Electrochemical Hydrogen Contaminant Detection

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Project ID
SCS029

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Overview

Timeline

- Project Start Date: 08/01/16
- Project End Date: 07/31/18

Barriers

- C. Safety is Not Always Treated as a Continuous Process
- G. Insufficient Technical Data to Revise Standards

Budget

- Total Project Budget: $999,999
  - Total Recipient Share: $302,766
  - Total Federal Share: $999,999
  - Total DOE Funds Spent*: $350,318

* As of 3/31/17

Partners

- University of Connecticut – Center for Clean Energy Engineering
- Sustainable Innovations, Inc., Project Lead

SBIR Phase II Electrochemical Hydrogen Contaminant Detection
Relevance

- Use of H₂ as Feedstock for Fuel Cells in Transportation has Driven Requirements for H₂ Purity From ppm/Low % Level, to ppb/ppm
- Purity Requirements - SAE J7219, and ISO 14687-2 Place 3 Orders of Magnitude Increase in Accuracy of Instruments Necessary to Detect Extremely Low Levels of Contaminants
- New Standards Have Driven a Need for Cost-Effective/Reliable Instrument That Can Sample H₂ Near the Nozzle of a Delivery Pump, and Either Certify Acceptability or Provide a Signal to Shut off the Fuel Distribution System
- Instrument Requirements
  - Detect Extremely Low Levels of Contaminants Over a Very Large Range of Temperatures and Pressures
  - Be Sufficiently Cost Effective, Reliable and Robust to be Installed at Hydrogen Refueling Pumps
Approach

Main Technical Objective - Define, Design, Fabricate, and Verify Operation of a Hydrogen Contaminant Detector for Use as a “Go – No Go" Sensor at or Near the Nozzle of a High-Pressure Hydrogen Storage/ Dispensing System

Phase II Efforts Focus on:

• Evaluating Sensors With a Larger List of Contaminants
• Identifying/Developing Materials for Improved Selectivity and Response Times
• Developing a Field Prototype
Collaborations

• The University of Connecticut
  – University Sub-Contractor Investigating the Fundamental Electrochemistry of the Sensor, Defining Sensor Requirements, Sensor Functionality, Creation of a Library of Responses for Each Contaminant at Different Concentrations

• DURO-SENSE Corporation
  – Industrial Partner/Vendor Aiding in Defining the Commercial Manufacturability of the Hydrogen Contamination Detector

• Los Alamos National Laboratory
  – SBV Targeted at Supporting Electrochemical R&D and Materials Development
Electrochemical Hydrogen Detector Development Pathway

Early Development
Concept Creation & Validation

Phase I SBIR
Benchtop Single Electrode Testing

Phase II SBIR
Prototype Construction and Validation

Prototype Validation Testing by Outside Partner

Field Testing Prototype Unit With Commercial Partner(s)

SBV Program

Product Commercialization
## Current Phase II Schedule

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Sensor Available for Outside Lab Testing
Accomplishments and Progress
Rapid CO Response

- When Subjected to 20ppm CO in the H₂ Gas Stream, the Sensor Responds Clearly to Presence of CO

Sensor Response to 20ppm CO in H₂

Signal Processing Algorithm (Developed in Phase I) Enables Rapid Detection of CO in H₂ Fuel

CO Applied to Sensor Yields Clear and Immediate Response
Accomplishments and Progress
Electrolyte Degradation Controls The Sensor Performance

- Electrolyte Delaminates From the Electrode Surface
  - Edges of the Pt Electrodes Remain in Contact with the Electrolyte
- Improving Electrolyte Stability is Key For Sustained Sensor Response

Lab Testing Identified an Important Problem Relating to Sensor Durability
Accomplishments and Progress

Alternative Electrolyte Application: Dense Ionomer Sol.

- Low Concentration Electrolyte Solution (5% Nafion®)
  - Poor Electrolyte Coverage on the Sensor Tip Causes Degradation
- Higher Concentration Electrolyte Solution (20% Nafion) to Promote Better Electrolyte Coverage
  - Fully Coated the Sensing Tip With a Much Thicker Electrolyte Layer
    - 0.6 mil Thick Electrolyte With 20% Solution Vs. 0.1 mil Thick Electrolyte With 5% Solution

Electrolyte from 5% Solution

- Lower Current Compared to Previous Sensors
  - Increased Gas Transport Resistance
- Response to CO is Significantly Delayed
  - ~35 Minutes Compared to <1 Minute

Electrolyte from 20% Solution

Working to Achieve Improved Sensor Durability and Lifespan Through Electrolyte Modification
Accomplishments and Progress

Alternative Electrolyte Application: Nafion® Film

- Thin Nafion Film Wrapped Around the Sensor Tip
  - Immersed in 5% Nafion Solution for Improved Contact
- Low Performance (0.33 ua vs >100 ua)
  - 2 mil Nafion has a Very Large Gas Transport Resistance
    - Measured Limiting Current is Similar to Measured Cross-Over Current in PEFCs With Nafion 112
- Very Slow CO Response (Limited CO Diffusivity)

Exploring Alternative Designs to Improve Electrolyte Contact W/O Impacting CO Response
Accomplishments and Progress

Alternative Electrolyte Application: ePTFE Support

- Sensor Tip is Covered With a Thin (0.5 mil) Porous, Hydrophobic PTFE Matrix and Saturated With Low Concentration Electrolyte solution
- Rapid CO Response: ePTFE has a Minimal Effect on Gas Transport

Future Alternatives:
- Mixed Wettability Porous Support
  - Electrolyte in the Hydrophilic Pores, Hydrophobic Pores Available for Gas Transport
- A catalyst Layer Like Electrolyte Ink (with Insulating Support)
  - A Porous Ionic Conducting Layer
- Holes in Thicker Electrolyte Layers
  - Optimized Hole Patterns for Gas Transport and Ionic Conductivity

Employing Thin Porous Substrates to Maintain Electrolyte Integrity
Accomplishments and Progress
Sensor Design

A Thermocouple Embodiment was Selected as a Cost Effective Contamination Detector Platform

- **Benefits Include**
  - Direct Commercial Availability
  - Proven History of Reliability and Robustness
  - Adaptability of Conductor Materials for Most Appropriate Catalyst for Each Contaminant
  - Ability to Incorporate up to 12 Conductors a Single Thermocouple, Reducing Fluid Stream Penetrations

A High Pressure Pass-Through was Identified to Integrate Sensor into Fluid Stream

- Pressure Rating of 30,000 psi, Using a Cone and Thread Style Fluid Connection

- **Detector Location is Anticipated to be in or Near Fueling Breakaway – Ready Access Close to the Nozzle**

Preliminary Design Complete, Commercially Available Components, Up to 12 Sensors in Single Housing
Accomplishments and Progress Testing And Evaluation

- **Low Pressure Testing**
  - To Date all Sensor Testing to Date Has Been Near Ambient Pressures

- **High Pressure Non-Functional Evaluation**
  - Hydrostatically Evaluated a Sealed Thermocouple Sensor to 9,000 psi
  - Hydrostatic Pressure Testing Capacity of 18,000 psi

- **High Pressure Functional Testing**
  - A High Pressure Test Stand has Been Designed and Components Have Been Ordered
  - System Rated for Evaluating Pressures Above 10,000 psi

**High Pressure Sensor Test Stand P&ID**

Test Stand Designed and Fabricated to Evaluate Sensors at Fueling Pressures for Real-Time Analysis
Accomplishments and Progress
High Pressure Testing Strategy

Technical Challenge: Gas Blending/Mixing to Evaluate Sensors at Pressures Greater than 320 psi was Cost Prohibitive and Technically Challenging

Solution: Employing Precision Blended Gas Cylinders and Operate Directly from Cylinder Pressure

- Initial High Pressure Sensor Functional Evaluation Will be up to 2,000 psi with Standard Cylinders
- Follow on Testing Will be up to 5,000 psi Using Ultra High Pressure Compressed Gas Cylinders

Working To Overcome Challenges With Respect to Extreme Pressure Testing
Responses to Previous Year Reviewers’ Comments

- This Project Was Not Reviewed Last Year
Remaining Challenges and Barriers

- Selection of the Proper Electrolyte Material and Application Procedure
- Full Hydrogen Refueling Pressure Functional Testing, Currently Limited to 5,000 psi
- Development of Integrated Fast-Acting Control Algorithm Capable of Recognizing a Contamination, Shutting Down Refueling, and Indicating Level of Contamination
Proposed Future Work

- Continue to Optimize Sensor on CO
- Continue Developing Electrochemical Framework on Additional Contaminants Besides Carbon Monoxide
- Evaluate Prototype Hydrogen Contamination Sensor at Typical Fueling Pressures of 70 MPa
Technology Transfer Activities

• Applied for Provisional Patents on Sensor Concept and Improvements

• Sustainable Innovations Initiating a Series A Equity Round – Sensor Represents a Commercialization Opportunity
Project Summary

• Relevance
  – New Standards Have Driven a Need for Cost-Effective/Reliable Instrument That Can Sample H₂ Near the Nozzle of a Delivery Pump, and Certify Acceptability or Provide a Signal to Shut off the Fuel Distribution System

• Approach
  – Define, Design, Fabricate, and Verify Operation of a Hydrogen Contaminant Detector for Use as a “Go – No Go” Sensor at or Near the Nozzle of a High-Pressure Hydrogen Storage/Dispensing System

• Technical Accomplishments:
  – Developed an Electrochemical Sensor Capable of Detecting CO Down to a Concentration of 20 PPM
  – Designed and Fabricated a Test Stand to Evaluate the Hydrogen Contamination Detector Pressures up to 10,200 psi

• Collaborations:
  – University of Connecticut – Electrochemistry
  – LANL – Materials and Testing SBV
  – Duro-Sense – Electrode Materials

• Proposed Future Work:
  – Continue to Optimize Sensor Performance, Evaluate Other Contaminants and Pressure
Acknowledgement

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