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Electrolytical Decomposition of Hydrogen Sulifide into Hydrogen and Gaseous Sulfur at 400°C.

Feasibility Study

By

Keilir Research Center and University of South Florida

Electrolytical Decomposition of Hydrogen Sulifide (H₂S) into Hydrogen and gaseous Sulfur at 400°C.

INTRODUCTION

Hydrogen sulfide is an environmental nuisance emitted from geothermal wells that can be captured and split into Hydrogen and Sulfur, both value added useful commercial products. NE in cooperation with Keilir and USF propose to develop an economical commercial system to split hydrogen sulfide into these useful products using an electrolysis method developed earlier in our research center. This proposal focuses on (a) optimization of the electrolytic cell for performance and easy separation of the products, and (b) test and demonstration of a prototype that can be scaled up to commercial applications. Hydrogen sulfide is a colorless gas with the characteristic foul odor of rotten eggs; it is heavier than air, very poisonous, corrosive, flammable and explosive. It is a component of geothermal fluid that requires disposal and has no market value. Since hydrogen sulfide has a small free energy of formation, a small amount of energy can decompose it into hydrogen and sulfur that can be sold. This project aims to develop an economical technique for achieving this decomposition at a cost below the value of these products.

Endurance Materials for Hydrogen Sulfide Splitting in Electrolytic Cell

by

Project Title
Hydrogen Production from Hydrogen Sulfide in IGCC Power Plants

Jonathan Chinwendu Mbah

Final Scientific /Technical Report

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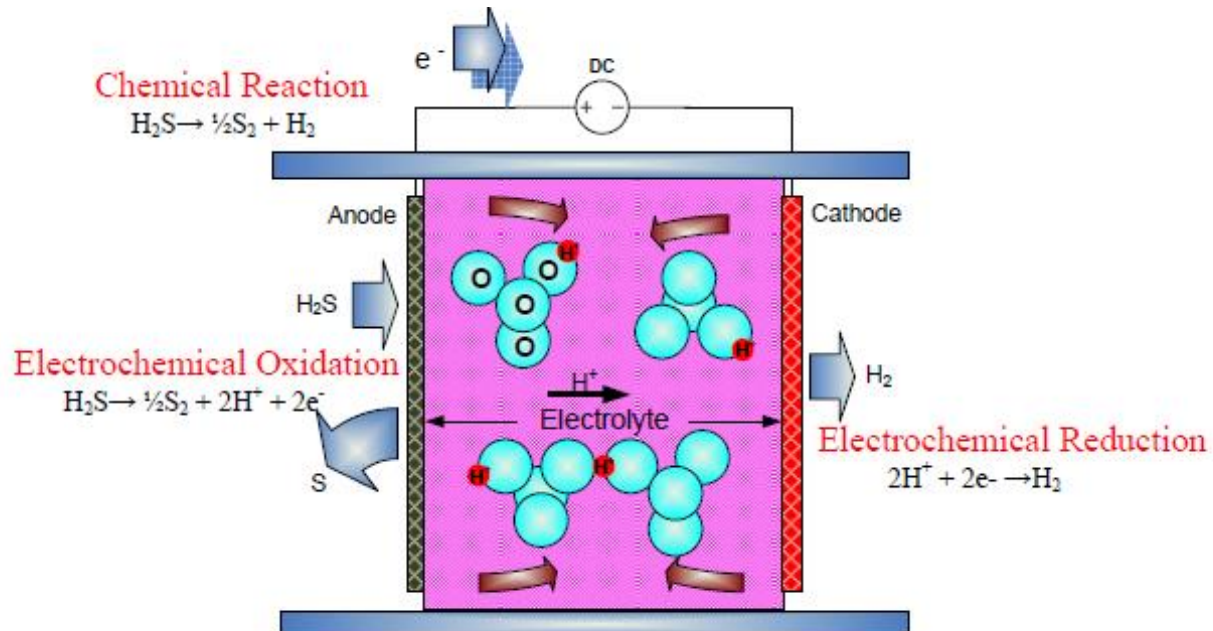
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Electrolytical Decomposition of Hydrogen Sulfide (H₂S) into Hydrogen and gaseous Sulfur at 400°C.

The previous studies at University of South Florida describes the development of a novel thin **membrane** exchange assembly (MEA) from a solid acid material, cesium hydrogen sulfate (CsHSO₄), and from a composite **anode** electrocatalyst for electrolytic splitting of (100 %) H₂S feed content gas operating at 135 kPa and 150 °C. A new class of anode electrocatalyst with the general composition, RuO₂/CoS₂, and an improved proton conductor, CsHSO₄, have shown great stability and desired properties at typical operating conditions. This configuration demonstrated stable electrochemical operation for 24 h with a (100 %) H₂S fuel stream at 423 K.(150°C). This same system showed a maximum current density of (19 mA/cm₂) at 900 mV.

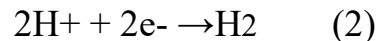
Electrolytical Decomposition of Hydrogen Sulifide (H₂S) into Hydrogen and gaseous Sulfur at 400°C.



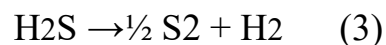
The fundamental principle underlying the splitting of H₂S electrochemically consist of having an anode and cathode compartments in which a solid proton conducting membrane separates an anode chamber from a cathode chamber see Figure. The process consists of passing H₂S containing gas through the anode chamber to contact a catalytic anode, where reaction (Eqn. 1) takes place to produce elemental sulfur, protons and electrons.



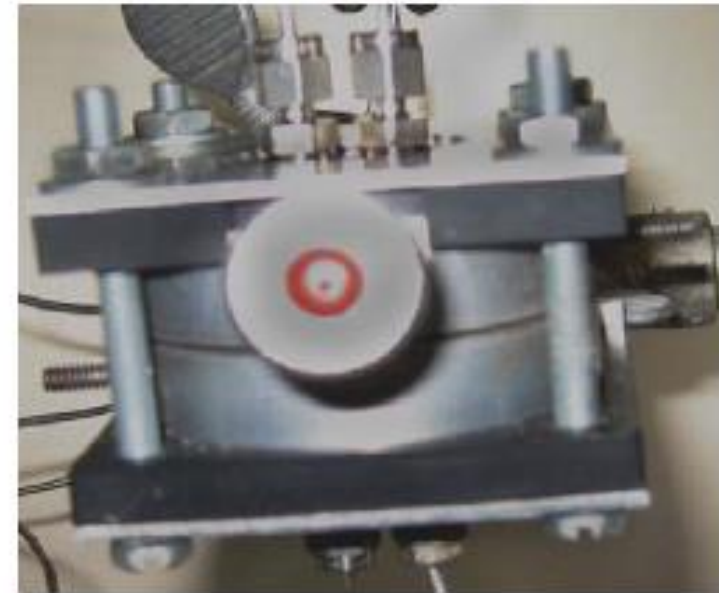
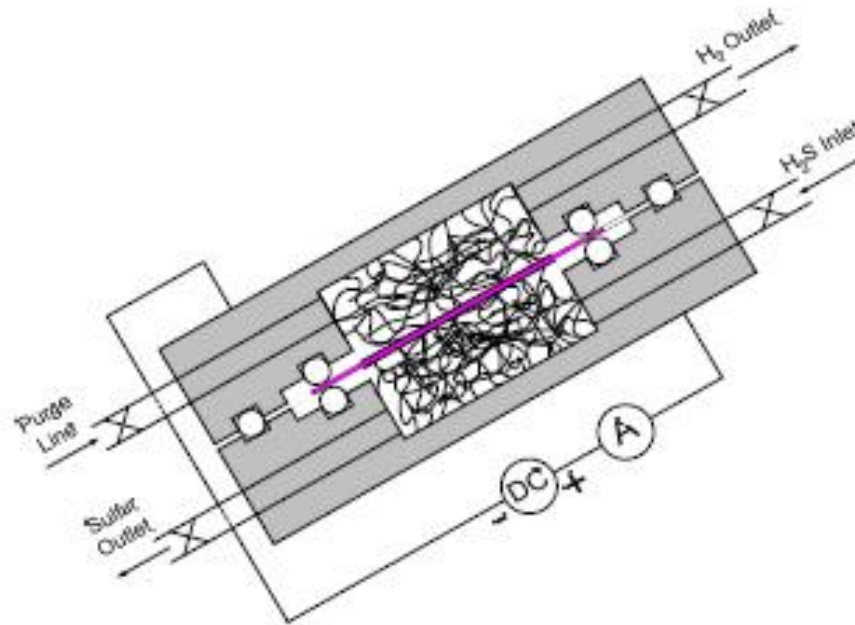
The protons pass through the membrane from the anode chamber to the cathode chamber, where reaction (Eqn..2) occurs with electrons from the catalytic cathode to produce hydrogen gas.



The chemical reaction taken place is given by reaction (Eqn. 3)



Electrolytical Decomposition of Hydrogen Sulphide (H_2S) into Hydrogen and gaseous Sulfur at $400^\circ C$.



Electrochemical Thermodynamics

Any electrochemical reaction involves the transfer of electrons between an electrode surface and a chemical species adjacent to the electrode surface. Thermodynamically favorable electron transfer processes is harnessed in order to extract the electrical energy requirement for the oxidation process.

Electrolytical Decomposition of Hydrogen Sulfide (H₂S) into Hydrogen and gaseous Sulfur at 450°C.

PROPOSED DEVELOPMENT WORK

In USF previous work, it was proved the principle using thick electrolyte films and a working temperature of 150 °C. In order to advance the development to achieve commercial viability USF is seeking higher current densities, lower overvoltages and lower material costs for electrolyte and catalysts. For this we will seek to make thinner MEAs and operate at higher temperatures. Mechanisms that degrade current density and overvoltage include: wetting of the membrane with liquid sulfur, inherently slower chemical kinetics at lower temperatures, random contacts and higher electrical resistance of thick films. We do not know the relative importance of these mechanisms and are not proposing to do basic research to get this information. Rather we are proposing to assemble an apparatus to alleviate them all. We propose to lower material costs by using less of the expensive electrolyte in thin films and lower loadings of cheaper catalysts at higher temperatures. The low strength of the thin films will be overcome by using cheap metal supporting structures.

Electrolytical Decomposition of Hydrogen Sulfide (H_2S) into Hydrogen and gaseous Sulfur at 400°C .

Experimental Electrolysis System

Figure 1 shows the experimental electrolysis system used with the cesium hydrogen sulfate electrolyte at 150°C . A similar system will be used in this project. However, the new system will be operating at higher temperatures ($400\text{-}500^\circ\text{C}$) with the sulfur collection vessel accepting hot gaseous sulfur and cooling it to condense it to liquid. The line from the electrolysis cell to the sulfur collection vessel will be heated and larger and some H_2S carried through it together with the sulfur will be recycled. A flow controlling H_2S pump will be needed.

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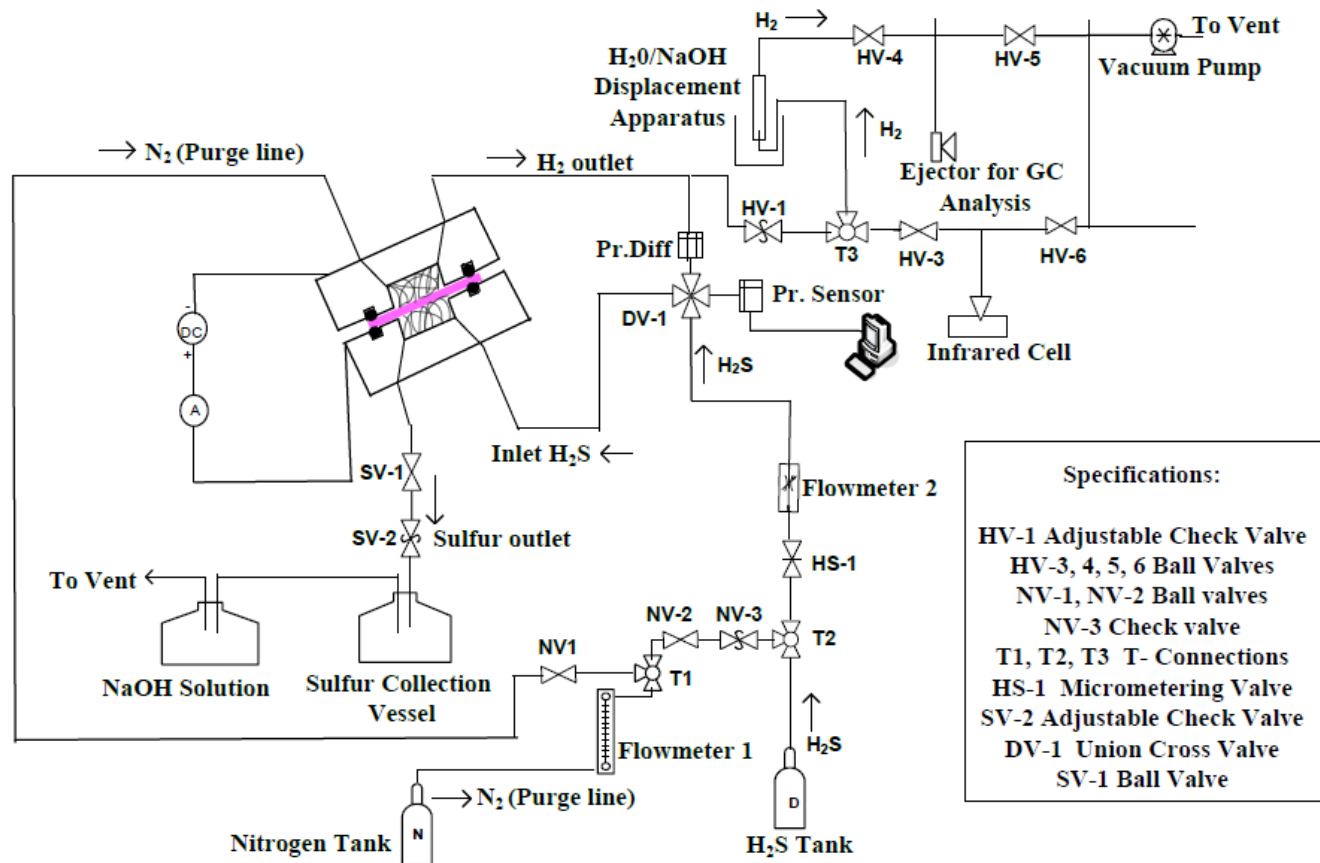


Figure 1. Schematic set-up of the electrolytic decomposition system.

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The MEA and Electrolyte Membrane

To make thinner MEAs we intend to structure it so that electrolyte, electrodes, substrate and insulation will mutually support each other to maximize the strength of the unit. An example of such a structure is shown schematically in Figure 2. We are seeking materials with which we can make thinner MEAs that have the required traits and operate at higher temperatures where the sulfur could be extracted as vapor. A temperature of 400 °C may be a good compromise between enhanced performance and modest material demands.

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Membrane Electrode Assembly (MEA)

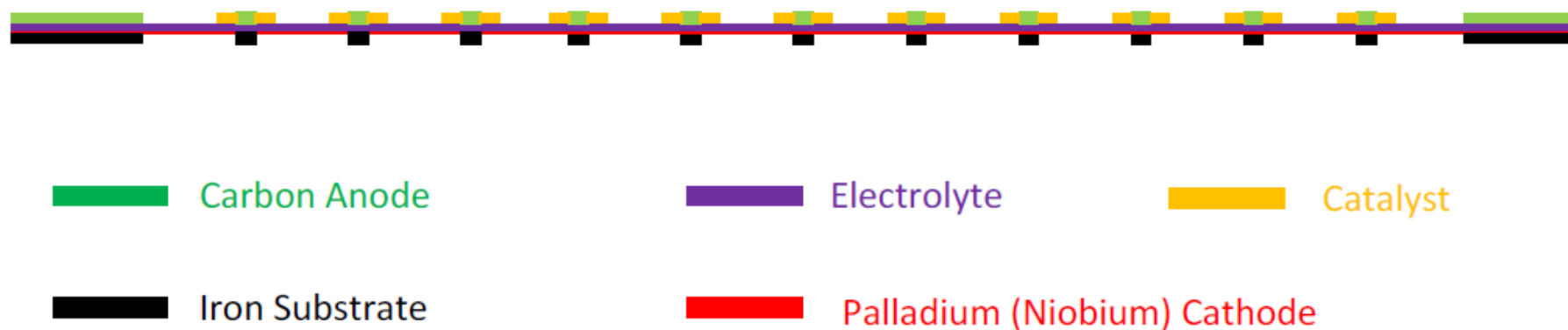


Figure 2. The proposed membrane electrode assembly (MEA) that can operate at higher temperatures (400-500°C)

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The Membrane Electrode Assembly (MEA)

The membrane electrode assembly consists of 5 layers of material assembled in order to serve the various required functions. The fabrication process and layer functions of the MEA will be as follows:

1. A layer of iron foil is the foundation and support on which the other layers are serially deposited.
2. A one micron thick film of Pd, Nb or Ta is deposited on the iron foil by electron beam evaporation. This serves as cathode, hydrogen atom conductor and catalyst.
3. A two micron thick film of proton conducting electrolyte is deposited on the cathode by electrophoresis or sol-gel deposition. Doped barium zirconates and cerates will be used for this application.
4. A carbon anode grid will be screen printed on the electrolyte. This can have catalytic as well as electrode actions.
5. The anode catalyst will be screen printed on the electrolyte at the edges of the anode grid lines. Ruthenium oxide was the best anode catalyst observed in our previous work at lower temperatures. A cheaper catalyst may prove adequate for this higher temperature reaction. Sulfides will be considered for their stability in H₂S and sulfur.
6. Holes will be photo etched through the iron foil to provide paths for exit of the hydrogen molecules released by the cathode.

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DEVELOPMENT PHASE 1. EXPERIMENTS

During the experimental portion of the phase 1 work, USF plan to investigate the chemical stability of doped barium zirconates and cerates in the H₂S electrolysis cell environment. The following steps will be followed:

1.1 Component Development

- Compare deposition techniques (sol-gel and electrophoresis) for depositing electrolyte membranes. Test criteria will be impermeability, conductivity, stability and strength.
- Contrast the practicability of palladium, niobium and tantalum cathodes.
- Structure MEA so that electrolyte, electrodes, catalyst, substrate and insulation will mutually support each other to maximize the strength of the unit.
- Develop seals for operation at the cell temperatures.

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DEVELOPMENT PHASE 1. EXPERIMENTS

During the experimental portion of the phase 1 work, USF plan to investigate the chemical stability of doped barium zirconates and cerates in the H₂S electrolysis cell environment. The following steps will be followed:

1.2 System Development

A small scale prototype system will be assembled and tested.

- Test thin MEA for impermeability, conductivity and strength.
- Test thin MEA performance in electrolysis of hydrogen sulfide.
- Study procedures for operating the sulfur collection vessel and H₂S recycling system.
- Evaluate the performance, application and loading choices for catalysts.

Techniques used in the manufacture of solid oxide fuel cells will be examined and employed where applicable.

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DEVELOPMENT PHASE 2.

SCALE- UP DESIGN FOR FABRICATION AND DEMONSTRATION

2.1 Design for scale-up of component manufacture

The prototype design will be evaluated at the end of Phase I. The design for manufacture will be evaluated in Phase II. Dialogue will be established with capable and qualified large scale product manufacturing industries that can collaborate with the University of South Florida and Keilir University to meet demands of a bulk volume of components. Considerations will also be given to tooling costs and other nonrecurring manufacturing costs. Initial cost models, manufacturing plans, and business models will be developed for commercialization of the designs and materials and fabrication approaches developed in Phase II. In defining possible manufacturing approaches, considerations will be focused on high rate processes and continuous processes that will minimize labor costs of our optimized structure. With feedback from manufacturers, laboratory experiments will be used to examine the impacts of manufacturing recommendations on performance.

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DEVELOPMENT PHASE 2.

SCALE- UP DESIGN FOR FABRICATION AND DEMONSTRATION

2.2 Design for field demonstration

In collaboration with Keilir University, we will focus on the integration of the designed electrolysis concept into a geothermal system and an analysis of its overall efficiency and costeffectiveness.

Intensive guidance will be sought from the geothermal field operators in designing the first field prototype that they might use on a slip stream.

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Timeline and Milestones

Research Activities	Year 1					Year 2					Year 3				
Phase 1.1 Component Development	■	■	■	■	■										
Phase 1.2 System Development		■	■	■	■										
Phase 2.1. Design for scale-up of component manufacture						■	■	■	■	■					
Phase 2.2. Design for field demonstration											■	■	■	■	■
Reporting:					■						■				■