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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**

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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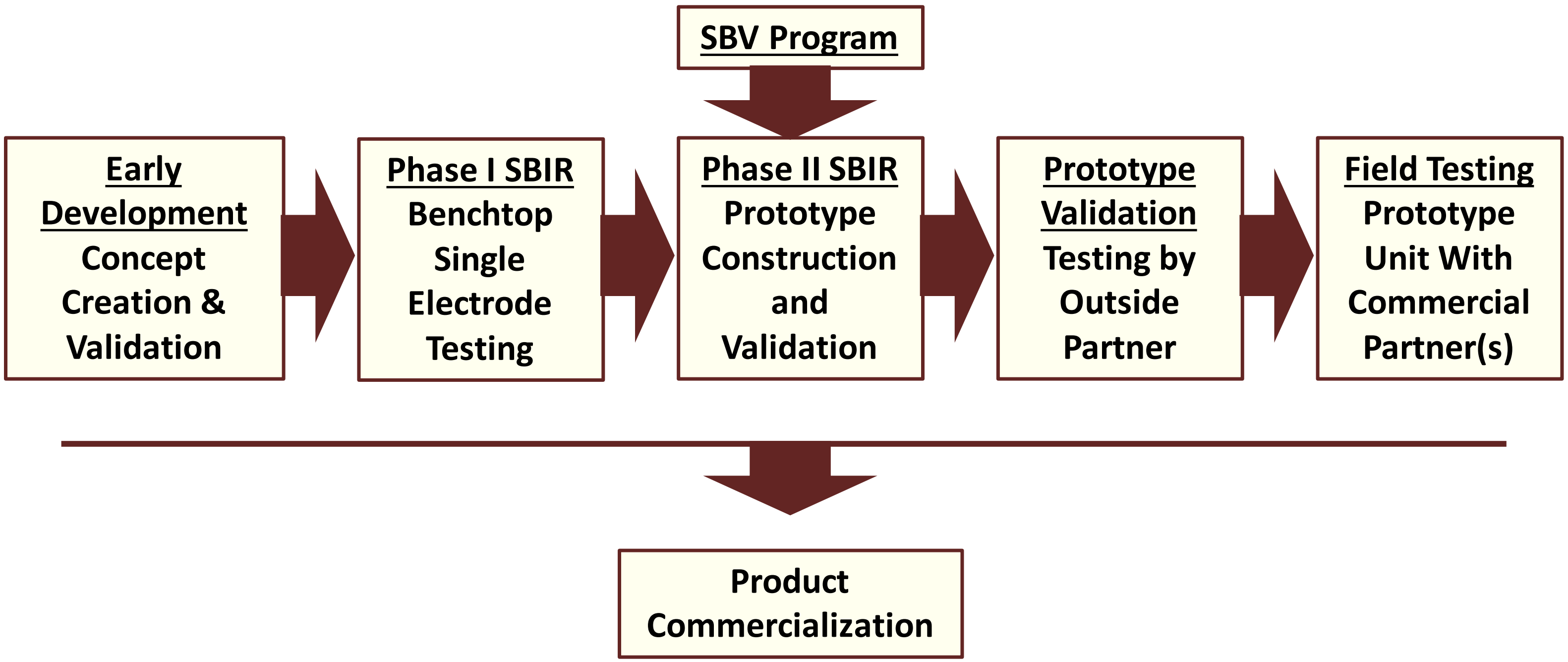
Electrochemical Hydrogen Detector Development Pathway



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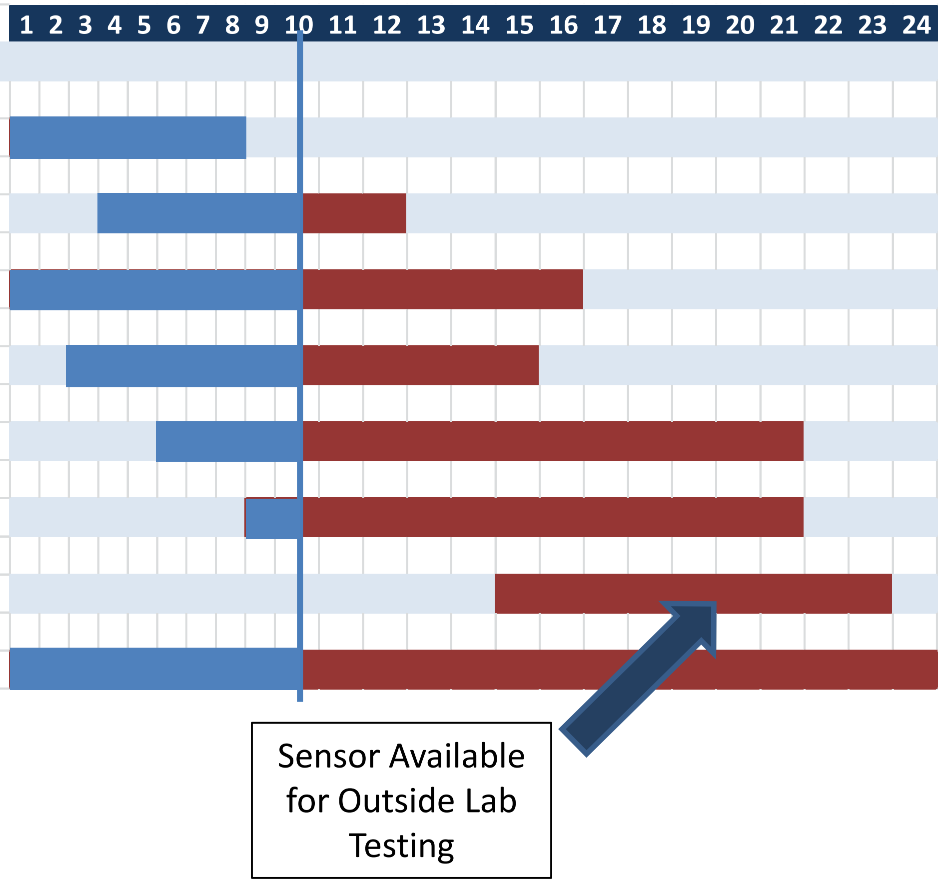
Current Phase II Schedule

	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

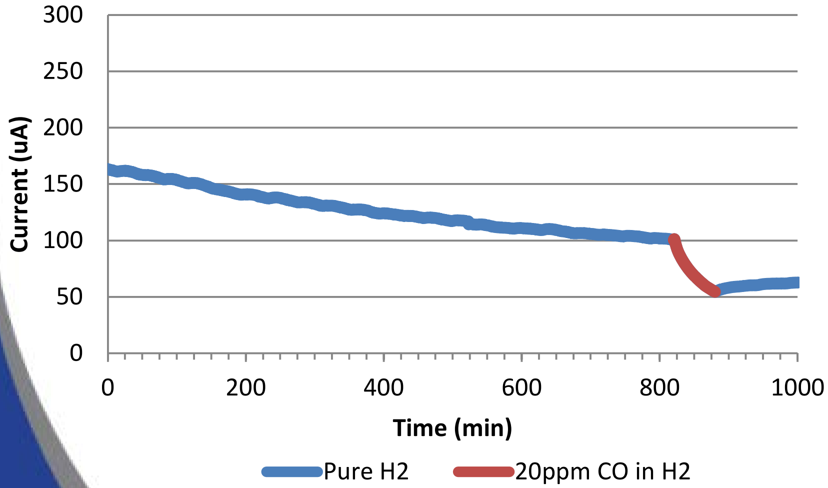


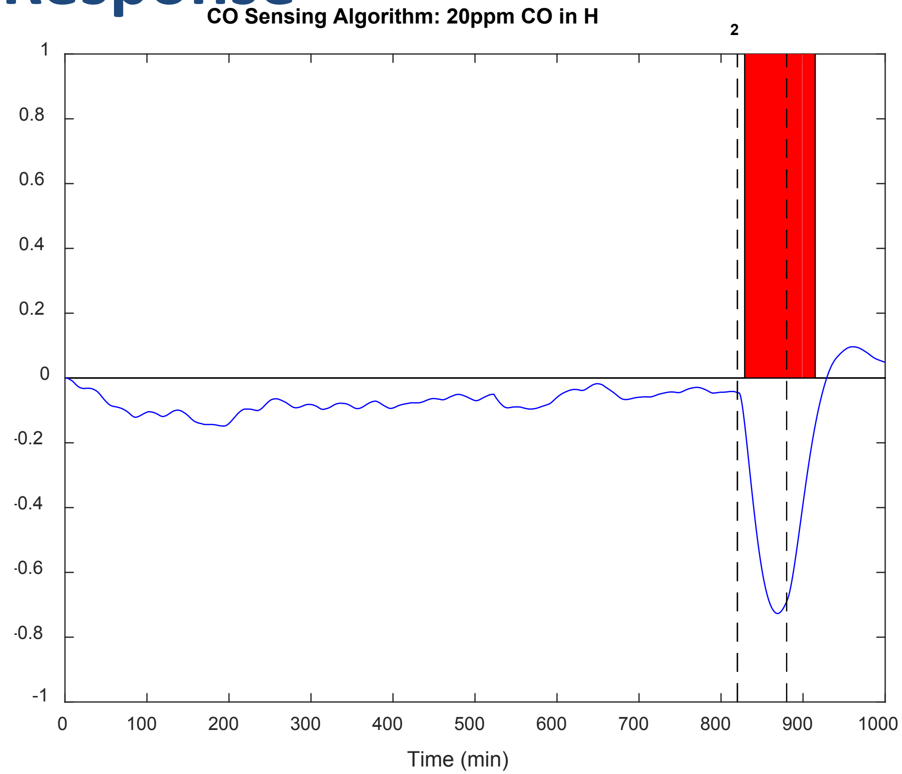
Accomplishments and Progress

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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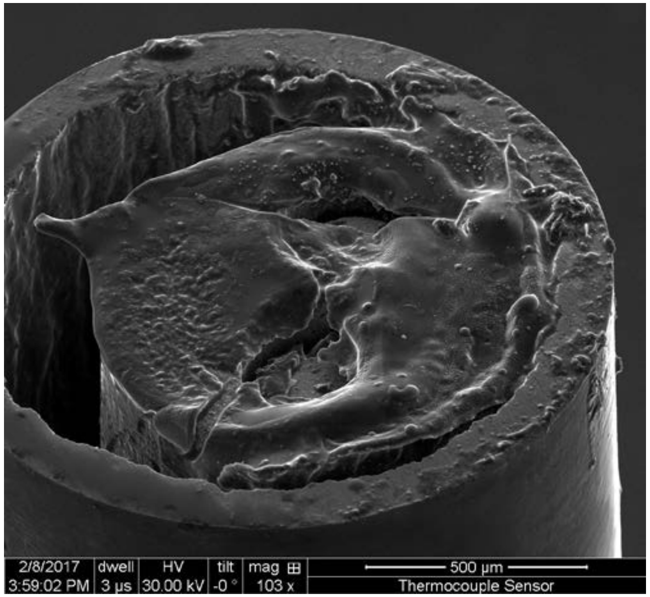
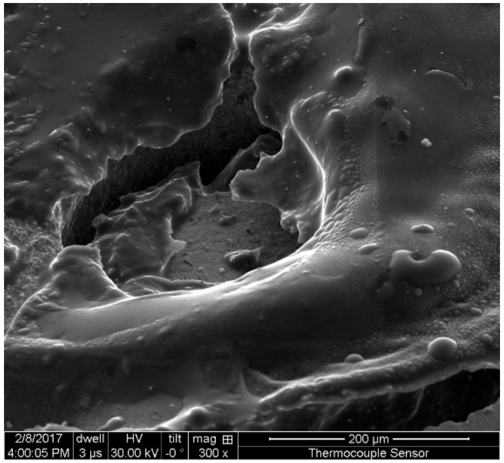
Accomplishments and Progress

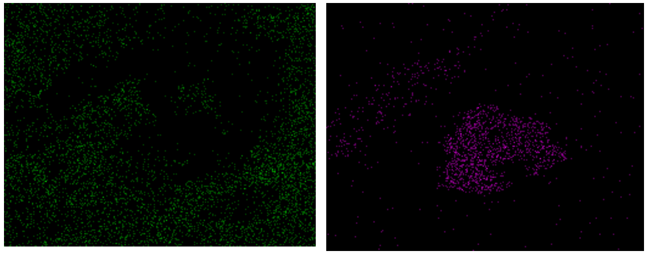
Electrolyte Degradation Controls The Sensor Performance

- **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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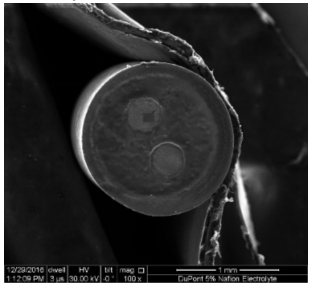
Accomplishments and Progress

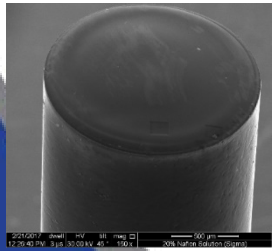
Alternative Electrolyte Application: Dense Ionomer Sol.

- **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**

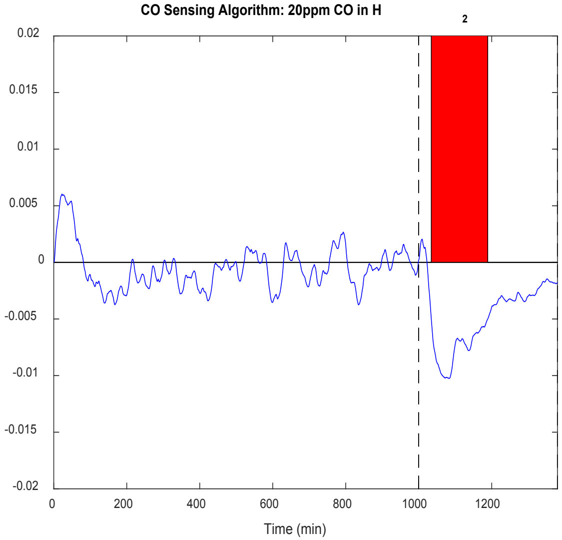
Electrolyte from 5% Solution



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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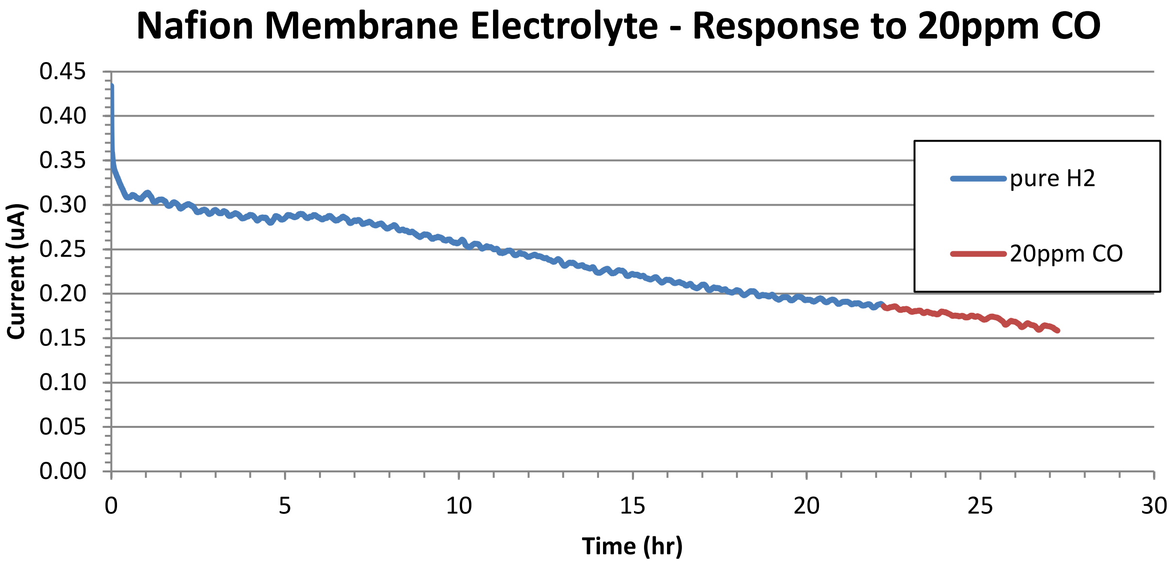
Accomplishments and Progress

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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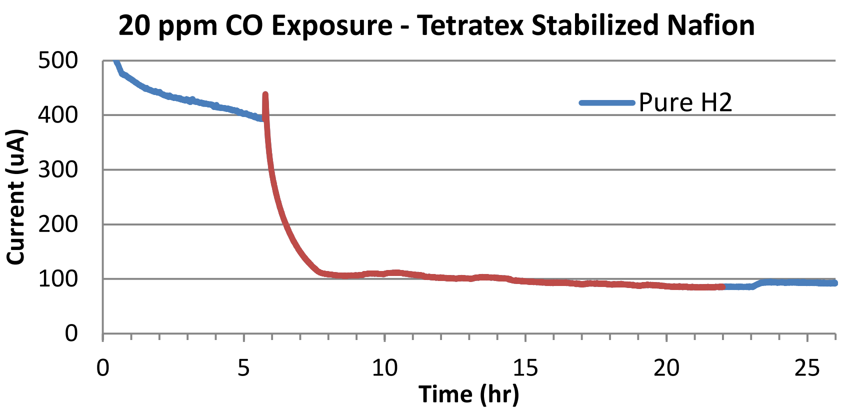
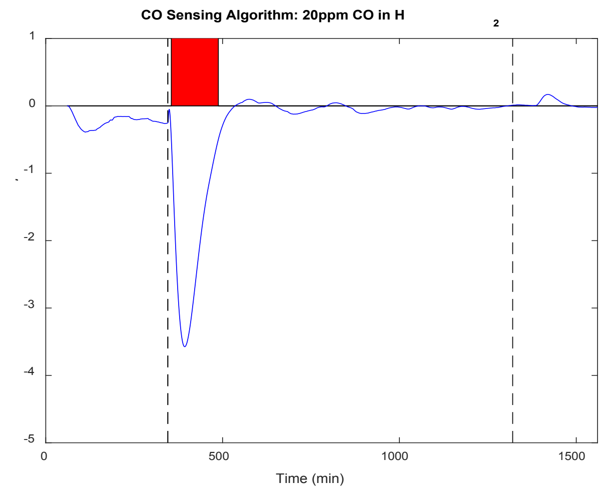
Accomplishments and Progress

Alternative Electrolyte Application: ePTFE Support

- **Sensor Tip is Covered With a Thin ($0.5mil$) 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

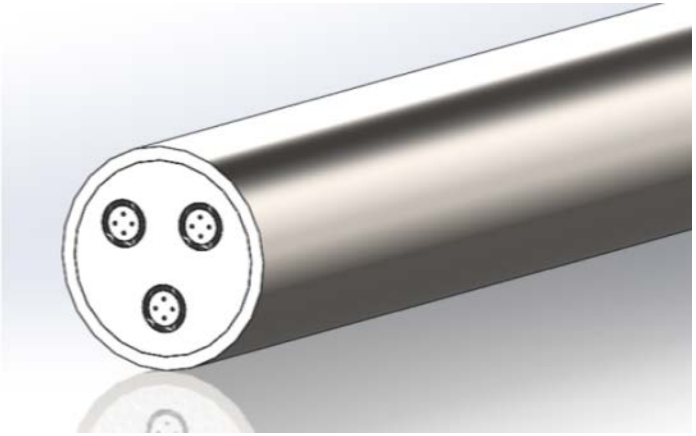
A Thermocouple Embodiment was Selected as a Cost Effective Contamination Detector Platform

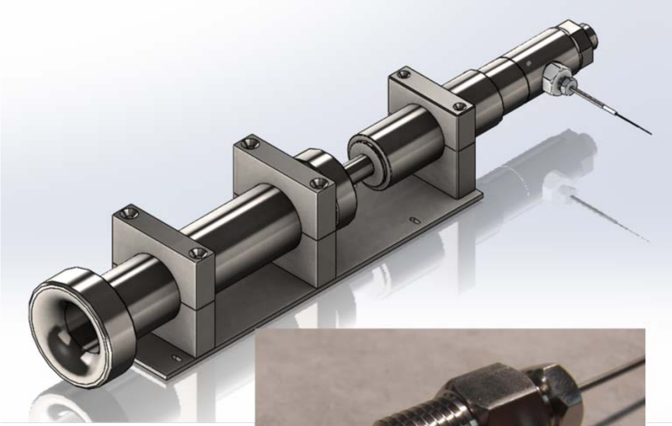
- **Benefits Include**
  - Direct Commercial Availability
  - Proven History of Reliability and Robustness
  - Adaptability of Conductor Materials for Most Appropriate Catalyst for Each Contaminant
  - Ability to Incorporate up to 12 Conductors a Single Thermocouple, Reducing Fluid Stream Penetrations

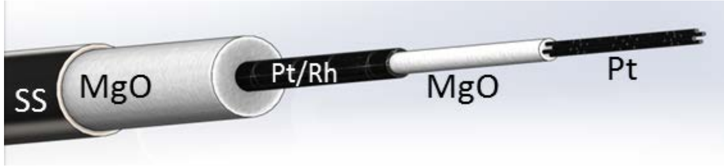
A High Pressure Pass-Through was Identified to Integrate Sensor into Fluid Stream

  - 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

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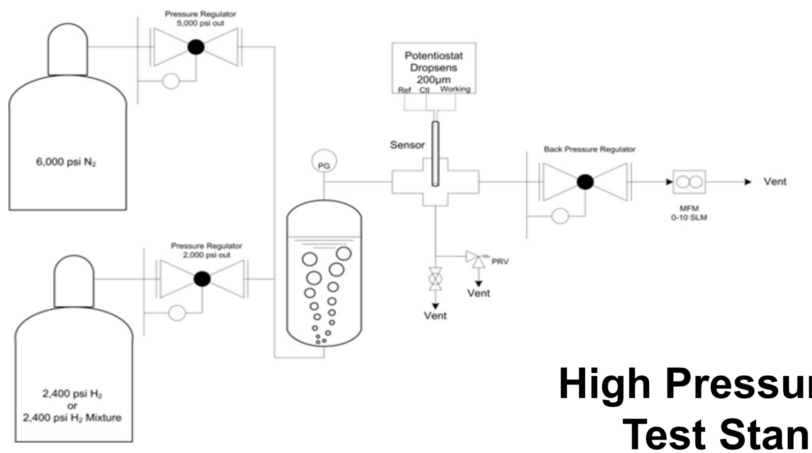
Accomplishments and Progress
Testing And Evaluation

- **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**

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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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