt-Au-V system will be explored to identify highest activity compositions.

# High-Throughput Electro-chemical Analysis

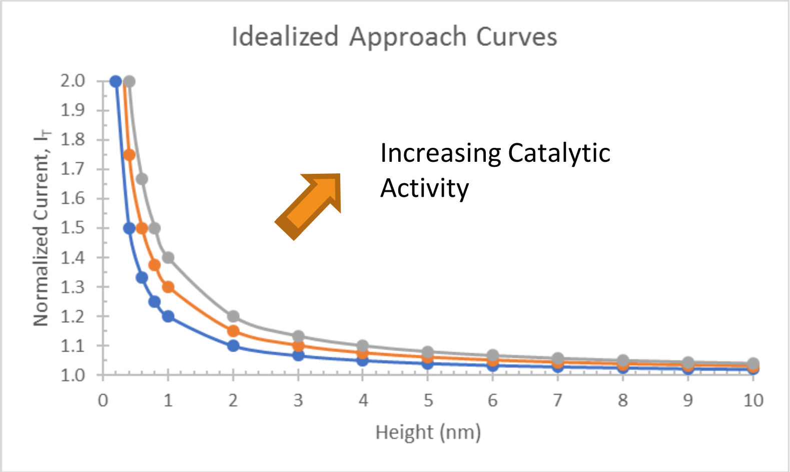
- Scanning Electrochemical Microscope (SECM) will be used to analyze binary and ternary electrocatalyst matrixes prepared via physical vapor deposition.
- Approach method will be used to identify most active catalyst compositions.
- Each substrate within the matrix will be analyzed for S(IV) → S(VI) oxidation in aqueous $H_2SO_4$ solution
  e.g., $SO_2 + 2H_2O \rightarrow H_2SO_4 + 2e^-$




Depiction of the ultramicroelectrode, substrate, and the surface redox reaction

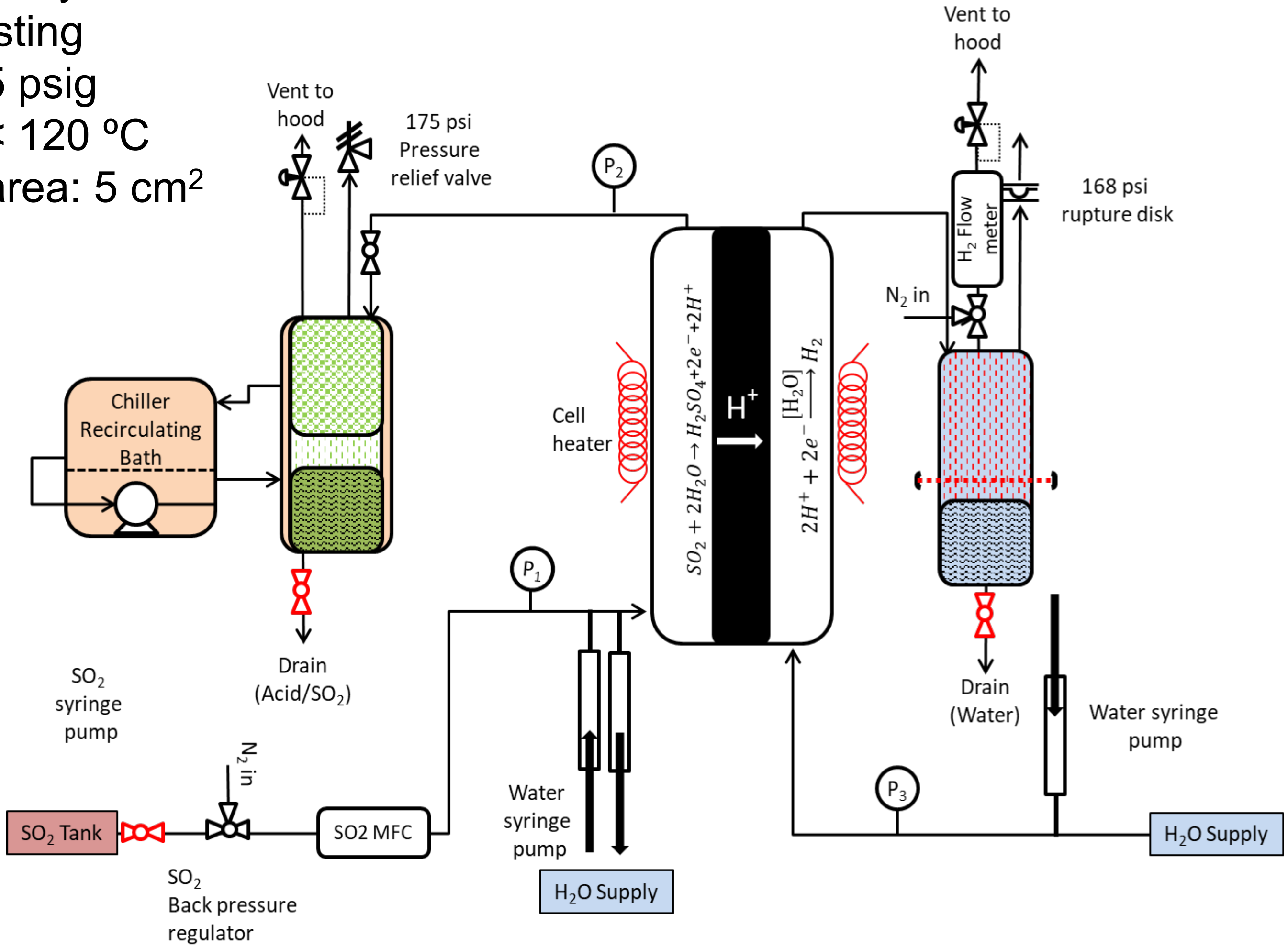


Uniscan Instruments Model 370 Scanning Electrochemical Workstation



# Gaseous Feed Electro-Chemical Cell Development

- System under construction will allow rapid screening of catalysts and membranes
- Simplify lab scale testing
- Test Pressures: < 25 psig
- Test temperatures: < 120 ºC
- Nominal active cell area: 5 cm$^2$



# Future Work - Tasks

## Task 1 System Design and Analysis

**Task 1.1** IMSR 3HX Integration Design Study

**SCS** and **TEUSA** will provide baseline properties of the molten salt (inlet and outlet temperature ranges, flowrates, compositions).

**Task 1.1.1** SRNL will conduct flowsheet analyses of IMSR 3HX and HyS mass and energy.

**Task 1.1.2** INL will model heat transfer from the IMSR 3HX to the HyS

**Downselect:** Based on the modeled scenarios, one or two will be selected for further review. SCS and TEUSA will review this work and concur with the process design.

**Task 1.2 Process Design**

Performance data for advanced MEAs will be in an Aspen® flowsheet analyses to develop a conceptual design of the MSR-HyS plant.

**Task 1.2.1** 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.

**Task 1.2.2** INL will provide a conceptual design for heat recovery process meeting a +/-30% capital cost and +/-10% operating and maintenance cost.

**Deliverable**: Develop a conceptual plant design for MSR-HyS in collaboration with TEUSA and SCS.

**Task 1.3 Economic Analysis and Hydrogen Production Cost Estimate**

**SCS** and **TEUSA** will provide plant capital and operational cost data

**Task 1.3.2** SRNL will use that cost and the process design to estimate hydrogen production cost using DOE H2A tool.

**Task 1.3.2** INL will estimate the cost of the MSR process heat. The INL work is a continuation of **Task 1.1.2,** and will be completed include materials costs, maintenance, and energy used.

**Deliverable**: Develop a techno-economic analysis of H2 production via MSR-HyS.

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

# Future Work – Tasks (cont.)

**Task 2 Sulfur Depolarized Electrolyzer (SDE) Development**

**Task 2.1** MEA Gaseous/Liquid Test Facility

SRNL will upgrade the gaseous membrane electrode assembly (MEA) Test Facility to a Gaseous MEA Test Facility.

**Deliverable:** Validated operation of the gaseous MEA Test Facility. This facility will be used throughout the project duration for MEA testing.

**Task 2.2** High Temp Membrane Development

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

**Deliverable:** SNL will develop an SPP membrane composition showing better ion conductivity than Nafion®112 in 6 M sulfuric acid.

**Task 2.3** Electrocatalyst Development

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

**Deliverable:** Develop electrocatalyst that show a 20 mV performance improvement over Pt/C in 30% sulfuric acid solution containing dissolved sulfur dioxide or sodium sulfite.

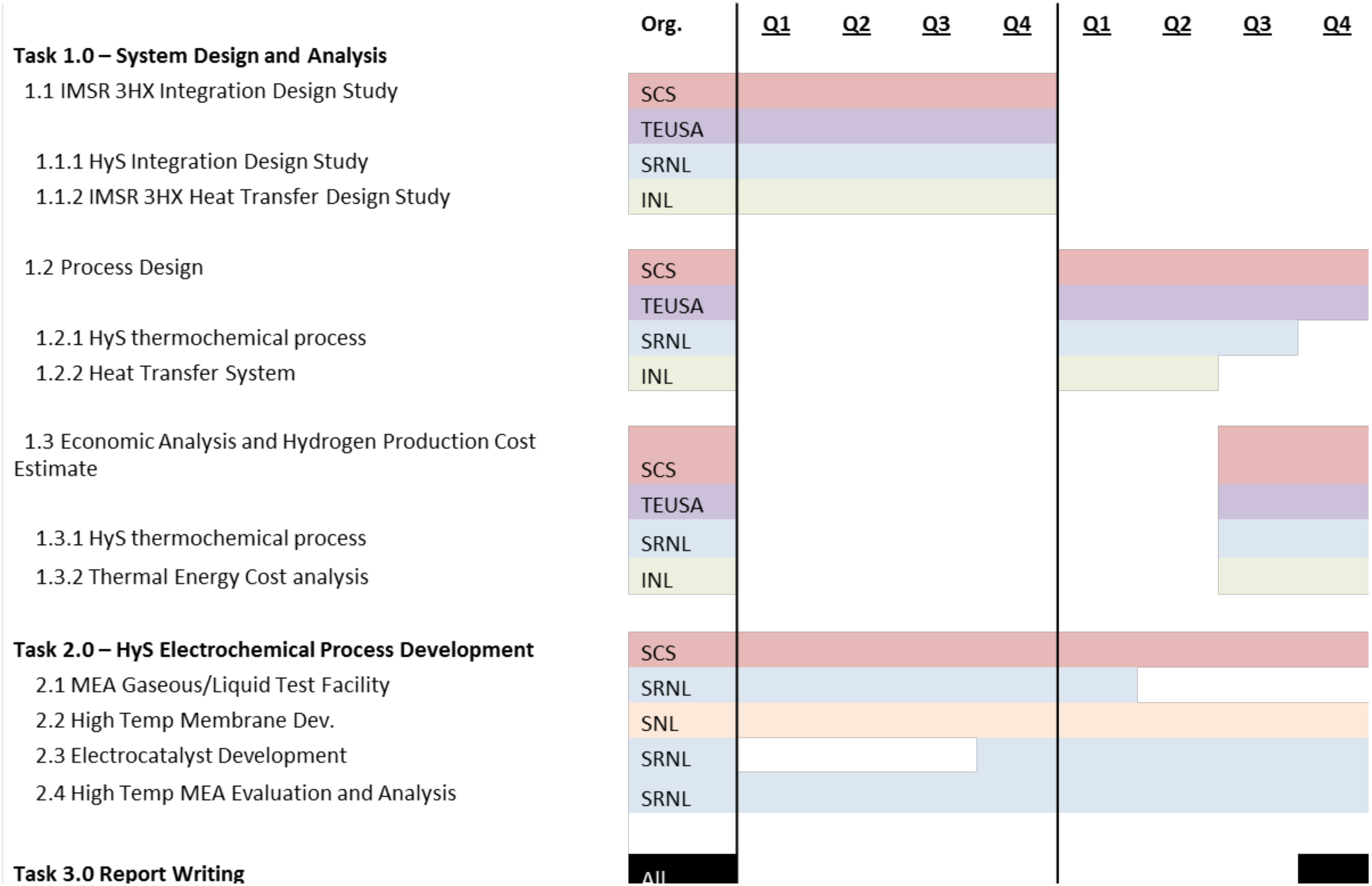
**Task 2.4** High Temp MEA Evaluation and Analysis

SRNL will perform rapid screening of MEA using advanced membranes and electrocatalysts, utilizing the upgraded Gaseous/Liquid MEA Test Facility.

**Deliverable:** Demonstrate performance of at least 100 mV lower cell voltage than Nafion® of an MEA using higher temperature membranes and improved catalysts.

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

# Future Work - Schedule




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

# Summary

- Molten Salt Reactor (MSR) 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 transfer of heat from molten salt to HyS process needs to be obtained
- Efficient utilization of <650$^{o}$C MSR thermal output needs to be integrated into HyS process.
- Electro-chemical step identified as key technical barrier to efficient $SO_2$ oxidation
- Potential high temperature membrane with minimal $SO_2$ permeation identified as SDAPP 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.
- Combinatorial approach identified to optimize $Pt_xAu_yV_z$ catalyst alloy.
- Upgraded gaseous MEA test facility will validate operational endurance of SDAPP/ $Pt_xAu_yV_z$ MEA.