Fuel Quality Assurance Research and Development and Impurity Testing in Support of Codes and Standards

#SCS007

Team:

Eric L. Brosha, Rangachary Mukundan (Program Manager), Tommy Rockward (Principal Investigator), Christopher J. Romero

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"This presentation does not contain any proprietary, confidential, or otherwise restricted information"

Overview

Timeline

- Project 1 start date: 10/1/06
- Project 1 end date: 9/30/18
- Project 2 start date: 10/1/18
- Project 2 end date: 9/30/12

Budget

- Total project 1 funding: $5,475K
  - Total analyzer funding $1,900K (2013-2018)
- Total project 2 funding: $1,400K over 4 years planned
  - In-line analyzer FY19 funding: $350K

Barriers

- Barriers addressed
  - G. Insufficient Technical Data to Revise Standards
  - K. No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

Partners/Collaborators

- **H2Frontier (Burbank, CA)**
- **SKYRE (Formerly Sustainable Innovations)**
- **Southwest Sciences, Inc.**
- **NREL, Bill Buttner**

Outline

- Project Background: Scope and Approach
- Developing the Hydrogen Contaminant Detector (HCD): Timeline
- HCD Field Testing at H2 Frontier filling station
  - HCD Status
  - Field Results
  - Next Steps
- New HCD(Oct 2019)
  - Work Scope
  - Progress/status
- Summary
- Future Work

Relevance : HCDs for Offline or Inline Analysis

Scope

Develop a device to measure impurities in a dry fuel stream at and above the SAE J2719 levels that can quickly respond (**t < 5min**).

Objective: Offline Analysis

Initial Challenges: (ended Sep 2018)

- No oxygen or water
- Device operated H^+ pump **(No oxygen required.)**
- Hydration provided using ***Wicking Scheme/water reservoir***
- Optimization of best materials and their configuration
- Technology developed and validated in field trials

Objective: Inline Analysis

New Challenges: (began Oct 2018)

- HCD inside fuel stream/at nozzle
- Ability to **operate without water reservoir**
- Tolerant to flowrate changes
- Operate under higher pressures and lower temperatures

Reviewer Comment: "It is a bit misleading that the analyzer is installed at the Burbank station, but it is not in-line, and it does not analyze fuel at 700 bar. The placement of the analyzer is a problem for detecting CO and H_2S; the location could be moved, but then there may be a temperature or pressure problem."

Developing the Analyzer : Timeline

- **FY 15: Proof-of-Concept was shown**
  - Sensitivity and response times obtained for CO and H_2S at the SAE J2719 level.
- **FY 16: Prototype Developed and Tested**
  - Wicking scheme allowed operation in dry H_2
- **FY 17: Provisional Patent applied for in November 2016**
  - HCD responds 200ppb CO ≈ 2.5 mins
- **FY 18: HCD installed in Field**
  - Analyzer demonstrated stable baseline; no false positives or negatives in the field
  - Reservoir refills and gas flow rates need to be maintained
  - Applied for technology commercialization funds (TCF) for further development
- **FY19: Initiated new approach for true in-line detection**
  - Initial results show promise

LANL HCD installed at H2F, Burbank,CA

HCD Status (Approach 1)

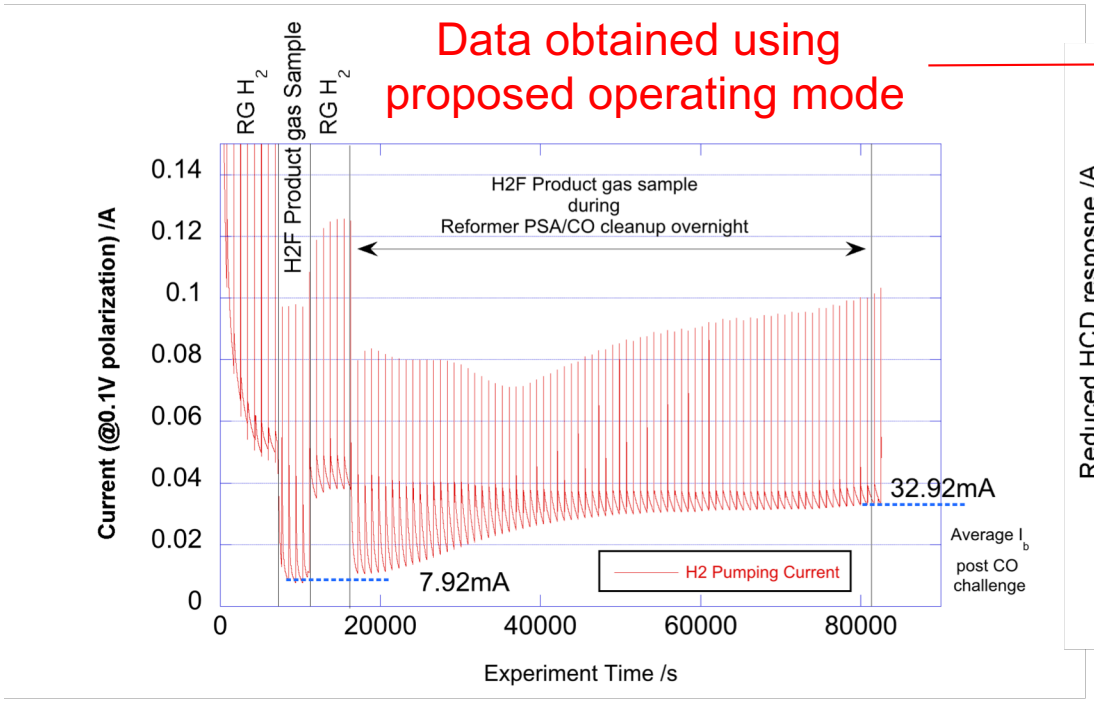
- Installed HCD at H2Frontier, Burbank CA. **(March 28-30, 2018)**
  - New compressors, new dispenser, new explosion proof conduit installed at the H2F station.
- Initial HCD field testing **(Mar 28 – Sept 19, 2018)**
  - Tested HCD control hardware, defined testing approach, methods, etc.
  - **LANL system interfaced with H2F E-stop alarm for safety purposes.**
  - Experiments are controlled remotely using GotoMyPC®
  - 10 and 1 ppm CO challenges performed and baseline stability studied.
  - H2F tested reformer on May 9, 2018 and August 14, 2018.
- Station testing/certification: **(October 16, 2018)**
  - 1st reformer restart attempt during "Milestone window" for LANL field tests.
- H2F reformer restarted. Production cycle began. **(October 22, 2018)**
  - Start of 30+ day HCD field trials experiment.
- Submitted proposal for DOE Technology Commercialization Fund
  - Collaborating with SKYRE to commercialize. Supporting SKYRE's SBIR applications

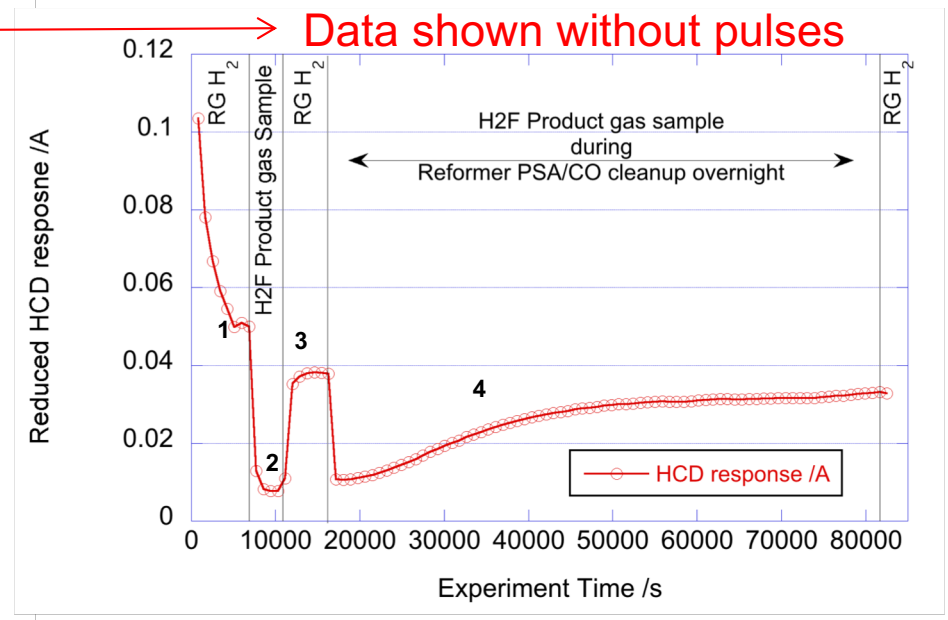
Reviewer Comments:

"The project should find a partner who can commercialize the prototype."

"A question remains about who will develop this prototype into a commercial piece of equipment."

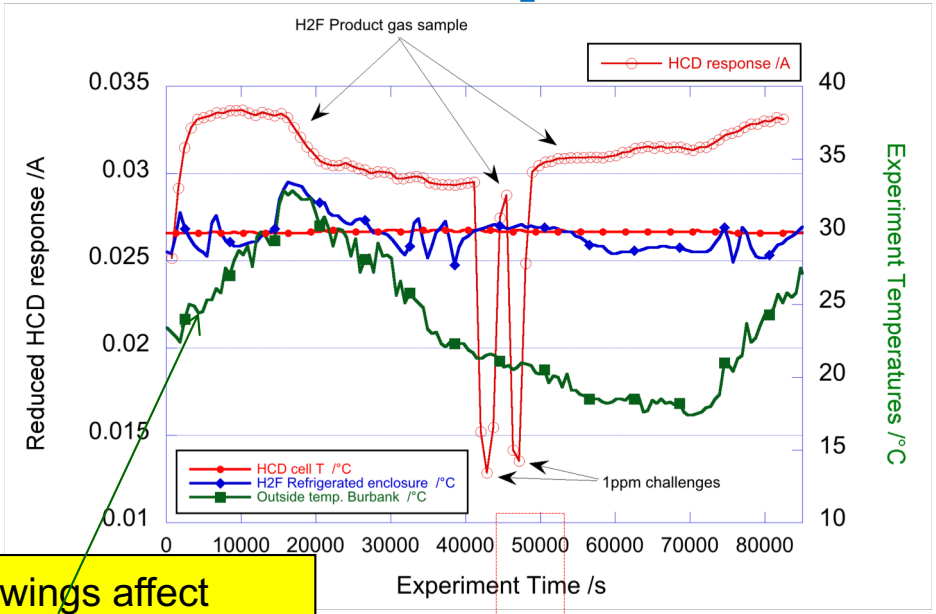
HCD Results : Field Trials



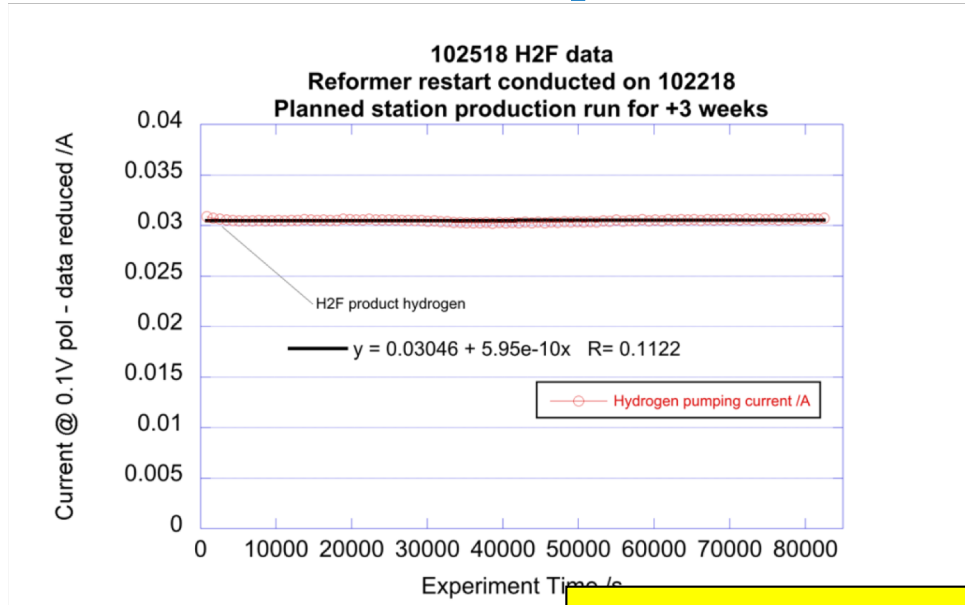


- Operating mode: 0.1V hold with periodic cleaning pulse applied, 1.5V. **(left graph)**
- Data shown without pulses **(right graph)** :
  1. Research grade (RG) H_2 sampled until reformer began.
  2. CO present during reformer start-up evident by sharp current decay.
  3. Performance recovers after returning to RG H_2
  4. Current increases as product gas becomes cleaner.

Impact of Ambient Temp

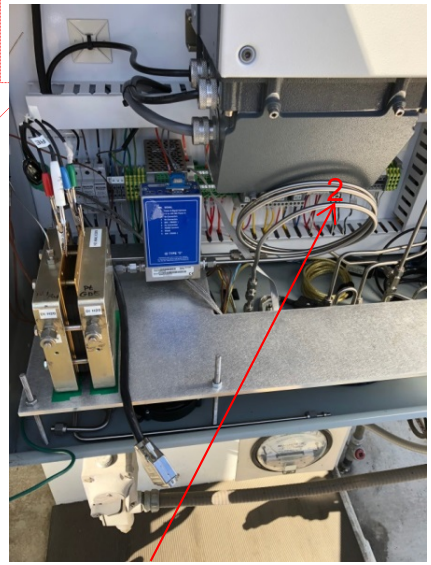


T swings affect baseline stability



Modifications provided stable baseline.

Insulation applied



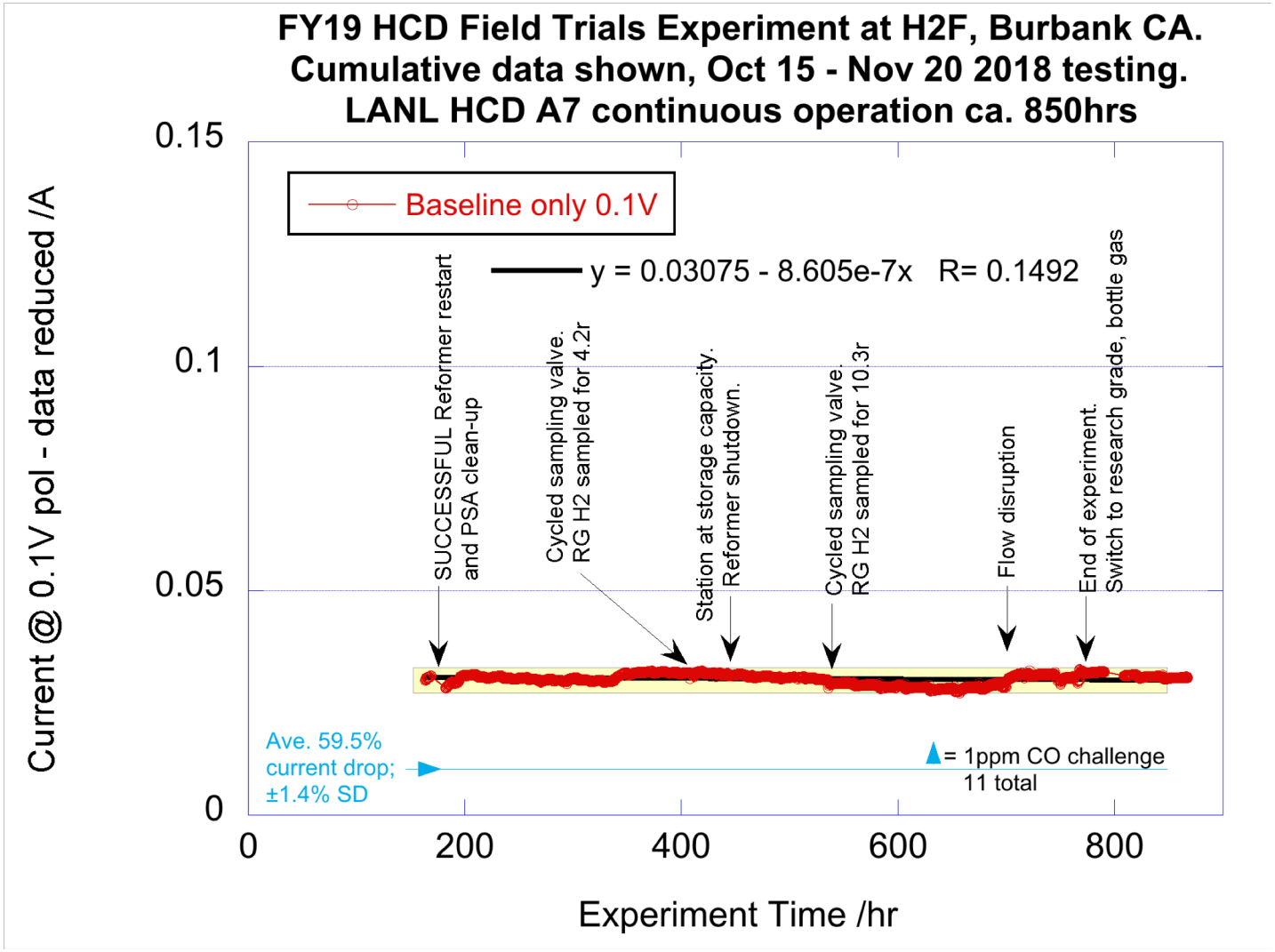
Gas sample loop

Modifications made to mitigate impact of local temp:

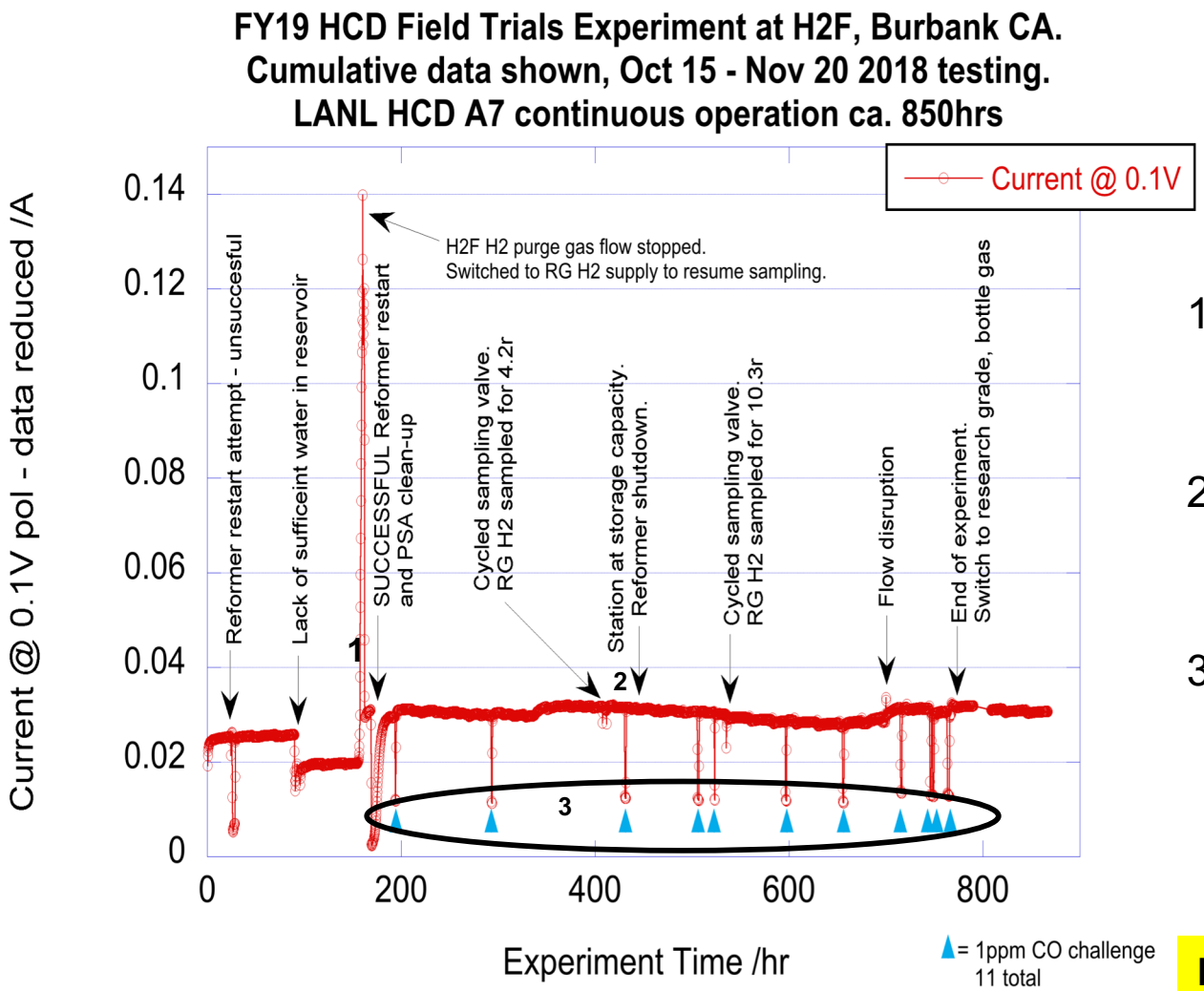
1. Insulation applied to exterior manifold and supply gas lines.
2. Internal sample loop installed to allow sample gas temp more time to equilibrate.

FY18 Milestone

- Data show only pumping current data during periods without CO present from the successful reformer restart event until end of the experiment.
- Baseline variation well below 1ppm detection threshold.
- **Analyzer baseline stability can meet < 1ppm detection limit (June 2018 milestone)**



FY18 Milestone



≤ 1ppm CO detection in ≤ 1min demonstrated September 2018 Milestone

1. Monitored HCD response during start-up and subsequent PSA clean-up process.
2. Measured product gas stream until station storage tanks achieve full capacity
3. Challenged HCD periodically with 1ppm CO; a response **observed every time within ± 1.4% error**.

HCD operated >35 days

Cycles: 0.1V for 830s,1.5V(clean-up pulse) for 30s

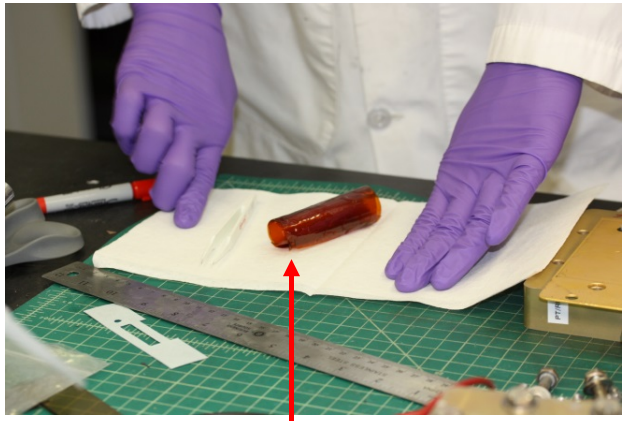
Polybenzimidazole (PBI) based HCD work

Motivation/Relevance

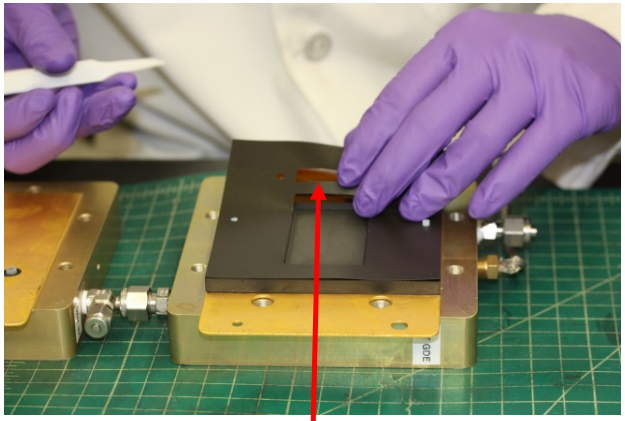
Develop a hydrogen contamination detector that functions like the technology shown today without need for water. Reduce system complexity and cost and potential to operate ***inline*** at the nozzle. Successful implementation of a true in-line HCD can have an enormous impact on FC vehicle viability.

Approach

Replace Nafion® with a proton-conducting thermoplastic membrane that will not require water to function.

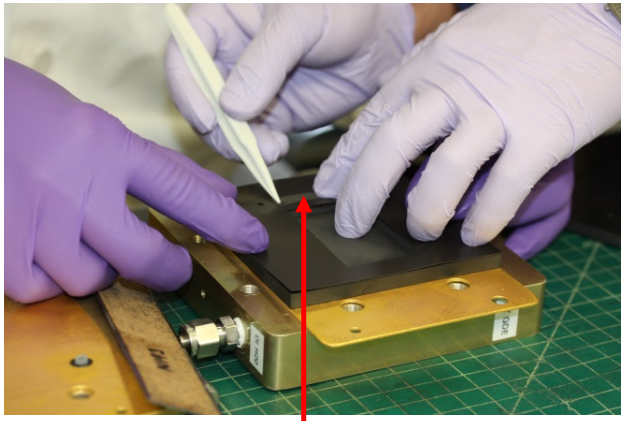


PBI membranes prepared by LANL researchers with 5, 10, and 15% H_2PO_4.



Same HCD hardware used but humidification scheme not used.

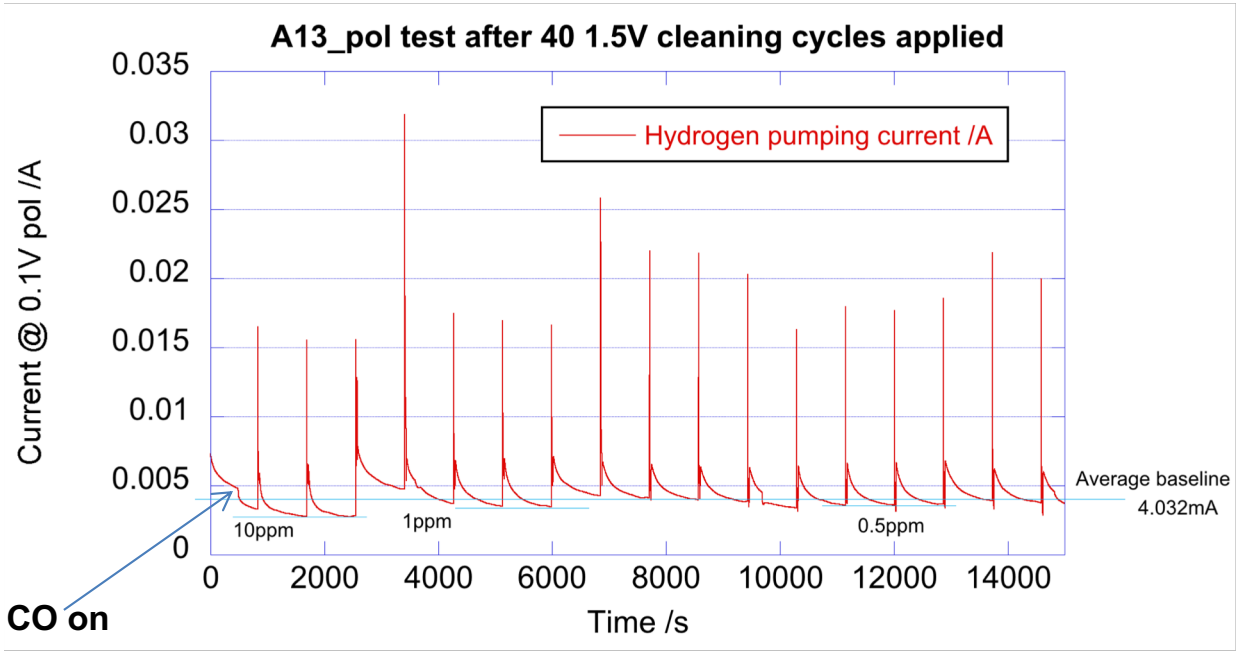
Excess H_2PO_4 applied to GDE/GDL before assembly.

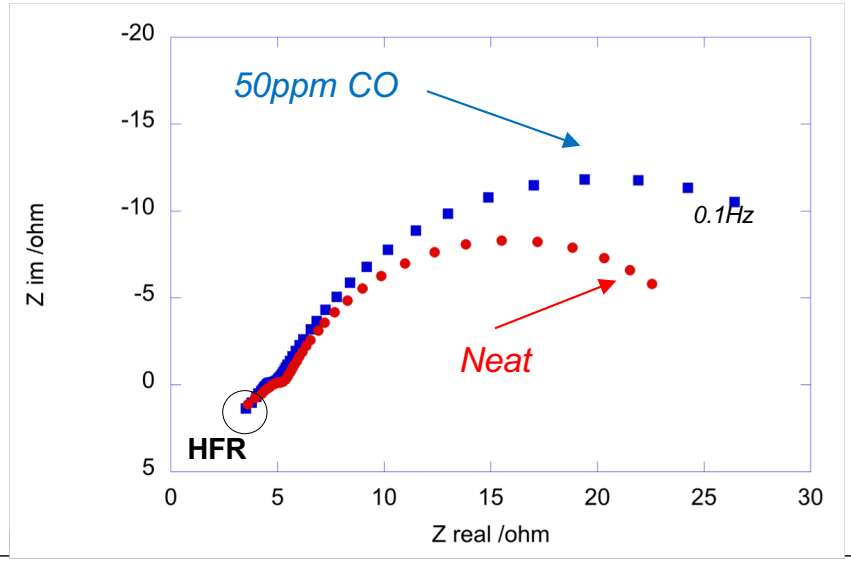


Same sputtered, low-Pt loaded GDL used / PtRu CE. With or without ionomer.

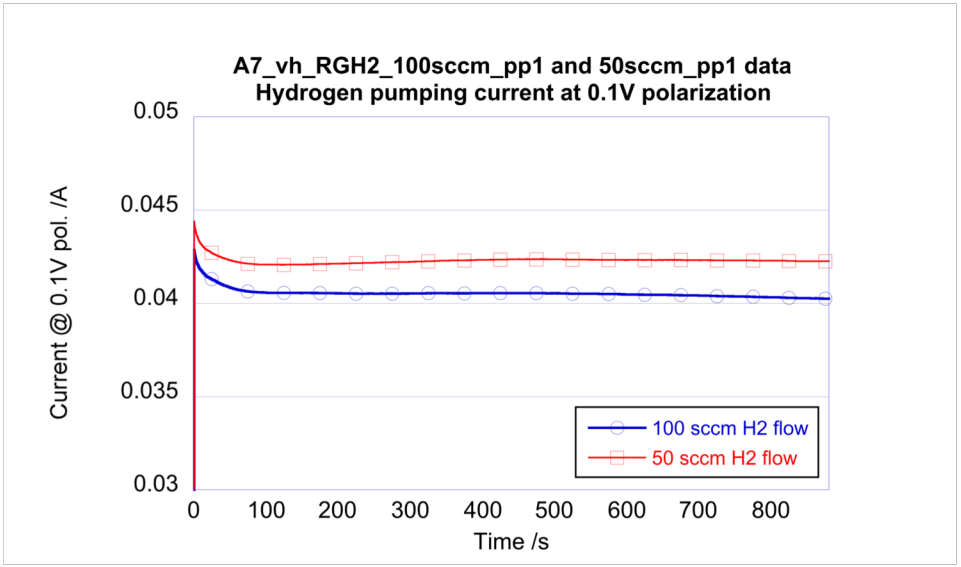
HCD: Initial PBI Results

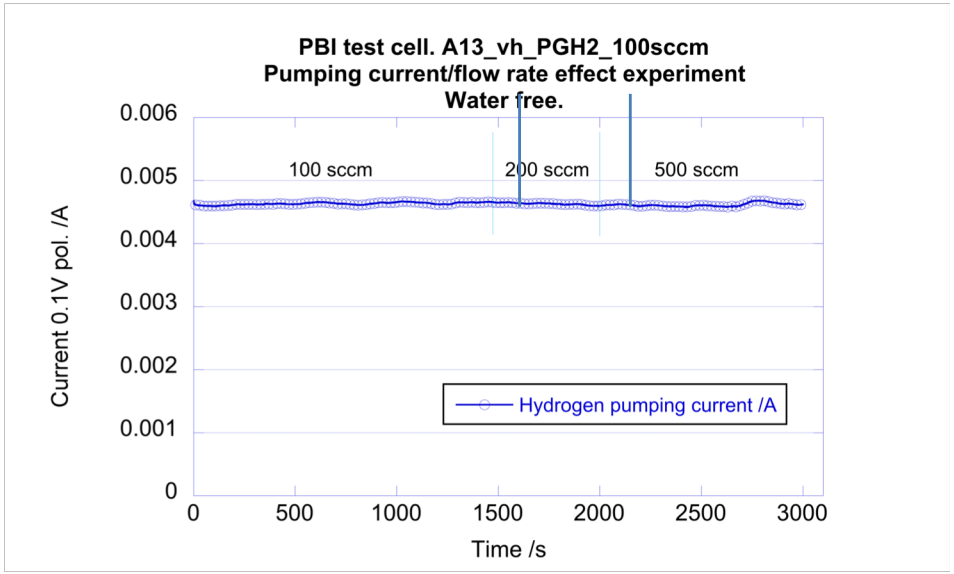
- Use identical operating mode
- Current response to higher concentration CO similar to Nafion® HCD.
- Impedance spectra: an increase in charge transfer resistance is indicative of catalyst poisoning (i.e. CO adsorption)
- No response to CO at the SAE level
- Cell conditioning different from Nafion® based HCD.





HCD Flowrate Impact: Nafion® vs. PBI



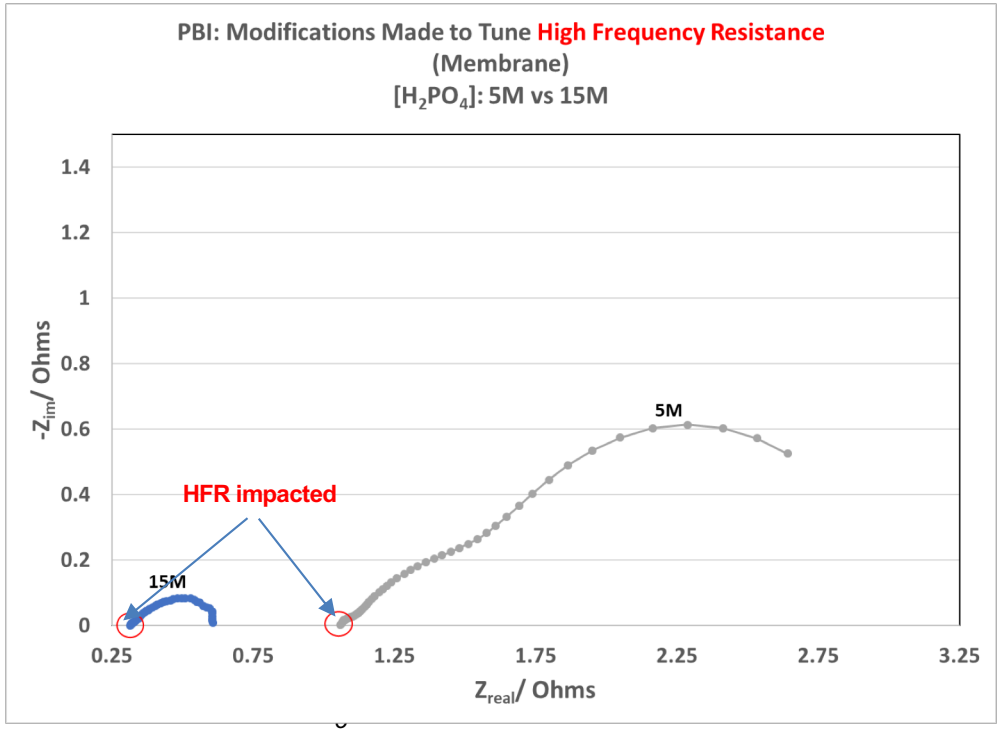


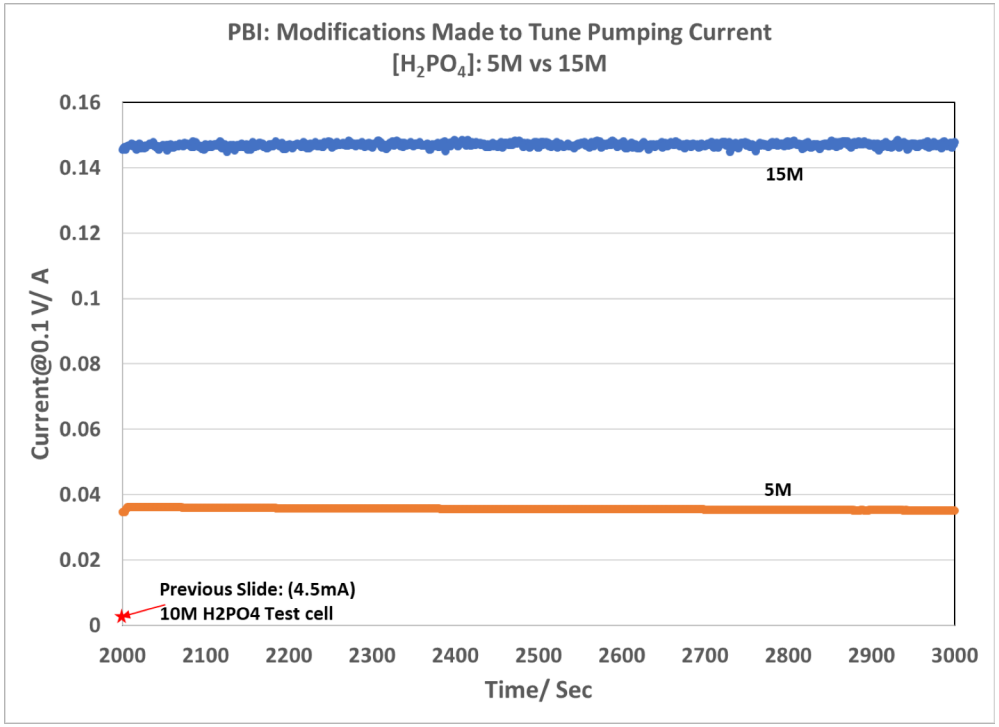
- *Nafion® based HCD requires water reservoir to provide the necessary hydration*
- *Clear flowrate dependence observed –higher flows cause membrane drying (higher HFR)*

- *PBI based HCD without water reservoir;*
- *Flow independent baseline current*
- *Initial performance lower*

PBI-based HCD operated in completely water-free, dry H_2 stream. The current response remained constant even after a 5X increase in flowrate.

PBI HCD: Sensitivity Tuning





- Test conditions: 30°C, ambient pressure, 500sccm flowrate, identical reference electrodes
- Previous Slide: **Pumping Current: ~0.0045 A** (Ultra-low Pt loadings with 10M H_2PO_4)
- Modified [H_2PO_4] and Pt loading
- **Left graph:** Varying local [H_2PO_4] significantly changes membrane conductivity (HFR).
- **Right graph:** Pumping Current is influenced by both [H_2PO_4] and Pt loading
- **Met Dec 2018 milestone**

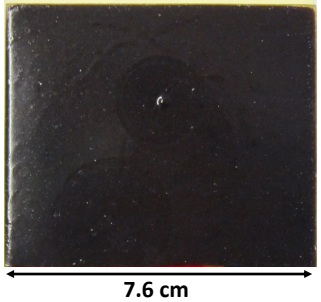
Successfully varied the HCD pumping current!!!

TinPyrophosphate based membranes

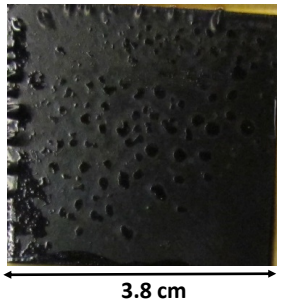
Three different Tin Pyrophosphate (TPP) membranes prepared

(1) TPP-Nafion – 80:20 P/M = 4.6

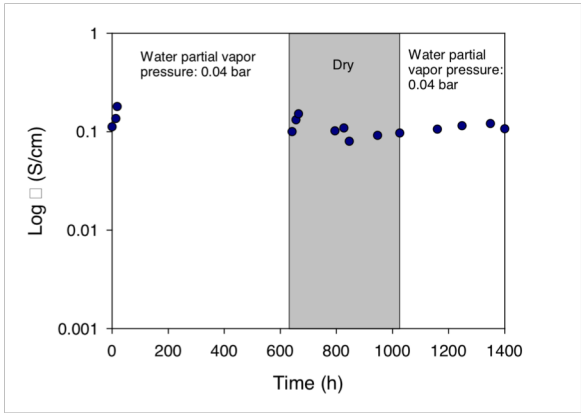
(2) TPP-Nafion – 90:10 P/M = 4.6



(3) TPP-Nafion – 80:20 P/M = 9.3



- TPP powder was prepared by mixing $SnSO_4$ with 0.5M sulfuric acid followed by oxalic acid and phosphoric acid. The resulting mixture was dried overnight at 140 °C followed by sintering at 650 °C for 2 hours.
- The membranes were fabricated by mixing appropriate ratio of TPP and Nafion in 1,2 pentane diol by probe sonication and magnetic stirring at 100 °C. The resulting homogeneous solution was cast and dried in an oven kept at 120 °C for 3 hours followed by vacuum drying at 160 °C for 4 hours.



Conductivity of SnP_2O_7 in dry and wet gases at 200 °C ***Energy Environ. Sci.***, 2018,**11**, 979-987

- Higher TPP content (90:10 vs 80:20) should result in better conductivity
- Higher P/M ratio (9.3 vs 4.6) should result in better conductivity

On track : March 2019 milestone

Milestones

6/30/2018	Regular	Obtain real-world performance data of a novel in-line analyze in an existing hydrogen fueling station to identify issues with analyzer sensitivity and stability to inform further direction of R&D.	Complete
9/30/2018	Annual	Implement new findings from field test in to analyzer prototype to advance the design to be capable of detecting < 1ppm CO with an order of magnitude improvement in response time (< 1 minute) in a dry hydrogen stream.	Complete
Quarterly Progress Measure	Evaluate PBI membranes to enable down-selection of ideal membrane for operation of analyzer with stable conductivity under defined conditions.	Report the conductivity of three different compositions of PBI membranes in dry H_2 at 30 °C	12/31/2018	Complete
Quarterly Progress Measure	Evaluate TPP membranes to enable down-selection of ideal membrane for operation of analyzer with stable conductivity under defined conditions.	Report the conductivity of three different compositions of Tin pyrophosphate membranes in dry H_2 at 30 °C	03/31/2019	90% Complete
Quarterly Progress Measure	Develop membrane electrode assemblies based on down-selected PBI or TPP membranes	Synthesize a membrane electrode assembly based on the down-selected membrane and incorporate it into a H_2 pumping cell	06/30/2019	In progress
Annual Milestone	Membrane Development	Report performance of analyzer membrane electrode assembly capable of maintaining baseline pumping current within ±5% when exposed to dry H_2 at 30°C for 1 week.	09/30/2019	In Progress

Collaboration and Coordination

- H2Frontier (Dan Poppe)
  - Field trials partner (no cost)

- Skyre (Trent Molter)
  - Support to Skyre's high pressure HCD under the SBIR and SBV (Small business voucher) programs
  - Written collaborative proposals for TCF and SBIR

- NREL (Bill Buttner)
  - LANL currently developing an HCD for independent evaluation at NREL (under laboratory and HRS conditions)

- Southwest Sciences Inc. (Mark Paige)
  - Under guidance from SCS TDM, LANL provided support to SSI's SBIR Program
  - LANL staff evaluated the response of SSI's Optical HCD to CO, NH_3, and H_2S contaminants in H_2.
  - SSI's staff presented data from LANL at CSTT meeting (Jan. 2019).

Summary of field trials work

- A Nafion® based, electrochemical hydrogen contaminant detector was tested at H2Frontier hydrogen filling station in Burbank CA during its refit and recommissioning.
- A 100 sccm sample was taken from the H2F production skid and **without requiring humidification**; both real-time product gas and storage gas was sampled. **The self-humidifying approach using an internal reservoir worked with minimal baseline drift.**
- The LANL HCD easily detected CO byproduct during reformer restart (as high as 18ppm) and 10, 1ppm challenges were performed during an 850h experiment after initial installation and 10ppm testing/commissioning.
- The 10ppm and 1ppm challenges produced ≈ 75% and ≈ 60% reductions in pumping current respectively. **Twelve, 1ppm challenges decreased pumping current on average 59.5% with an error of ±1.4% over 12 challenges during a 6 month time period.**
- Long term baseline data show a drift rate of 9×10^{-7} A/h over a 600h period of testing. The addition of a 1.5V, 600s pulse approximately once a day eliminated any long term drift.
- **No false positives or false negatives were seen during the field tests to date.**
- Average water consumption rate is estimated to be ~250µl/day at 100sccm.
- Project milestones successfully met.

Summary of new HCD

- PBI membranes can function in a HCD
  - Eliminates the need for water wicking system. Provides ability to operate inline and under pressure
  - Eliminates the need for precise flow control of the hydrogen stream
  - Long term stability needs to be evaluated

- Sensitivity of PBI based HCD demonstrated
  - Ionomer in the electrode and Pt loading of the electrode needs optimization
  - Develop understanding of CO and H_2S poisoning of electrodes in these novel systems

- Tin Pyrophosphate (TPP) /Nafion® composite membranes have been prepared with 2 different TPP contents and 2 different P/Sn ratios
  - Assembly of TPP composite membranes with GDEs to measure conductivity and HCD performance underway

Proposed Future work

- Commercialize Nafion® based HCD **(Technology Transfer Activity)**
  - Submitted TCF proposal with SKYRE (Trent Molter)
  - Extend to H_2S and other gases
  - Improve sensitivity and response time with improved designs
  - Develop electronics
  - Continue successful relationship with H2F
- Develop PBI based analyzer (lower TRL work started in Oct of 2018 based on 4 year proposal)
  - Evaluate conductivity of anhydrous membranes and select appropriate membrane either PBI or TPP (Tin Pyrophosphate)
  - Develop understanding of poisoning mechanisms and design sensitive electrodes
  - Understand clean up mechanisms and develop operating modes with improved sensitivity, selectivity and response time
  - Evaluate operation at different temperatures and pressures
- Evaluate new analyzer prototype in the field and transition to commercialization.

Any proposed future work is subject to change based on funding levels.

Acknowledgements

LANL staff would like to thank:

- Kannan Ramaiyan, Sandipkumar Maurya and Cortney Kreller
- DOE-EERE Fuel Cell Technologies Office
  - Laura Hill: Technical Development Manager
- Codes & Standards Tech Team
- The Audience…

Reviewer's Comments

Major Strengths: This is a very intriguing technology, and it is showing very impressive results. The expertise of the laboratory is a project strength. The project includes good partnerships between national laboratories and industry.

Weakness: The principal investigator and DOE need to recast the specific application with respect to fueling stations to redirect some of the goals and targets to more closely align with realistic timescales and sensitivities. A previous reviewer remarked on not having enough time and money to work at a faster pace, noting that fuel quality assurance technologies are needed in place now, because hydrogen fueling stations are being deployed in California now and in the Northeast soon. A question remains about who will develop this prototype into a commercial piece of equipment.

LANL has reworked the project with DOE based on priorities of the Industry and directions of FCTO research. The current analyzer (with wicking system) has demonstrated enough promise to be commercialized, and funding for this will be pursued through other independent means in collaboration with Industry

Having the analyzer function with a response time of under five minutes is critical. It is a bit misleading that the analyzer is installed at the Burbank station, but it is not in-line, and it does not analyze fuel at 700 bar. The placement of the analyzer is a problem for detecting CO and H2S; the location could be moved, but then there may be a temperature or pressure problem.

LANL's current project is a lower TRL project aimed at solving this critical problem. The development of membranes with conductivity independent of ambient water content or flow rate or pressure will be a critical step towards the development of an inline analyzer.