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

D. Anton, H. Colon-Mercado, M. Gorensek, Savannah River National Laboratory
S. Hancock, R. Boardman, Idaho National Laboratory
C. Fujimoto, Sandia National Laboratory
N. Meeks, Southern Co.
J. Kutsch, D. Carleton, Terrestrial Energy USA, LLC

April 30, 2019

This presentation does not contain any proprietary, confidential or otherwise restricted information
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: $ 259,000
  (as of 1/1/19)
- Cost Share: $ 525,000

Partners
- SRNL
- Southern Company
- INL
- 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 SO₂, to be used to generate hydrogen as required to minimize generation and storage costs.
Advanced Nuclear Power + Hydrogen = Economy–wide Energy Decarbonization

Renewable Power

intermittent power

Zero-carbon Power

baseload power

Electric Grid
BEV Transportation

High-Quality, Zero-carbon Heat from IMSR®

peaking power

Green Hydrogen

Hybrid Sulfur Process

Industrial Utilization
FCEV Transportation
Distributed Generation
Thermal Energy
**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

Wind, Solar or Nuclear

**Electrical Power**

- Electrolyzer and Auxiliaries
  - Sulfuric Acid Decomposition
  - Sulfur Dioxide / Oxygen Separation

**Thermal Power**

- IMSR® Nuclear
  - Wind, Solar or Nuclear

H₂O, SO₂ → H₂SO₄

H₂O, SO₂, O₂

H₂O Feed

H₂O, SO₂

Electrolyzer is key component to be investigated

H₂ Product

O₂ by-product

H₂ Product

>600°C

22% 78%

Savannah River National Laboratory

We put science to work™
Integration of Hydrogen Generation with an Integral Molten Salt Reactor IMSR®

IMSR® CORE-UNIT

Secondary Coolant Salt (non-radioactive)

Fuel-Salt Pump Drive Motors

600° C INDUSTRIAL SOLAR SALT LOOPS

POWER GENERATION

GRID SERVICES

Thermal Storage

PROCESS HEAT USES

H₂ Generation

H₂ Generation

TERRESTRIAL ENERGY USA

Savannah River National Laboratory
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS
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 SO₂ depolarized electrolyzer (SDE).
- All fluid processing minimizes entropic losses due to phase changes.

**HyS Process**

\[
\begin{align*}
H_2SO_4 & \rightarrow H_2O + SO_2 + \frac{1}{2} O_2 & \text{Thermochemical: } 600-900^\circ C \\
SO_2 + 2 H_2O & \leftrightarrow H_2SO_4 + H_2 & \text{Electrochemical: } 0.17 \, v_{th} \, 80-140^\circ C \\
H_2O & \rightarrow H_2 + \frac{1}{2} O_2 & \text{Net Reaction}
\end{align*}
\]

vs. Low Temperature Electrochemical

\[
H_2O \rightarrow H_2 + \frac{1}{2} O_2 & \quad \text{Electrochemical: } 1.23 \, v_{th}
\]
Approach

- **System Analysis**
  - Develop a plausible path to hydrogen production cost less than $2/kgH₂ based on the process design and cost estimation.
  - Develop a conceptual plant design for MSR-HyS
  - Develop a techno-economic analysis of H₂ 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.
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 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\textsubscript{2} permeability and durability in SO\textsubscript{2}/SO\textsubscript{3} environment required.
- New catalysts and supports resulting in 600mV potential at 500mA/cm\textsuperscript{2} required.
- Membrane electrode Assembly (MEA) required having >10% degradation in potential after 700 hrs. operation.

**Kinetics (catalyst)**
- \(\uparrow\) Operating temperature
- \(\uparrow\) Intrinsic higher activity

**Cell resistance (membrane)**
- \(\uparrow\) Operating temperature
- \(\uparrow\) Ionic conductivity

![Graph showing electrochemical performance targets](image-url)

- **Catalysts** ~400mV
- **Membrane** ~150 mV
- **Mass Transfer** ~10 mV
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

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


\[ 2H_2S + SO_2 \rightarrow \frac{3}{8}S_8 + 2H_2O \]
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
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

- 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

Substrate and catalyst patch each having a uniform but varying composition

High-Throughput Electrochemical Analysis

Uniscan Instruments Model 370 Scanning Electrochemical Workstation

SECM ultramicroelectrode probe for reversible redox reactions

Variable height Scan distance

Sheath (insulator) Ultra-microelectrode (Pt wire)

Cyclic voltammetry

Approach curves

Uniscan Instruments Model 370 Scanning Electrochemical Workstation

Scanning droplet system (SDS) probe for irreversible redox reactions

Sheath (insulator) Ultra-microelectrode (Pt wire)

Sample

Quickly scan many different metal compositions to find ideal catalyst for SO₂ oxidation

Cyclic voltammetry

Approach curves

Surface reactivity mapping

Savannah River National Laboratory OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS
**Ex-situ Catalyst Evaluation: Rotating Disk Electrode**

Rotating disk electrode with Na$_2$SO$_3$ 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, SO2/O2 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 SO2 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 SO₂ or H₂SO₄ indefinitely as required.
- Efficient utilization of <650°C IMSR® thermal output needs to be integrated into HyS process.

**Electro-chemical step key to efficient SO₂ oxidation**
- Potential high temperature membrane with minimal SO₂ permeation identified as SPP which needs to be optimized for SO₂/SO₃ environment.
- Potential PtₓAuᵧVₜ alloy catalyst identified to greatly reduce required cell potential.
- Upgraded gaseous MEA test facility will validate operational endurance of SPP/ PtₓAuᵧVₜ MEA.