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Title: Measurement of local electrode potentials in an operating PEMFC exposed to contaminants

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Measurement of local electrode potentials in an operating PEMFC exposed to contaminants

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Introduction

Motivation

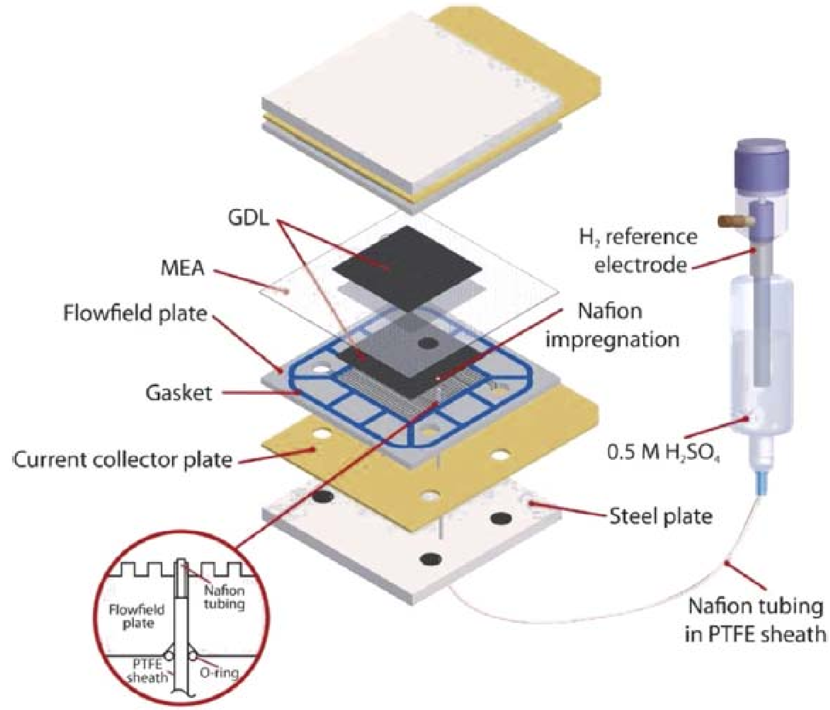
- Fuel cell voltage is routinely measured, but measurement of individual electrode potentials in operating PEMFCs is rarely performed
- The PEMFC anode can function as a pseudo-reference electrode, but this functionality isn't available when dealing with anode contaminants, non-H_2 fuels, or very low anode catalyst loadings
- Various methods of incorporating reference electrodes have been described in the literature, but typically suffer from one or more drawbacks:
    - Lack of cathode vs. anode specificity
    - Disrupted current density distribution
    - Influence of edge effects

This Work

- This presentation describes a new capability at LANL for measurement of electrode potentials in operating PEMFCs using external reference electrodes
- The method of reference electrode incorporation is based on methods developed by Gareth Hinds and coworkers at the National Physical Laboratory (UK)
- Multiple reference electrodes can be used simultaneously, enabling accurate measurement of lateral potential distributions without disturbing cell operation

Methods

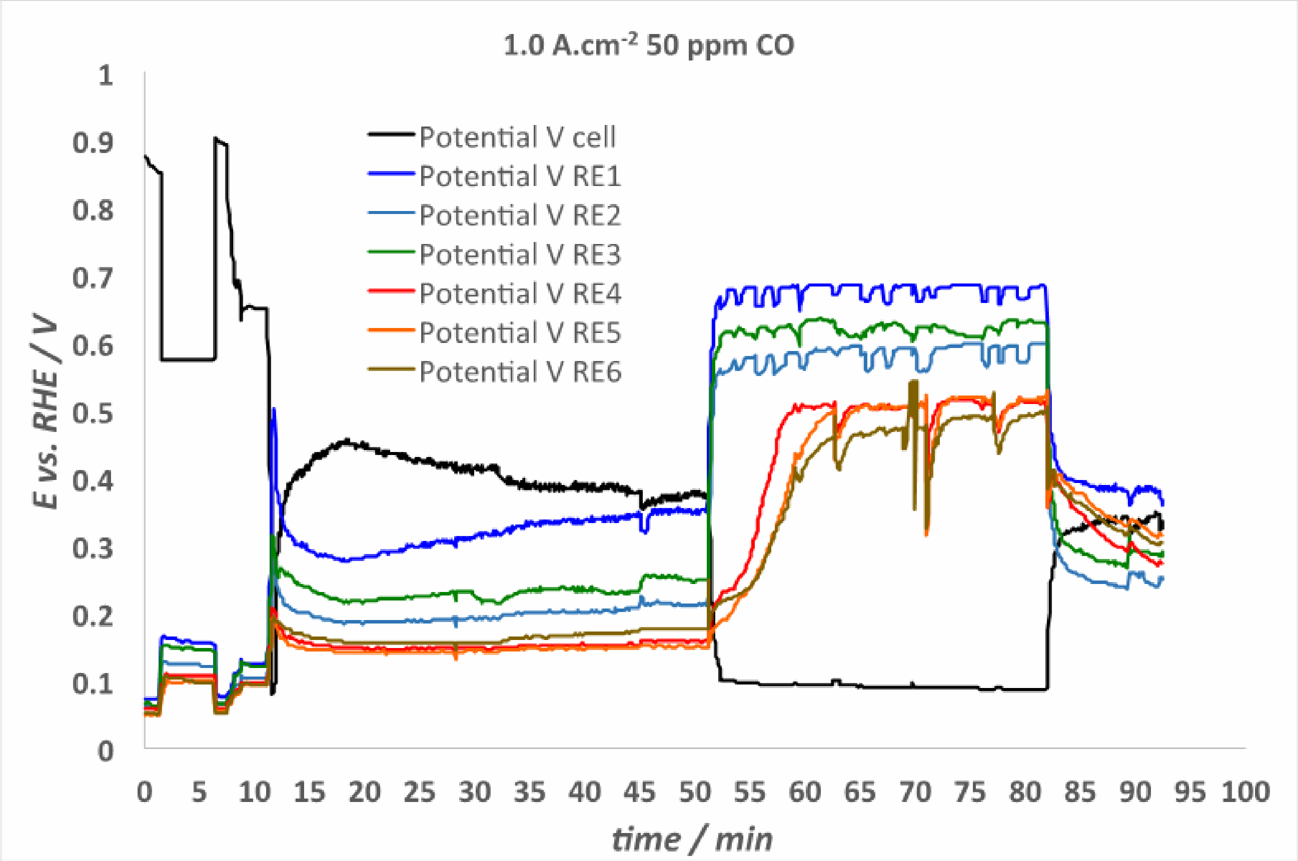
- Reference electrodes are connected to the back side of the MEA (anode or cathode) via a salt bridge, which passes through a hole drilled in the cell hardware
- Reference electrode components are located entirely outside the MEA, so they do not affect cell operation
- Salt bridges are based on Nafion tubes (PermaPure), which are filled with water and enclosed within a PFA sheath
- Ionic conductivity through the GDL is provided by puncturing with a needle and locally impregnating the GDL with Nafion solution
- Proper o-ring sealing of the salt bridge within the hardware enables ionic conductivity to be maintained without allowing gas leakage



E. Brightman, G. Hinds, Journal of Power Sources 267 (2014) 160-170

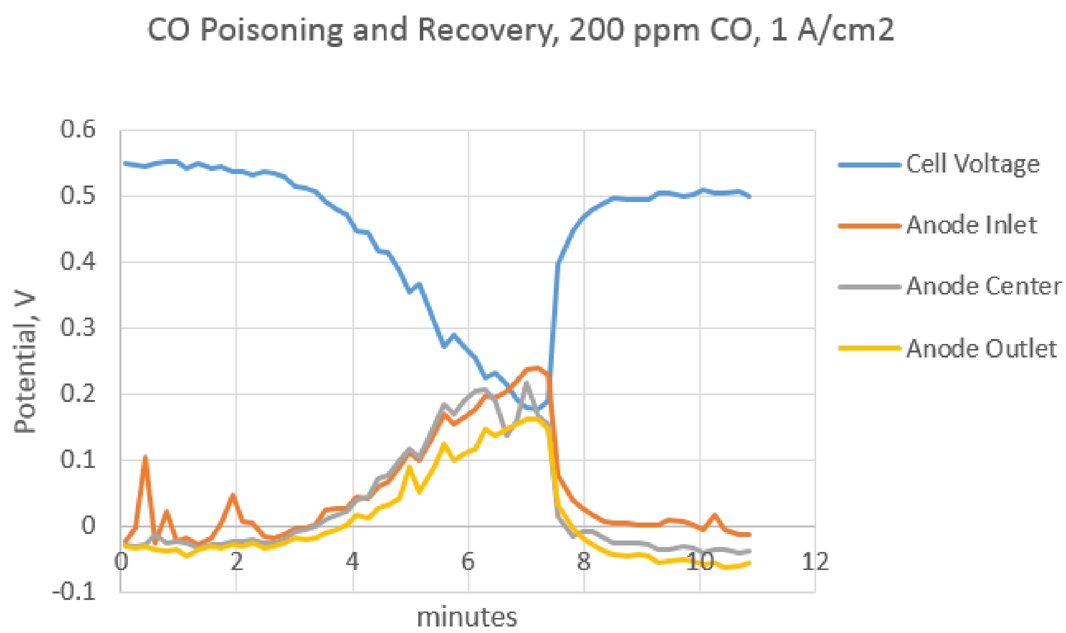
CO Poisoning and Recovery at NPL

- CO poisoning of the HOR on PEMFC anodes was selected as a simple, easy to control system to test and demonstrate reference electrode setup
- Initial work on CO was done in collaboration between LANL and NPL



CO Poisoning and Recovery at LANL

- LANL results show smaller difference between CO poisoning at inlet and outlet
- No difference in recovery between inlet and outlet
- Change in anode potential measured vs. reference electrodes (~0.2 V) is significantly smaller than cell voltage change (~0.35 V) – possibly due to excessive impedance between reference electrode and anode

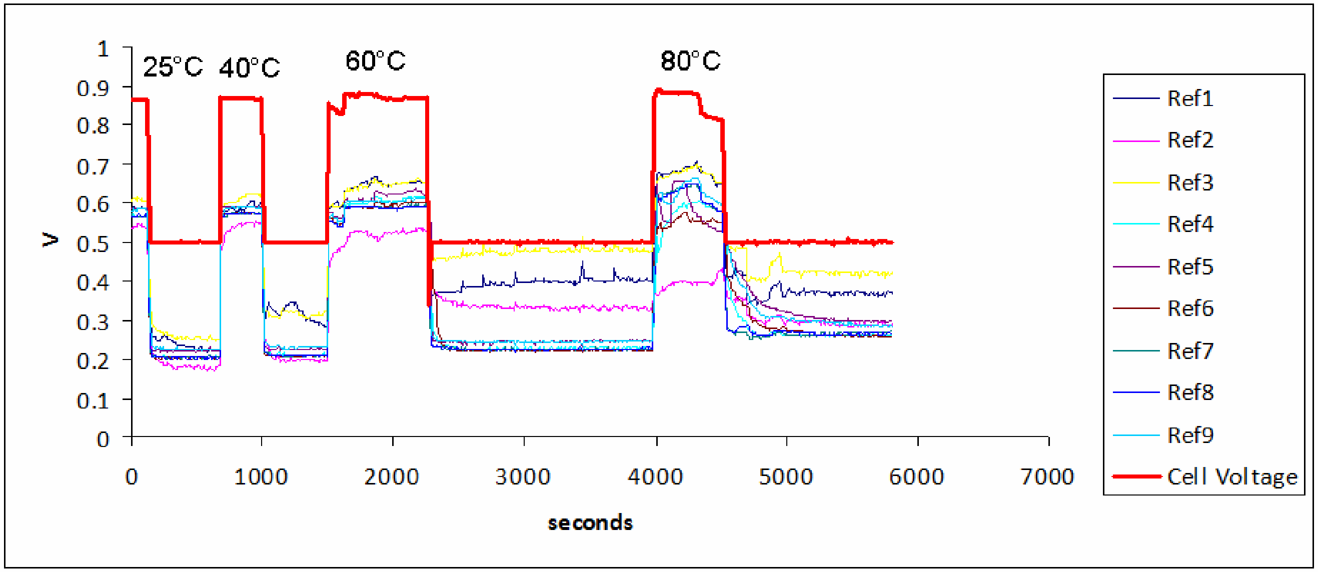


Gore 710, 0.4 mg/cm^2 anode, 0.1 mg/cm^2 cathode
80°C, 150 kPa, 1.2/2.0 stoich

Quantitative Reference Electrodes

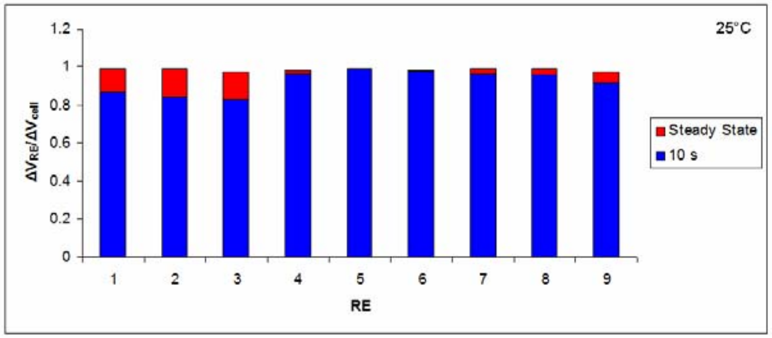
How quantitative are RE measurements?

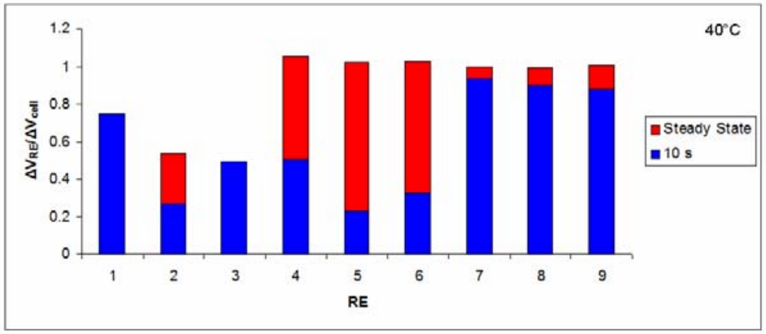
- Tube/GDL interface stabilized with Nafion solution
- High input impedance measurements required
- RE potentials vs. cathode measured during potential stepping

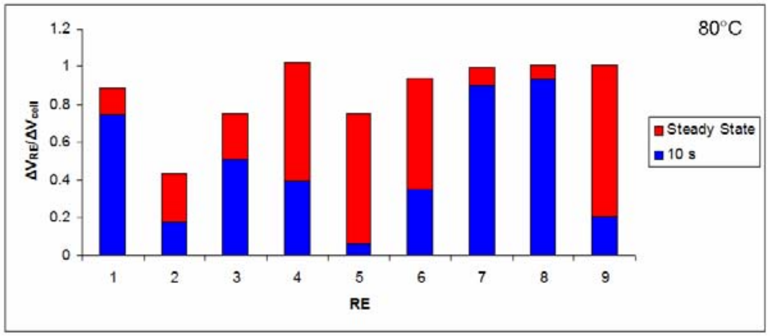


Quantitative Reference Electrodes

- At 25°C, some REs show delayed response, but each RE ΔV quantitatively matches cell ΔV at steady state
- At 40°C all REs are slower to reach steady state, and some are non-quantitative at steady state
- At 80°C, only 4 out of 9 REs were quantitative at steady state, and only 2 responded on a reasonable time scale

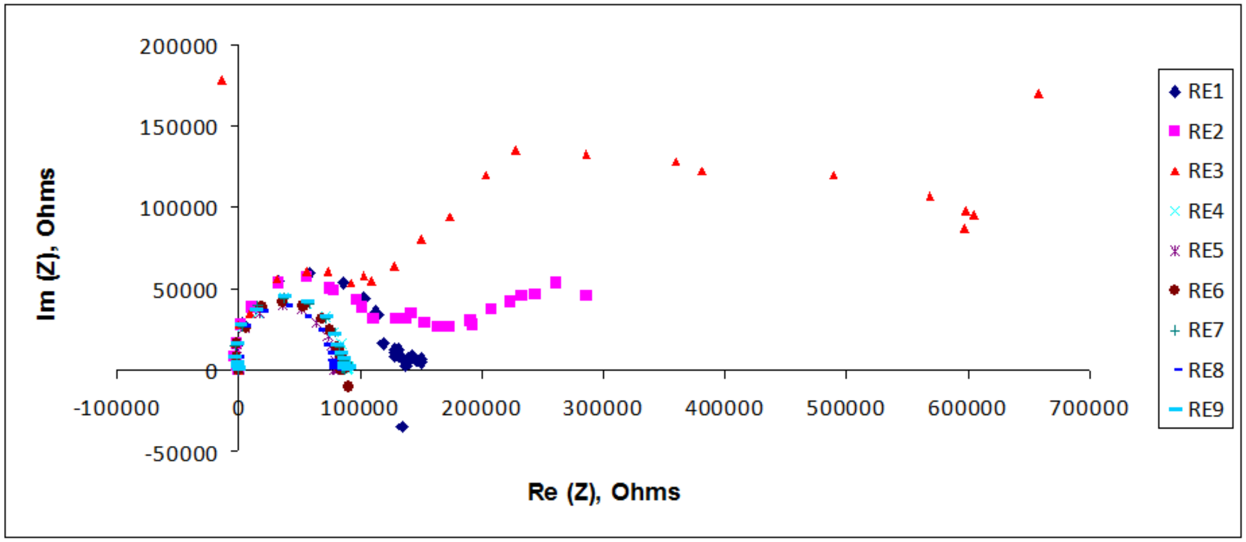






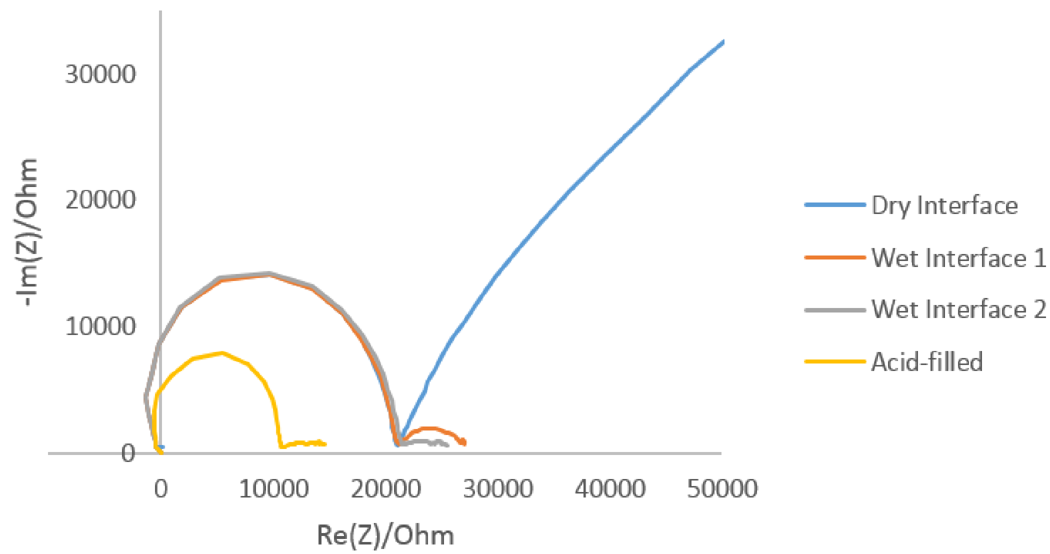
RE Impedance

- Impedance measured between MEA and REs shows Ohmic resistance ~ $10^5\ \Omega$ on "good" REs
- "Bad" REs have higher intercept or do not intercept Re(Z) access at all
- RE response time affected by RC time constant – higher impedance → slower response



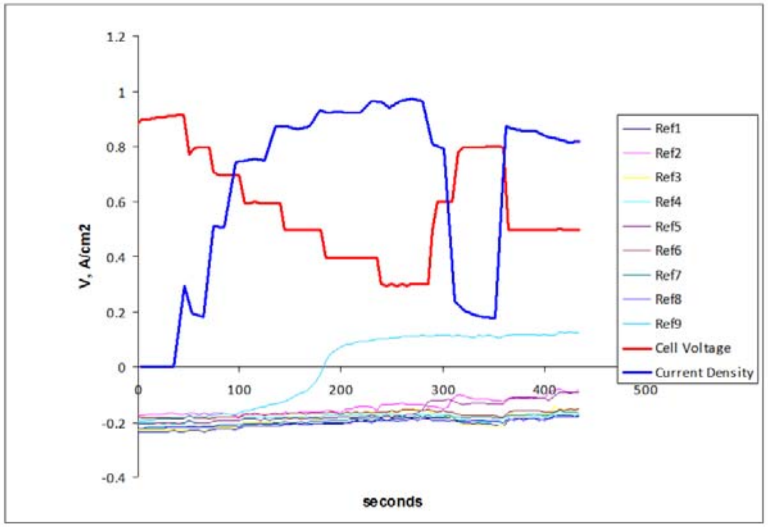
RE Impedance

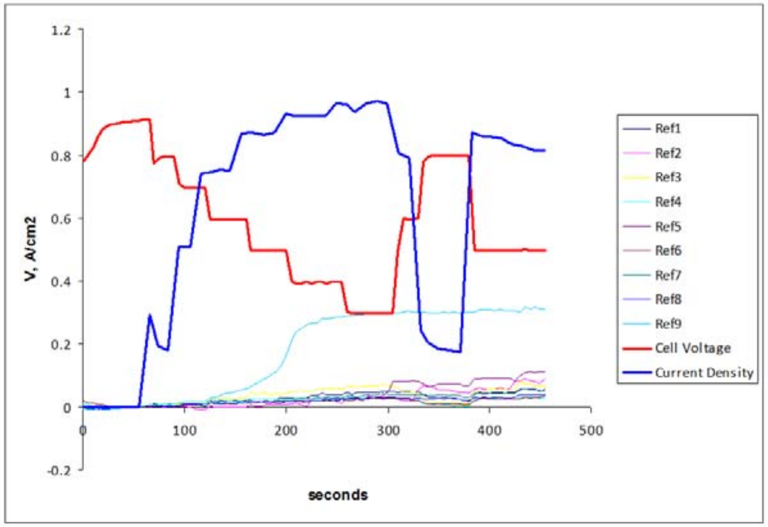
- Impedance can be reduced by using shorter Nafion tube or by filling tube with acid solution
- For good performance, entire pathway between MEA and RE must have low impedance
- Even if high-frequency semicircle is small, RE performance may suffer due to additional impedance loops



RE Anode Measurements

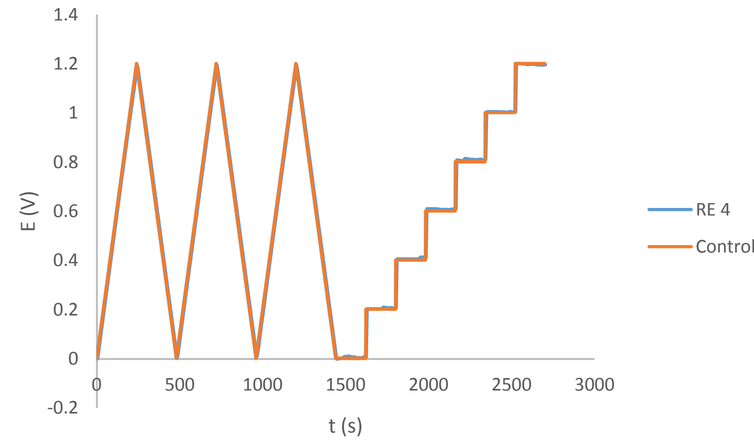
- With REs connected to anode, little change in RE potential observed when changing cell voltage
- Each RE is ~ 0.2 V vs. anode at OCV ($E_{Ag/AgCl}$ = 0.21 V vs. SHE)
- Anode at OCV used as internal calibration for Res
- Some drift observed at longer times

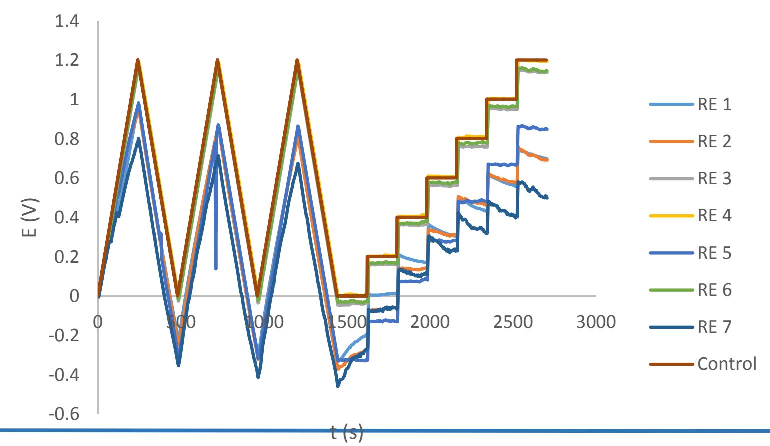




Long-term Stability

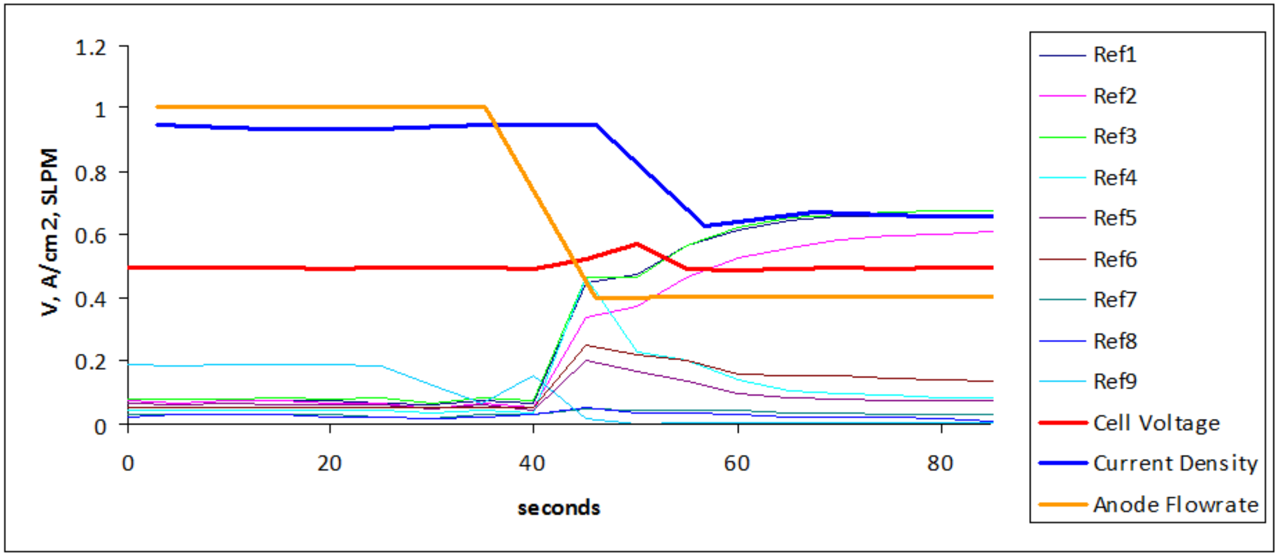
- Stability and quantitative accuracy of REs measured by controlling cell voltage in H_2/N_2, 80°C, 100%RH
- Out of seven REs during 2500 s of potential sweep and step experiments:
  - One tracked control perfectly (always within 10 mV, no drifting)
  - Two tracked control perfectly over short periods, but showed long-term drift (60 mV over 2500 s)
  - Four showed poor tracking and significant drift





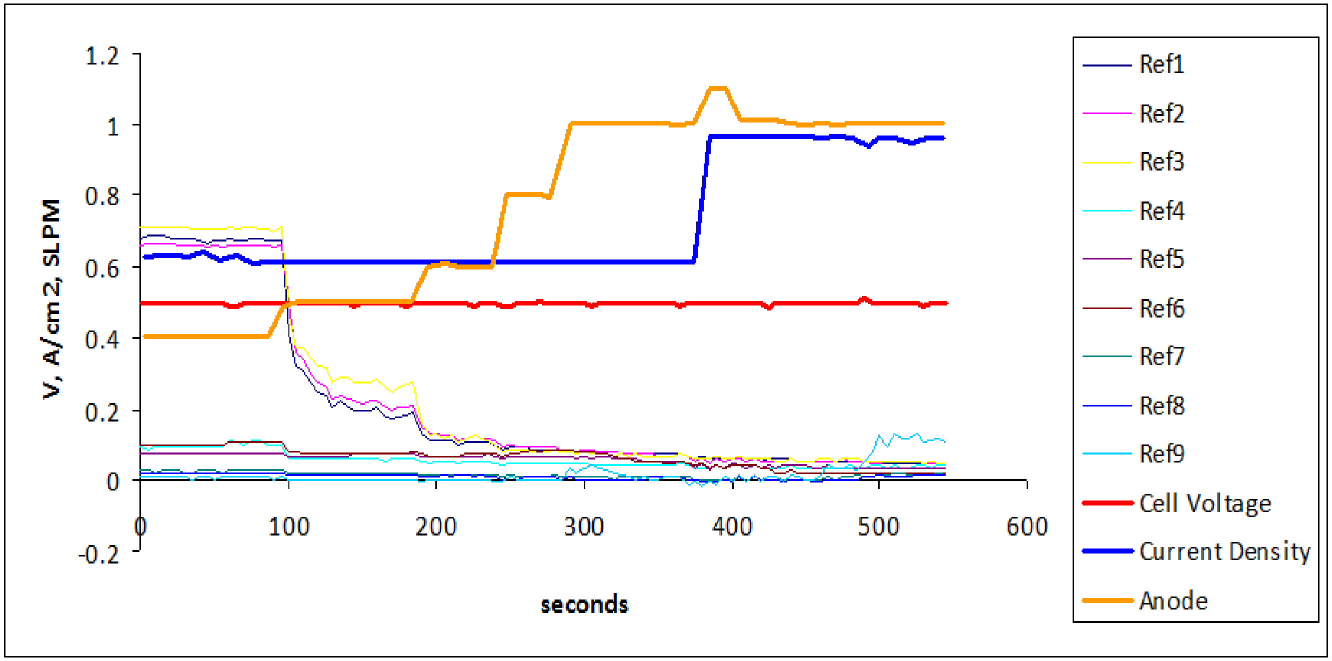
H_2 Starvation

- Decrease of H_2 flowrate to sub-stoichiometric levels has different effects throughout cell
  - strong effect on anode potential near outlet
  - moderate effect on mid-cell region
  - little effect on inlet
- H_2 starvation can cause localized cell reversal

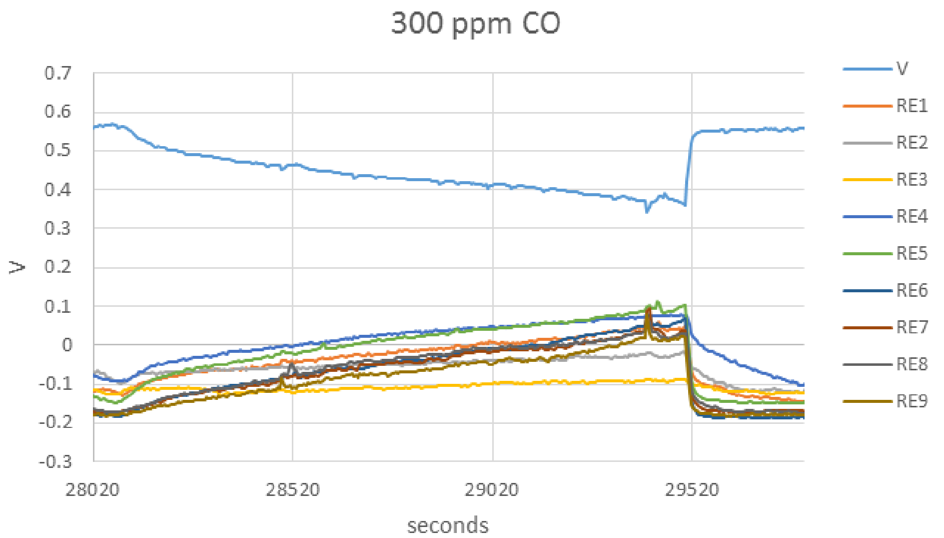


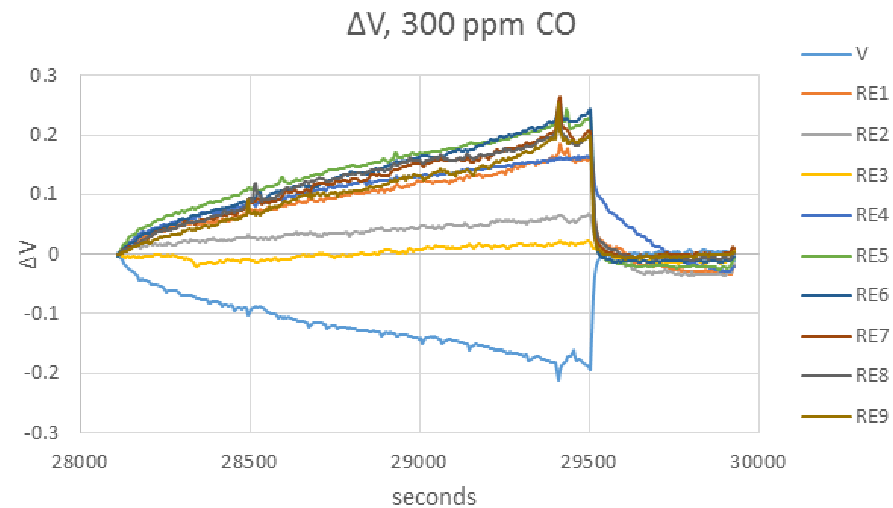
H_2 Starvation

- Increasing flowrate causes local voltage recovery
- Current density doesn't recover as quickly

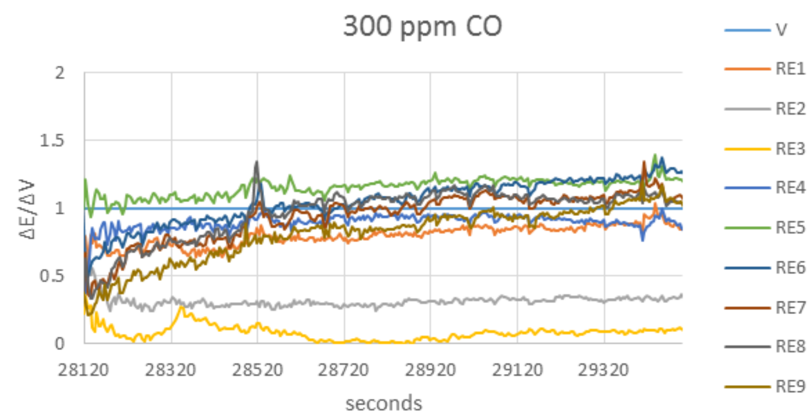


CO poisoning at 300 ppm



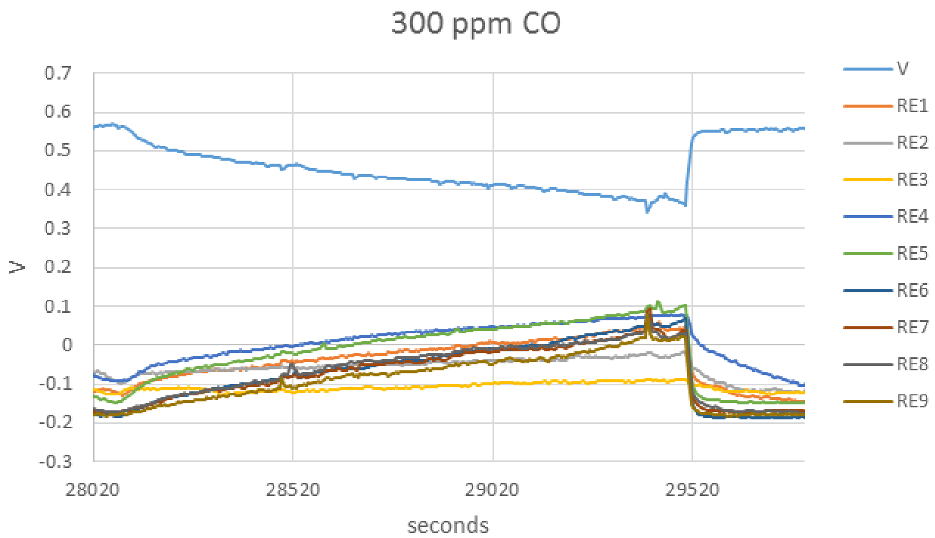


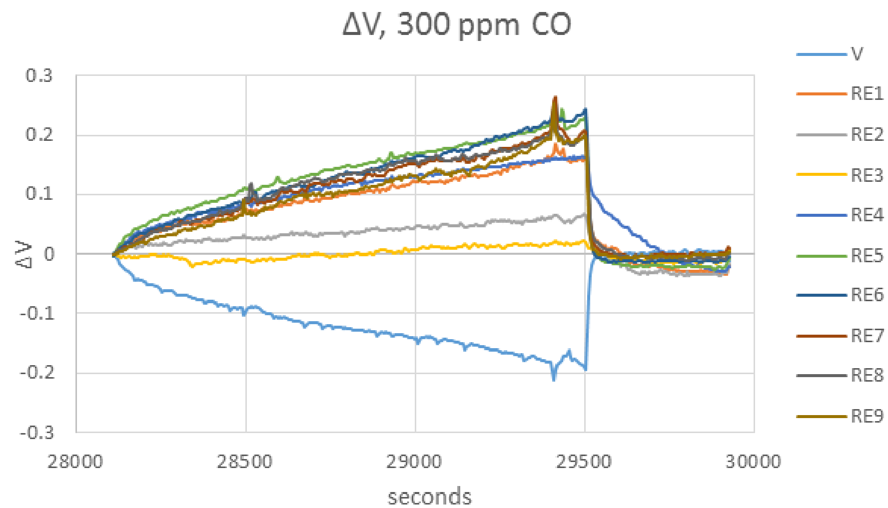
- “Good” reference electrodes respond quantitatively to CO poisoning



Gore 710, 0.15 mg/cm^2 anode, 0.1 mg/cm^2 cathode
40°C, 150 kPa, 600/1500 sccm

CO poisoning at 300 ppm





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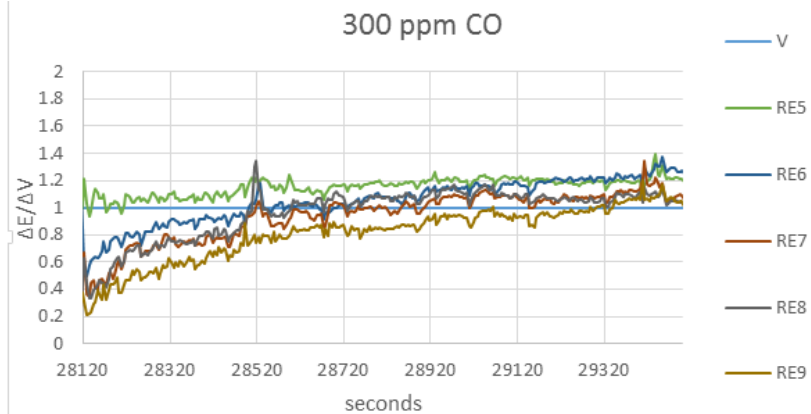


Gore 710, 0.15 mg/cm^2 anode, 0.1 mg/cm^2 cathode
40°C, 150 kPa, 600/1500 sccm

Future Work

- Achieve quantitative accuracy during long-term tests at elevated temperature
- Implement simultaneous reference electrode measurements on cathode and anode
- Study contaminants that poison both cathode and anode
- Transient effects, startup/shutdown, fuel starvation
- Incorporation of reference electrodes into a segmented cell
- Use of reference electrode in AEMFCs

Summary/Conclusions

- Use of reference electrodes to measure individual PEMFC electrode potentials can be achieved without affecting cell behavior by connecting via Nafion salt bridges attached to the back side of the MEA
- CO poisoning of the HOR and H_2 starvation were used to demonstrate reference electrode technique
- Improvements to technique have enabled quantitative measurements, but further improvement needed for consistent measurements at elevated temperature
- Further development of the technique will allow reference electrode measurements in more demanding applications, including measurement of dual anode/cathode contaminants and use in segmented cells

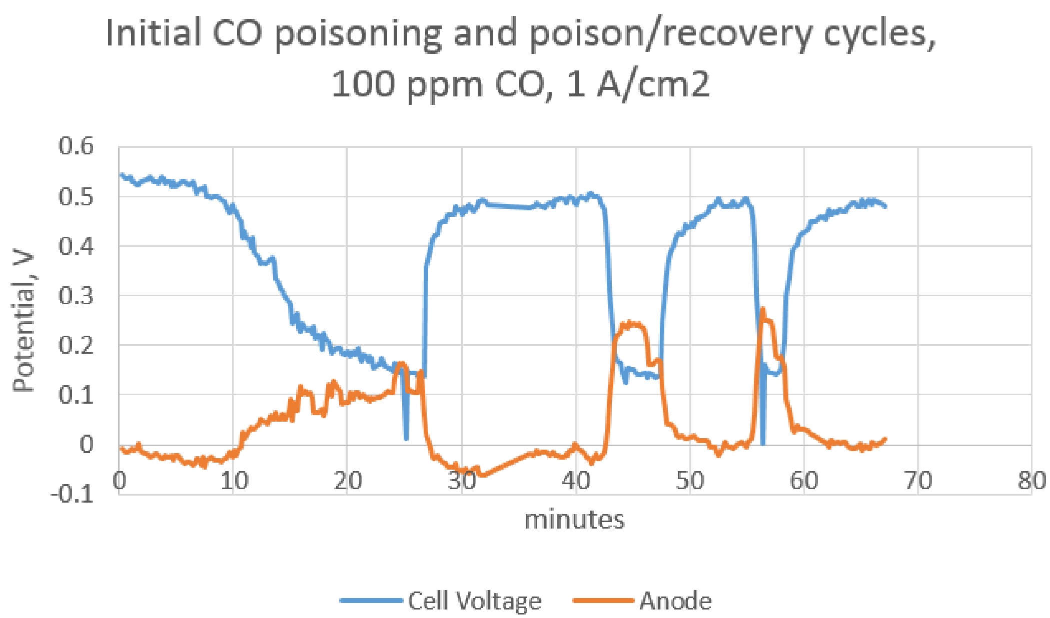
Acknowledgments

- The LANL reference electrode setup is based on a similar setup at NPL. Luis Castanheira and Gareth Hinds of NPL provided assistance and advice on designing and operating the apparatus.
- Funding was provided by the US Department of Energy, Energy Efficiency and Renewable Energy, Fuel Cell Technologies Office, through the FC-PAD consortium.
- Program managers: Dimitrios Papageorgopoulos and Greg Kleen

Extra Slides

Initial Poisoning vs. Re-Poisoning

- Initial CO poisoning is slow – HOR has low overpotential even at significant CO coverage
- Initial recovery is rapid, but 100% recovery is not achieved – still significant CO on surface
- Re-poisoning is rapid – since most of the adsorbed CO was retained on the surface, only a small amount of additional CO is needed to significantly slow HOR kinetics



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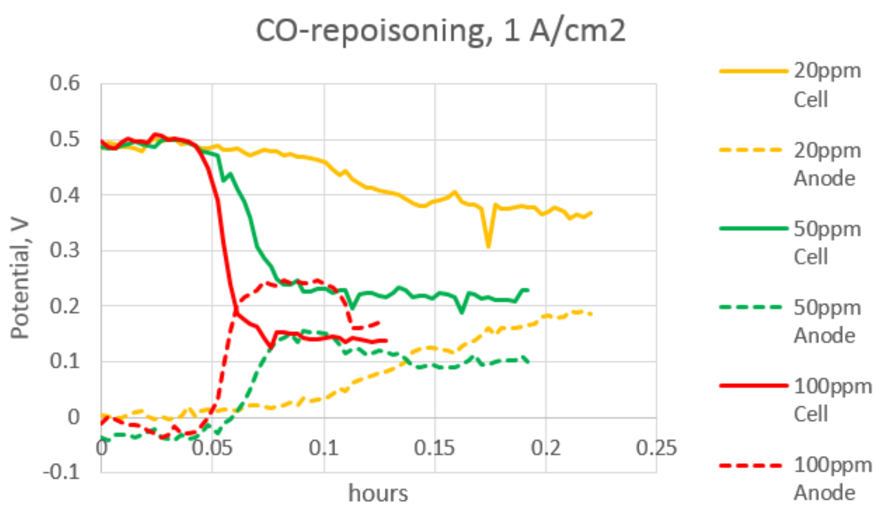
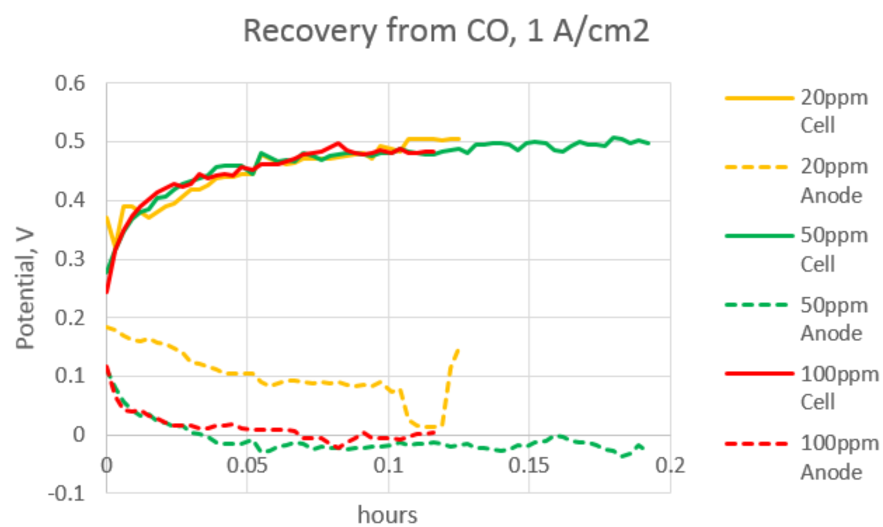
80°C, 150 kPa, 1.2/2.0 stoich

Effect of CO Concentration



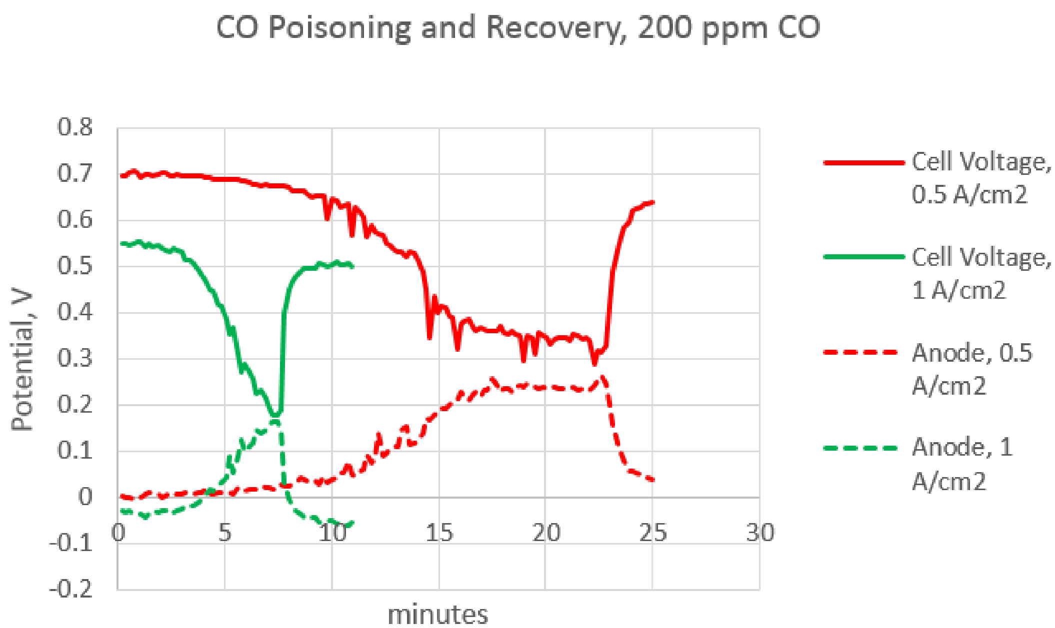


- CO poisoning occurs faster with higher concentrations
- Recovery from CO poisoning is approximately the same regardless of CO concentration used when poisoning

Gore 710, 0.4 mg/cm^2 anode, 0.1 mg/cm^2 cathode
80°C, 150 kPa, 1.2/2.0 stoich

Effect of Current Density on CO Poisoning

- CO poisoning occurs faster at higher currents
  - Higher gas flowrate brings CO in faster
  - Performance is more sensitive to CO coverage as HOR current increases



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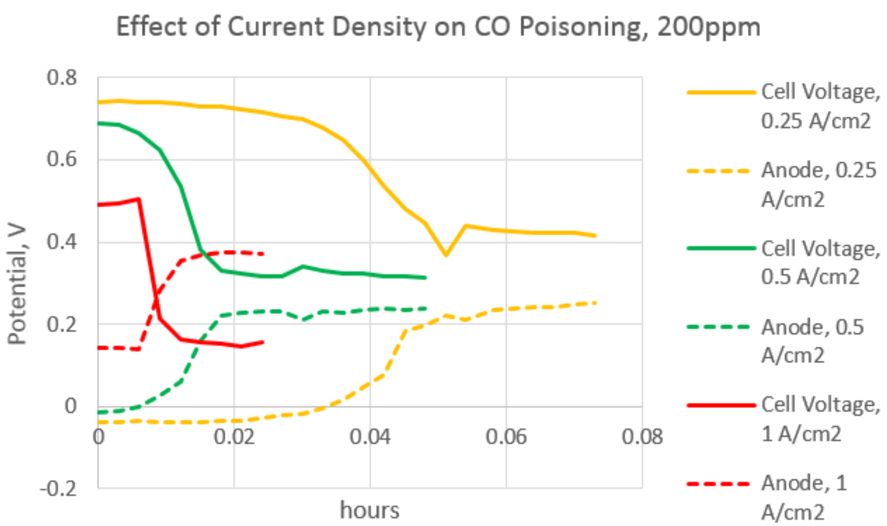
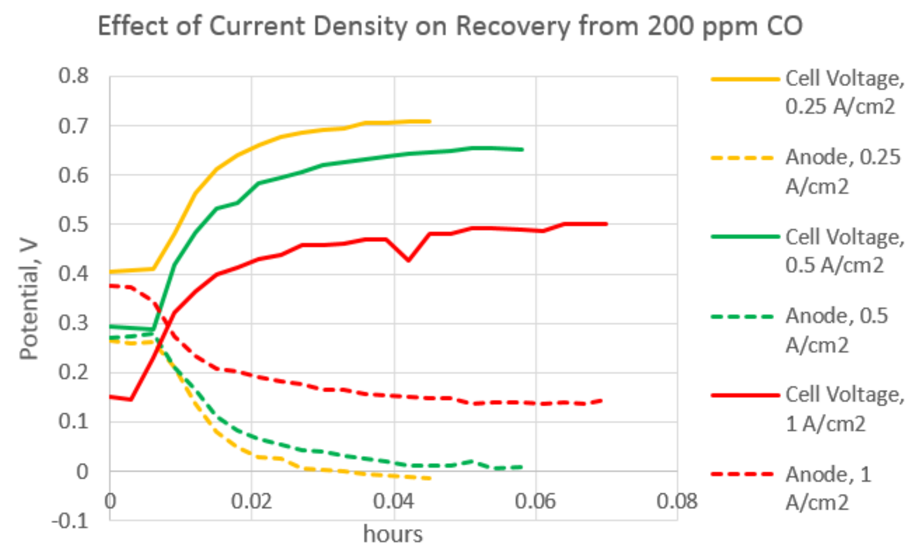
Effect of Current Density on CO Re-poisoning





- Re-poisoning occurs faster than initial poisoning at all current densities
- Recovery for re-poisoning is the same as for initial poisoning

Gore 710, 0.4 mg/cm^2 anode, 0.1 mg/cm^2 cathode
80°C, 150 kPa, 1.2/2.0 stoich