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Electrochemical Hydrogen Contaminant Detection

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East Hartford, CT

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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

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Relevance

- Use of H_2 as Feedstock for Fuel Cells in Transportation has Driven Requirements for H_2 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 H_2 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

Intended Location for Hydrogen Contaminant Detector

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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**

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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

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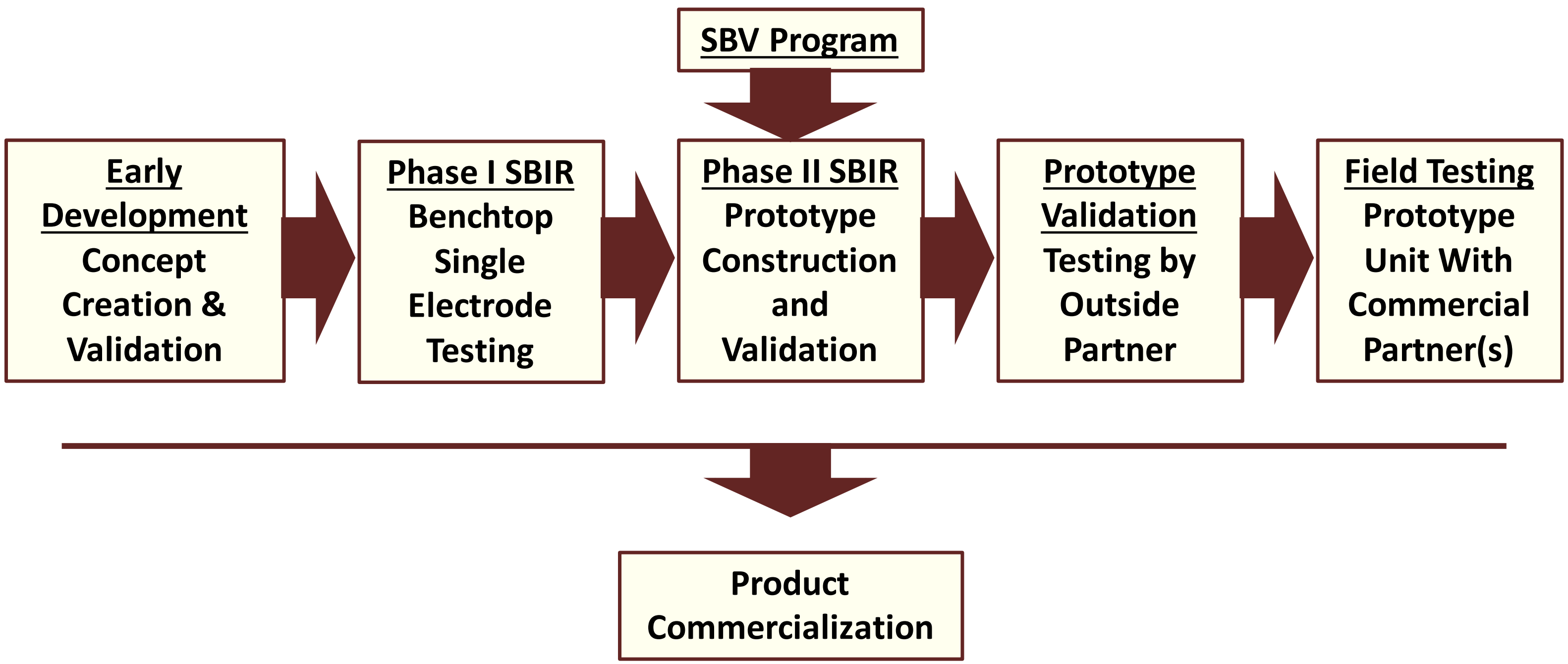
Electrochemical Hydrogen Detector Development Pathway



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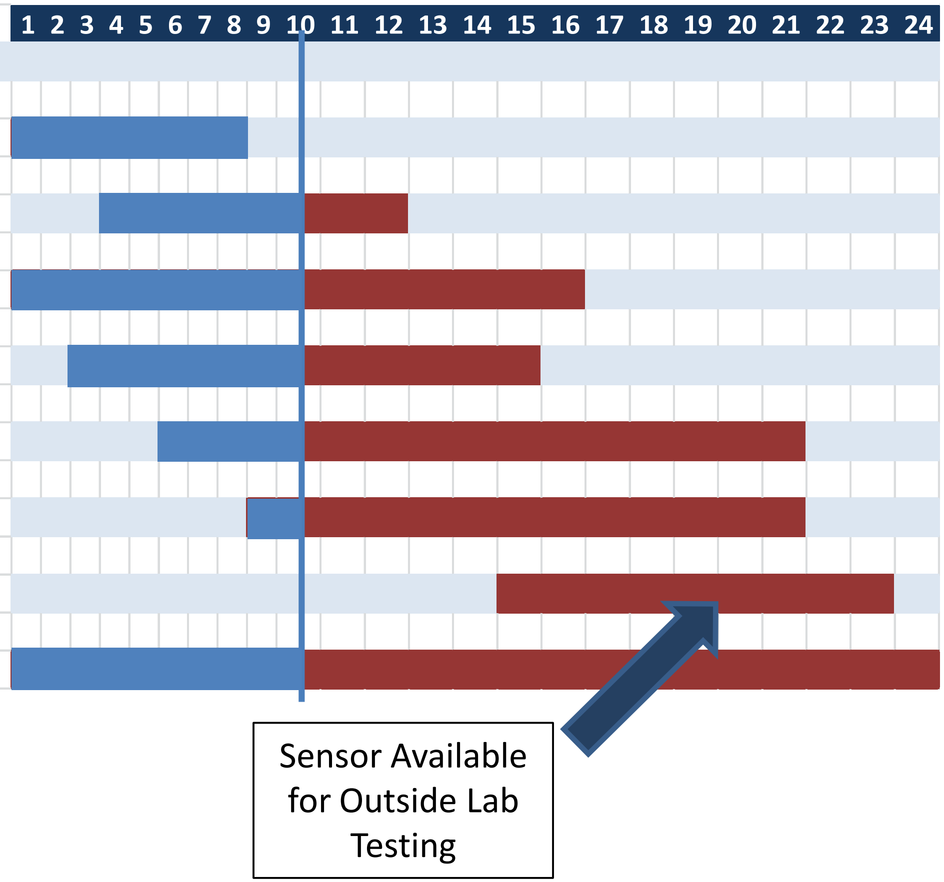
Current Phase II Schedule

	Task	Resp
1	Understanding Fluids Transport	UConn, SI
2	Materials Development	UConn
3	Single Electrode Characterization	UConn
4	Prototype Sensor Design	SI
5	Prototype Sensor Fabrication	SI, UConn
6	Impurity Response: Signal Processin	UConn
7	Prototype Bench-Scale Evaluation	SI
8	Project Management and Reporting	SI



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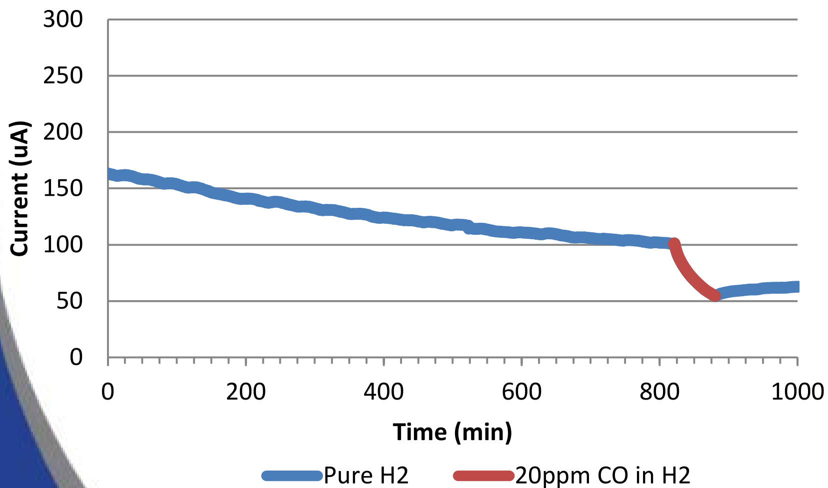
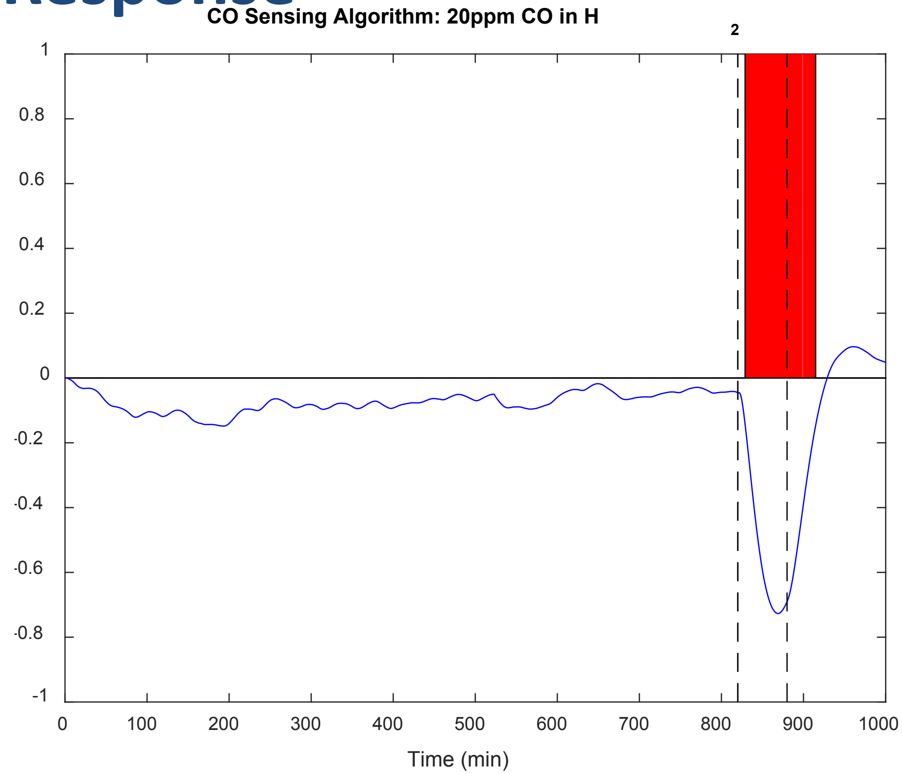
Accomplishments and Progress

Rapid CO Response

- **When Subjected to 20ppm CO in the H_2 Gas Stream, the Sensor Responds Clearly to Presence of CO**

Sensor Response to 20ppm CO in H_2





Signal Processing Algorithm (Developed in Phase I) Enables Rapid Detection of CO in H_2 Fuel

CO Applied to Sensor Yields Clear and Immediate Response

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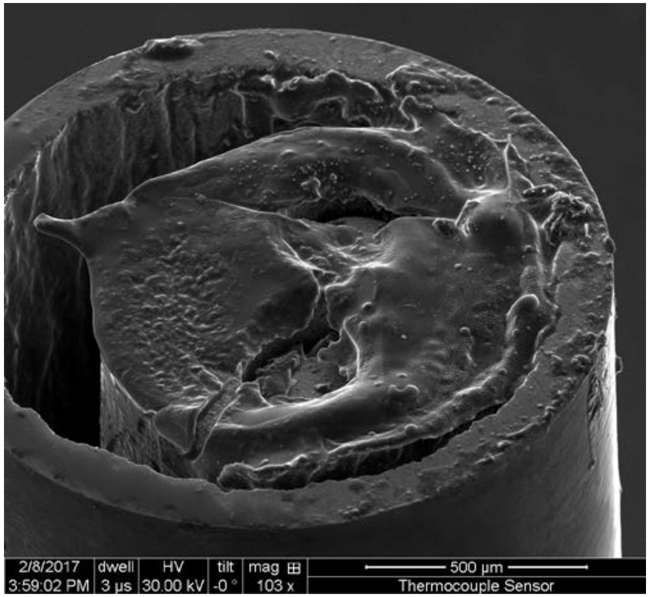
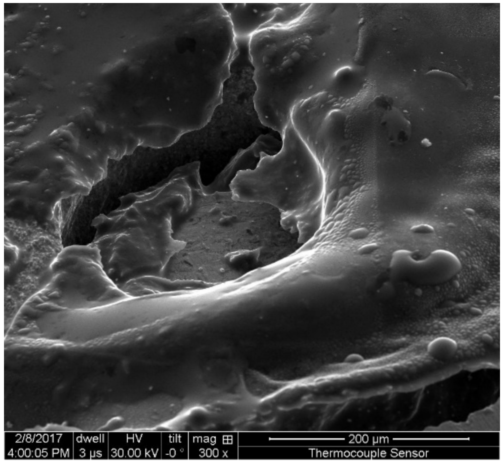
Accomplishments and Progress

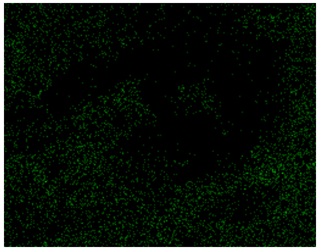
Electrolyte Degradation Controls The Sensor Performance



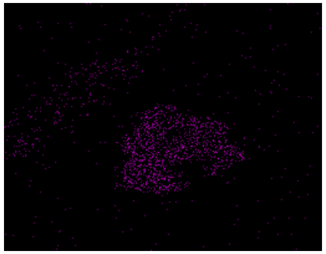
- **Electrolyte Delaminates From the Electrode Surface**
  - **Edges of the Pt Electrodes Remain in Contact with the Electrolyte**
- **Improving Electrolyte Stability is Key For Sustained Sensor Response**



Fluorine



Platinum



Lab Testing Identified an Important Problem Relating to Sensor Durability

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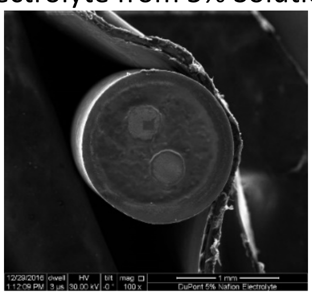
Accomplishments and Progress

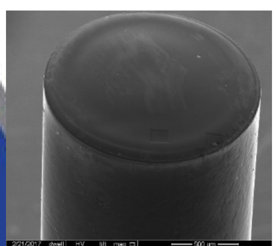
Alternative Electrolyte Application: Dense Ionomer Sol.

- 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
    - $0.6mil$ Thick Electrolyte With 20% Solution Vs. $0.1mil$ Thick Electrolyte With 5% Solution

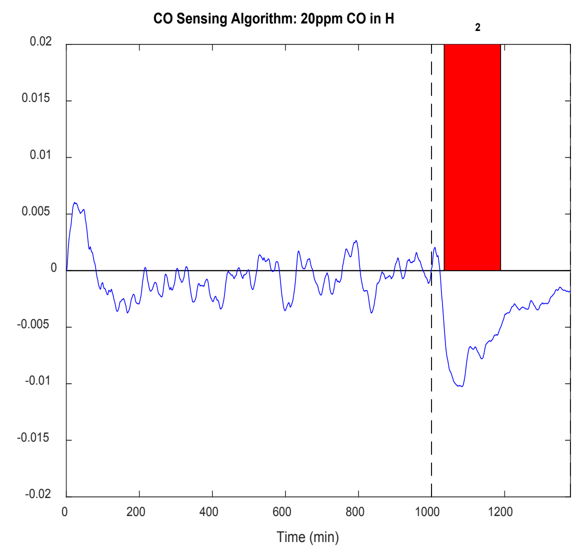
Electrolyte from 5% Solution



Electrolyte from 20% Solution



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



Working to Achieve Improved Sensor Durability and Lifespan Through Electrolyte Modification

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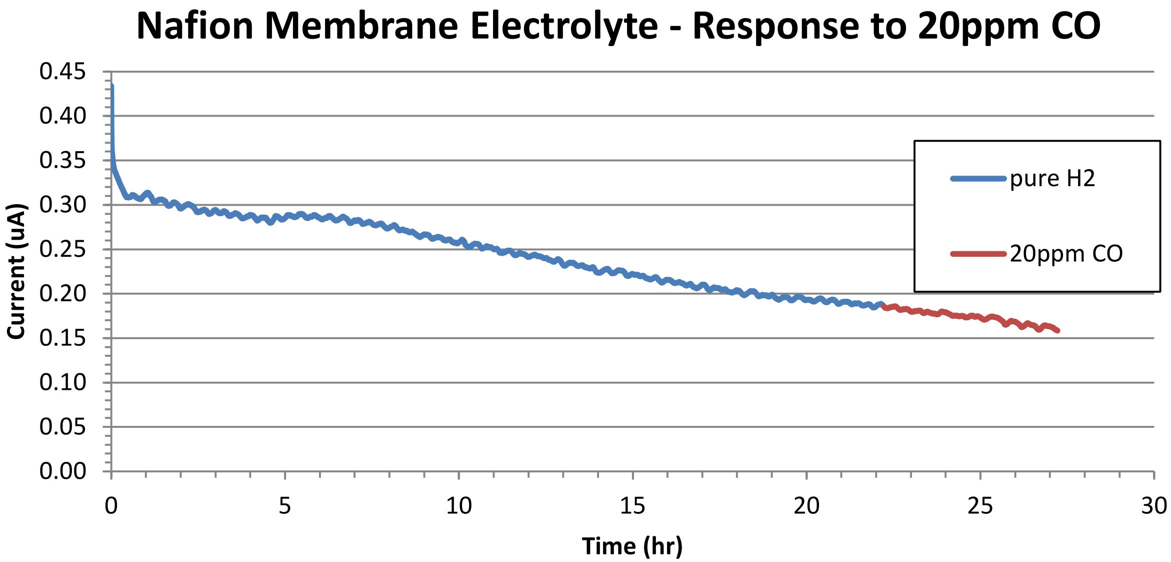
Accomplishments and Progress

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

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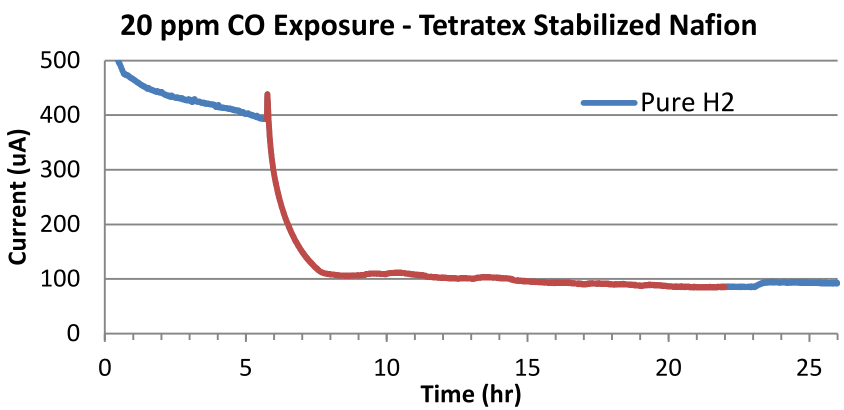
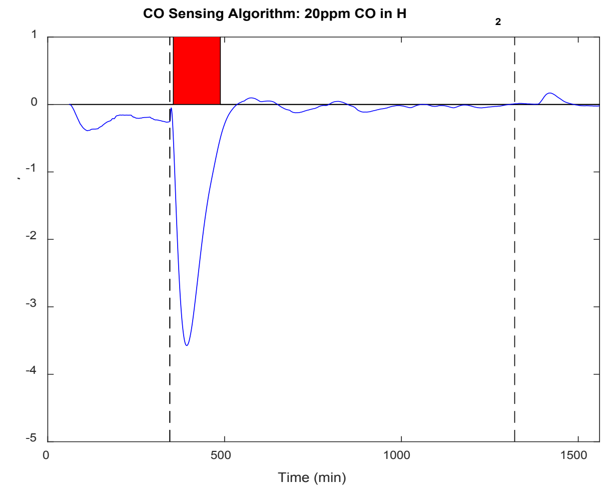
Accomplishments and Progress

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

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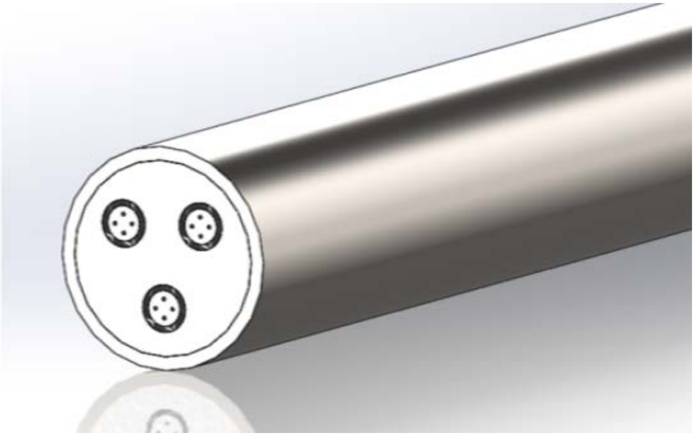
Accomplishments and Progress

Sensor Design



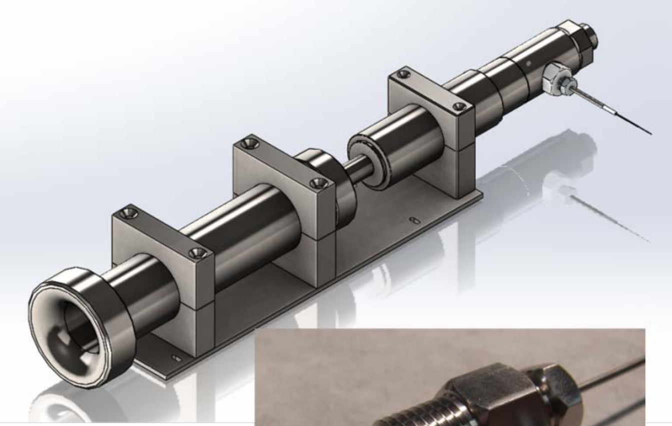
A Thermocouple Embodiment was Selected as a Cost Effective Contamination Detector Platform

- **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**

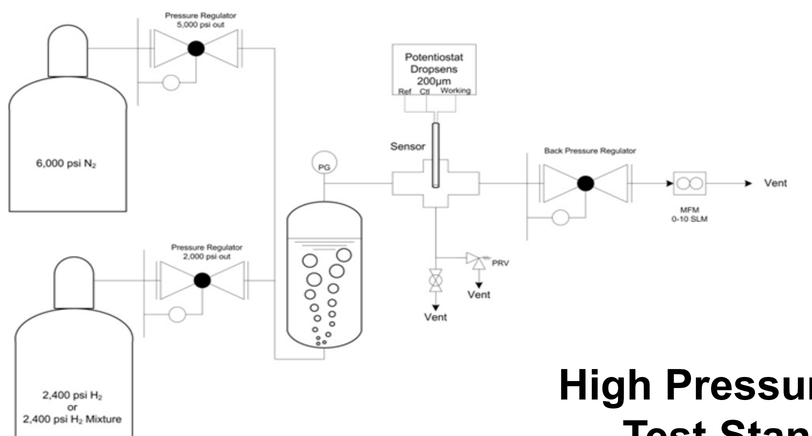


Preliminary Design Complete, Commercially Available Components, Up to 12 Sensors in Single Housing

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

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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

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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

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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**

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Project Summary

- **Relevance**
  - New Standards Have Driven a Need for Cost-Effective/Reliable Instrument That Can Sample H_2 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

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Acknowledgement

- DOE – Will James and Laura Hill
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