Florida Solar Energy Center

Creating Energy Independence Since 1975

Florida Hydrogen Initiative (FHI)

DOE Contract # DE-FC36-04GO14225

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Project ID#: TV012

Overview

Timeline

- Project Start Date: 10/1/04
- Project End Date: 11/15/10
- Percent Complete: 44%

Barriers

- Barriers addressed
  - Research and Development
  - Creating Partnership
  - Facilitating Technology Transfer

Budget

- Total project funding
  - DOE share: $3,946,155
  - Contractor share: $928,045
- Funding for FY09: None
- Funding for FY10: None

Partners

- Florida Solar Energy Center
- EnerFuel, Inc.
- Chevron Technologies
- Orlando Science Center
- Rollins College

Project Objectives/Relevance

This project seeks to develop DOE and Florida's Hydrogen and fuel cell infrastructure by:

- **Creating partnerships for applied demonstration projects;**
- **Sponsoring research, development and demonstrations in hydrogen and fuel cells technology;**
- **Facilitating technology transfers to create, build, and strengthen high-growth, high technology companies;**
- **Developing industry support for applications;**
- **Develop unique university level education programs.**

FHI Background

- Previously operated by the Florida Hydrogen Iniative, Inc.
- Contract for operation and management received by the University of Central Florida (UCF) in October 2009.
- Project management and technical oversight provided by the Florida Solar Energy Center/UCF.
- Approximately $2.5 million in funds available for new projects.

Approach

- Project has solicited proposals to conduct work
- Initially selected four projects
- Solicited new projects in October 2009
- Selected three R & D projects in January 2010
- Solicited new projects (RFP) in April 2010

New Funding Status

I. Letters of Interest (LOI) ≈ $1 million

1. Request for projects at FSEC released on October 15, 2009
2. Proposed projects received on November 16, 2009.
3. Five member peer review committee evaluated proposals.
4. Three projects selected January 2010. Project details follow.

New Funding Status (continued)

II. Request for Proposals ≈ $1.5 million

1. **Request for Proposals issued March 17, 2010.**
2. **Proposals due April 23, 2010.**
3. **Five member peer review committee has been appointed.**
4. **Planned new project contracts issued by July 2010.**

FHI Task Status

Task 1. FL Hydrogen Refueling Infrastructure, Rollins College. Project is complete and final report written.

Task 2. FHI Project 2005-02, EnerFuel, Inc., "Hydrogen Technology (HyTech) Rest Area: Demonstration of a Multi-kW Integrated Methanol Fuel Cell Power Plant for a Highway Rest Area". Project continuing. Work has been completed on locating a more appropriate location for the demonstration project.

Task 3. Hydrogen Exhibit, Orlando, Science Center, Assessment of Public Understanding of the Hydrogen Economy Through Science Center Exhibits. This project is complete and final report completed.

Task 4. FHI Executive Director. Task is complete.

Task 5. FHI Project 2005-05, University of Central Florida and Chevron Technology Ventures, "On-Site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications". The project is complete and a final report written.

Task 6. FHI Temporary Executive Director. This task is complete.

Three New Projects – Just Beginning

Task 7. Chemochromatic Hydrogen Leak Detectors for Safety Monitoring.

Task 8. High Efficiency Low Cost Electrocatalyst for Hydrogen Production and PEM Fuel Cell Applications.

Task 9. Understanding Mechanical and Chemical Durability of Fuel Cell Membrane Electrode Assemblies.

Collaborations

1. Task 1 – FL Hydrogen Refueling Infrastructure, Rollins College, Winter Park, FL
2. Task 2 – Hydrogen Technology (HyTech) Rest Area: Demonstration of a Multi-kW Integrated Methanol Fuel Cell Power Plant for a Highway Rest Area, EnerFuel, West Palm Beach, FL
3. Task 3 – Hydrogen Exhibit, Orlando Science Center, Orlando, FL
4. Task 5 – On-Site Reformation, Chevron Technology Venture, LLC, Houston, TX

Task Status Summary

Tasks 1, 3, 4, and 6 – Complete

Task 2 – Continuing

Task 7, 8, and 9 – New and just beginning.

Summary

Relevance: Conduct R & D, demonstrations, create partnerships, facilitate technology transfer

Approach: Solicit proposals to meet objectives

Technical Accomplishments and Progress: Completed three projects, one continuing, three new

Technology Transfer/Collaboration: Active partnership with project participants – EnerFuel and Chevron

Proposed Future Research: R & D on developing H_2 sensing chemochromatic tape, R & D on improving catalysts and on understanding fuel cell mechanical and chemical durability

References

- Lines, L., Kuby, M., Schultz, R., & Xie, Z. (2007). Hydrogen refueling infrastructure and rental car strategies for commercialization of hydrogen in Florida (Final Report for Florida Hydrogen Initiative Agreement No. 2005-01/Department of Energy Grant Award No. DE-FC-36-04GOI4225). Winter Park, FL: Rollins College.

- Newman, J., & Hunter, K. (2010). Assessment of public understanding of the hydrogen economy through science (Final Report for Florida Hydrogen Initiative Agreement No. 2005-03/Department of Energy Grant Award No. DE-FC36-04GOI4225). Orlando, FL: Orlando Science Center.

New Project Descriptions

Task 7. Chemochromatic Hydrogen Leak Detectors for Safety Monitoring – Drs. Nahid Mohajeri and Nazim Muradov, FSEC.

The aim of this project is to develop and demonstrate a cost-effective, high specific chemochormic (visual) hydrogen (H2) leak detector for safety monitoring at any facility engaged in handling and use of hydrogen. The work will lead to a new generation of versatile chemochromic hydrogen detectors that employ “smart” materials that cost less, possess fast discoloration kinetics, are user-friendly, are reliable and have superior field worthiness. Of particular practical importance is the development of multi-functional visual hydrogen leak detectors that have the capacity to function in either reversible or irreversible mode by facile modification of their chemistry. DOE = $281,549.

Applications

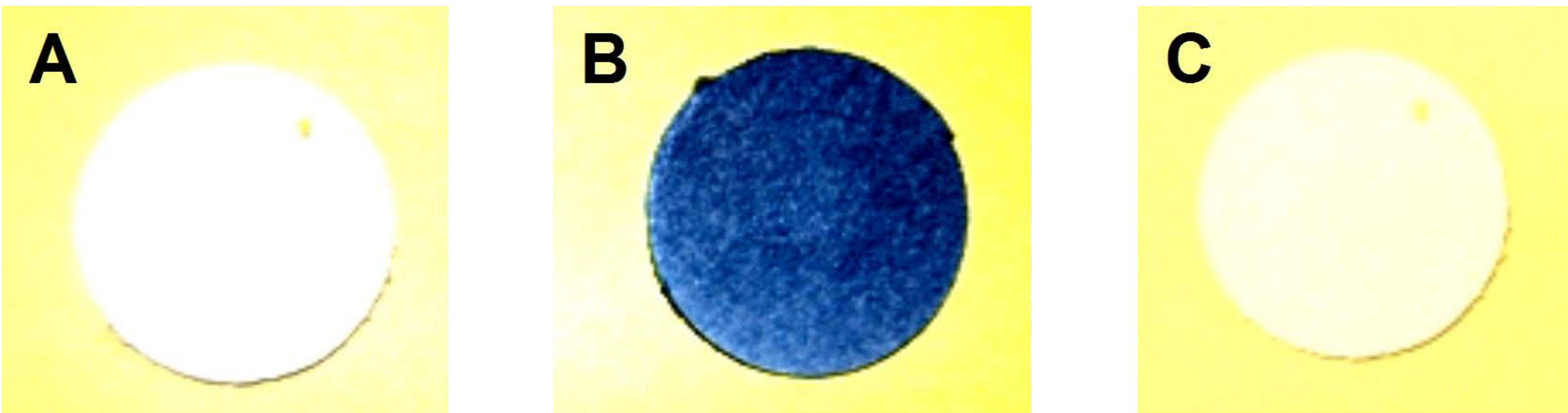
- Hydrogen Generation
  - *Ammonia plants*
  - *Oil refineries*
  - *Water electrolyzers*
- Hydrogen Storage/Distribution
  - *NASA – Kennedy Space Center*
  - *Hydrogen pipelines*
- Hydrogen Utilization
  - *Combustion Systems*
  - *Fuel Cell Applications*

Chemochromic H_2 Sensing Materials

(1st Generation)

Chemochromic Hydrogen Detectors is nominated for a 2010 NASA Blue Marble Environment and Energy Award

Reversible Mo-POM Based Pigments



H_2 sensor based on Mo-POM activated by Pt nanoparticles

A- before H_2 exposure,

B- immediately after exposure to hydrogen

C- left overnight

Proposed Tasks

Task 1 – Review of available literature data on existing chemochromic hydrogen sensors.

Task 2 – Determine the selectivity of the chemochromic sensor toward hydrogen detection in the presence of other reducing gases.

Task 3 – Optimize the sensor performance by the noble and non-noble metal doping and nano-engineering.

Task 4 – Optimize the method of encapsulation of chemochromic pigments as it relates to ease of hydrogen and oxygen diffusion into the pigmented matrix.

Task 5 – Determine the effect of different parameters (temperature, hydrogen partial pressure and flow rate, UV light) on the performance of the chemochromic pigments/matrix system.

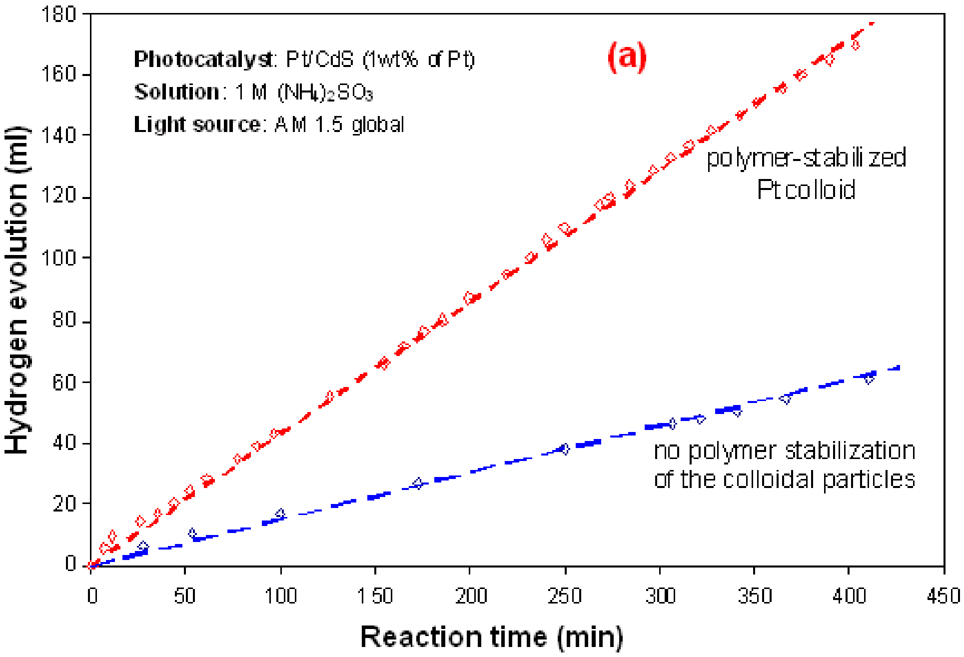
Task 6 – Perform field testing of the prospective visual hydrogen leak detectors.

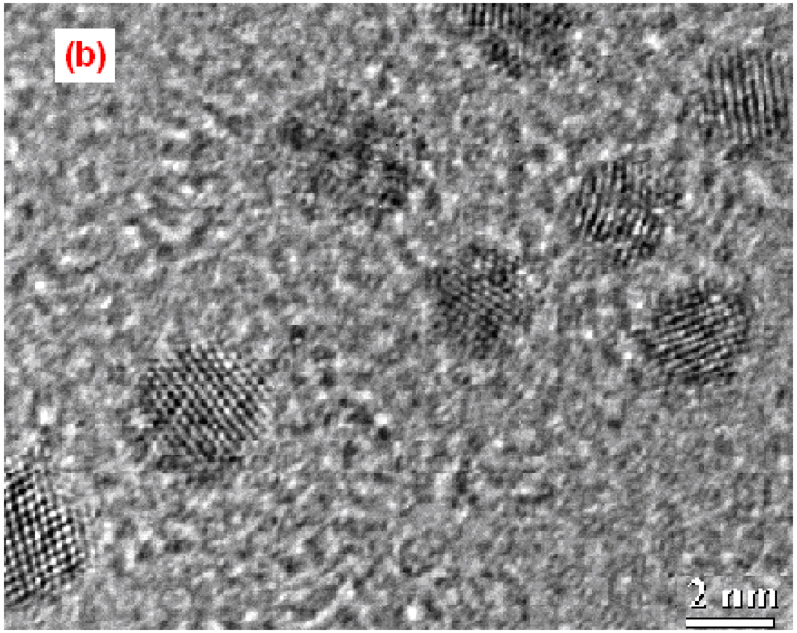
New Project Descriptions (continued)

Task 8. High Efficiency Low Cost Electrocatalyst for Hydrogen Production and PEM Fuel Cell Applications – Drs. Cunping Huang and Pyoungho Choi, FSEC.

The objectives of this project are to develop highly active metal alloys with low Pt loading and metal-metal oxide based electrocatalysts having nanosized grains. The project will conduct research and development for enhanced hydrogen evolution at low cost. The new catalysts will be evaluated for their activity toward H_2 evolution via electrolysis of water as well as applications for PEM fuel cells. DOE = $351,862.

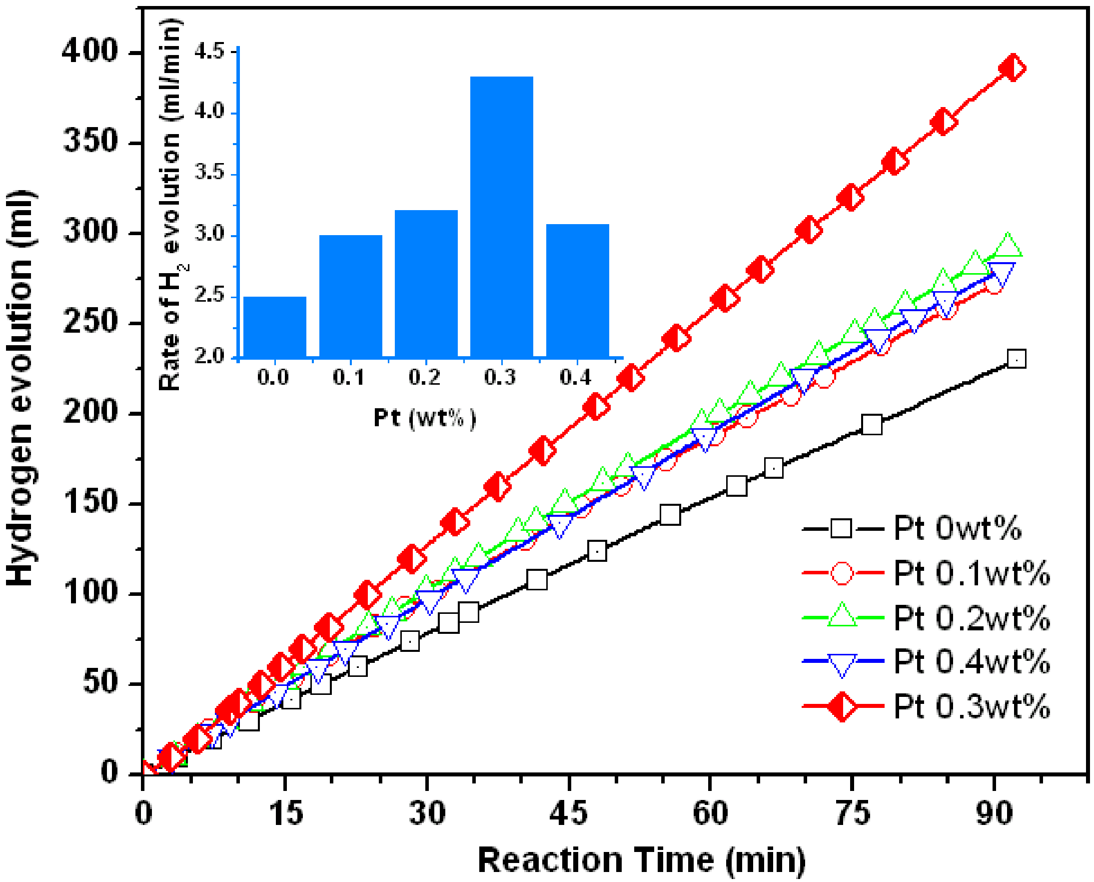
Size, Distribution Shapes and Defects can be Critical Parameters





Based on our previous experiences in the preparation of Pt nano particles, small size and uniform distribution of Pt can significantly increase the rate of hydrogen production.

Pd-Cr_2O_3-Pt Based Catalysts



Small amount of Pt added to Pd-Cr_2O_3 catalysts can significantly increase the hydrogen evolution rates and efficiencies.

Project Tasks

- Task 1 – Establishing a standard catalyst synthesis technique
- Task 2 – Screening of the carbon supports
- Task 3 – Syntheses of the Pt alloy based electrocatalysts
- Task 4 – Screening of the Pt–metal or Pt–metal oxide based catalysts
- Task 5 – Screening of the Pt-lanthanide based electrocatalysts
- Task 6 – Palladium based catalysts
- Task 7 – Characterization of the high activity catalysts

New Project Descriptions (continued)

Task 9. Understanding Mechanical and Chemical Durability of Fuel Cell Membrane Electrode Assemblies – Drs. Darlene Slattery and Len Bonville, FSEC.

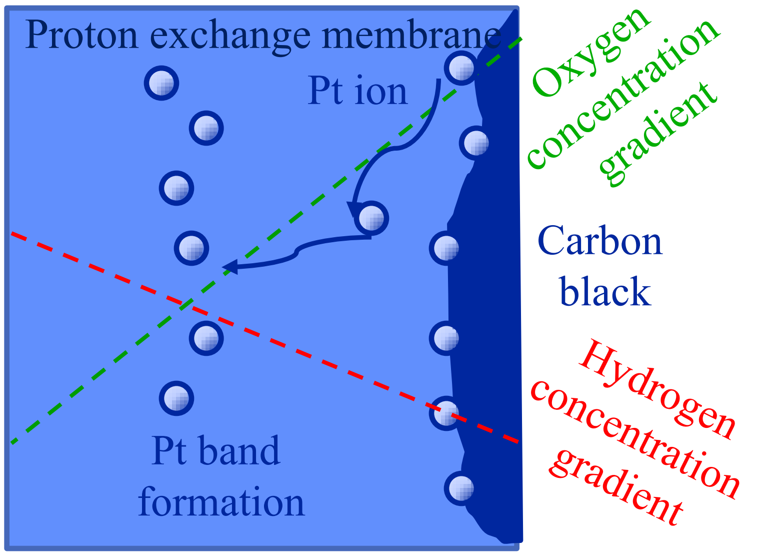
The objective of this project is to increase the knowledge base of the degradation mechanisms for membranes used in PEM fuel cells. Approaches to mitigate membrane degradation can be classified into three areas: membrane composition changes; radical quenching; and platinum band formation mitigation. In the first approach, membrane composition is altered to be less sensitive to radical attack. The second approach is to include compounds within the membrane that will quench the radicals preferentially, before they have an opportunity to attack the membrane. The third approach is to limit or control the formation of the platinum band within the membrane.

Program Motivation

- Membrane Degradation
  - Polymer attacked by radicals
  - Membranes weaken, pinholes/cracks form
  - Ex-situ decay accelerated by Fenton's Test
  - In-situ decay accelerated by OCV
- Pt Dissolution
  - Driven by potential cycles and high potential
  - Pt migrates into membrane
  - Pt ions encounter crossover H_2 and form Pt band
  - Pt band contributes to membrane decay through radical generation within membrane

Pt Migration through the Membrane

- After dissolution:
  - Pt diffuses from the cathode into the membrane
  - Pt is deposited by reduction from crossover H_2
- Pt band forms where Pt becomes stable (Zero V)
- High concentration of O_2 and H_2 at Pt band generates radicals



Relevance - Approach

- Four tasks
  - Chemical mitigation of membrane degradation
  - Evaluation of platinum band formation
  - Development of Pt band formation mitigation strategy
  - Combination of radical scavenging and Pt^{2+} band reduction

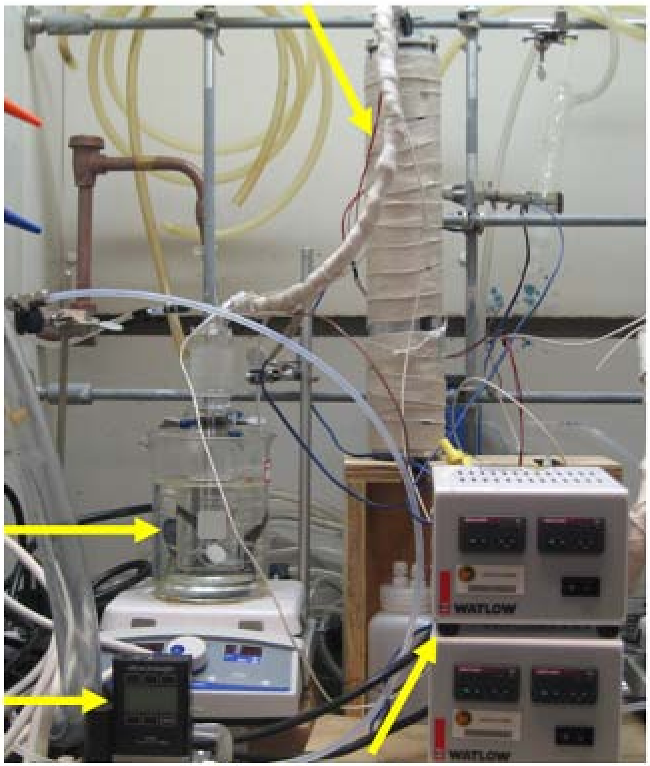
Program Goals

- Identification of mitigator that best prevents membrane degradation
- Characterization of Pt band formation and its influence on membrane degradation
- Identification of a heteropolyacid that reduces or prevents Pt band formation
- Method by which a more durable fuel cell can be produced

Modified gas phase Fenton's test setup

Chemical degradation + Mechanical stress

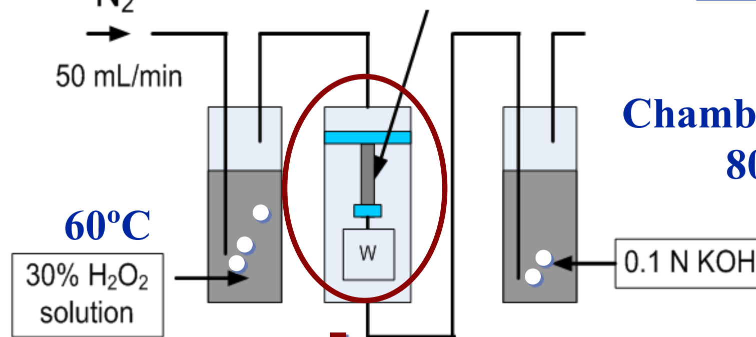
Membrane chamber



30% H_2O_2

Gas flow controller

Temperature controller



NRE 211

Chamber Temp. 80°C

Membrane chamber

Aluminum cylinder & Heat cartridge

PC tube

PTFE top

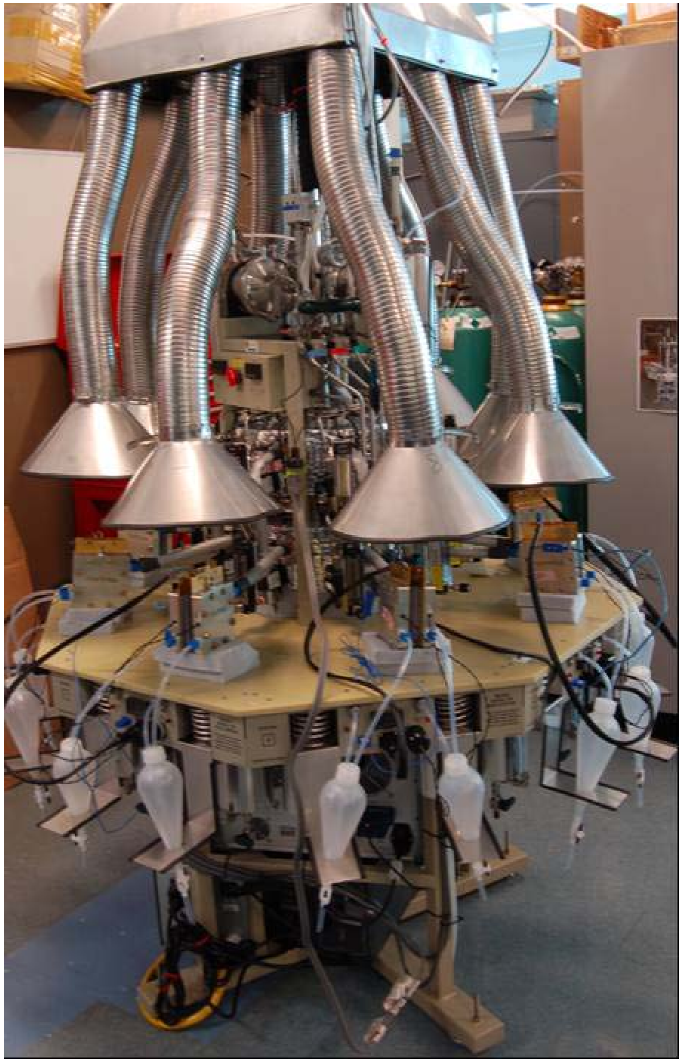
PTFE coated Metal grip

Mechanical load (metal ball inside) HDPE

Gas sealing parts

Membrane Electrode Assembly Durability System

- Simultaneous, independent operation of 8 cells at or near open circuit voltage (OCV)
- Capable of operating at various relative humidities from RT to 100 °C



EnerFuel

Hydrogen Technology (HyTech) Rest Area

Michel Fuchs

EnerFuel, Inc.

June 10, 2010

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Project Overview

Timeline

- Start – Oct 2006
- Finish – Dec 2010
- 80% complete

Budget

- Total project funding
  - DOE - $607K
  - Contractor - $632K
- Funding received for FY07
  - $191.0K
- Funding received for FY08
  - $160.9K
- Funding received for FY09
  - $35.7K
- Funding for FY2010
  - $219.3K

Barriers

- **Barriers**
  - **C**. Performance
  - **E**. System Thermal and Water Management
  - **G**. Startup and shut-down time and Energy/Transient Operation
- **Targets**

	2003	2005	2011
Electrical Energy Eff.	30%	32	40
Transient response time	<3ms	<3ms	<3ms

Subcontractors

- **Florida Atlantic University (FAU)** – Demo site design and construction
- **Technology Research & Development Authority** – Assist in demo site preparations & public relations

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Objectives

Overall	• Design, construct and demonstrate a 10kW$_{net}$ PEMFC stationary power plant operating on methanol • Achieve an electrical energy efficiency >32% • Demonstrate transient response time <3ms
2009	• Demonstrate fuel cell power plant operating on renewable methanol and providing power to service plaza • Evaluate fuel cell power plant performance • Present results of project
2010	•Change demonstration scope and location from rest area demo to electrical vehicle charge station due to budget constraints •Construct and commission charge station •Evaluate fuel cell power plant and charge station performance •Present results of project

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Milestone

Month/Year	Milestone or Go/No-Go Decision
Jan-09	Milestone: Identified commercial bio-methanol supplier able to provide entire 5000 gallons necessary for project
Apr-09	Milestone: Obtain all permits required for construction, including Florida Turnpike Enterprise, Fire Marshall and County permits.
Jun-09	Milestone: Complete construction of fuel cell demonstration site.
Sept-09	Milestone: Complete fuel cell power plant, operating on renewable methanol and providing power to service station, demonstration phase.
Aug-2010	Milestone: Complete construction of electric vehicle charge station demo site
Dec-2010	Milestone: Complete demonstration and evaluation of fuel cell and charge station performance

EnerFuel

Plan & Approach

100% Complete

- **Task 1: Citrus derived methanol**
  - Identify source
  - Clean-up methanol to fuel cell grade
  - Test methanol for compatibility w/ reformer
  - Work out transportation, storage logistics and associated NEPA compliance
  - Identify/establish safety protocols for use

85% Complete

- **Task 2: Demo site preps**
  - Obtain permitting & NEPA compliance for methanol storage
  - Identify electrical interface requirements
  - Establish location for fuel cell power plant and methanol storage

100% Complete

- **Task 3: Fuel cell power plant design**
  - DMFC vs. standard PEMFC trade study
  - Identify fuel cell stack source
  - Identify reformer source
  - Design system through modeling

85% Complete

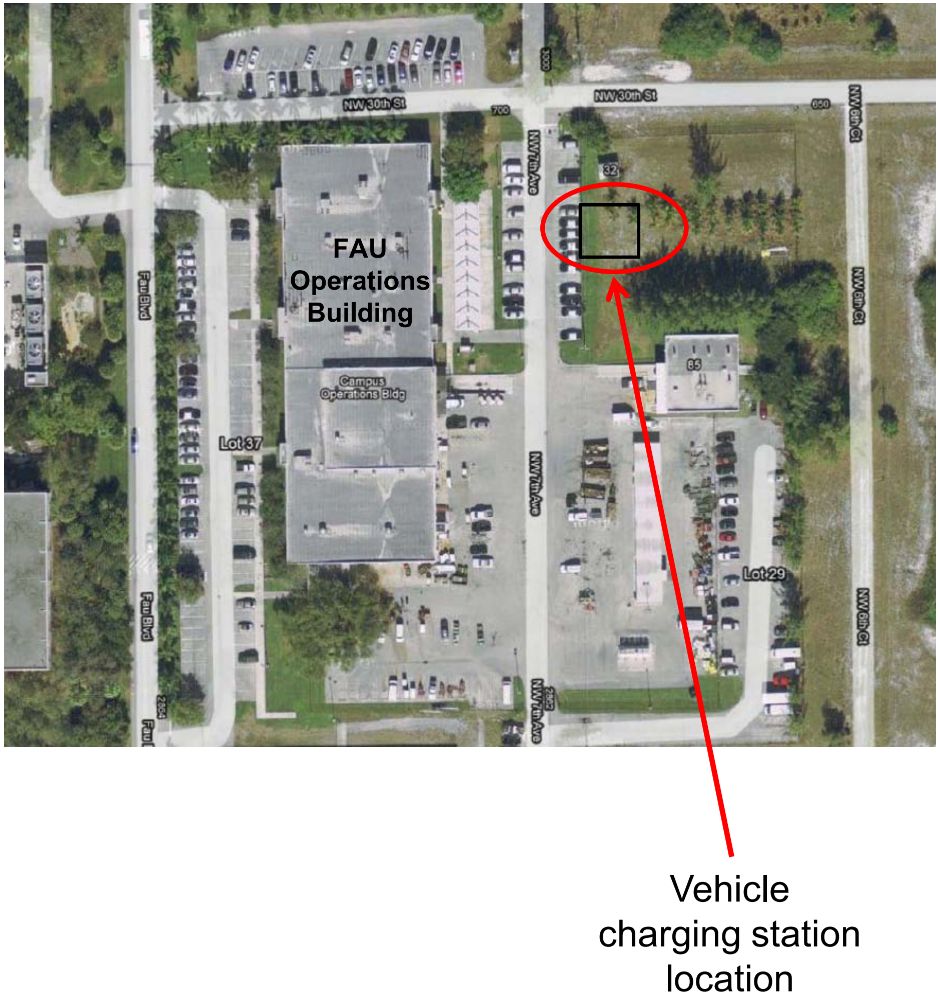
- **Task 4: Power plant construction and testing**
  - Construct power plant
  - Test and debug power plant
  - Benchmark performance

0% Complete

- **Task 5: Power Plant installation and demonstration**
  - Install power plant at demo site
  - Operate system for 3 months

Accomplishments

- Changed demonstration from powering a portion of a rest area to powering an electric vehicle charge station
- Selected demonstration site for electric vehicle charge station to be at Florida Atlantic University in Boca Raton, FL
- Secured the support of FAU to design, construct and evaluate charge station
- Successfully incorporated the existing inverter/fuel cell systems into the design of the charge station



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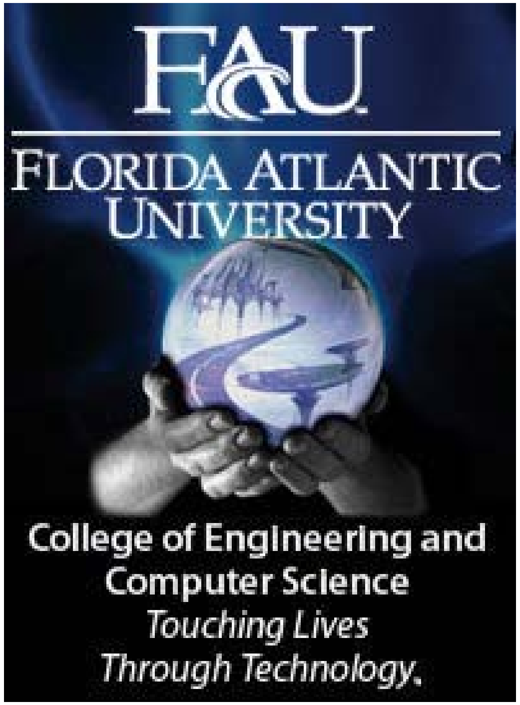
EnerFuel

Florida Atlantic University

FAU
FLORIDA ATLANTIC UNIVERSITY

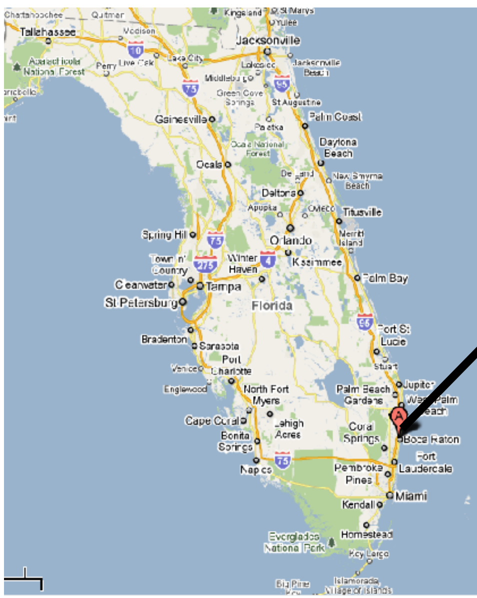
- Part of the State University System of Florida
- Has six satellite campuses in south FL with main campus on Boca Raton
- Established in 1961
- One of the fastest growing universities in FL
- 26,867 students enrolled (2010)
- Part of Florida Energy Systems Consortium
- College of engineering very active in energy conservation and research, as demonstrated in new Platinum LEEDS engineering building
- EnerFuel will be working with the Ocean and Mechanical Eng. Dept.

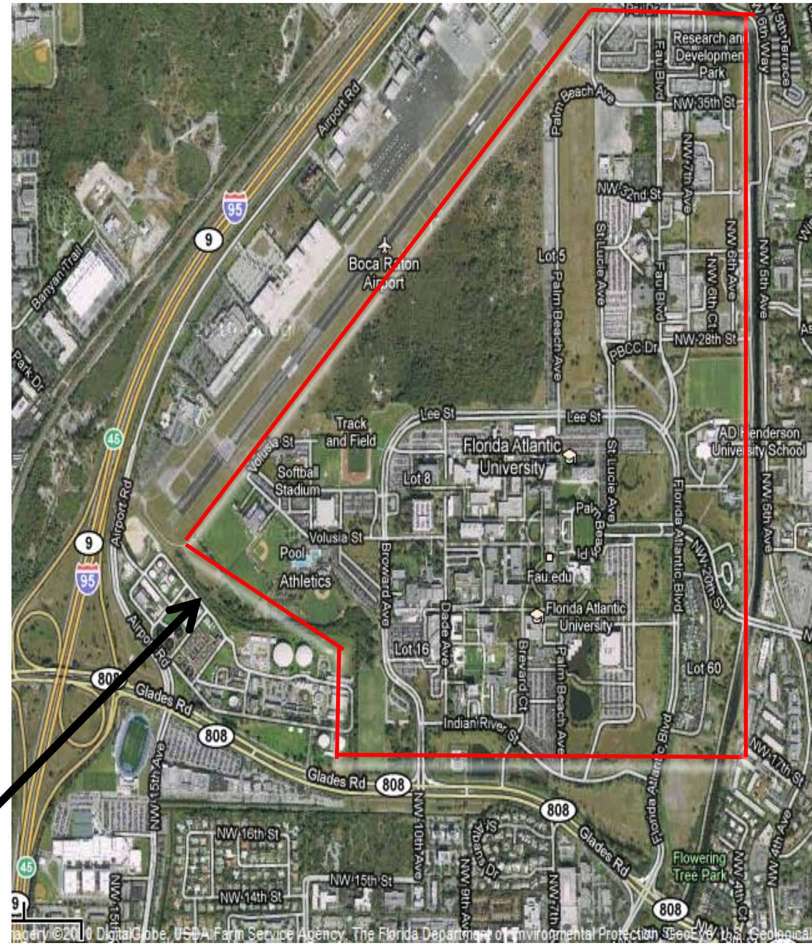


EnerFuel

Florida Atlantic University

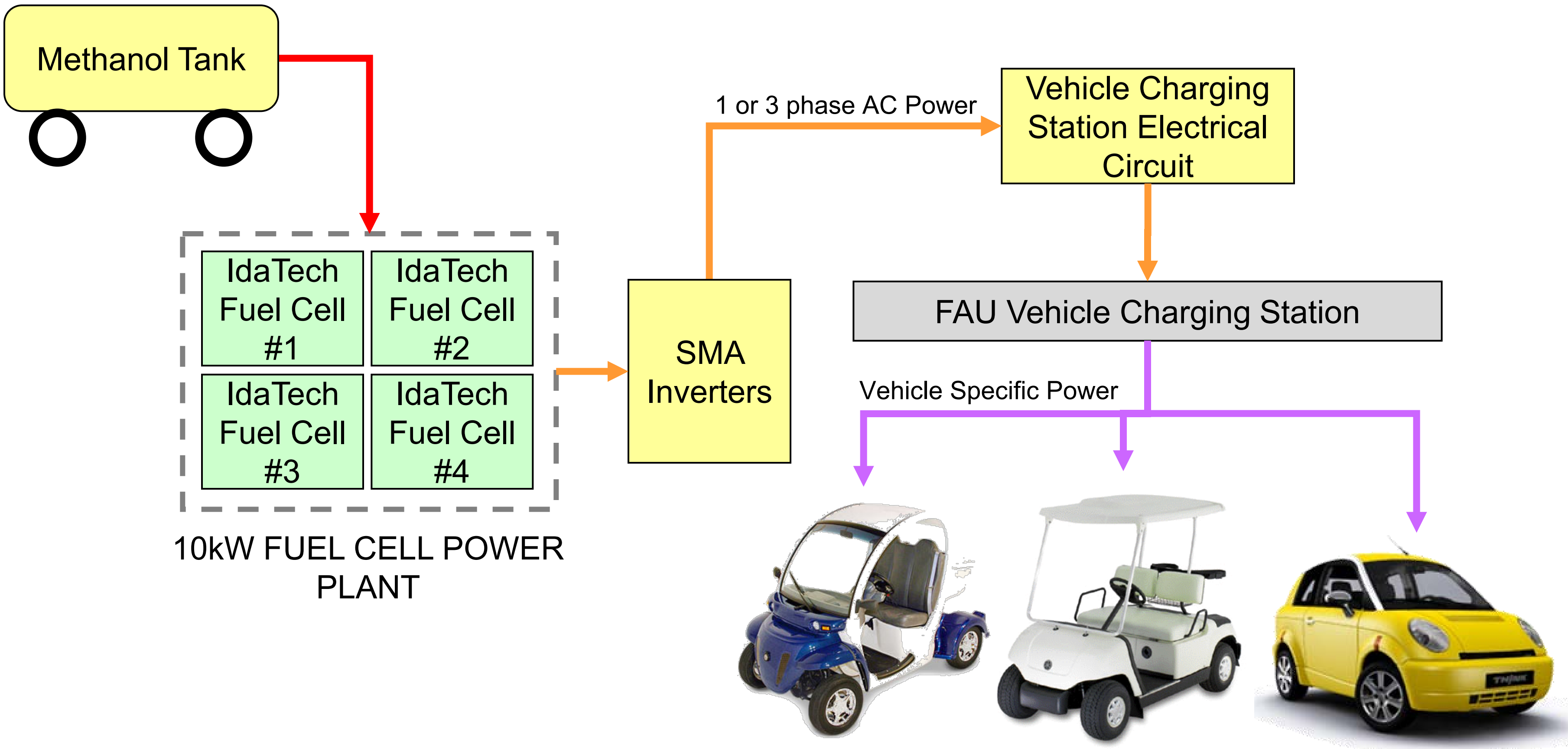
- 850 acres main campus in Boca Raton





New Demonstration Design

Electric Vehicle Charge Station, Boca Raton, Florida



Future Work (FY09 – FY10)

- **FY10 – Site preparation**
  - Design charge station using existing fuel cells and inverters
  - Secure all permits necessary to begin construction phase
  - Construct fuel cell demonstration site
  - Operate charge station for period of 3 months

- **FY10 – Analysis of fuel cell power plant under operation**
  - Determine overall electrical efficiency
  - Document system transient response to load changes
  - Determine overall performance and effectiveness of charge station
  - Assess requirements for future projects

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HyTech Rest Area Project Summary

- **Relevance**
  - Demonstrate a fully “clean” power solution for electric vehicle charging using a methanol fueled fuel cell system
- **Approach**
  - Utilize a PEM based fuel cell power plant, with onboard reforming, to convert methanol to usable electrical power
  - Demonstrate project in high visibility university environment
- **Technology collaboration**
  - Participation with the Technological Research and Development Authority (TRDA) of Florida to promote project objectives
  - Participation with Florida Atlantic University to host demonstration as well as design, construct and evaluate electric vehicle charge station
- **Proposed future projects**
  - Develop and participate in additional alternative power generation and renewable fuel projects that lead to the development of viable commercial “clean” power solutions

On-site Reformation of Diesel Fuel for Hydrogen Fueling Station Applications

Nazim Muradov[*], Karthikeyan Ramasamy[*], Cunping Huang[*], Ali T-Raissi[*] & James Stevens[**]

[*] Florida Solar Energy Center – University of Central Florida

[**] Chevron Technology Ventures, Houston, TX

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Overview

Timeline

- Project start date: 01/21/08
- Project end date: 03/31/10
- Percent complete: 100%

Budget

- Total project funding: $500K
  - DOE share: $300K
  - Contractor share:

    Chevron: $150K

    FSEC: $50K

Barriers addressed

Distributed Hydrogen Production & Storage:

B. Hydrogen Storage
C. Lack of Hydrogen Refueling Infrastructure Performance & Availability Data
D. Maintenance & Training Facilities
E. Codes & Standards

Partners

- Chevron Technology Ventures, LLC
- **Project lead:** UCF – FL Solar Energy Center

Objectives/Relevance

- Develop a compact, self-contained high-sulfur fuel utilization system for hydrogen fueling station applications.
- Develop an electrolytic desulfurization unit and stable catalysts for hydro-reforming of high-S diesel fuel.
- Operate & validate an integrated unit composed of pre-reformer & sulfur scrubber capable of generating gas containing less than 10 ppmv of H_2S.

Milestones

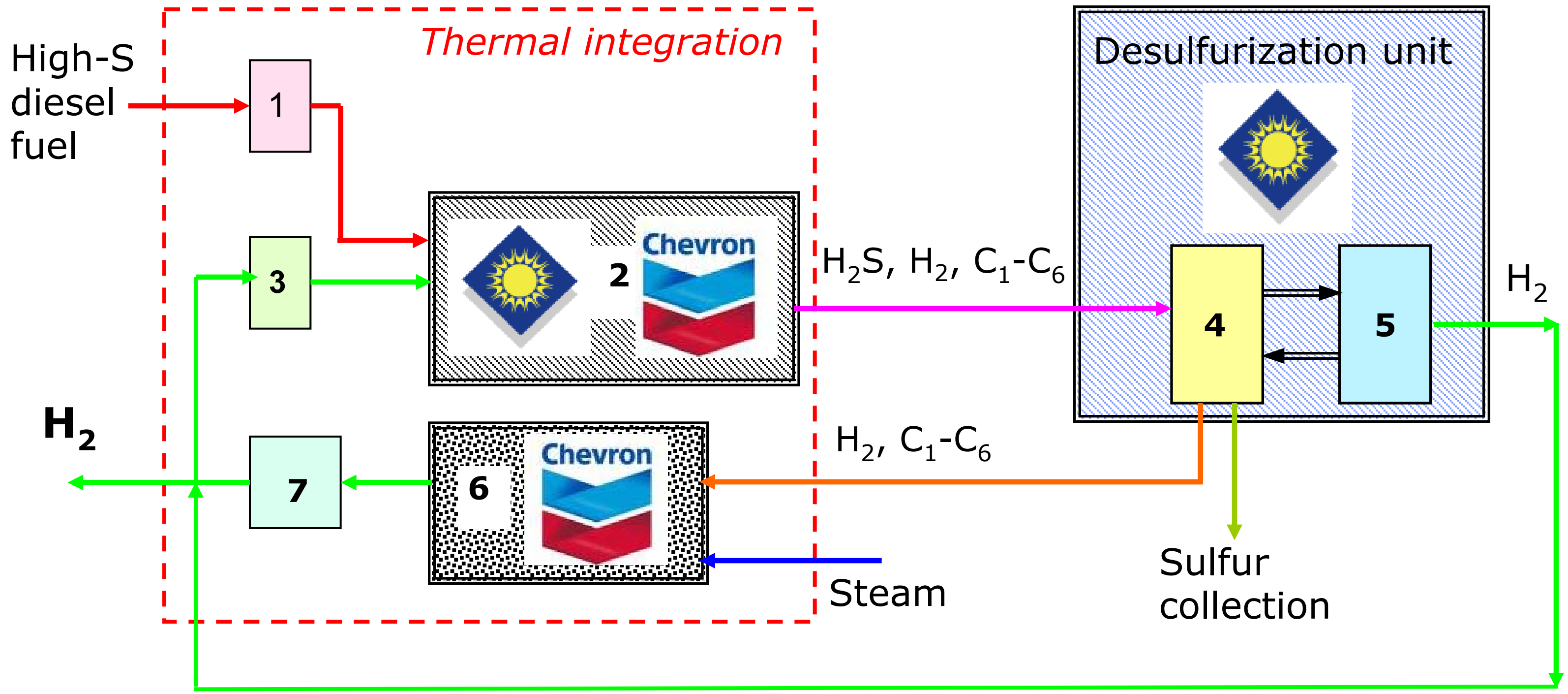
- This project has been completed.

Approach

- Used diesel and $C_{16}H_{34}$ spiked with ~5000 ppmw of thiophene as surrogate high-S hydrocarbon fuel.
- Performed catalytic hydroreforming-desulfurization of high-S fuel to light (C_1-C_6) hydrocarbons suitable for H_2 generation *via* steam reforming process.
- Developed a robust bi-functional catalyst for hydrocracking of high-S diesel & hydrogenation of sulfur-organics to H_2S with high selectivity.
- Designed and built a H_2S-scrubber capable of lowering [H_2S] in the pre-reformate to less than 10 ppmv.

Technical Accomplishments/ Progress/Results

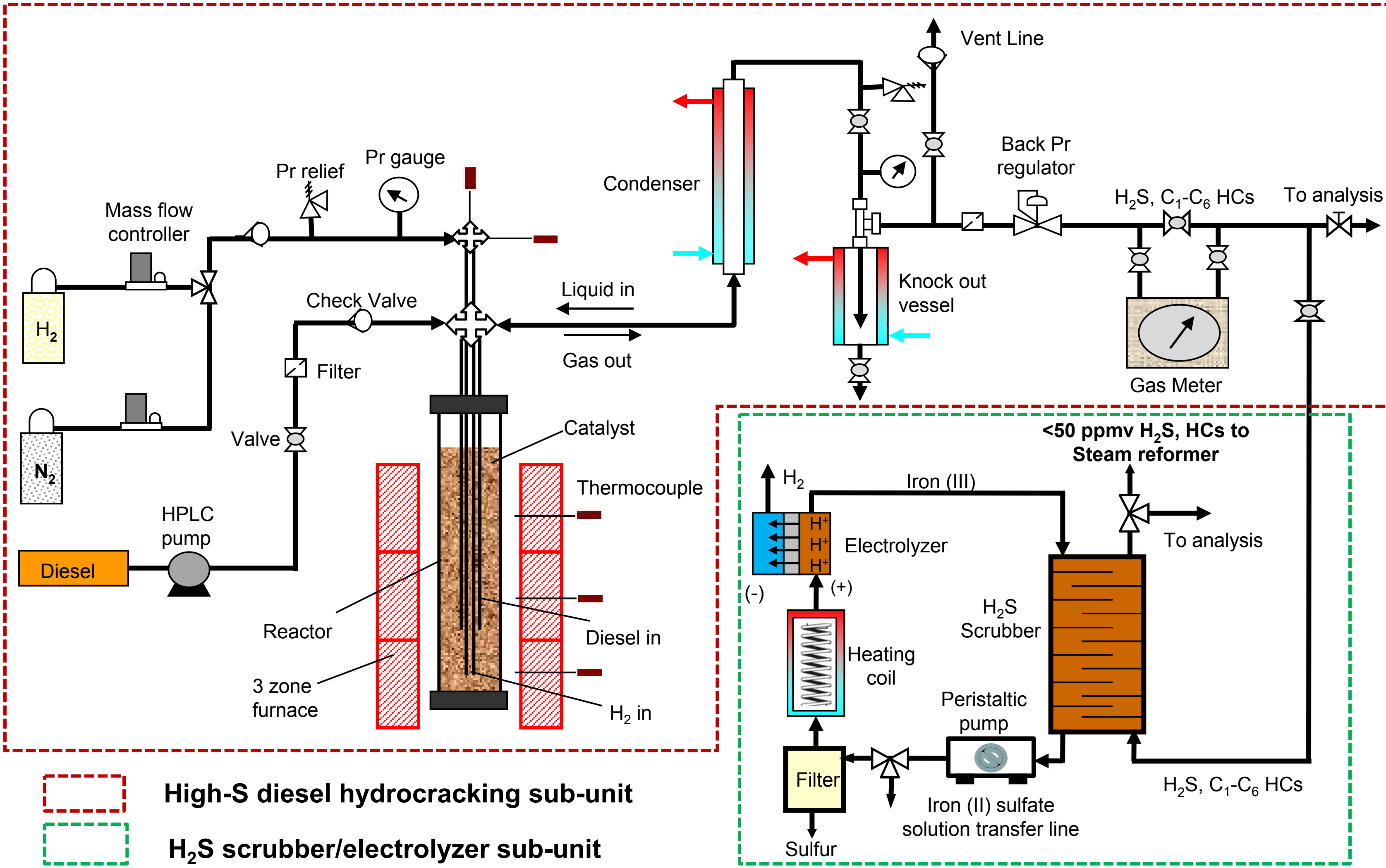
Division of Labor



1- vaporizer, 2- pre-reformer, 3- H_2 compressor, 4-H_2S stripper, 5- electrolytic regenerator, 6- steam reforming unit, 7- gas-conditioning and H_2 purification unit.

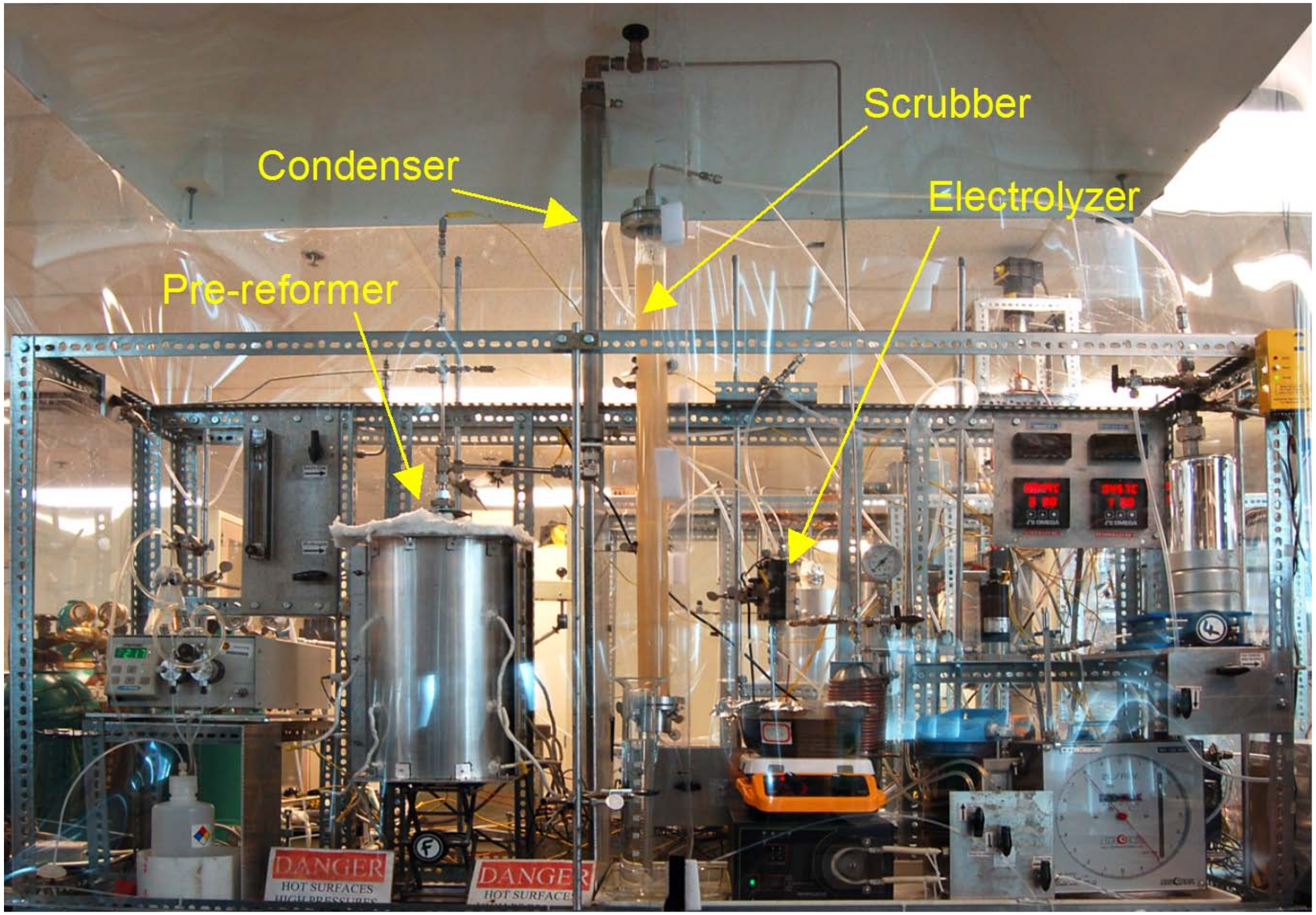
Technical Accomplishments/ Progress/Results

Schematic Diagram of Experimental Setup



Technical Accomplishments/ Progress/Results

Bench-Scale Unit at FSEC



Technical Accomplishments/ Progress/Results

- Developed a novel Fe-redox/electrolysis unit for H_2S scrubbing.
- Designed & built a compact pre-reformer for converting high-S fuel to light hydrocarbons at 97% yield.
- Fully integrated pre-reformer & sulfur-scrubber operated continuously for several days with sulfur removal efficiency of >95%.

Technical Accomplishments/ Progress/Results

Iron-based Redox System for H_2S Scrubbing & Splitting

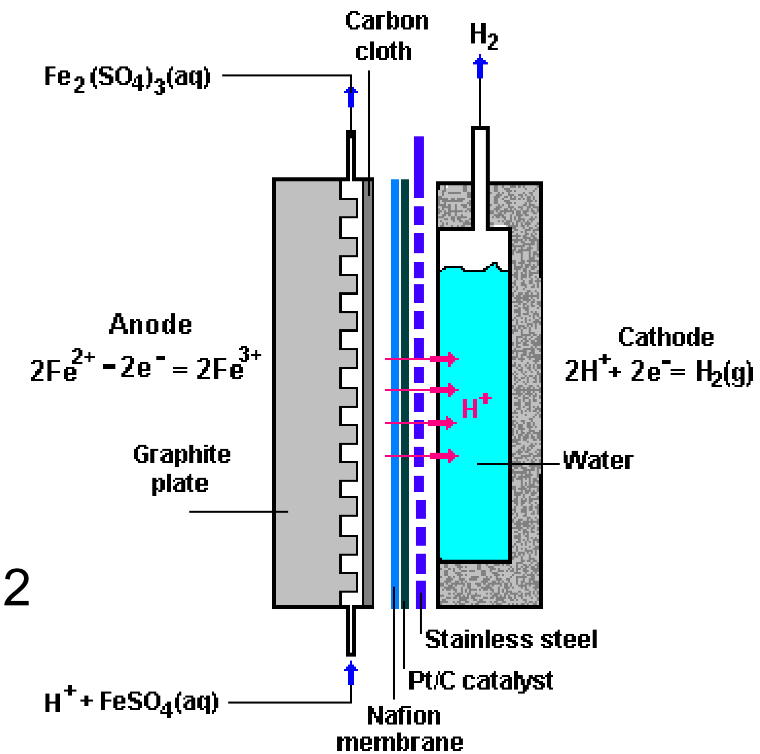
H_2S scrubbing:

$$H_2S(aq) + 2Fe^{3+} \rightarrow$$

$$S^o(s) + 2Fe^{2+} + 2H^+$$

Electrolytic regeneration:

$$2Fe^{2+} + 2H^+ \rightarrow 2Fe^{3+} + H_2$$

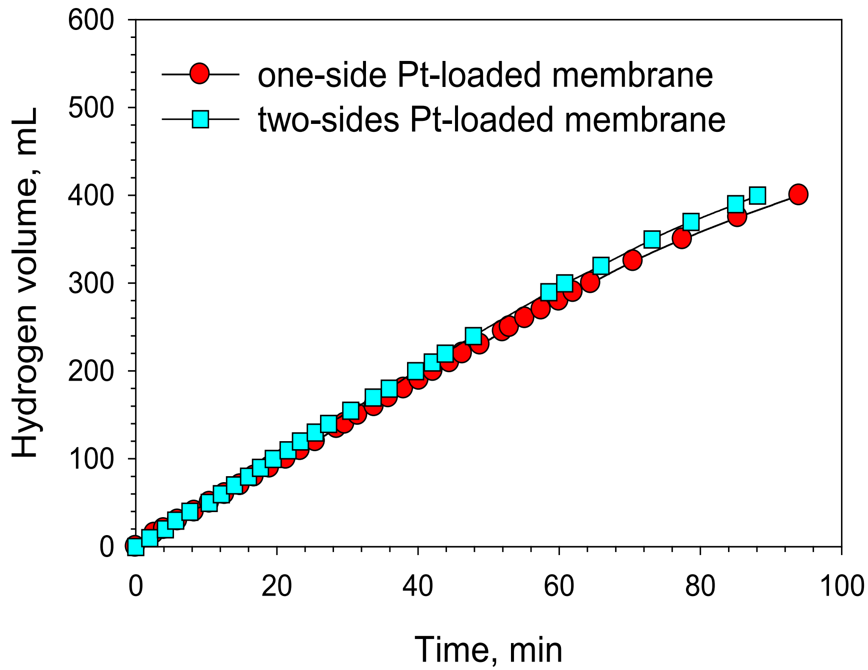


Concentration of H_2S in the reformate was reduced from hundreds to <10 ppm levels.

Technical Accomplishments/ Progress/Results

Electrolytic Regeneration of Fe^{3+}

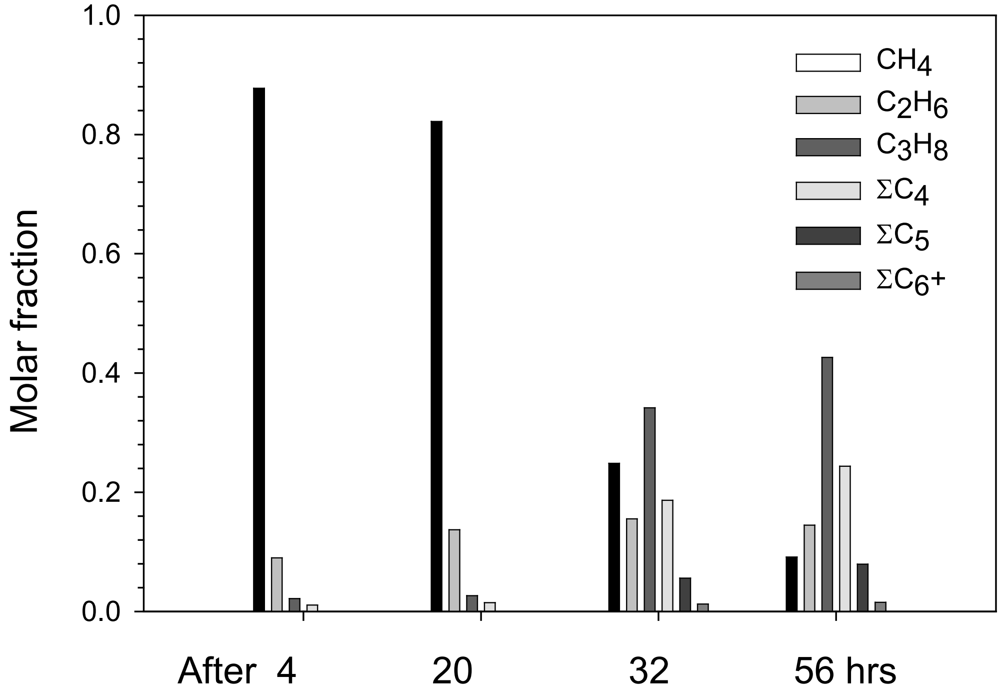
Effect of Pt Loading on One and Both Sides of MEA



Pt loading =1.8 mg/cm^2, *i* =30-50 mA/cm^2, E=0.95 V.

Technical Accomplishments/ Progress/Results

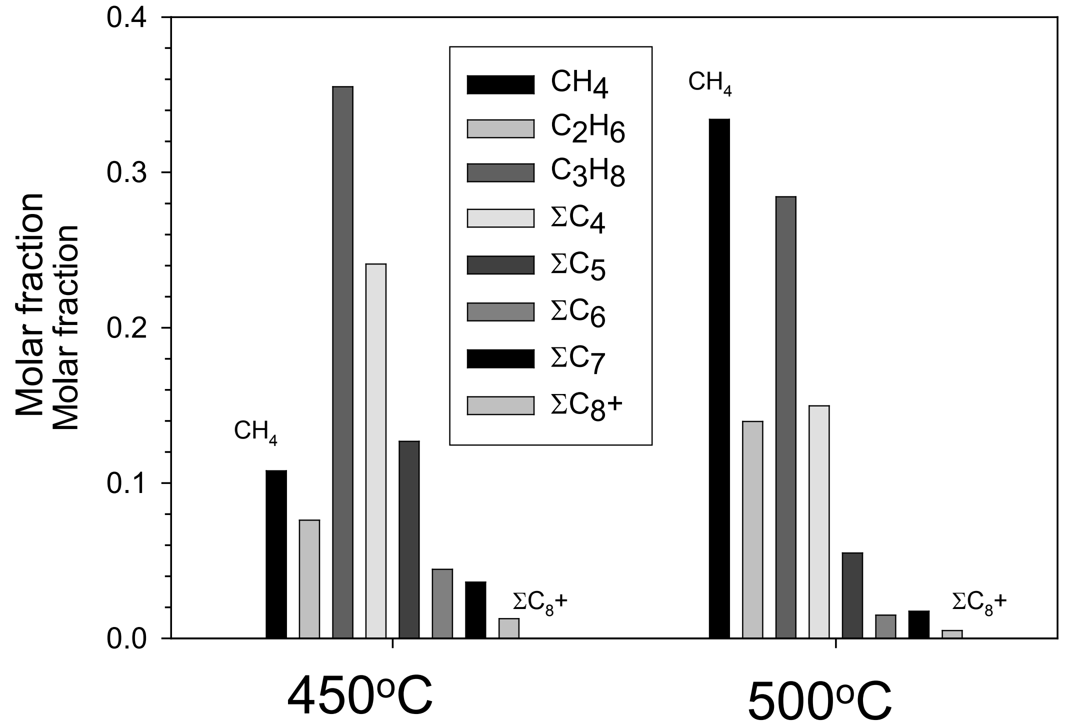
Hexadecane Hydro-reforming Products Distribution.
T= 470^oC, P= 13.7 atm.



Pre-reformate produced from hexadecane containing 5240 ppmw of thiophene. Catalyst: a mixture of zeolite and Ni-Mo/Al_2O_3 (2:1 weight ratio).

Technical Accomplishments/ Progress/Results

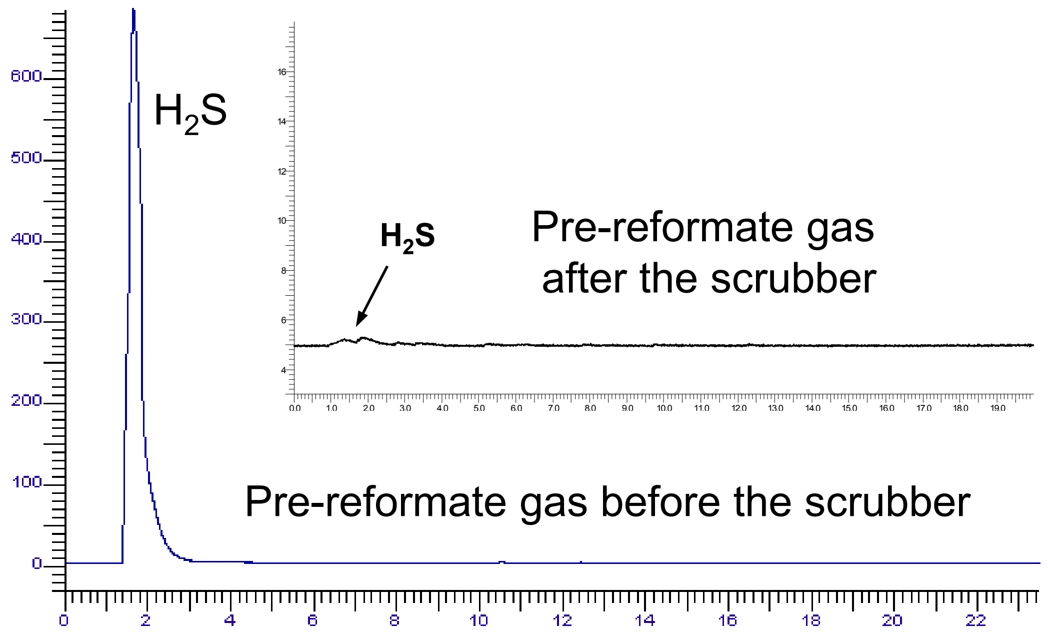
Effect of Temperature on Diesel Hydro-reforming Products Distribution (P= 13.7 atm).

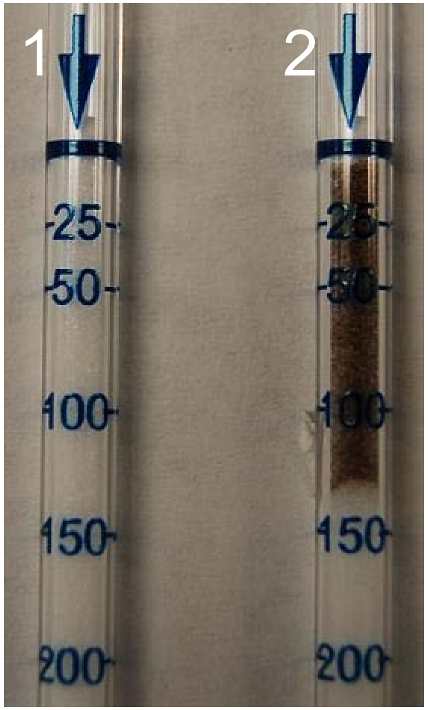


Pre-reformate gas produced from diesel fuel containing 5240 ppmw of thiophene. Catalyst: a mixture of zeolite & Ni-Mo/Al_2O_3 (2:1 by weight).

Technical Accomplishments/ Progress/Results

GC/FPD Chromatogram of Diesel Pre-Reformate





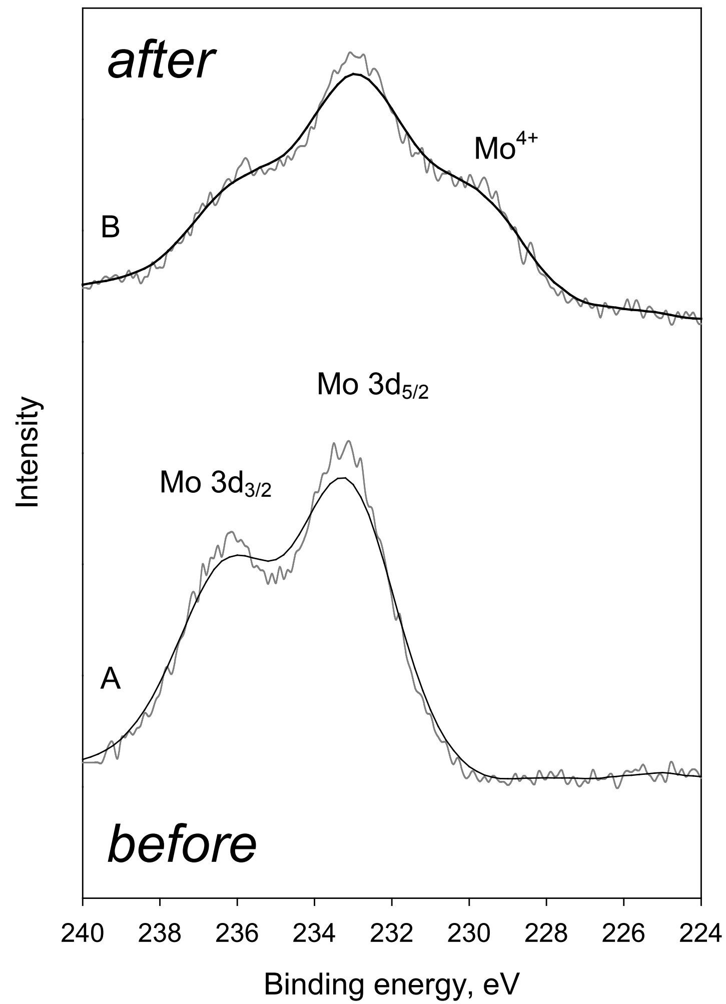
Determination of H_2S in the pre-reformate gas using gas detection tube method.
1- original tube,
2- tube after passing the pre-reformate gas.

Sulfur removal efficiency: >95%

$$\eta = \frac{(moles H_2 S)_{out} - (moles C_4 H_8 S)_{out}}{(moles C_4 H_8 S)_{in}} \cdot 100\%$$

Technical Accomplishments/ Progress/Results

High Resolution X-ray Photoelectron Spectra of Ni-Mo/alumina catalyst before and after high-sulfur diesel hydro-reforming



Molybdenum was reduced during diesel hydroreforming from Mo^{+6} to Mo^{+4}

Summary

- Developed a novel diesel-to-H_2 reformer by pairing a catalytic pre-reformation reactor to a sulfur scrubbing unit suitable for hydrogen fueling station applications.
- Built & operated a pre-reformer for converting high-S diesel to light hydrocarbons (C_1-C_6) at 97% yield.
- Developed an efficient & robust catalyst for hydro-reforming of high-S fuel.
- Built an efficient regenerable Fe-redox/ electrolyzer for H_2S scrubbing and splitting to H_2 & S.
- Demonstrated continuous operation of a fully integrated pre-reformer-desulfurization unit for several days, with sulfur removal efficiencies exceeding 95% & [H_2S]< 10 ppmv in the reformate.

Team Members

FSEC tasks:

- Design, fabrication & evaluation of a compact, self-contained desulfurization unit.
- Development & testing of the pre-reforming catalysts.
- Integration of the pre-reformer & desulfurization units.

CTV tasks:

- Pre-reforming catalyst development & analysis.
- Design of the pre-reforming reactor & advising FSEC on the operation and troubleshooting of the pre-reforming reactor.