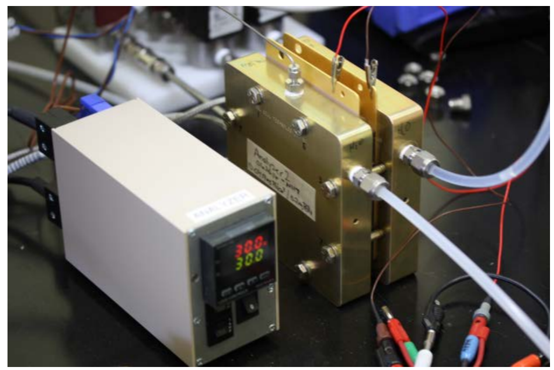
Fuel Quality Assurance R&D and Impurity Testing in Support of Codes & Standards

The U.S. Department of Energy 2017
Hydrogen and Fuel Cells Program
and Vehicle Technologies Office
Annual Merit Review and Peer Evaluation Meeting



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Project ID # SCS007

June 6, 2017

Overview

Timeline

- Project start date: 10/1/06
- Project end date: 9/30/17*

* Project continuation and direction determined annually by DOE

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

Budget

- Total project funding: $4775K
- Funding received in FY16: $700K
- Total funding planned for FY17 $750K

Partners/Collaborators

- Japanese Automotive Research Institute
- SAE
- CEA-Liten France
- VTT- Helsinki, Finland
- ISO TC197/WG 27 & 28

Outline

- **Fuel Quality Analyzer**
  - **Relevance/Impact**
  - **Progress in FY17**
- **Hydrogen Fuel Quality**
  - **Background**
  - **Motivation**
  - **Experimental Set-Up**
  - **Results with CO and H_2S**
    - **Fuel: Single-pass mode vs. Re-circulation mode**
    - **Pre-Dosing**
- **Summary**
- **Future Plans**

Fuel Quality Analyzer: Relevance/Impact

The development of a device to measure impurities in the fuel stream would be useful to the fuel cell community, hydrogen fueling stations and suppliers. Some of the more important qualities of the device:

- Inexpensive
- sensitive to the same impurities that would poison a fuel cell stack (e.g. CO, H_2S, and NH_3)
- quick response time to fuel contaminants

Such a device could be used as an early alert monitor and prevent damage to fuel cell stacks!!!

Approach

- This device operates as an electrochemical pump using a MEA-type Configuration. **(no air or water available). Measure pumping current before, during and after contaminant exposure.**

- Use similar components to a fuel cell stack (e.g. Ionomer, PGM, and GDLs)

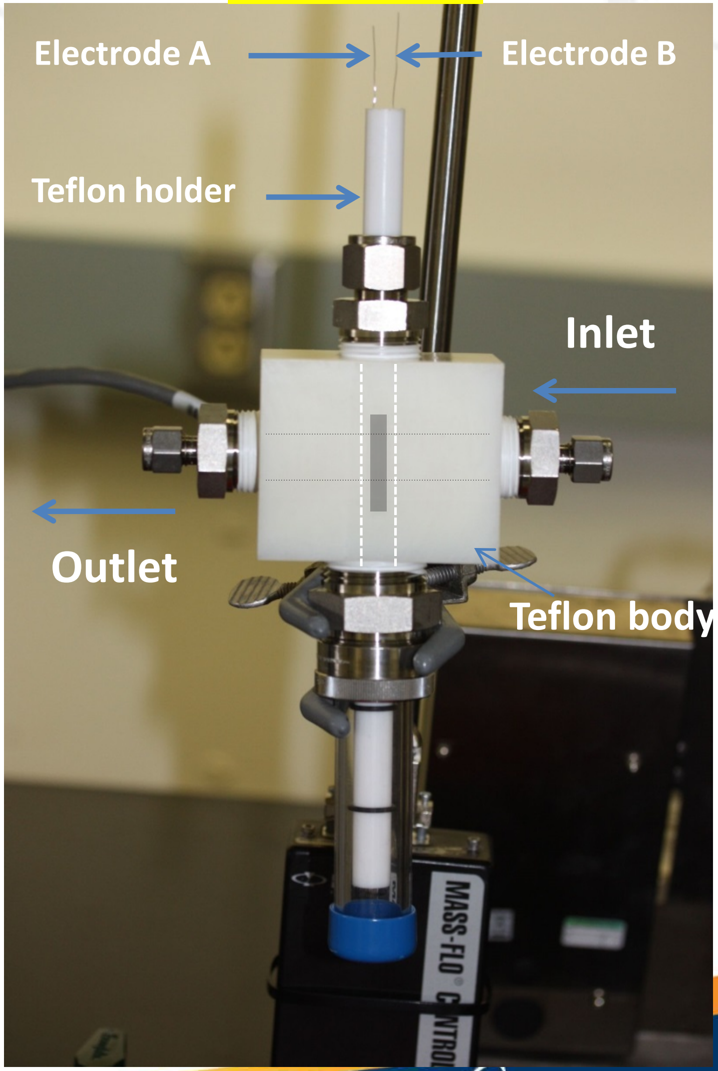
- Reduce overall Pt loading and utilize low surface area catalyst

- Identify best materials and their configuration

Developing the Prototype FY16

Approach

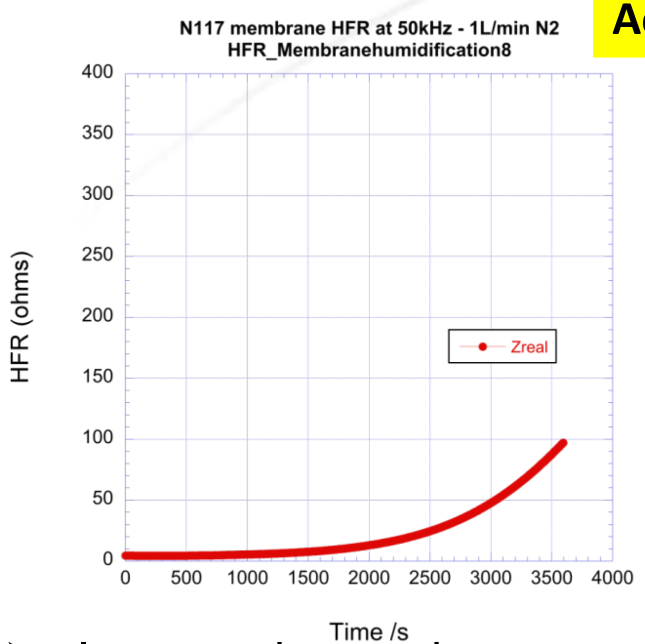
- **Membrane Hydration Challenging**: Identifying conditions needed for constant membrane humidification
  - Characterize and confirm by measuring HFR and CV
  - Vary flow conditions
  - Vary Membrane thickness
- Determine a **fuel flow-rate** that will not compromise sensitivity or response time

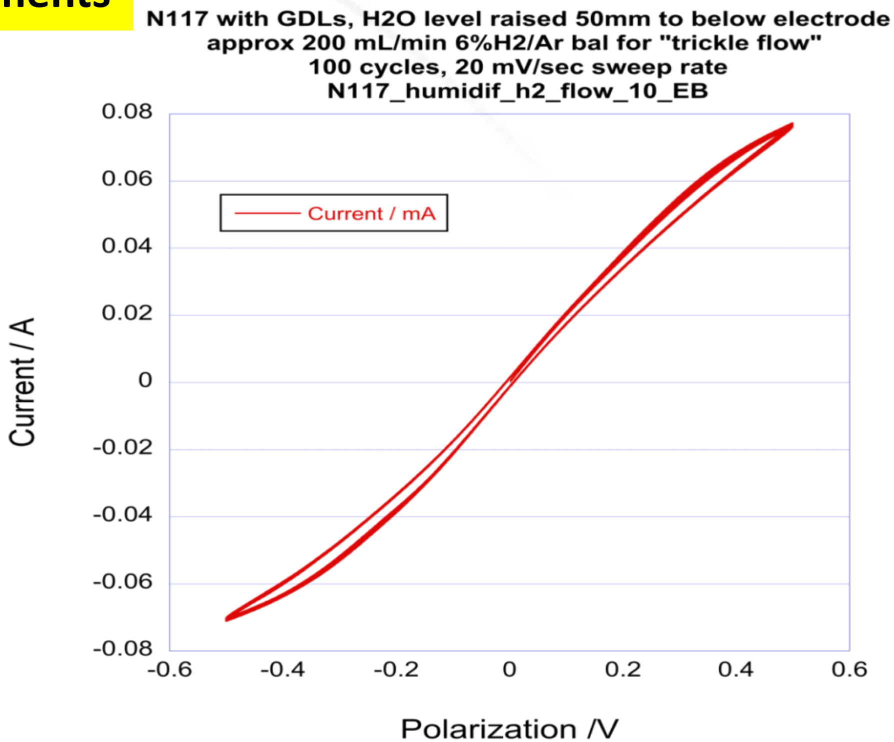


Membrane Hydration Tests: Achieved Stability (FY 16)

N117

Accomplishments



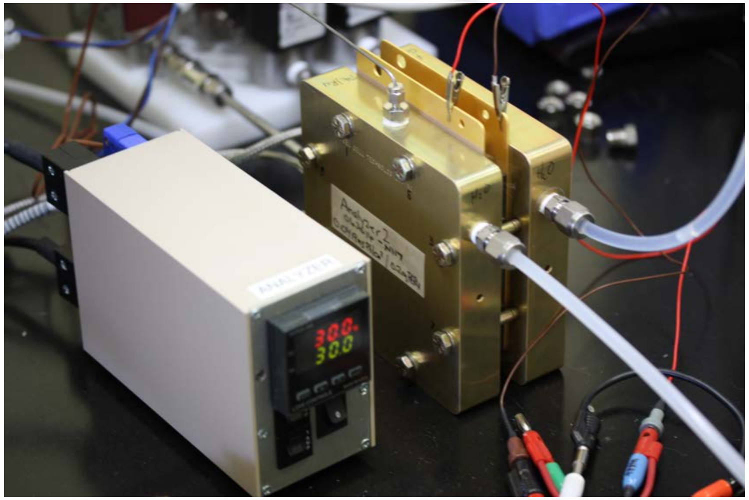


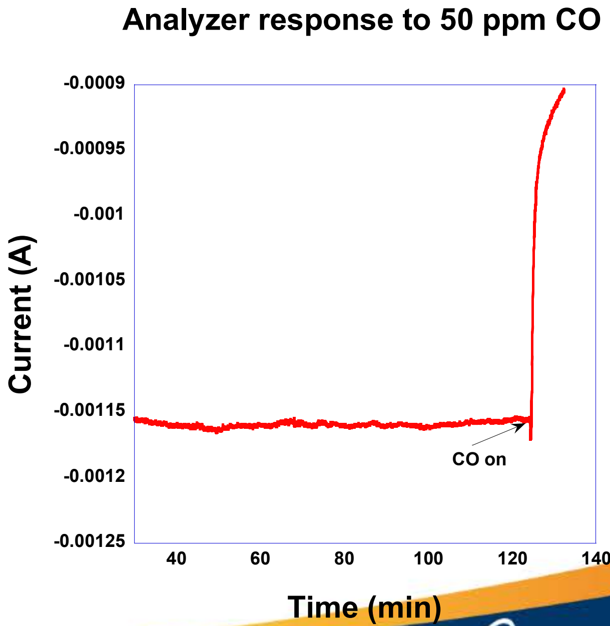
- Increase in membrane conductivity during flow of dry gas evident and more pronounced in N212 (FY16)
- Thicker membrane (N117) maintains hydration longer.

Re-designed hydration scheme with GDLs: 100 cycles are shown overlapping (constant HFR)

Prototype Developed in FY 16

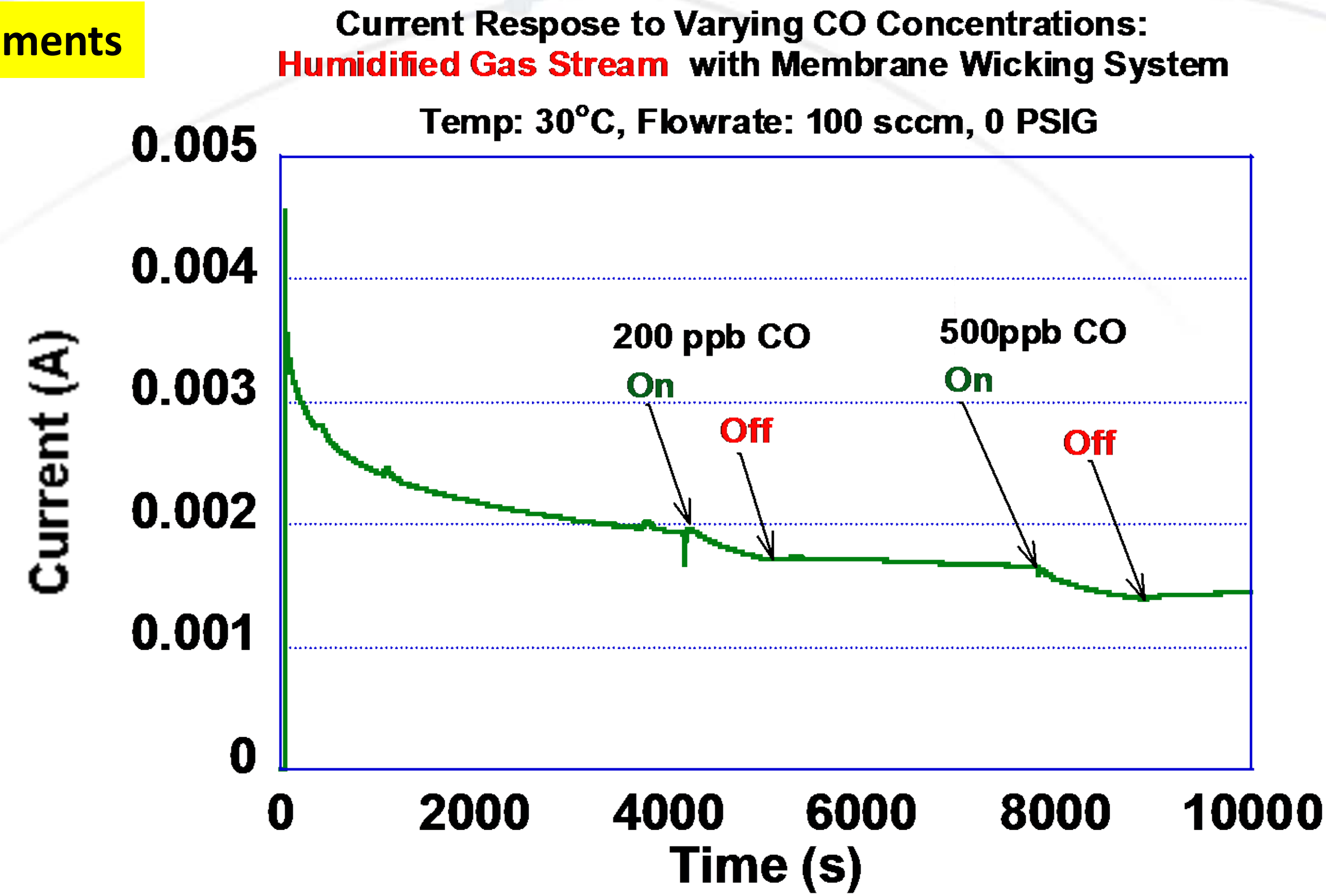
- Incorporate design elements from experiments into analyzer prototype- standard PEMFC hardware
  - Better current collection, uniform compression, etc.
  - Use as much common hardware as possible.
  - Allow for pressurization.
- Use LANL membrane humidification approach. Test complete analyzer prototype before applying for Patent.
- Test HFR stability and determine maximum dry gas flow rate.
- Test analyzer with SAE J2719 contaminant levels
- Plan for field testing! Requires precise control of sensor T regardless of changes in ambient T.





SAE Level Studies: Baseline Measurement

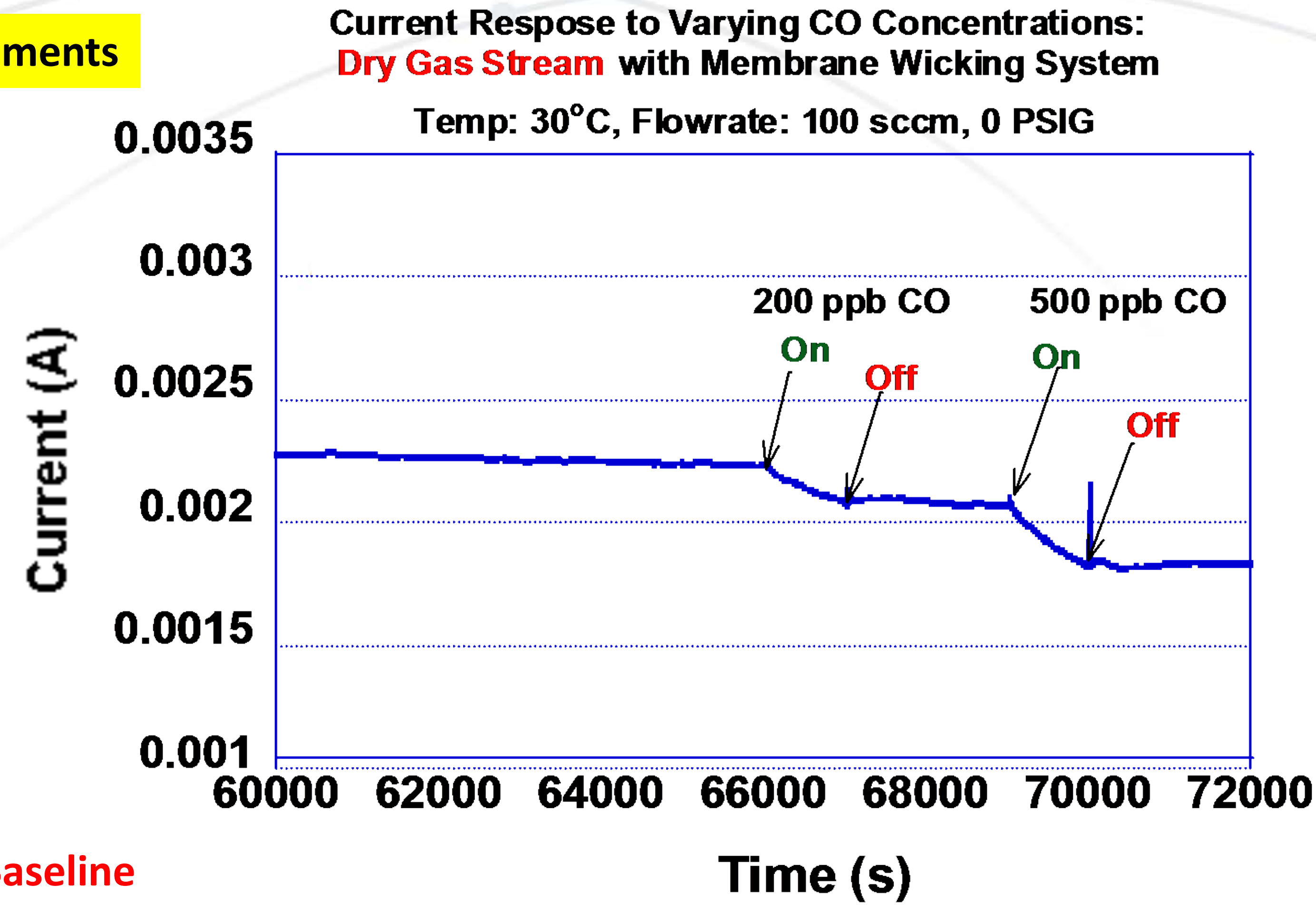
Accomplishments



- 0.039 mg Pt/cm^2; Low Pt GDE working electrode (25BC) & Counter: 0.2 mg PtRu/cm^2
- Baseline conducted at 30oC and ambient pressure for comparison
- Gases were externally humidified and membrane wicking humidification system employed
- 0.3V hold , 200 ppb CO and 500 ppb CO exposure shows clear response (current decay)
- No natural recovery observed

Membrane/GDL Wicking : Clear Response at SAE Level

Accomplishments



Improved Baseline

- Dry gases along with the membrane and GDL wicking humidification system
- Gas Diffusion Media changed to a less hydrophobic material
- Initial baseline before CO exposure **more stable** than previous 'Baseline'
- Response to 200 and 500 ppb CO similar to 'Baseline;
- No natural recovery observed

NNSA
National Nuclear Security Administration

Patent Application Filed for Analyzer Prototype in FY17

Accomplishments

- An application for US patent was filed November 2016 for a prototype fuel quality analyzer that uses a novel membrane humidification scheme the permits the use of Nafion® membrane in dry environment. Incorporates latest design improvements to double sample gas flow rate while maintaining membrane and electrode HFR.

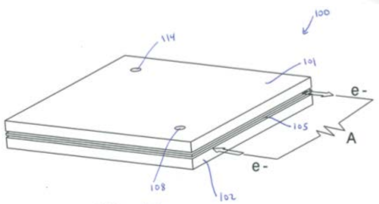


FIG. 1A

- Docket No. 127686/LANS(S133399), "Hydrogen Fuel Quality Analyzer with Self-Humidifying Electrochemical Cell and Methods of Testing Fuel Quality"
- Experimental data provided showing detection of 200ppb CO in dry H_2 with equivalent performance to conditions of external humidification of test gases.

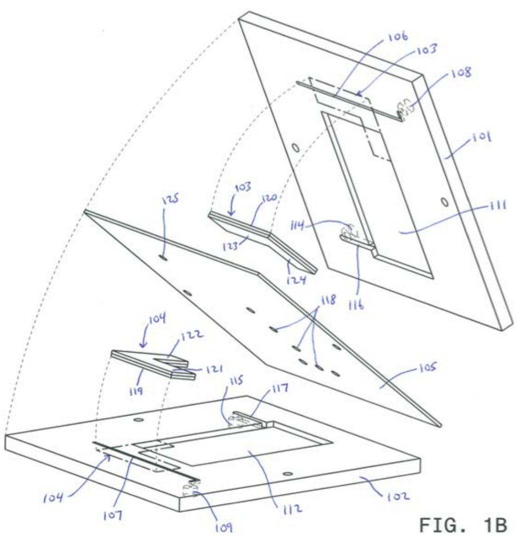
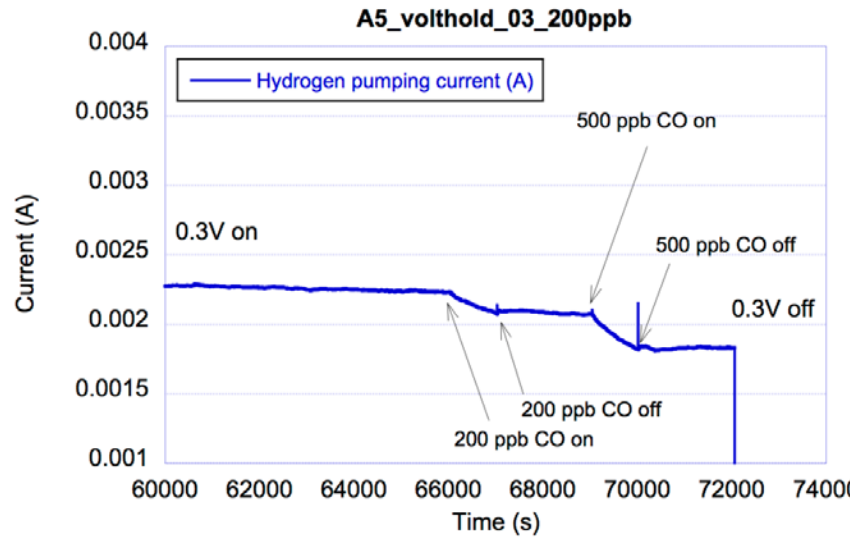
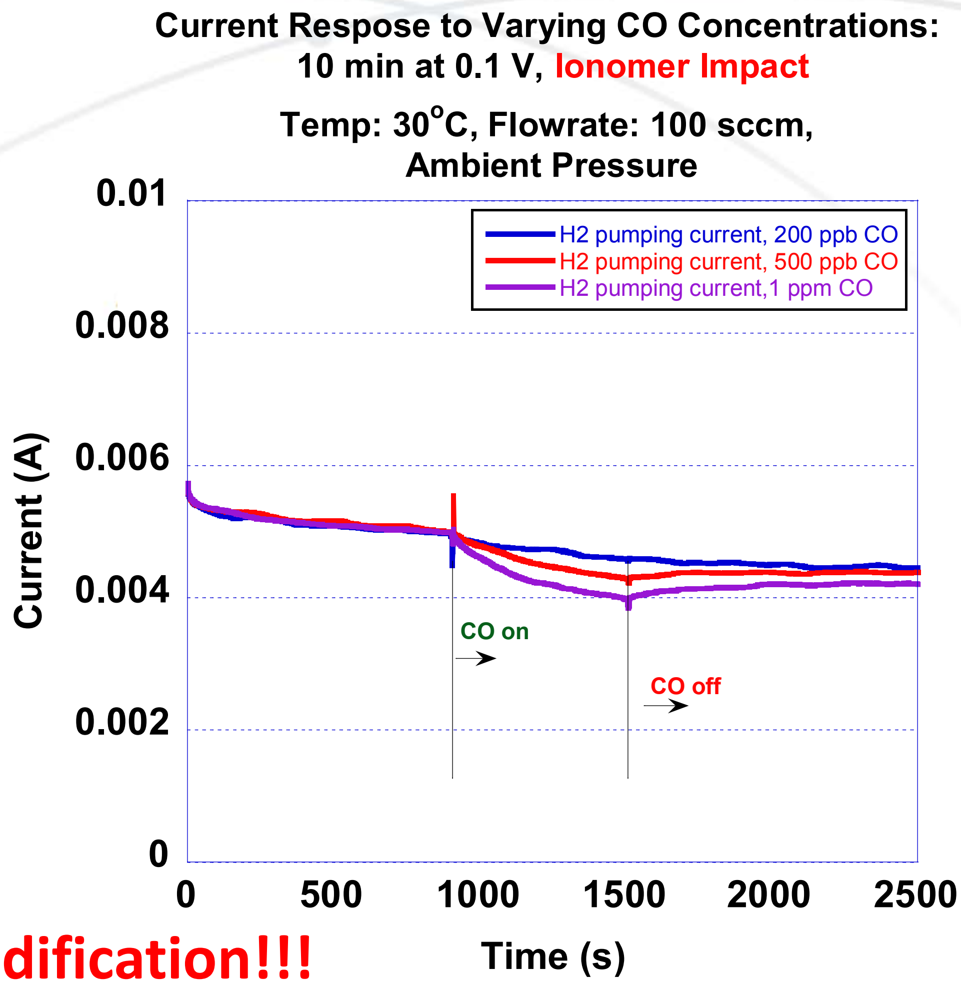


FIG. 1B



Impact of Ionomer

Accomplishments



Improved humidification!!!

Electrode resistance high without ionomer; any water alters electrode resistance significantly

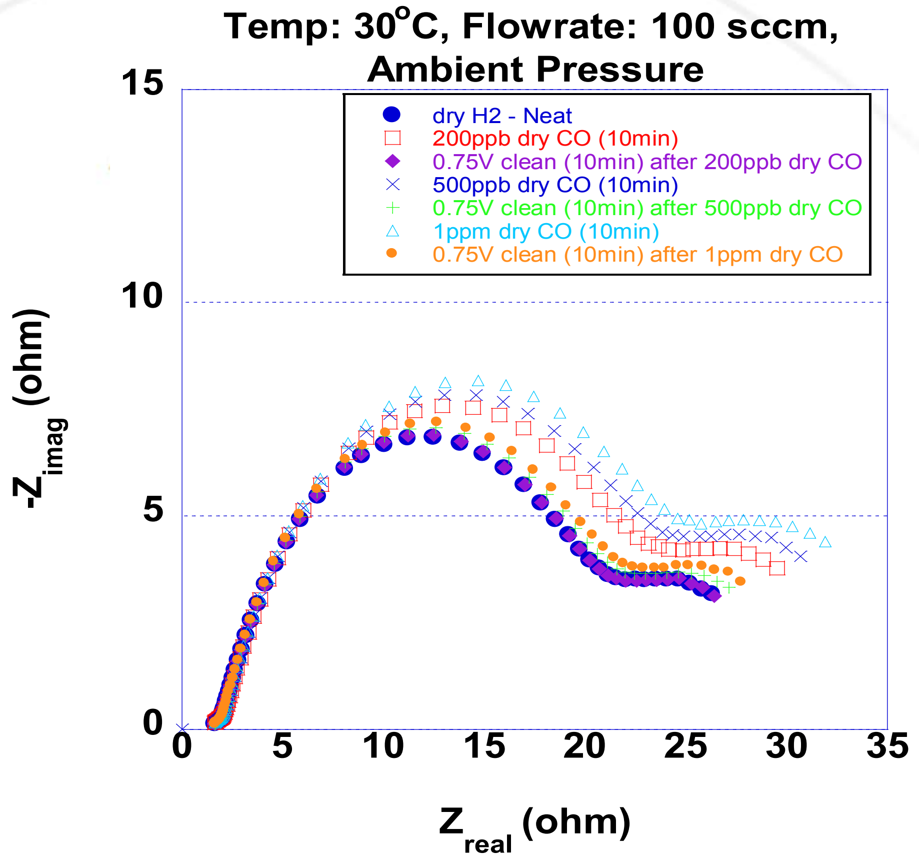
Ionomer was added to the working electrode to help stabilize electrode water content

Current decay rate and extent increases with CO concentration

Investigating Clean-Up Strategy

Accomplishments

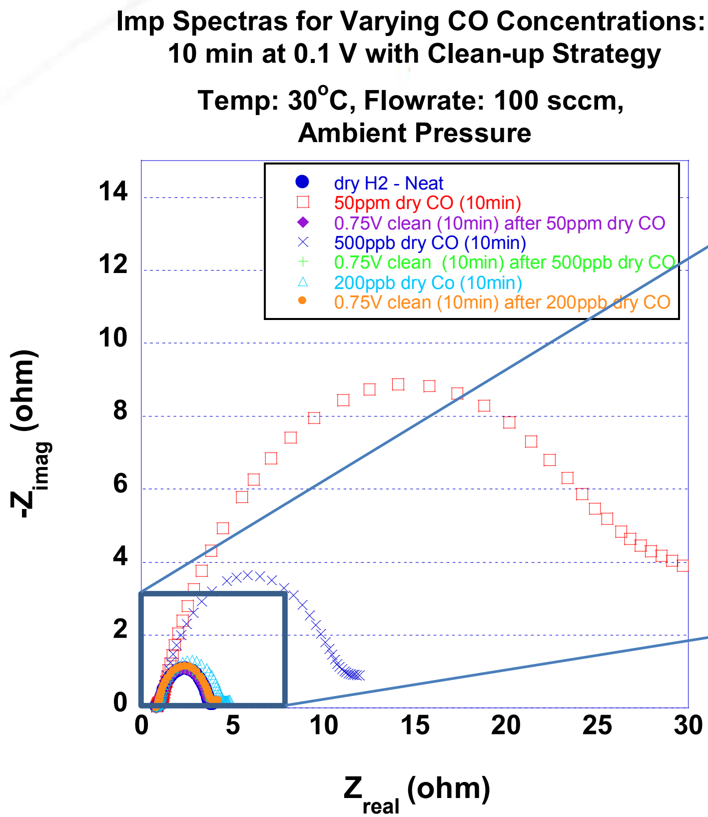
Imp Spectras for Varying CO Concentrations:
10 min at 0.1 V, Ionomer Impact

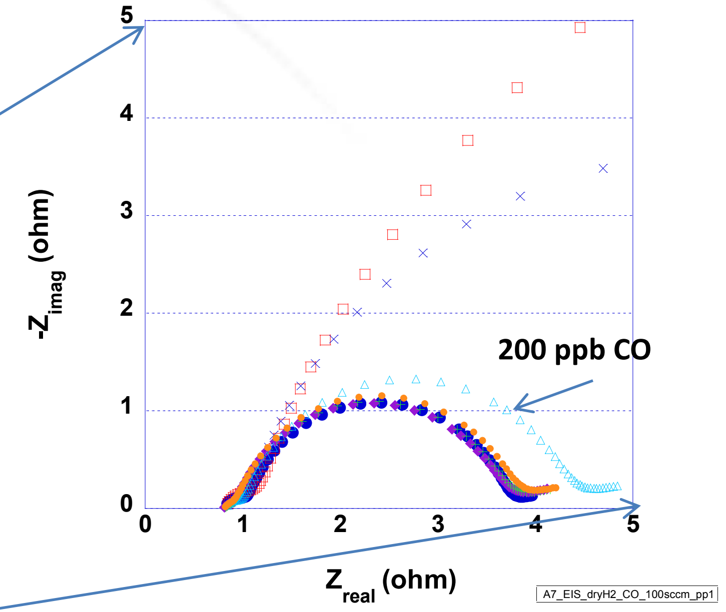


- Applied 0.75V as a ‘Clean-Up’ Method
- Analyzer reset after 200 ppb CO
- **Recovery not complete at higher concentrations**

Changed the Ionomer to Catalyst Ratio/Investigating Clean-Up Strategy

Accomplishments





- Reduce Ionomer by a factor of 10
- Similar responses to CO observed

- Responses still observed to 200 ppb CO
- 0.75 V applied after CO exposures
- **Clean-up shown at 5 times SAE level!!!**

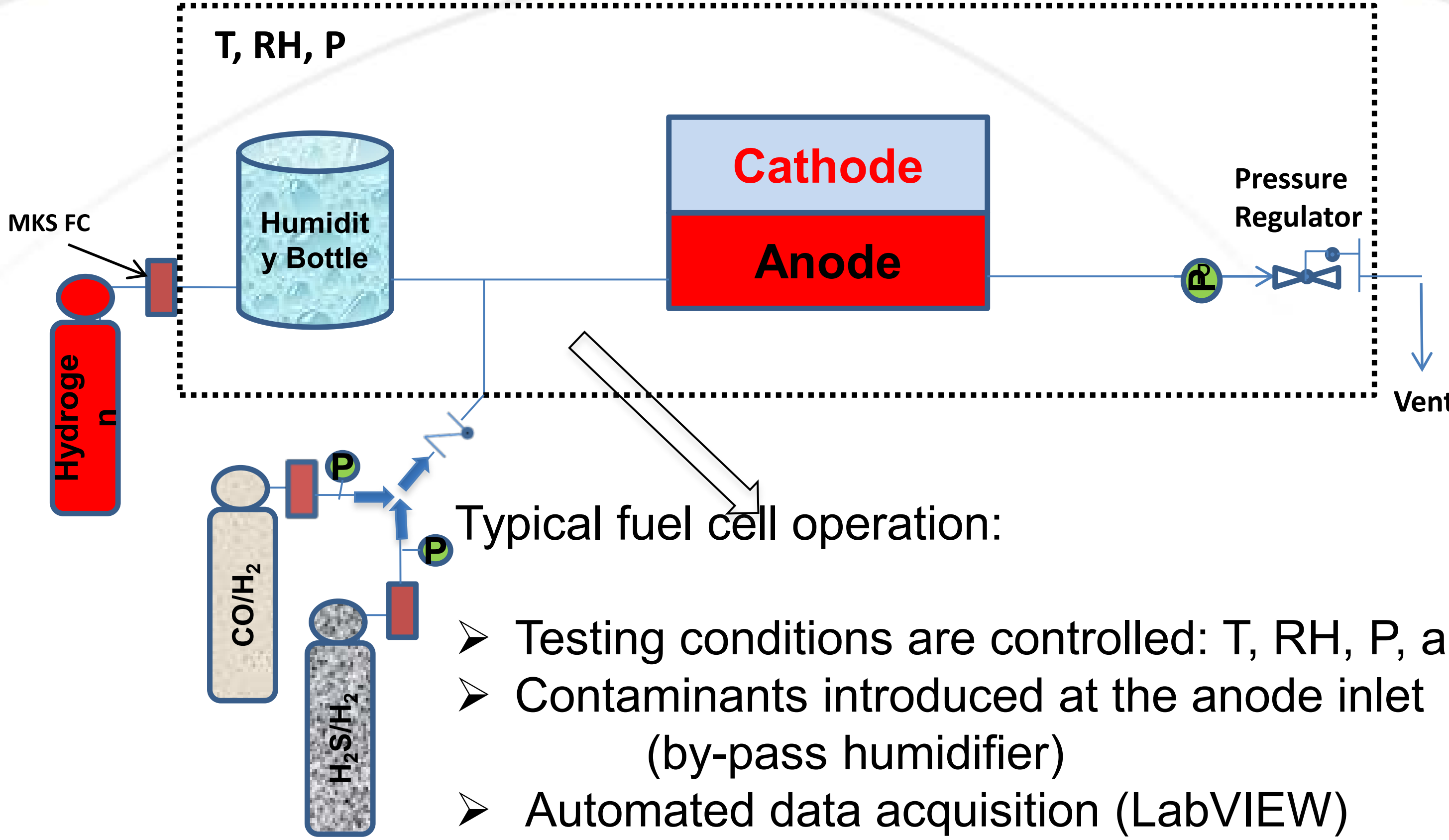
Hydrogen Fuel Quality: Background

- Current fuel specifications: ISO 14687-2 and SAE J2719 allow 200ppb CO, 4ppb H_2S, others
- Previous FC studies were instrumental in their development; higher loaded Pt electrodes (≥ 0.4 mg_{Pt}/cm^2) were used, tests were conducted in single-pass at constant current densities
- U.S. DOE 2020 target loading calls for 0.125 mg_{Pt}/cm^2 which results in an anode loading approaching 0.025 mg_{Pt}/cm^2
- **Focus: Low loaded electrodes tested in both single pass mode and fuel re-circulation mode at impurity levels in the fuel specification**

Motivation

- Provide useful data to OEMs/ Modelers and FC Community; particularly modelers for predicting the impact under broader operating conditions
- Understand the impact of impurities with more realistic test conditions
- The question remains: Do the standards need revision? If so, ***Relaxed or Tightened***

Fuel Re-Circulation System: Single-Pass Mode



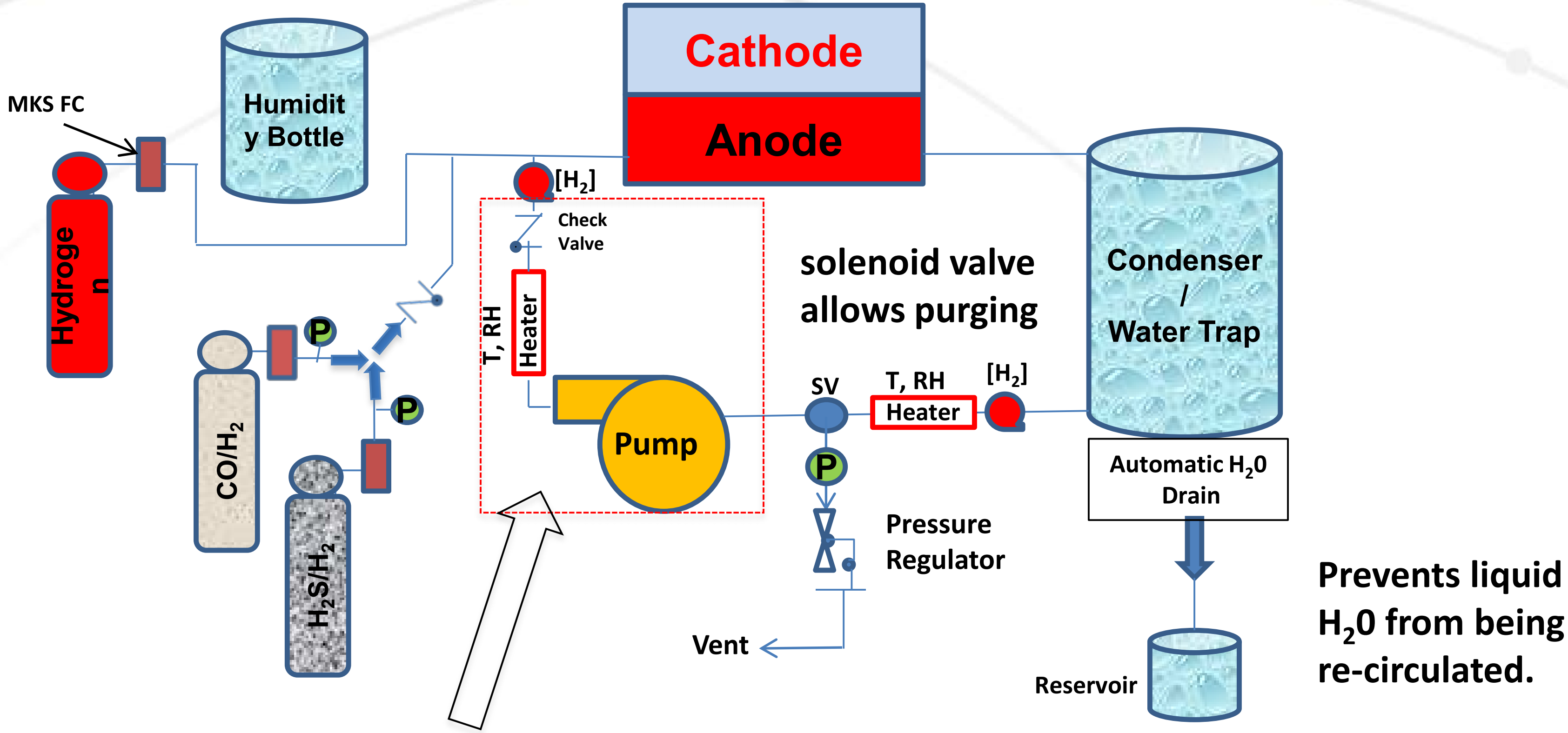
Typical fuel cell operation:

- Testing conditions are controlled: T, RH, P, and gas flows
- Contaminants introduced at the anode inlet (by-pass humidifier)
- Automated data acquisition (LabVIEW)

MEA: 25 cm2, A/C: 0.05/0.10 mg Pt/cm^2
NR211

Fuel stream exhaust gets released to atmosphere.

Fuel Re-Circulation System for Fuel Quality Testing



- Hydrogen fuel enters the anode feed dry and gets humidified via in-situ cross-over cathode water
- It is **critical** to remove liquid water from the system! H_20 is condensed and released automatically
- The return fuel is monitored: H_2 concentration, relative humidity, and temperature
- Purging can be activated via: [H2] %, cell voltage limits, or timed duty cycles
- The pump speed is controlled along with the return gas relative humidity via the local temperature

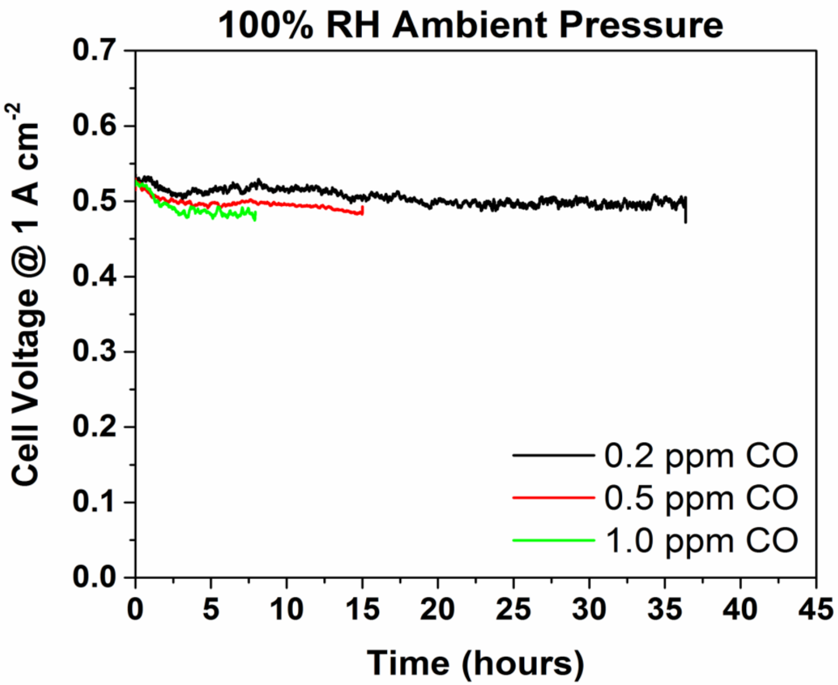
Approach: Parametric Study of CO Tolerance

T: 80 °C		Tolerance of [CO] in PEM Fuel Cells								completed
Pressure (kPa)		80	150	275	80	150	275	80	150	275
[CO] (ppm)		1	1	1	0.5	0.5	0.5	0.2	0.2	0.2
RH (%)	32	0	0		0	0		0	0	
	50	51 mV	42 mV		25 mV	9 mV		2 mV	0	
	100	51 mV	51 mV		29 mV	10 mV		13 mV	0	

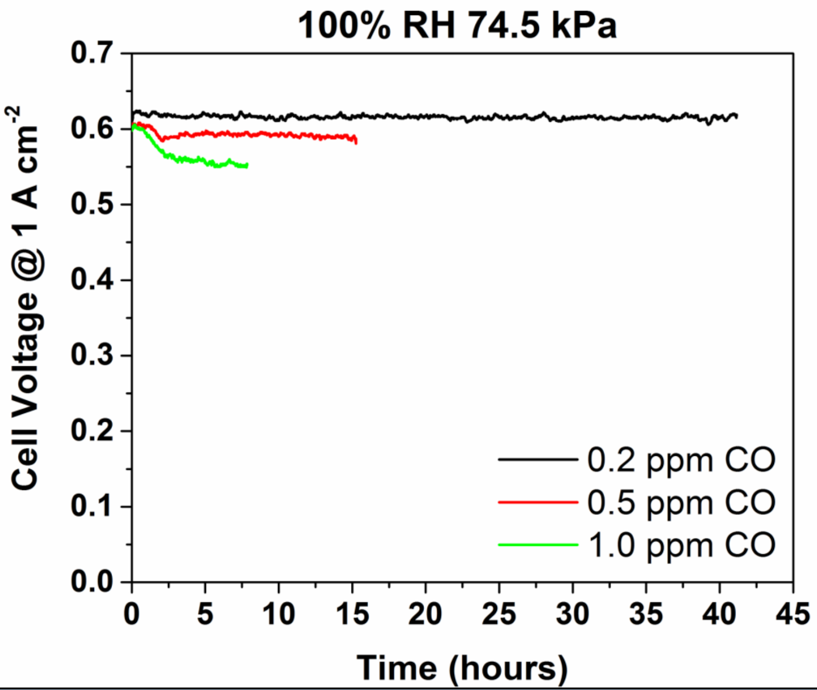
- Is there a need to revise standards?
  - Evaluate tolerance on MEAs with low anode loadings ($0.05 mg_{pt}/cm^2$)
  - Compare re-circulation vs single pass
  - Effect of RH and pressure and concentration
- Presented two talks at ECS (10/2016)
- Create database to provide to modelers

CO Effects: Constant Dosage (Higher loading)

Accomplishments



The anode was exposed to 1.0 ppm, 0.5 ppm and 0.2 ppm CO for 7, 14, and 35h

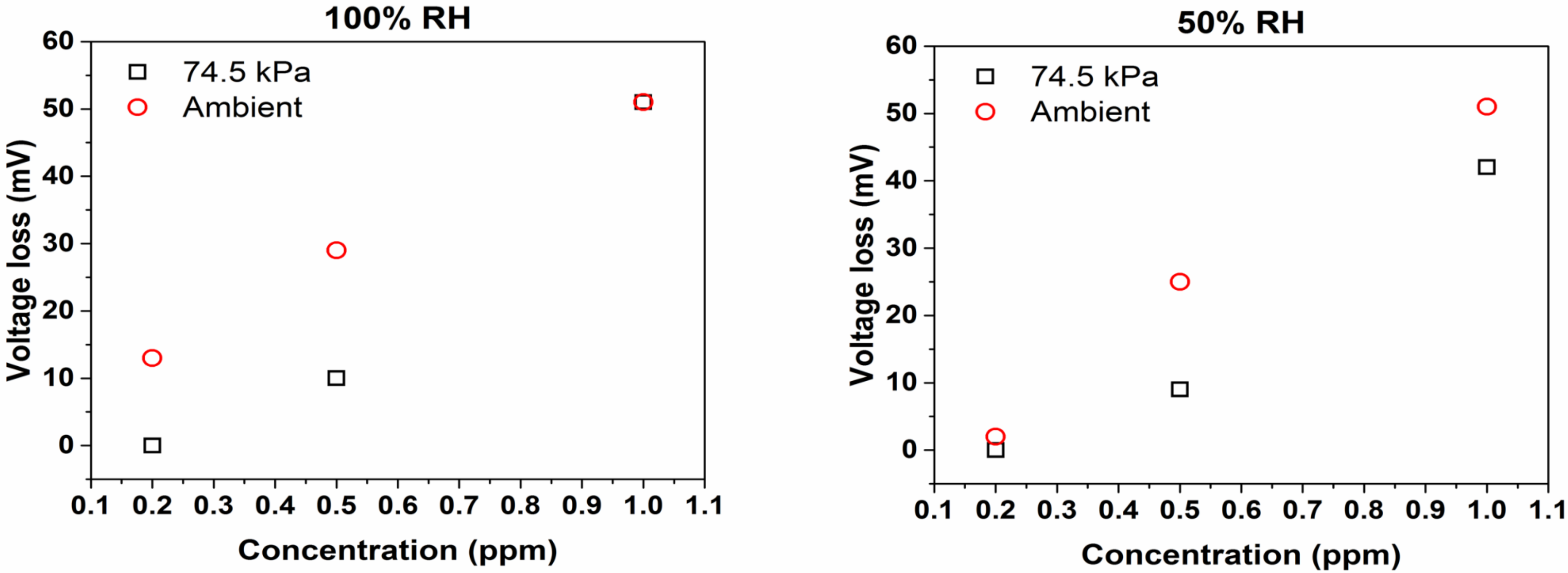


Anode: 0.2 mg cm^{-2} Pt/C, 209 sccm H_2,
Cathode: 0.2 mg cm^{-2} Pt/C, 833 sccm Air,
Membrane: Nafion® 211; **Cell**: 80ºC @ 1A/cm^2

- Cell voltage was recorded while cell operated at 1 A/cm^2 under ambient and 74.5 kPa (10.8 Psig) back pressure.
- XRF Loading showed higher Pt loadings than DOE target

CO Effects: Constant Dosage/RH Impacts

Accomplishments

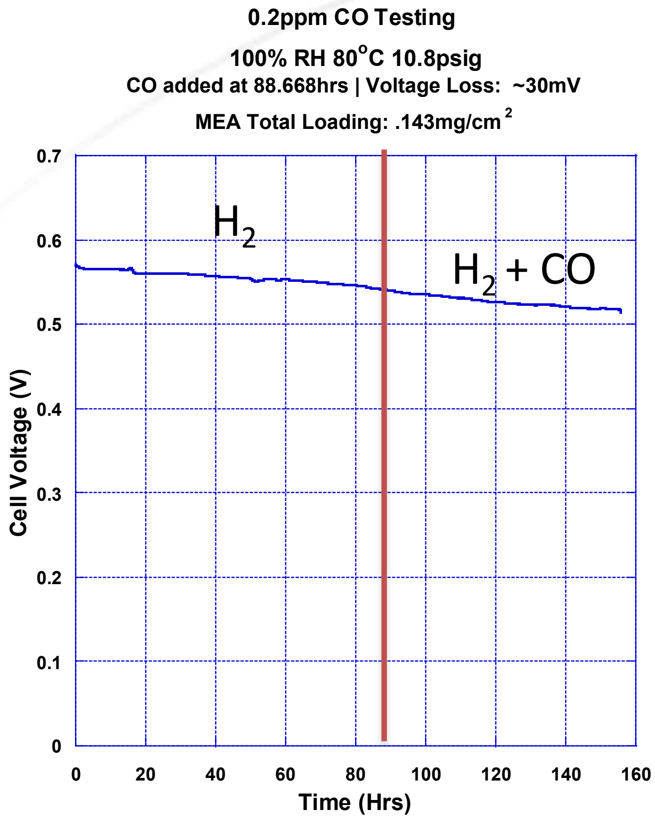


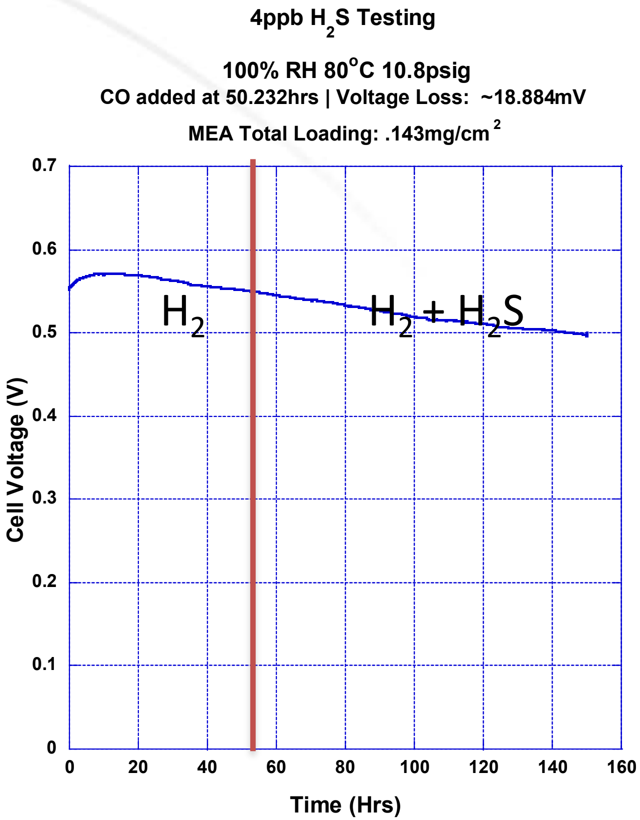
Voltage loss versus CO concentration was plotted for both pressures 74.5 kPa tolerated 0.2 ppm CO (35hrs) and Ambient pressure showed a 13mV decay @ 100% RH **(Left graph)**

Constant dosage expt's were repeated at 50% RH both pressures were able to tolerate 0.2 ppm CO within the accuracy of the load box **(Right)**

CO, H_2S Effects (Lower loading)

Accomplishments



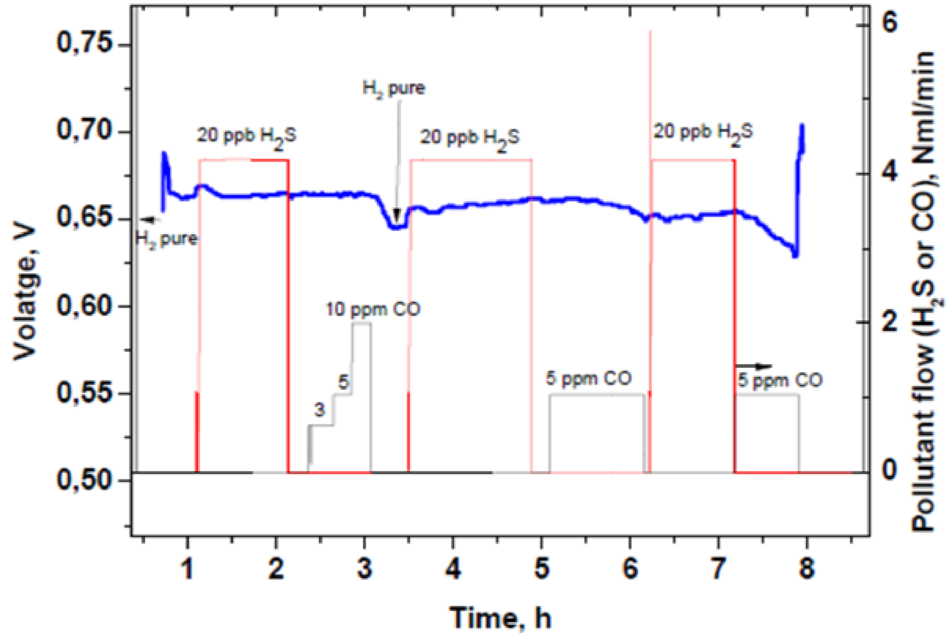


- Voltage drops 13mV after 35 hrs of exposure to CO, whereas the higher Pt loading MEA was tolerant. 30mV losses observed after 100 hrs of exposure. (**left graph)**
- Natural voltage decay observed during H_2S poisoning: Losses computed by the difference in decay rates before and during exposure **(right graph)**

Pre-Dosing Experiments

- What happens if there is an unlikely event that releases S?
- Our international collaborator, CEA (France), is also engaged
- in these studies. (HyCoRA)
- 25cm[2], Low Loading MEAs
- Data collected at CEA facility
- with LANL hardware and components

LANL/CEA Single-Pass Results



Subsequent exposures to CO and H_2S shows both regions are impacted

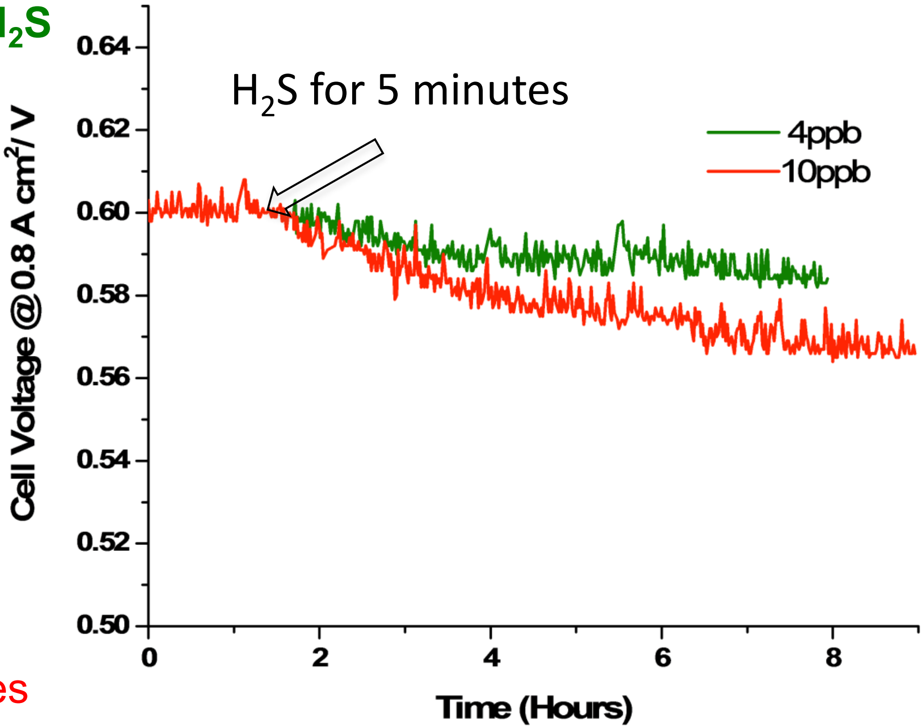
H_2S regions are decreasing with successive exposures

CO impacts become more severe as S coverage increases

Pre-Dosing Experiments:200ppb CO in Hydrogen

Accomplishments

- **In re-circ mode, we introduce 4ppb H_2S for 5 minutes**
- No voltage loss during S exposure
- 200ppb CO is introduced for 7h
- Voltage losses with CO ~10mV
- **Similar scenario except with 10 ppb H_2S pre-dose**
- Losses are enhanced as concentration of pre-dose gas increases. 2X the losses
- A system upset containing sulfur can be detrimental to cell performance. At the SAE/ISO levels the CO impacts become more severe.



1.2 ppm H_2S for 1 second should have the same effect (dosage controlled)

Summary

- Fuel Quality Analyzer:
  - FY17 Improvements
    - One order of magnitude improvement in baseline
    - Dramatic improvement in CO sensitivity (sensitive to < 50 ppb)
    - Operation under dry H_2 for > 1 month
  - Successful prototype developed **(Patent applied for)**
- Hydrogen Fuel Quality:
  - Determined that low loaded MEAs are not tolerant to SAE J2719 level of impurities
  - Parametric study of impurities underway to quantify CO and H_2S tolerance levels of low loaded MEAs
  - Testing under dynamic conditions including impurity mitigation strategies will ultimately determine the future of fuel quality standards (relax or tighten?).

Future Plans

Analyzer

- Repeat results
- CO dosage experiments: Can we quantify contaminants?
- Add inline gas filters to clean H_2
- Employ Research Grade H_2 (99.9999%)
- Investigating Field Deployable Electronics
- Test other impurities: H_2S, NH_3
- Test new flow-field configuration for improved sensitivity and response time
- Demonstrate analyzer in the field after independent evaluation

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Fuel Quality

- Modify the Re-Circulation System to include Gas Chromatography for mass balance experiments
- Incorporate Start-Stop capabilities to mimic vehicle behavior and investigate it as a recovery strategy
- Test with the entire fuel cell specification (minus particulates) and apply start-stop protocol
- Test using an accepted Drive Cycle

Acknowledgements

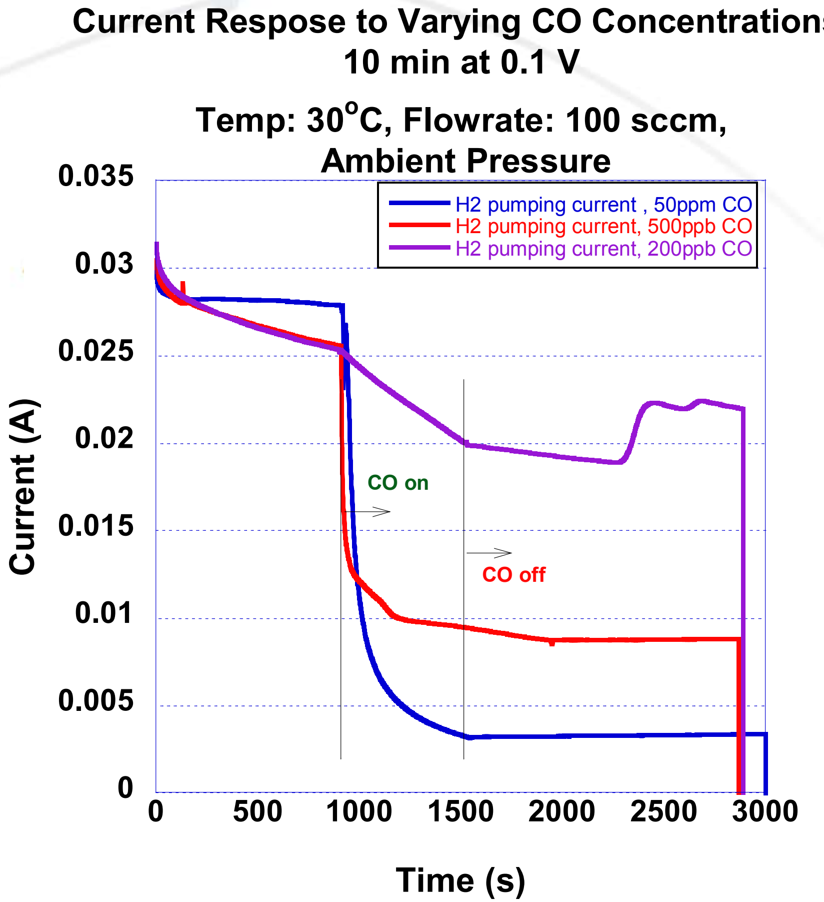
- DOE- Will James, SCS Manager
- Jari Ihonen, VTT
- Jay Keller
- CEA (Grenoble, France)
- SAE

- And you the Audience!!!!!

Additional Slides

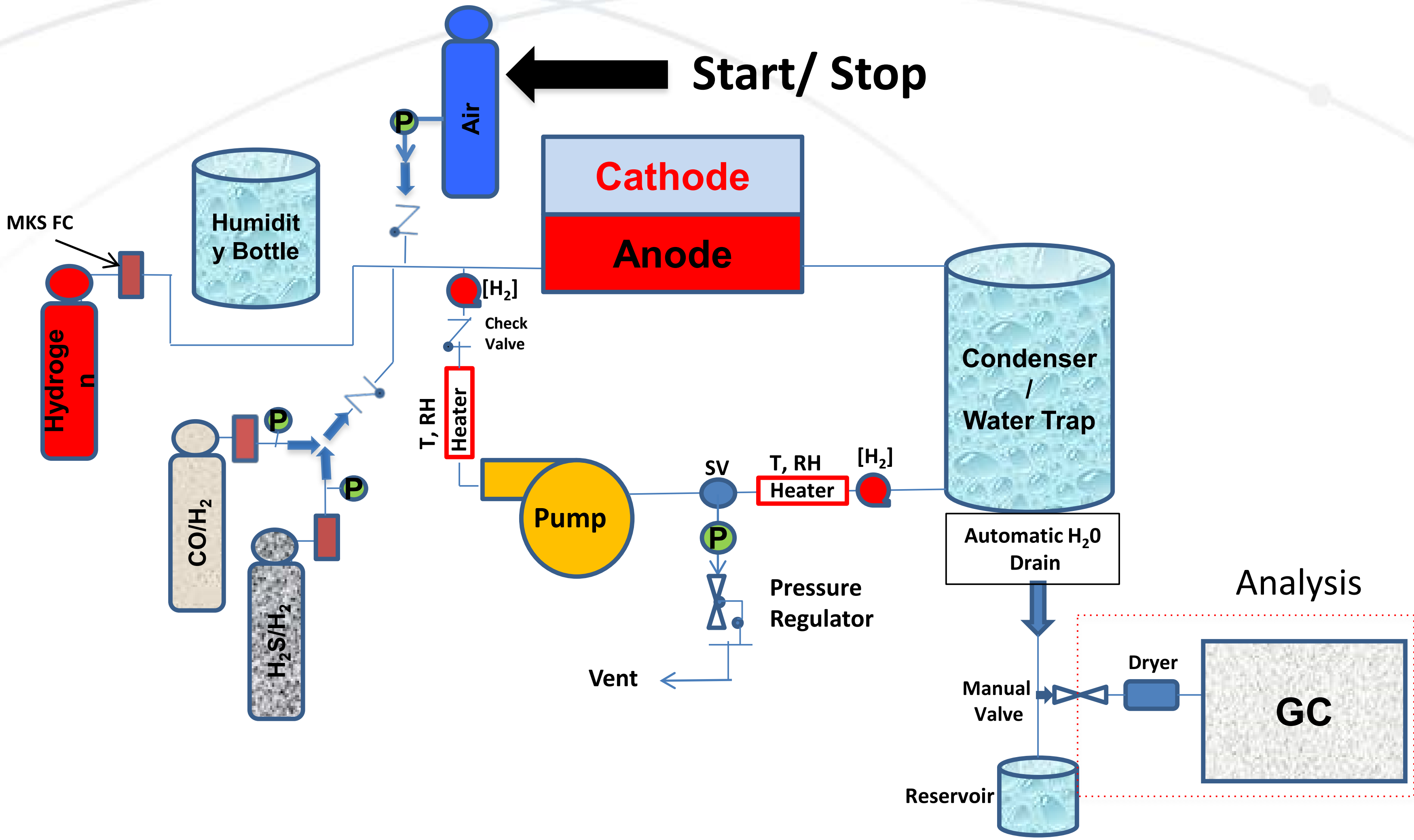
Optimizing the Ionomer to Catalyst Ratio

Accomplishments



- Reduce Ionomer by a factor of 10
- **Response is almost instant!!!**
- Activation step are being explored

Fuel Re-Circulation System: Future Work



Incorporate Drive cycles and Start/Stop protocols.

Reviewers Comments

"Project strengths are the project's strong knowledge, experimental base, and international partnership."

Continuing and strengthening international collaborations and creating extensive data base that will guide future standards.

"Development of an in-line analyzer for hydrogen fuel quality will facilitate deployment of FCEVs and hydrogen refueling dispensers."

Accelerated development of analyzer. Significant progress made in designing and building prototype analyzer. Developed IP.

"Project weaknesses are the lack of time scale for publication of ASTM standards"

Resources diverted from ASTM work to Analyzer work.

"The weakness of the project is the under-appreciation of the noise factors that could change the gas analyzer signal"

Project specifically looking into that. Plans to do field testing after developing electronics