



High temperature reactor catalyst material development for low cost and efficient solar driven sulfur-based processes

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Project ID: P169

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Lawrence Livermore National Laboratory



Project Overview

Project Partners

Corgnale C (co-PI), Summers W (GWE)

Monnier J (*co-PI*), Regalbuto J, Shimpalee S, Weidner J, Tengco J, Diao W (*USC*)

Ginosar D, Adhikari B (*INL*), Ma Z, Davenport P, Martinek J (*NREL*), Gorensek M, Caudle B (*SRNL*)

Project Vision

Development of:

- <u>New catalyst material</u> using our demonstrated surface free energy (SFE) and electro-less deposition technique,
- Novel integrated <u>direct solar reactor-receiver</u>, based on a demonstrated cavity solar reactor,
- New effective <u>solar-thermochemical plant process</u> <u>integration</u>

Objective:

<u>efficient and low cost</u> solar thermochemical process

Project Impact

- Increase of the <u>energetic efficiency</u> (solar to H₂ energy efficiency > 20%),
- Projected reduction of the <u>H₂ cost to < 2 \$/kg</u>

* this amount does not cover support for HydroGEN resources leveraged by the project (which is provided separately by DOE)

HydroGEN: Advanced Water Splitting Materials

Award #	EE0008091
Start/End Date	9/01/2017 - TBD
Year 1 Funding*	\$250,000

* this amount does not include cost share or support for HydroGEN resources leveraged by the project (which is provided separately by DOE)



Test conditions included temperature of 800 °C, pressure of 1 bar and H_2SO_4 concentration of 91 wt %. The catalyst used were 1%Pt/BN, 1%Pt/5%Ir/BN and 1%Pt/7.5%Ir/BN.





Results of Phase 1

- Baseline catalyst novel formulation identified with almost absence of degradation (≈ 100 h test) – *Provisional Patent Applied*
- Novel solar receiver-reactor concept for H₂SO₄ decomposition identified and numerically verified, allowing effective reaction and heat recovery – *ROI*
- Novel solar plant design and flowsheet identified allowing higher efficiency and cost reduction

Key Impact – Proposed targets

Metric - Milestones	State of the Art	Proposed	Achieved (Phase 1)
Catalyst Activity (molSO ₂ /h/g _{Cat}) Degradation (%/hour)	0.23 0.030	0.28 0.015	1.8 No degradation (75 hours)
Sun to H ₂ efficiency (%)	16 (LHV)	20% (LHV)	21.2 (LHV)
H ₂ cost (\$/kg)	3.6 – 7.6	2.0	2.0

Barriers	Solutions
Catalyst activity and lifetime	Bimetallic catalyst - ED technique
Materials of construction and BOP at high temperature	SiC material - Modeling and experimental stress tests
Efficient and cost effective solar- HyS plant integration	Unified intensified solar receiver- reactor
Efficient and cost effective solar HyS plant design	Augmented cross sectional heat recovery – Enhanced heat exchangers

Partnerships

GWE – Techno-economic analysis, design solutions and detailed transport phenomena model

USC – Catalyst development and CFD analysis

INL – Catalyst performance analysis under realistic conditions

SRNL – HyS process modeling and analysis

NREL – Solar plant design and cost assessment

HydroGEN: Advanced Water Splitting Materials

ED = Electroless deposition BOP = Balance of plant

Approach- The HyS process



The high temperature decomposer is the key component for the solar driven process energy efficiency and cost reduction

Approach-Innovation



Relevance & Impact Milestone accomplishment overview

activity

Catalvst

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degradation

Catalyst



Test conditions included temperature of 800 °C, pressure of 1 bar and H_2SO_4 concentration of 91 wt %. The catalyst used were 1%Pt/BN, 1%Pt/5%Ir/BN and 1%Pt/7.5%Ir/BN.

- Catalyst deactivation reduction required to reduce the lifetime costs of the plant and achieve 2 \$/kg target
 - HydroGEN node Idaho Nat Lab Unique capability to test catalytic decomposition of H_2SO_4 at the required operating conditions (T ~ 800 °C, concentrations ~ 90 wt%)

<u>Milestone 1.1</u>: Preparation of the new catalyst, measurement of its nominal (fresh material) properties. The success of the milestone will be based on the following criteria: (1) catalyst activity at least 20% higher than the corresponding current baseline values obtained at Idaho National Laboratory (INL), i.e. <u>SO₂ production</u> rate of 0.28 mol_{SO2}/h/g_{catalyst} (the current baseline value is about 0.23 mol_{SO2}/h/g_{catalyst} obtained with concentrated sulfuric acid at 1123 K and atmospheric pressure*)

> All BN-based catalytic formulations achieved the catalyst activity (Milestone 1.1) targets

<u>Milestone 1.2</u>: Measurement of catalyst activation reduction after 100-hour tests. The success of the milestone will be based on the following criteria: (1) catalyst activity reduction 50% less than the corresponding current values obtained at INL, i.e. <u>less</u> than 1.5% reduction after the 100-hour tests, corresponding to a <u>maximum 0.015% activity reduction</u> <u>per hour</u> (the current baseline value is 0.03% activity reduction per hour obtained with concentrated sulfuric acid at 1123 K and atmospheric pressure*). The values will be measured after the catalyst reaches an initial stable condition with a possible statistical analysis of the data.

The novel catalyst formulation, 1%Pt/7.5%Ir/BN (Provisional Patent Applied) achieved the catalyst degradation (Milestone 1.2) targets

* Petkovic LM et al, Applied catalysis A, 338 (2008) 27-36

Relevance & Impact Milestone accomplishment overview

- High-efficiency and low-cost plant configuration developed and demonstrated
 - HydroGEN node Savannah River Nat Lab Unique capability to develop process models for H₂SO₄ based thermochemical processes
 - HydroGEN node National Ren Energy Lab Unique capability to model and optimize the overall CSP and BOP components



Milestone 1.3: Assessment of the techno-economic performance of the solar driven HyS process. The success of the milestone will be based on the following criteria: (1) mass and energy balances of the HyS process (available from the HyS flowsheet) will be provided; (2) efficiency of the thermochemical plant (HyS) higher than 35% (based on LHV of hydrogen), (the current value is 32%, see Ref. 2); (3) overall solar plant efficiency higher than 18%; (4) hydrogen production cost showing a viable path to \$2 /kg H₂.

Novel reactor (being patented) and plant flowsheet HyS efficiency of >37% and S2H efficiency of 21%

<u>Go/No-Go</u>: The decision will be made based on the following criteria: (1) <u>catalyst activity</u> at least equal to a production rate of 0.28 molSO₂/h/gcatalyst (20% higher than the corresponding current baseline value of 0.23 molSO₂/h/gcatalyst obtained with concentrated sulfuric acid at 1123 K and atmospheric pressure); (2) <u>catalyst activity reduction</u> (100 hour test) lower than 1.5% after 100 h tests (50% lower than the corresponding current baseline value of 0.03% per hour obtained with concentrated sulfuric acid at 1123 K and atmospheric pressure); (3) the solar plant cost showing an <u>overall plant efficiency</u> > 18% (thermochemical plant efficiency > 35%) and a viable path to reach a <u>H₂ cost</u> of 2 \$/kg_{H2}

Current H_2 cost 2.43 \$/kg with a viable path to 2.0 \$/kg

LHV = Low Heating Value (120 MJ/kg) CSP = Concentrating Solar Plant S2H = Solar to hydrogen BOP = Balance of plant

Accomplishments - Sintering of monometallic catalysts on TiO₂

- Monometallic catalysts prepared by dry impregnation method. After reduction at 300°C, metal particles were too small for detection by XRD (< 1.5 nm).</p>
- Calcination then done in air at 800°C.
- > Pt sintered to ~35 nm particles, while Ir and Ru are very stable on TiO_2 surface.
- Higher loading Ir and Ru provides more surface for Pt anchoring. Core catalysts of Ir and Ru made with 5% weight loading of metal on pretreated TiO₂ (calcined at 800°C)



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XRD = X ray diffraction

Accomplishments - Bimetallic TiO₂ catalysts



Test conditions included:

temperature of 800 °C, pressure of 1 bar and $\rm H_2SO_4$ concentration of 91 wt %.

- Monometallic and bimetallic PGM/TiO₂ catalysts showed appreciable deactivation.
- Ir based catalysts had lower reaction rates than the monometallic catalyst.
- Increasing Ir content decreased reaction rates and did not reduce deactivation.

Accomplishments - Boron Nitride (BN) support

- BN is more stable support than TiO_2 with small loss of surface area at 800°C.
- At T ≥ 900°C, surface area increases dramatically due to large decrease in pore diameters.
- Pore diameters of $\sim 3 5$ nm likely not useful during reaction.



Sample	Surface area (SA, m²/g)	V _{pore} (cm³/g)	D _{ave} (nm)
BN-fresh	61	0.21	13.7
BN-600 °C	54	0.18	13.8
BN-800 °C	53	0.17	13.1
BN-900 °C	73	0.13	7.4
BN-950 °C	100	0.11	4.6
BN-1000 °C	135	0.11	3.5

Accomplishments - Bimetallic Pt-Ir catalysts supported on BN



- BN was calcined at 800°C before Ir impregnation.
- Ir/BN reduced at 300°C in H_2 /Ar gas mix.
- Pt deposited on Ir using ED.
- Deposition of Pt on Ir/BN faster than Ir/TiO₂ because of smaller Ir particles on BN.

[DMAB] : [EN] : [PtCl₆²⁻]

wt of base catalyst

Wt% Pt deposited

Volume

pН

5:4:1

500 mL

1 g

1%

10

Accomplishments - Bimetallic Pt-Ir catalysts supported on BN



- BN was calcined at 800°C before Ir impregnation.
- Fresh catalyst shows the presence of broad Ir peaks and absence of Pt peaks → presence of Ir on the surface not well dispersed
- Calcined has only Ir oxides and broad and less intense Pt peaks → metal Ir well dispersed, Pt more stable on BN than TiO₂

HydroGEN: Advanced Water Splitting Materials

ED = Electroless deposition

1%Pt on 5%lr

1%Pt on 7.5%lr

Calcined (Pt)

TiO₂

27

22

BN

11.4

16.4

Accomplishments - Bimetallic BN catalysts tests



Test conditions included:

temperature of 800 °C, pressure of 1 bar and H_2SO_4 concentration of 91.28 wt %.

- Both bimetallic Ir/BN catalysts showed less deactivation then the momometallic catalyst.
- 1% Pt-7.5% Ir/BN catalyst showed nominal activity of 1.75 molSO2/h/gCat, <u>surpassing Milestone</u> <u>1.1</u>.
- 1% Pt-7.5% Ir/BN catalyst showed no deactivation in 75 hours of testing surpassing <u>Milestone 1.2</u>, deactivation rate of 0.015%/hour.
- Increasing Ir content decreased reaction rates.

Accomplishments - Novel solar receiver/reactor concept



Novel GWE-NREL H₂SO₄ decomposition reactor configuration (ROI filled)

Level 2

- Compact and intensified design
- External solar heating and internal heat recovery accomplished in a single SiC unit
- Technical feasibility demonstrated (AMR 2018) with CFD detailed transport modeling

Accomplishments - Solar reactor preliminary scale up Level 2



assembled units on top of the solar tower

Single receiver-reactor

← 100 *←* (W4) 24.2 (W6)

units

(H1)

Sizing of the solar receiverreactor for large scale production

Initial configuration achieved

Matching between heat exchange power requirements and geometry constraints

Single unit receiver/reactor		
L (m)	0.5	
W4 (m)	0.1	
H ₂ SO ₄ flow rate (kg/s)	0.285	
Assembled units for 95.3TPD H ₂ peak production		
D (m)	11.5 (single tower)	
Y (m)	2-4 (projected total length) 1-1.5 (SO ₃ catalytic decomposition section length)	
Number of reactor	364	

Accomplishments - Solar reactor process analysis

Level 3









Accomplishments - Low T process flowsheet Level 3



Novel HyS cycle flowsheet based on the vapor fed SDE section – 24/7 operation

- SDE section (leveraged from externally financed USC work)
 - Increase of SDE efficiency at about 140 C
 - V= 575 mV, I= 500 mA/cm²
 - W_{el} = 110.2 kJ/molH₂
 - Production of high concentration sulfuric acid
 - Higher temperature SDE waste heat (140 °C) internally recoverable to concentrate H₂SO₄ up to 80wt%

Accomplishments - High T process flowsheet



High T section (not optimized version)

- Decrease of the decomposer heat duty
- Total internal heat recovery of undecomposed flow (> 200 °C) to concentrate H₂SO₄ up to 90wt%
- Increase of the overall efficiency need for small low T heat provided by solar vacuum tubes

Accomplishments - Process pinch analysis Level 3



LT = Low temperature

SDE = SO₂ depolarized electrolyzer

	Total	HyS HT	HyS LT
HyS thermal input (kJ/mol)	347.3	347.3	-
HyS electric input (kJ/mol)	123.1	10.6	112.5
HyS efficiency (%)	37.6		
	35.7 (with LT heat)		
Solar plant efficiency	56.4		
S2H efficiency (%)	21.2		
	20.1 (with LT heat)		

Thermochemical (37.6%) and Solar to Hydrogen (S2H) (21.2%) efficiencies meet the **Milestone 1.3 target**



Accomplishments - Design nominal point



Accomplishments - Solar HyS plant cost evaluation



Baseline hydrogen cost = 2.43 \$/kg

Main baseline economicfinancial assumptions

- Heliostat field cost = 75 \$/m² (Sunshot value)
- Electricity cost = 2 c\$/kWh
- Plant lifetime = 30 years
- Financial assumptions = H2A default

Results

- H₂ baseline cost = 2.43 \$/kg
- Utility cost (electricity) depending on efficiency and specific electricity cost
 - Capital cost is the main cost item

Level 3

Accomplishments - Solar HyS plant capital cost



Accomplishments - Receiver-reactor cost



Insulated inner structure support

Outlet reacted fluid distributor

Caps

Accomplishments - Viable path toward 2 \$/kg



Not included

- Oxygen byproduct cost
- Heliostat cost reduction
- Sulfuric acid concentration and SO₂/O₂ separation membranes
- Wind tower

*Wei M, et al. LBNL report on High T Fuel cell membranes, https://www.energy.gov/sites/prod/files/2017/06/f34/fcto_tco_model_hich_temp_pem_fc.pdf

HydroGEN: Advanced Water Splitting Materials

PCF = Plant capacity Factor HyS = Hybrid Sulfur HT = High temperature section PBI = Polibenzminide membranes Analysis based on <u>KNOWN,</u> <u>VIABLE and ACHIEVABLE</u> conditions

- Heliostat efficiency:
 63.9 → 67.5 % (Edisun company discussions)
- Plant Capacity Factor (PCF)

 $63 \rightarrow 73$ % (different location, previous analyses)

 HyS HT cooling utility and low T heating

Novel optimized flowsheet being developed with reduced low T heating ($35 \rightarrow 8 \text{ kJ/mol}$) and cooling (power reduction of about 60%)

• Solar reactor T

Increase up to 900-920 C, reduction of heat duty $347 \rightarrow 343$ kJ/mol

Enhanced catalyst

Being proposed a bimetal formulation with Co substituting Ir

• Product purification

Initial analysis with less expensive adsorbents and optimized flowsheet (projected -35% cost)

SDE membrane cost

Enhanced second generation PBI* with about 100-200 systems/year (still initial market) (PBI cost reduction 23%)

 $SDE = SO_2$ depolarized electrolyzer

Collaboration: Effectiveness

Level 1 Action	Institution	Need for the AWSM	
Novel BN catalyst development and synthesis (Patent)	USC	- INL \rightarrow unique capability to run of H ₂ SO ₄ decomposition	
		tests at the required T, P and concentration – <i>Milestone 1.1 and 1.2</i>	
Level 2 Action	Institution	Need for the AWSM	
Detailed model of the new reactor	GWE – USC	- NREL → critical to identify, optimize the novel direct solar reactor, leveraging lab expertise and previous results for electricity production (ROI filled) – <i>Milestone 1.3</i>	
Level 3 Action	Institution	Need for the AWSM	
Novel HyS Flowsheet	GWE – SRNL	 - NREL → design and characterization of solar tower plant and BOP - <i>Milestone 1.3</i> - SRNL → development of HyS process flowsheet – <i>Milestone 1.3</i> 	
Solar plant design with chemical storage	GWE – NREL		
Solar plant techno-economic analysis	GWE – SRNL - NREL		

HydroGEN: Advanced Water Splitting Materials

ROI = Record Of Invention

Collaboration: Interactions

- Meetings and data sharing
 - By-weekly meetings between recipients (GWE and USC) and capable labs (INL, NREL, SRNL) → presentations uploaded in the NREL Sharepoint
 - Face to Face meetings
 - Meetings in GWE (August-December 2018) with GWE, USC, SRNL → identification of the baseline flowsheet concept for the high T section and variations of the configurations
 - NREL visit in GWE and USC (December 2018) → identification of the next steps especially about modeling and lab scale demonstration of the reactor concept
 - Teleconferences INL, USC and GWE (October-December 2018) for different catalyst testing
 - Interactions with the 'Benchmarking 2B' project
 - Defined the protocol for hybrid cycles (connections with both the electrolysis group and the STCH group) – Involvement of possible international partners
 - Reports uploaded in the NREL Sharepoint
- DataHub data
 - Flowsheeting data
 - Equilibrium data for sulfuric mixtures (based on the new ASPEN model by SRNL for high T and low T sections)
 - Solar plant design data (solar flux data, efficiencies, optimization and design data for solar tower and mirrors by NREL)
 - Novel BN catalysis test data



Additional collaborations and potential partners

- CoorsTek Design of the novel receiver-reactor with SiC structures, initial discussion for lab scale reactor and feasibility for large scale operations
- Edisun Microgrids Enhanced solar heliostat (higher efficiency and potential lower cost) available, NDA between GWE and Edisun being signed, high interest on on-sun demonstration for 10-100 kW plant with Edisun heliostat and HydroGEN HyS
- Proton Onsite, namely George Roberts Conceptual design, analysis and testing of compact heat exchanger loop to recover the SO₂ electrolyzer heat

Proposed Future Work

<u>Catalyst development and testing</u>

- Optimization of the new proposed BN catalyst
 - · Co ED of Pt and Ir to achieve higher stability
 - Structural stability determination
 - Different bimetallic concentrations and depositions
- Different first layer metal material, replacing Ir (e.g. Co)
- Development of non PGM catalyst (e.g. Fe based materials)
- Development of stable engineered catalytic geometries and structures
- Long term duration tests (i.e. > 400 hours)
- Kinetic rates determination for modeling and scale up
- Higher pressure (i.e. 30-50 bar) tests equipment to be built
- Parallel reactor tests reactors to be built

Reactor and system modeling

- Rector development and CFD analysis, including the two phase (liquid/vapor) flow
 - New reaction kinetics
 - Possibly different flow regimes
 - New geometries and configurations
- Feasibility of novel reactor system scale up
- Solar plant characterization and design
 - Analysis of different solar plant configurations (e.g. location, enhanced efficiency heliostat, wind towers, etc)
- Storage
 - Analysis of alternative chem storage using membranes to separate O₂ at the exit of the high T reactor
 - Use of nanomaterials to store energy, embedded in the catalyst bed
- HyS process
 - Optimization of the process flowsheet (P, T, concentrations)
 - Assessment of alternative solutions for H₂SO₄ concentration and SO₂/O₂ separation
 - Detailed component design and cost assessment based on optimized flowsheet (especially for nonconventional components)



- Catalyst development and tests (USC INL)
 - Novel BN-based bimetallic formulation identified
 - The catalyst performance meets the nominal activity target
 - The catalyst showed essentially no degradation for 75-hour tests
- Receiver reactor design (GWE USC NREL)
 - Initial scale up of the direct receiver-reactor carried out
 - > Initial contacts with industrial partners for lab scale demo
- HyS process flowsheet (GWE SRNL)
 - Novel vapor fed electrolyzer flowsheet developed
 - Baseline high T flowsheet identified
 - Thermochemical efficiency of 37.6% achieved
- Solar plant system design and analysis (GWE NREL)
 - Chemical storage configuration downselected as the baseline storage approach
 - Conceptual design of solar thermochemical plant assessed, achieving solar to hydrogen efficiency of 21%
 - Economic assessment of the solar plant carried out
 - Identified viable path toward the target of 2 \$/kg



- Patents
 - Record Of Invention on the solar reactor receiver for sulfuric acid decomposition: Ma, Z., et al., NREL Record of Invention ROI-18-62, 2018.
 - Patent being filled on the BN catalyst Invention disclosure: Monnier, J., et al., USC ID no. 1372, 2018
- Presentations/publications
 - Corgnale, C. et al. "Solar Driven Thermo-Electrochemical Hybrid Sulfur Process for Hydrogen Production" ECS AiMES Meeting 2018, Cancun (Mexico), October 2018.
 https://ecs.com/ecs/aimes2018/meetingapp.cgi/Paper/112622

https://ecs.confex.com/ecs/aimes2018/meetingapp.cgi/Paper/112622

 Corgnale, C. et al. "Numerical Modeling of a Novel Solar Driven Sulfuric Acid Decomposition Reactor" ECS AiMES Meeting 2018, Cancun (Mexico), October 2018.

https://ecs.confex.com/ecs/aimes2018/meetingapp.cgi/Paper/112623

- Adhikari, B. et al. "High temperature catalyst development and testing for low cost and efficient solar driven sulfur-based hydrogen production" AIChE Annual Meeting (514g), Pittsburg (PA), November 2018
- Ma, Z. et al. "Integrating thermochemical and electrochemical processes with a concentrating solar thermal system for hydrogen production" ASME Power & Energy Conference and Exhibition, Lake Buena Vista (FL), June 2018
- Gorensek, M. et al. Electrochem. Soc. Interface Spring 2018 volume 27, issue 1, 53-56



Technical Back-Up Slides (Note: please include this "divider" slide if you are including back-up technical slides [maximum of five].

These back-up technical slides will be included in the USB drive and Web PDF files released to the public.)

Bimetallic Pt-Ir catalysts supported on BN



- BN was calcined at 800°C before Ir impregnation.
- Fresh Ir on BN catalyst shows the presence of broad Ir peaks → presence of Ir on the surface not well dispersed
- Calcined Ir on BN catalyst has only Ir oxides on the surface but not Ir metal → metal Ir well dispersed



Bimetallic Core-Shell Structures:

Stabilization using differential Surface Free Energy (SFE) Level 1

- *Enhanced stability of active metal surface by anchoring lower SFE metal (Pt) as shell on higher SFE cores (Ir or Ru).
 - Pt can be selectively deposited on Ir or Ru surfaces using Electroless Deposition (ED) method.



Pt deposits Catalytically (on Ir) or Autocatalytically (on Pt)

 Stabilization using SFE difference in core-shell morphology has been demonstrated for other systems.





	Melting	Surface free energy
Component	point, (°C)	(ergs/cm ² surface)
Carbon	3550	506
SiO ₂	1600	605
TiO ₂	1843	670
Al_2O_3	2072	805
Ag	962	1302
Au	1064	1626
Cu	1083	1934
Pd	1554	2043
Ni	1453	2364
Pt	1772	2691
Со	1495	2709
Rh	1966	2828
Мо	2617	2877
Fe	1535	2939
Nb	2468	2983
Re	3180	3109
Ir	2410	3231
Ru	2310	3409
W	3410	3468

*US 10,016,751 "Supported, bimetallic nanoparticles for selective catalysis," July 10, 2018

Reactor simulation results Level 2







HydroGEN: Advanced Water Splitting Materiais

Heliostat dimensions

HyS heat recovery exchanger network design



LT section (40.9 TPD design)

- SDE waste heat recovered using 4 finned compact shell and plate heat exchangers (pressurized water)
- TO01 condenser waste heat rejected using water at 20 C
- All the heat exchangers and components are massive equipment with SS316, Carpenter 20 or Hastelloy B20 as materials

HT section (95.3 TPD design)

- Low T heat (SO₂ stripper reboiler, TO04) provided using intermediate heat exchanger (pressurized water) interfaced with evacuated solar tubes (almost 20 MW)
- Heat rejected using water at 20 C
- Components have been (initially) designed using Acid Brick Liners and cladding solutions, achieving important cost reductions

Questions?

Contact us by email: H2AMR@orau.org