SOFC anode degradation during operation in coal syngas with selected impurities.

Harry O. Finklea

NIFT

Professor, Bennett Department of Chemistry

West Virginia University

Morgantown, WV

Fellow, Institute of Advanced Energy Studies

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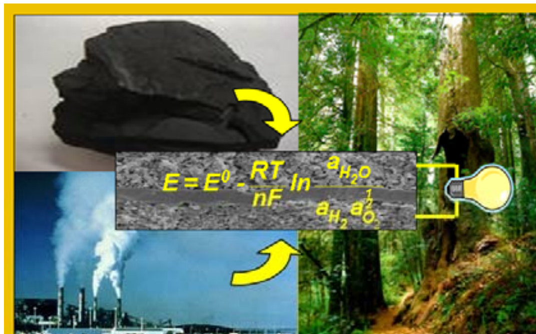

Outline

- Introduction to NIFT
- Phosphine
- Hydrogen sulfide
- Hydrogen chloride
- In-situ temperature measurements
- SOFC simulations
- Conclusions

National Institute for Fuel Cell Technology

- Established in Fall 2006 under the Implementation of US DOE EPSCoR and WV state EPSCoR Implementation
- Personnel
  - 10 faculty from 4 departments (MAE, Chem. Eng., Chem., Phys.)
  - 5 postdocs
  - 8 graduate students
- Vision - establish an internationally recognized, sustainable fuel cell research center for coal-based clean power generation
- Capabilities
  - Button cell manufacturing
  - Half-cell and full cell test benches
  - Unique in-situ optical test bench
  - High-end computational facilities

Acknowledge co-workers & support

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- Ismail Celik, Nick Wu, Bruce Kang, Xingbo Liu, Andrei Smirnov, Ed Sabolsky, Xueyan Song
- Chemical Engineering
- John Zondlo
- Chemistry
- Harry Finklea
- Physics
- Barry Cooper, Ning Ma
- National Research Center for Coal and Energy
- Dick Bajura
- plus the 5 post docs and 8 graduate students
- Support: DE-FG02-06ER46299 (Dept. of Energy)

Objectives of Current Research

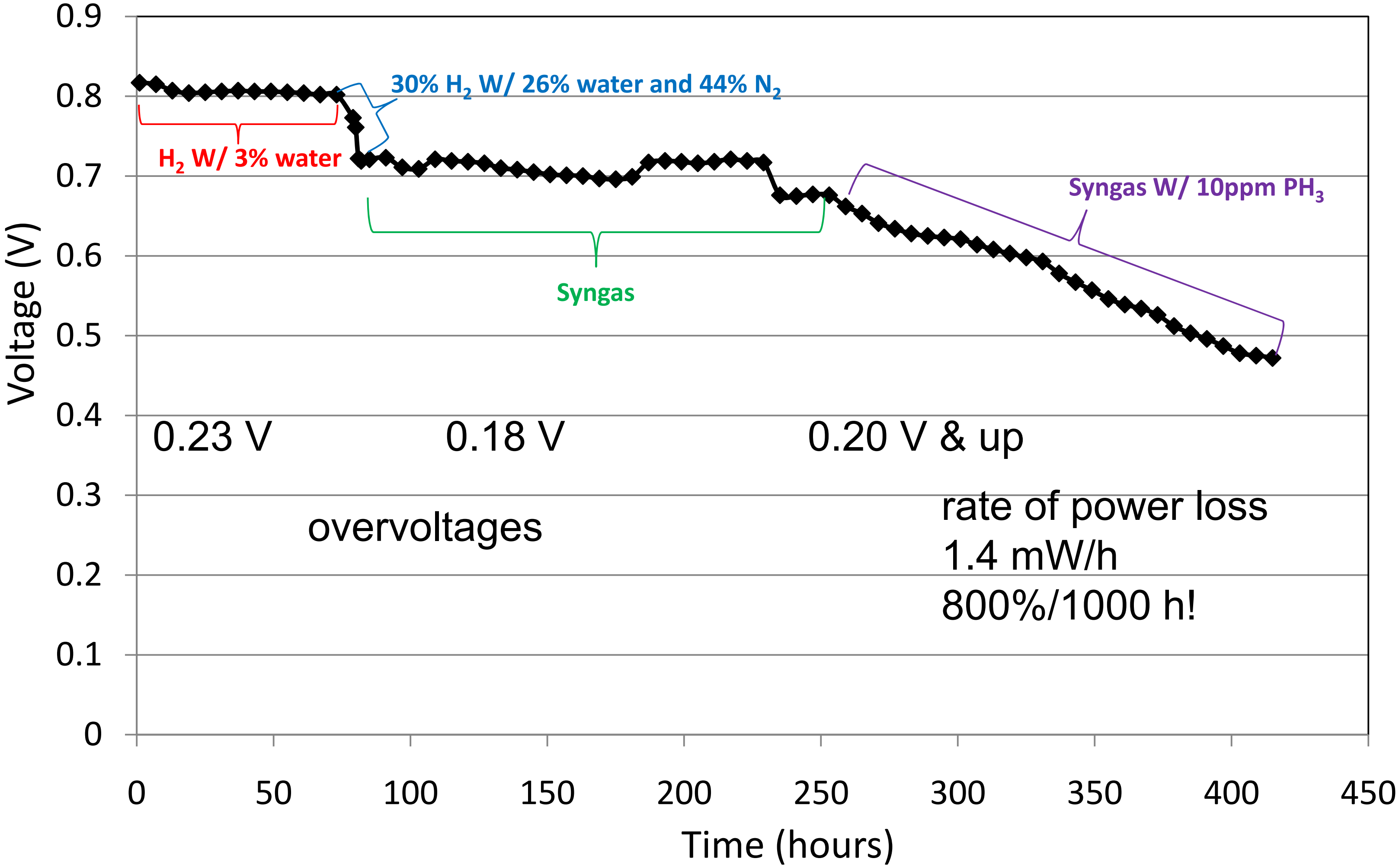
- Characterize the effects of major trace contaminants in coal syngas on fuel cell performance
- Identify the fundamental mechanisms through which these impurities affect performance
- Develop novel materials to minimize impact of contaminants
- Propose remedies for adverse effects of contaminants on fuel cell performance

Phosphine Protocol

- MSRI cells, 0.8 mm anode support, with 25 micron active anode layer, 20 micron YSZ electrolyte, LSM/YSZ cathode (2 cm^2).
- Anode current collector: anode center not covered with mesh or paste.
- Sequential exposure to wet hydrogen, syngas, and syngas with PH_3 at 800^{o}C.
- Syngas: 30% H_2, 26% H_2O, 23% CO, 21% CO_2.
- PH_3 conc. typically 10 ppm, injected after humidifier.

- In this section, focus on overvoltages ($\Delta E_{OCV} - \Delta E_{appl} + IR_s$).
- Ex. Apply 0.80 V, ΔE_{OCV} = 1.08 V, R_s = 0.10 Ω, I = 1.0 A
- Overvoltage = 1.08 – 0.80 + (1.0 A)(0.10 Ω) = 0.18 V

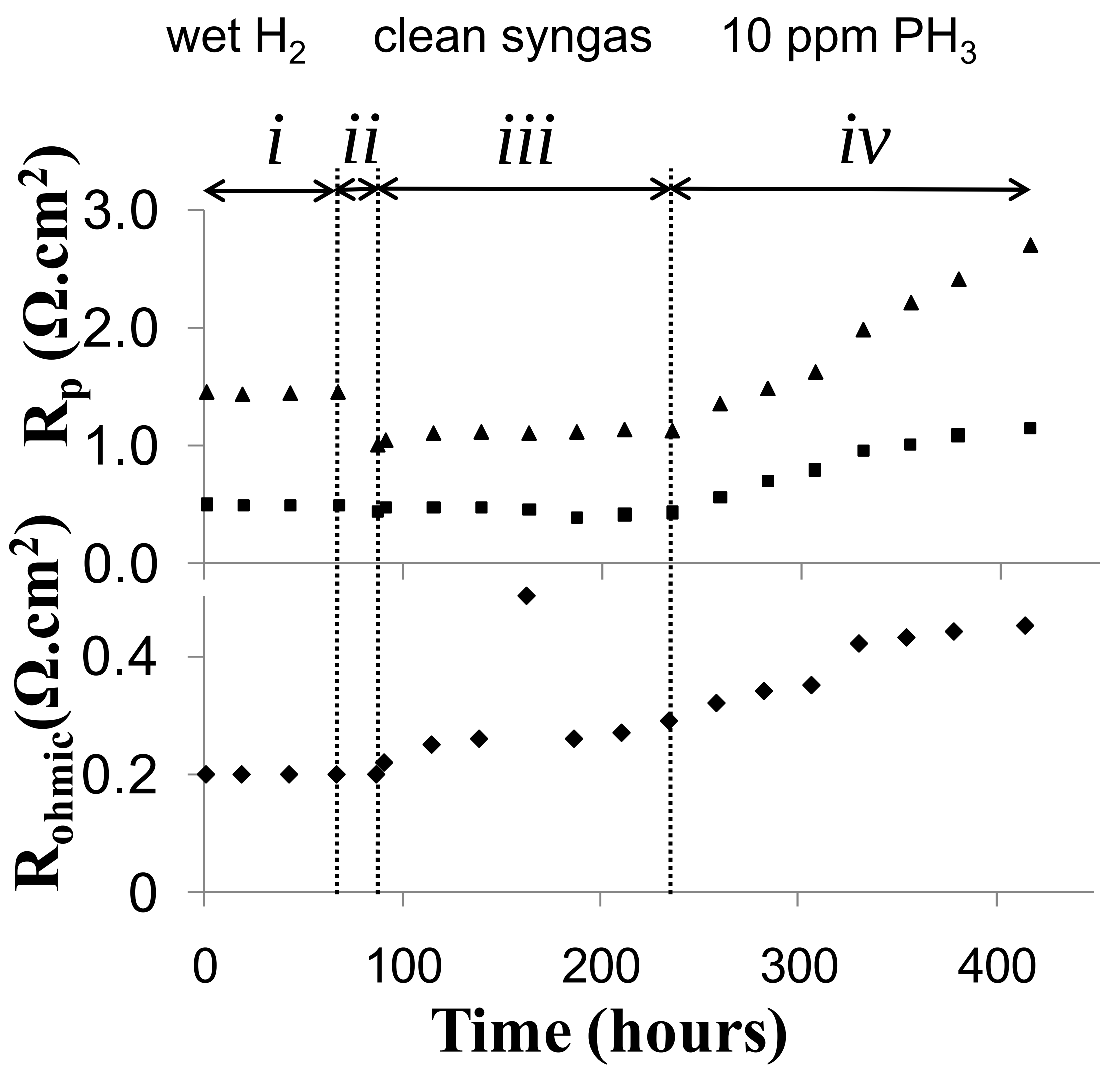
Long term Performance test at 0.25 A/cm^2



Ohmic and polarization resistances from EIS

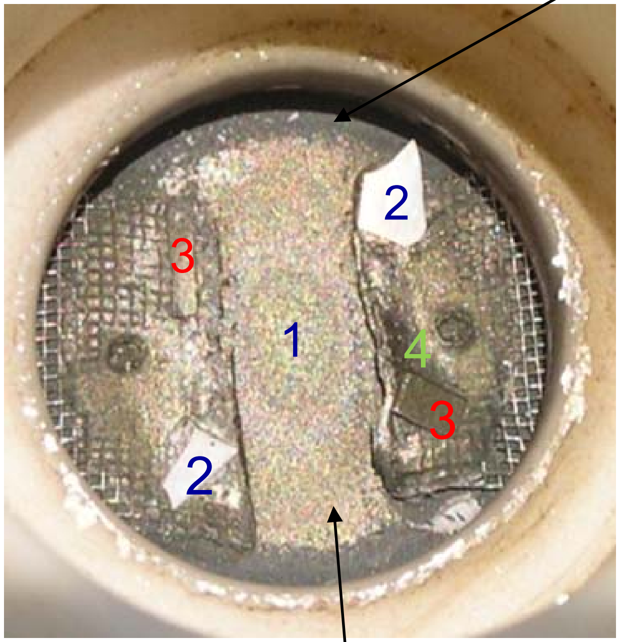
Both series & polarization resistances increase during PH_3 exposure

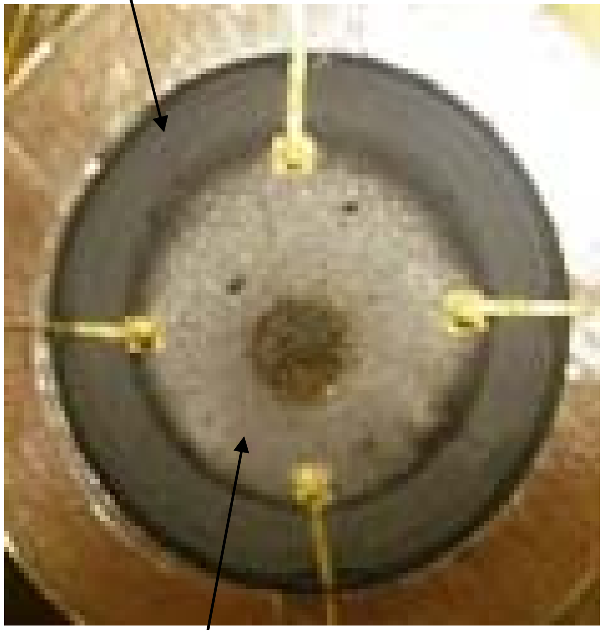
♦: R_{ohmic};
■: R_p at 400 mV overpotential;
▲: R_p at OCV



Anode appearance after PH_3 exposure

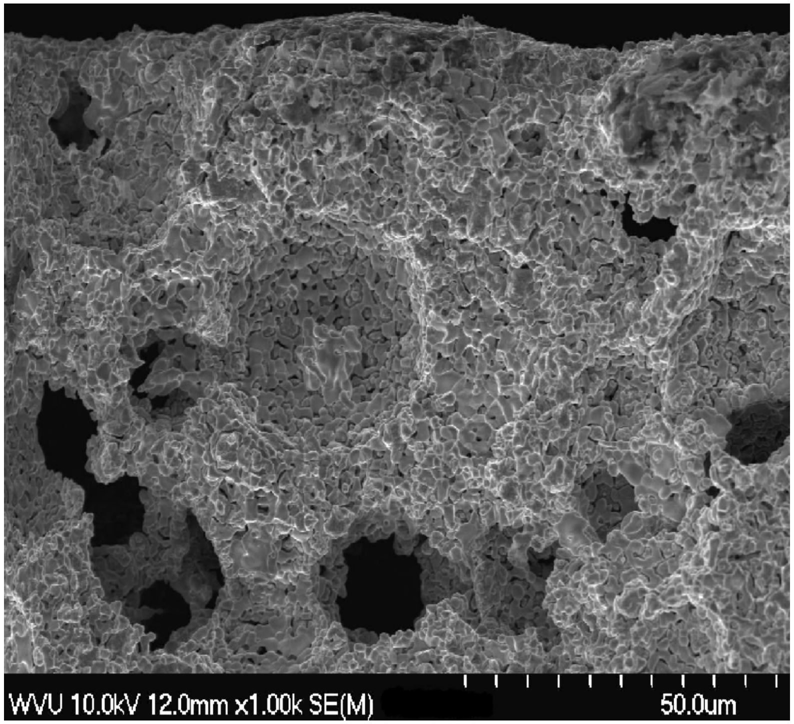
No metallic layer underneath mica seal

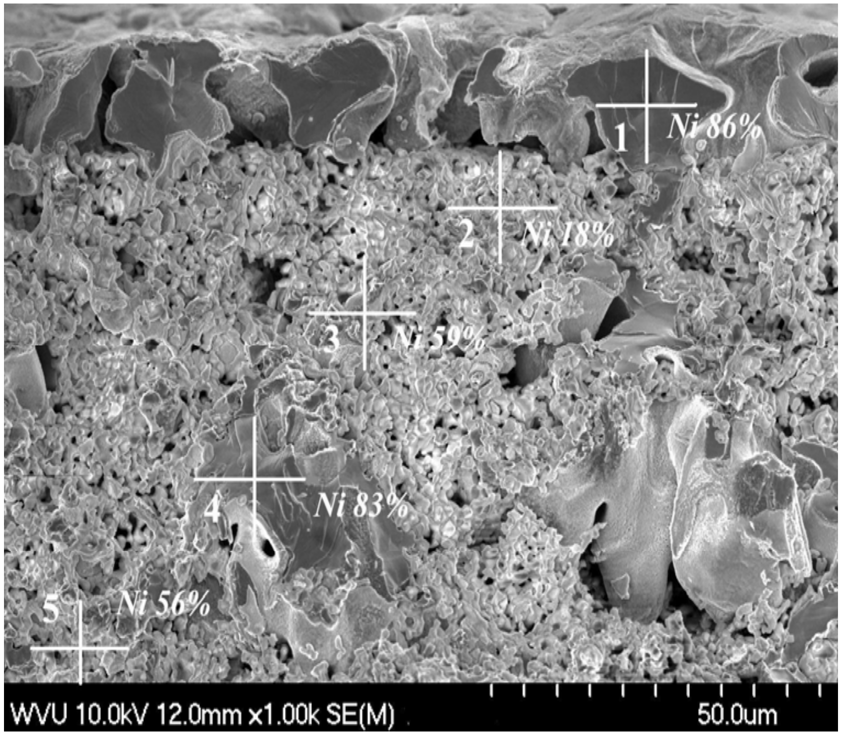




Metallic layer on exposed part of the anode

The nickel migrates!

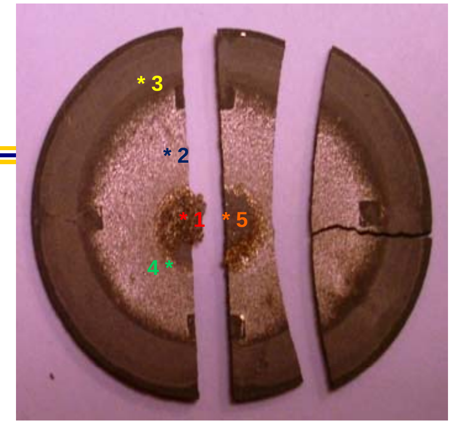


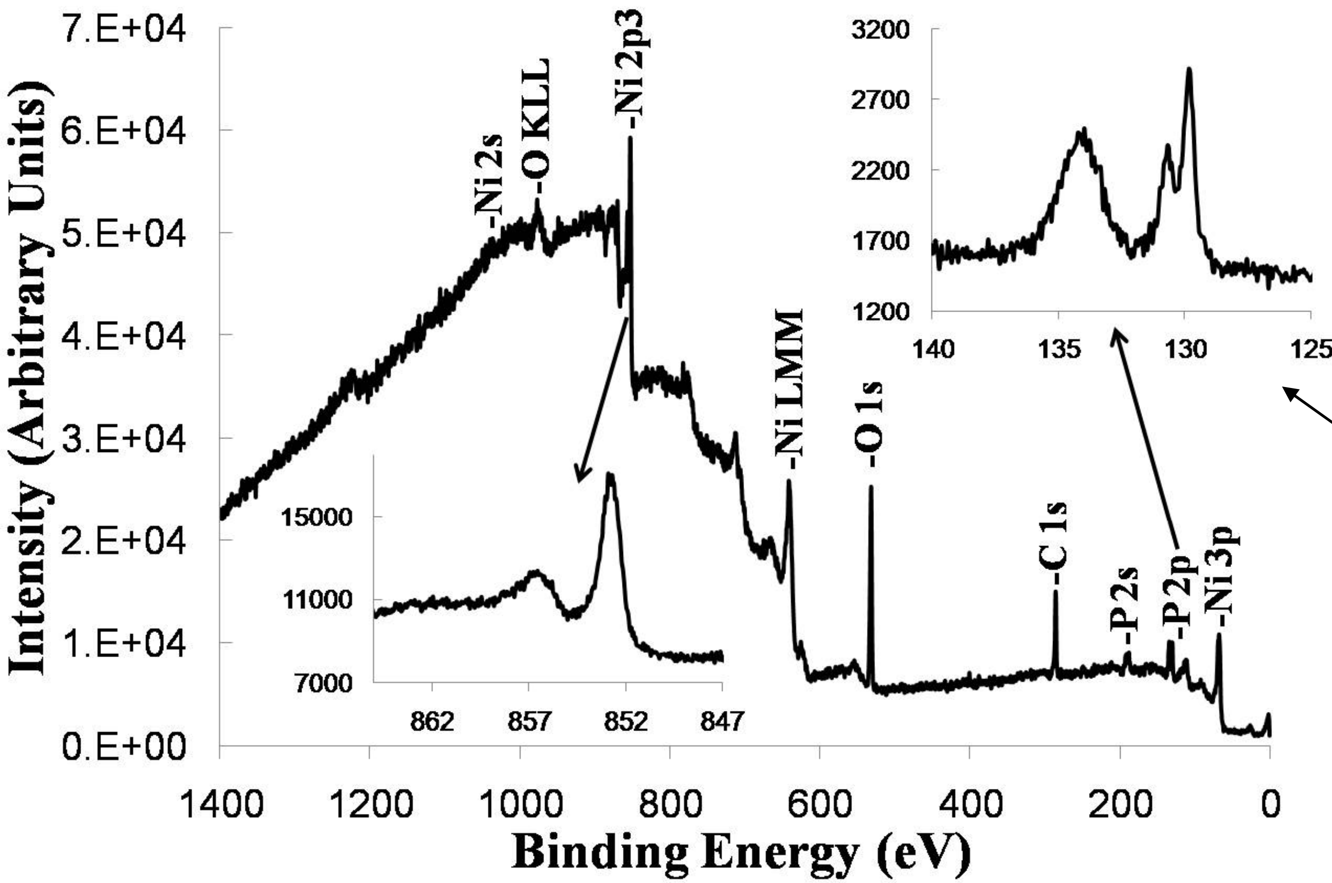


Virgin SOFC

After PH_3 exposure

XPS Analysis of Shiny grey area (2)

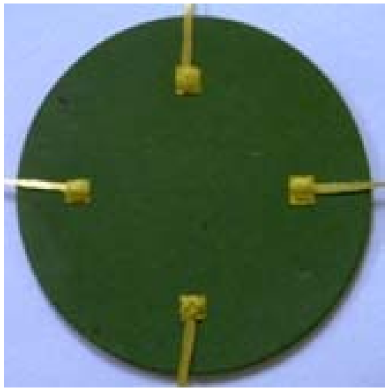


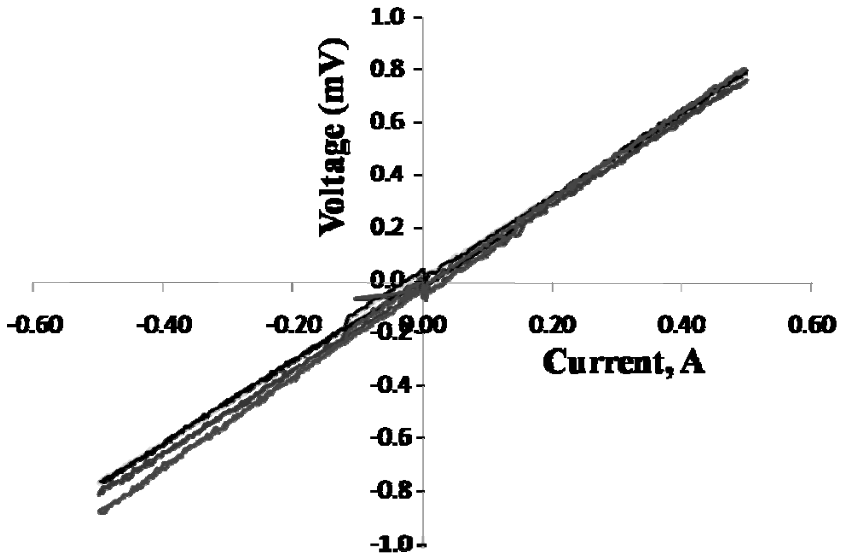


Ni, O, P,
But not
Y or Zr.
P(+5) and
P(0 or -3).

Van der Pauw measurements on the anode.

- Does Ni migration cause power loss through damage to the Ni percolation network in the anode?
- Perform in-situ van der Pauw measurements during exposure experiment.
- Linear plots, zero intercept imply pure ohmic behavior.
- All 4 connection combinations yield very similar resistances.
- Calculate sheet resistance and resistivity.





VDP results summary

	H_2 W/ 3% water	H_2 W/ 26% water	Syngas after 24 h	Syngas after 96 h	Syngas after 170 h	Syngas+PH_3 after 24 h	Syngas+PH_3 after 96 h	Syngas+PH_3 after 170 h
Resistivity (μΩ.cm)	575	585	588	608	610	606	605	608

Estimated uncertainty +/- 5% -> no significant change.

Loss of power not due to loss of percolation network in the supporting part of the anode.

Lit. value for pure nickel at 800°C = 45 μΩ.cm

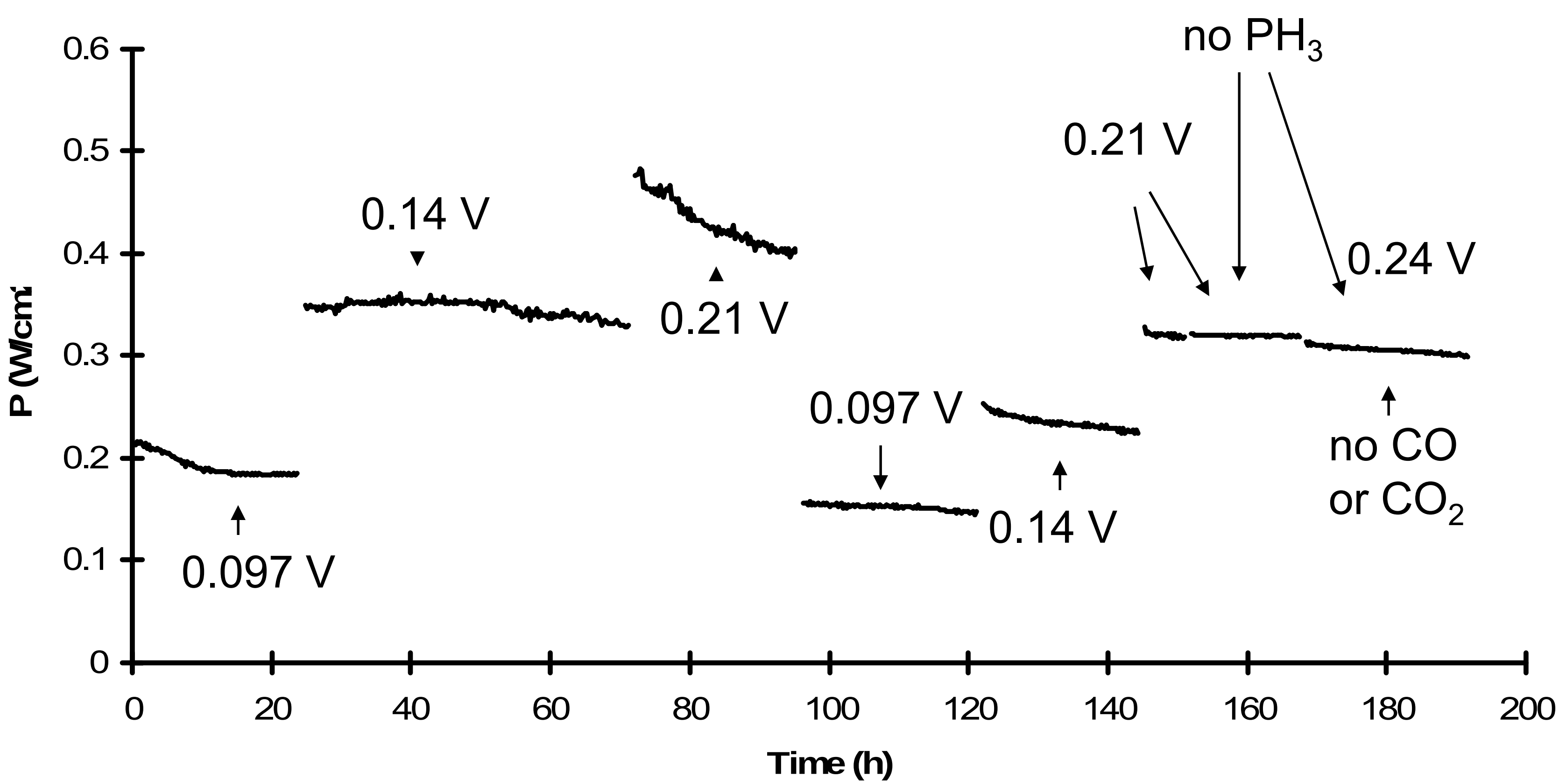
Recent overvoltage study

- Protocol
- After 200 hour burn-in using wet hydrogen, then clean syngas, expose the anode to 10 ppm PH_3 at fixed overvoltages for 24 hours.
- Applied overvoltage sequence: 0.1, 0.2, 0.3, 0.1, 0.2, 0.3 V (not corrected for iR drop) for 1-2 days each.
- Then expose the anode to clean syngas, and finally wet hydrogen for 1 day each.
- Collect measurements of OCV, polarization curves, EIS at OCV and at fixed overvoltages each day.

- Objective: see if there is a correlation between the overvoltage and the rate of power loss.

Power vs time during 10 ppm PH_3 exposure

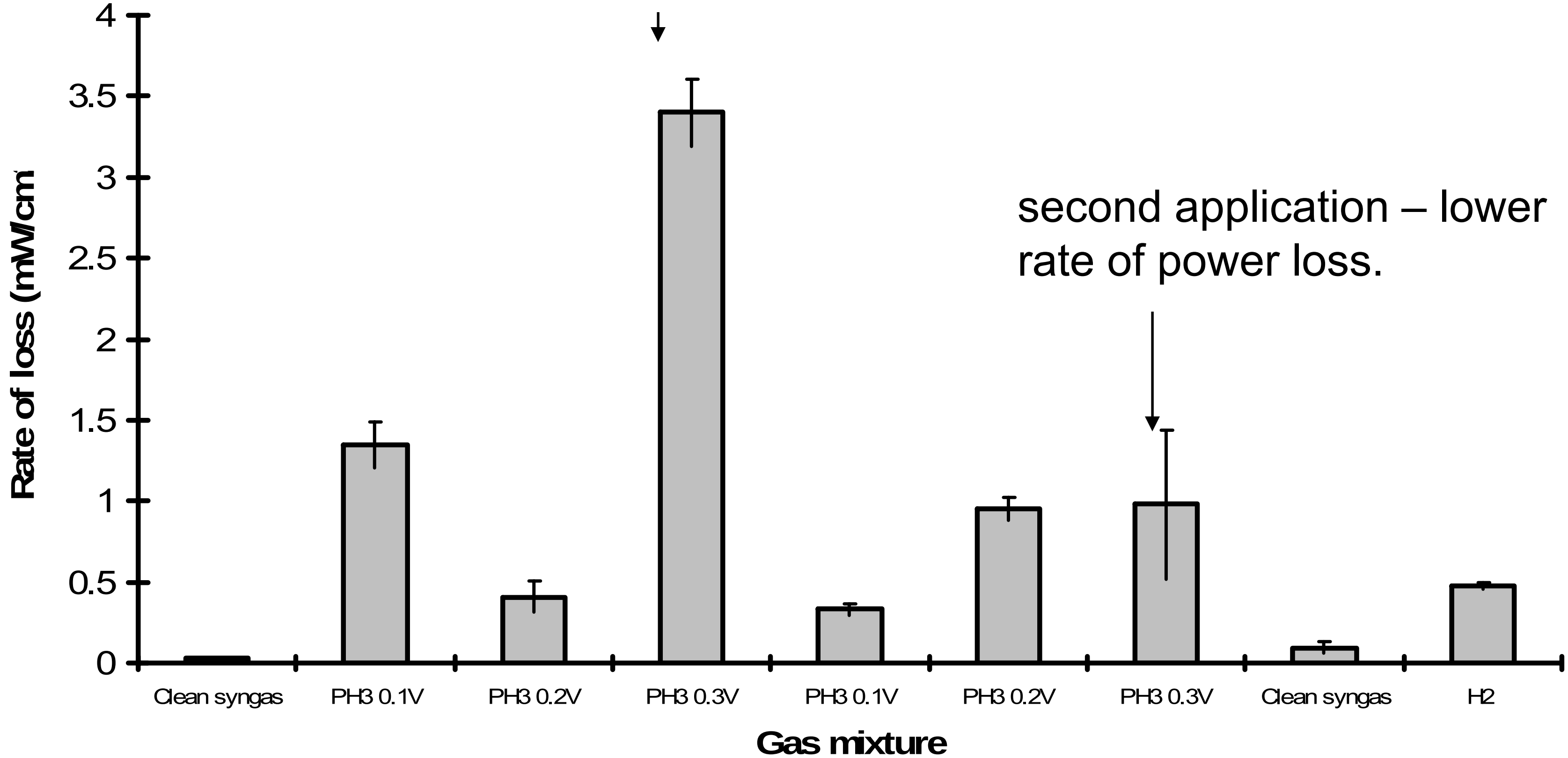
corrected overvoltages shown



Degradation continues after removal of PH_3.

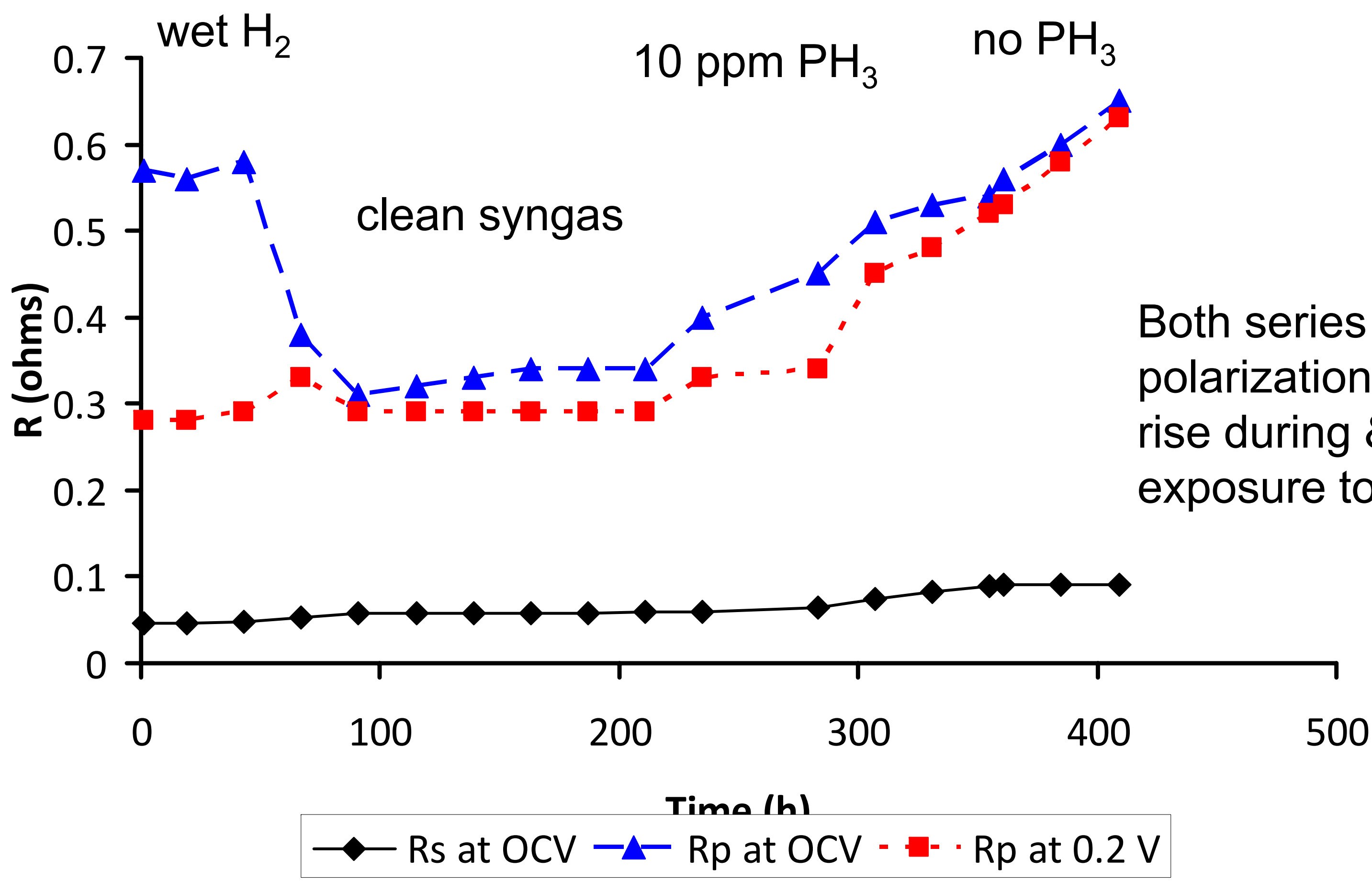
Rate of Power Loss vs Gas Mixture

first application of 0.2 V overvoltage results in highest rate of power loss



No clear correlation of rate of power loss with overvoltage.

Series and polarization resistances vs time

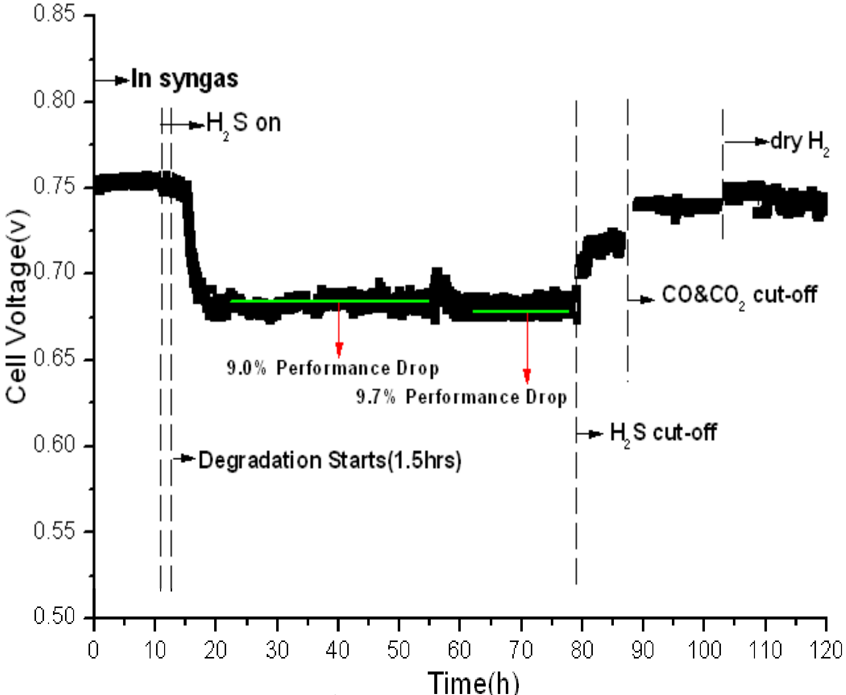


Both series & polarization resistances rise during & after exposure to PH_3.

Summary of phosphine results

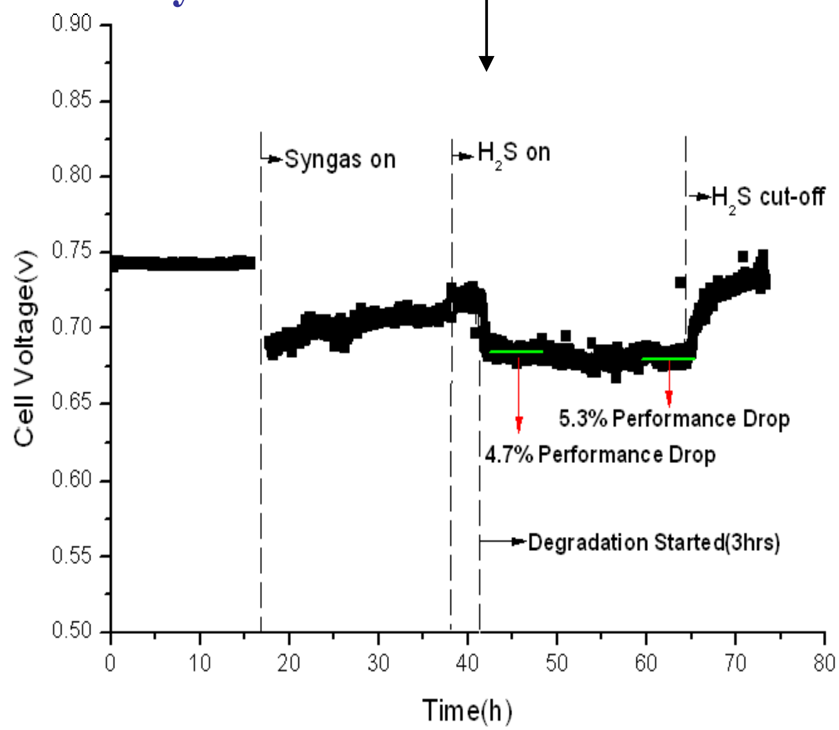
- Substantial loss of power (0.05 to 0.5 $mW/cm^2/hr$) during exposure to 10 ppm PH_3.
- Migration of nickel, possibly as nickel phosphide phases.
- No significant change in anode resistivity over 200 hrs.
- Power loss is not recovered using clean syngas.
- Higher rate of power loss on first exposure to higher overvoltage, but no subsequent correlation of power loss with overvoltage.
- Recent result – no degradation for 10 ppm PH_3 in dry H_2. Is water needed for the degradation process?

Sulfur-Tolerant SOFC Anode

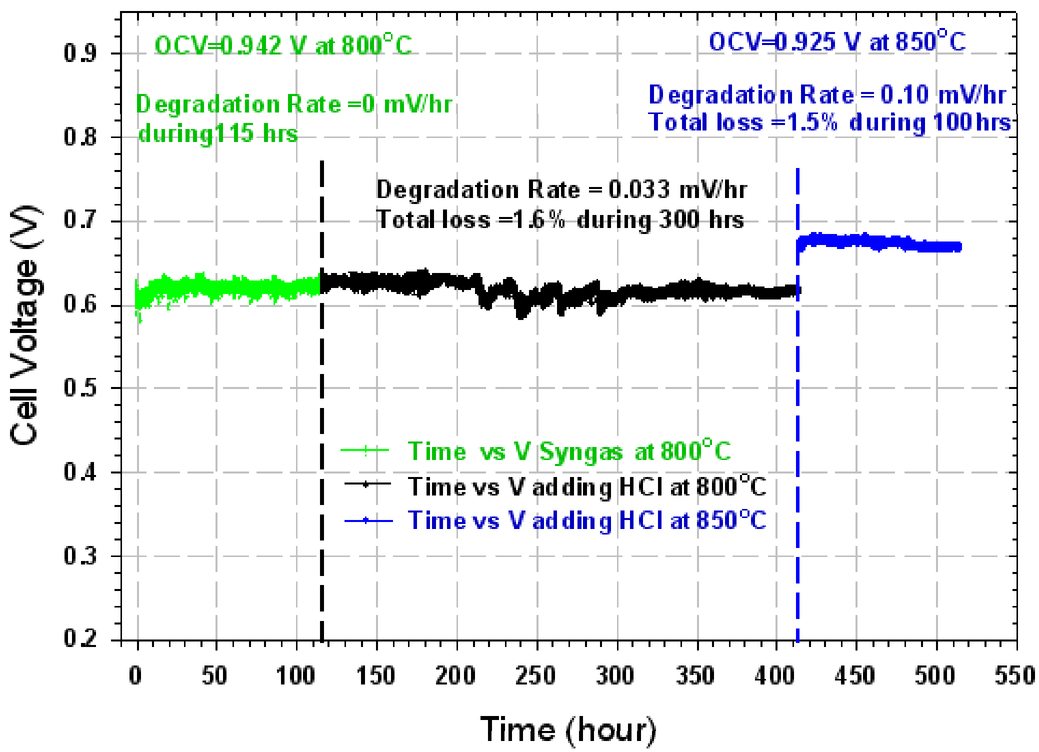


Baseline MSRI cell with Pt paste tested in syngas with 20 ppm H_2S and load of 0.25 A/cm^2.

MSRI cell impregnated with $La_xCe_{1-x}O_2$ coating tested in syngas with 20 ppm H_2S and load of 0.25 A/cm^2. Onset of decay delayed 2 to 13 hours.



Effect of HCl impurity

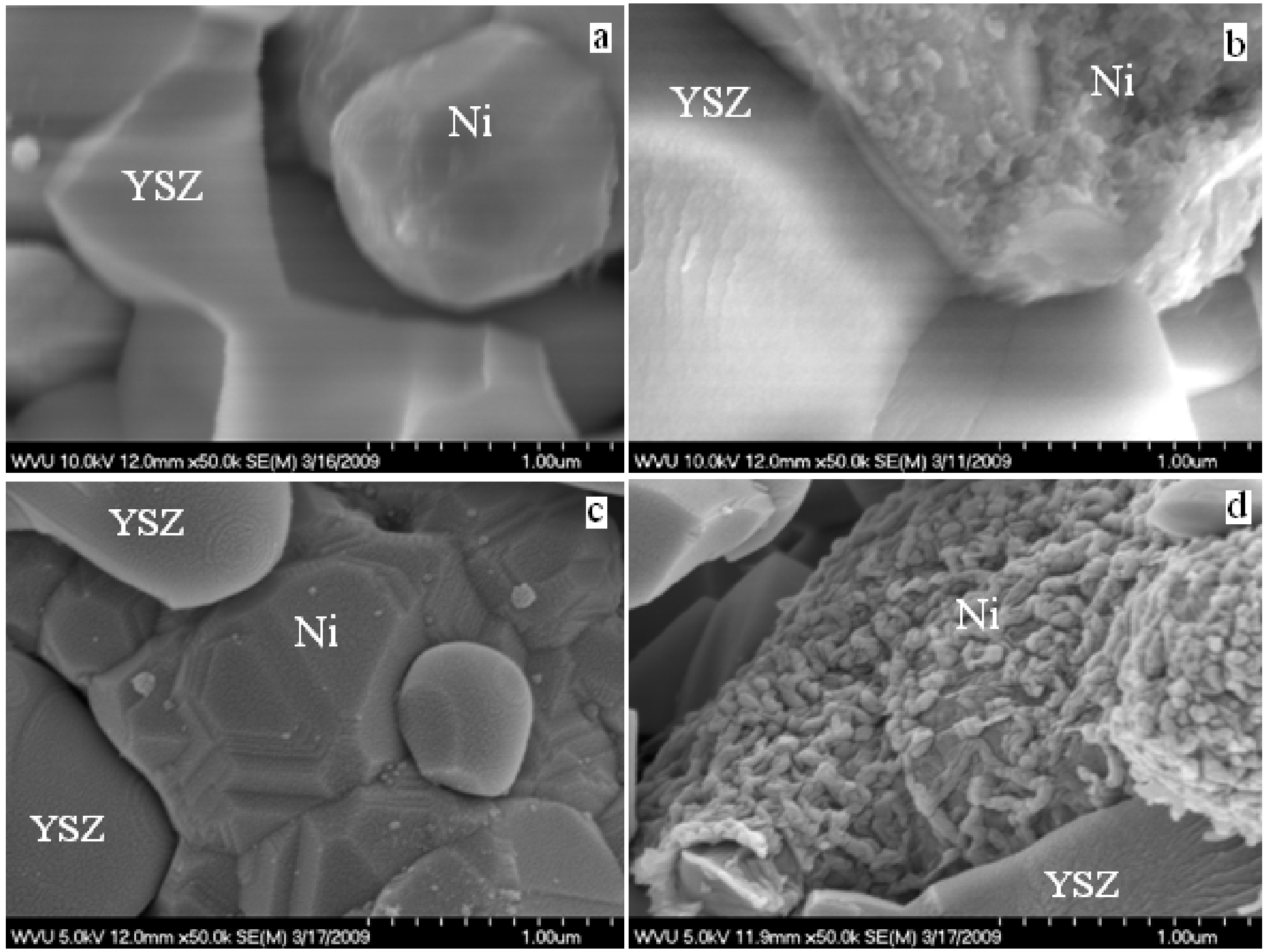


Cell voltage vs time at 0.5 A/cm^2 for a cell running on syngas before/after addition of 100 ppm HCl for 300 hours at 800ºC, 100 hours at 850ºC. Cell overvoltage ca. 0.2 V. No significant changes in ohmic or polarization resistances during HCl exposure.

After 400 hours exposure to 100 ppm HCl

cross-section of anode

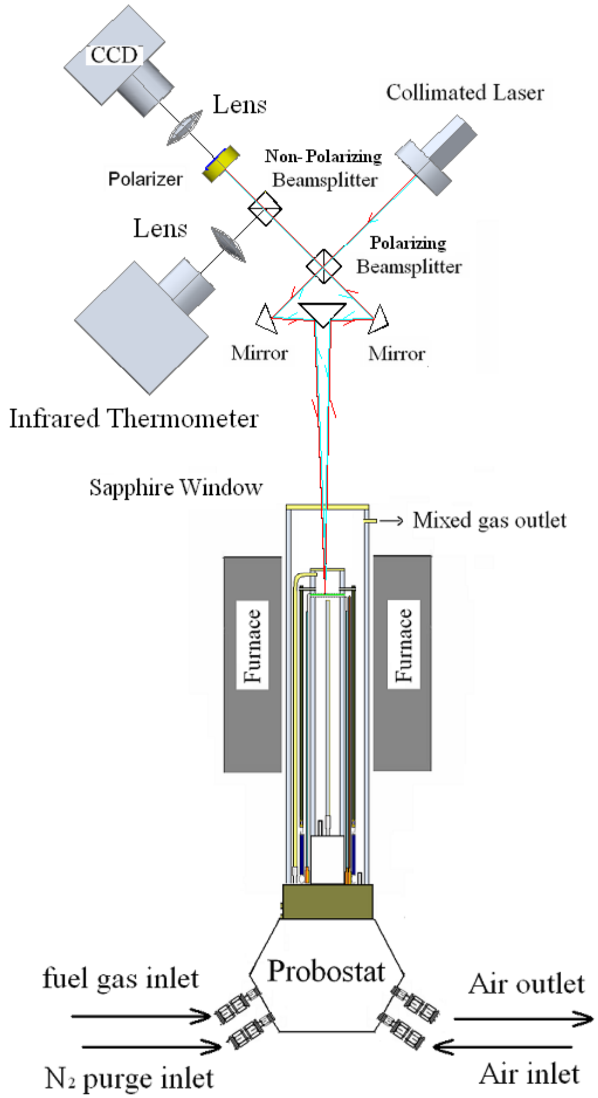
top surface of anode



clean reduced anode

after HCl exposure

In-situ measurements

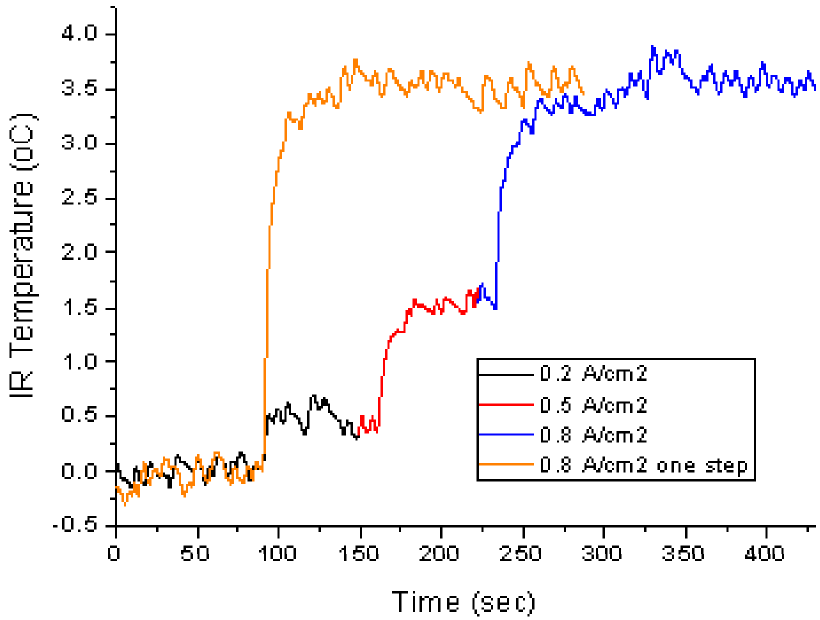


Probostat with sapphire window gives optical access to one electrode.

Use Sagnac interferometry to measure strain.

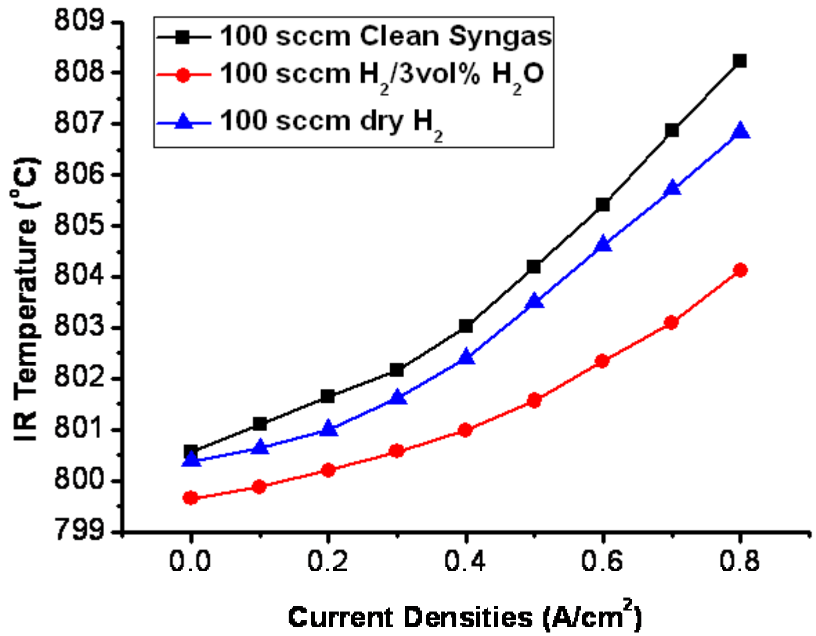
Use IR thermometer to measure directly the SOFC surface temperature.

Surface temperature results for the Ni mesh on the anode



<- time response to step changes in current density.

Effect of current density and gas composition ->

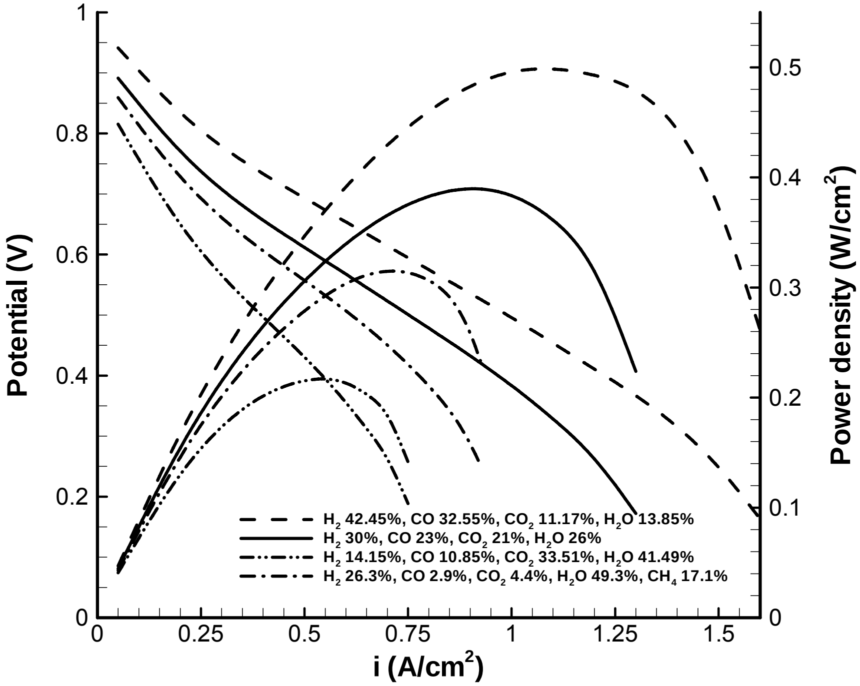


Accomplishments: Multiscale Continuum Modeling

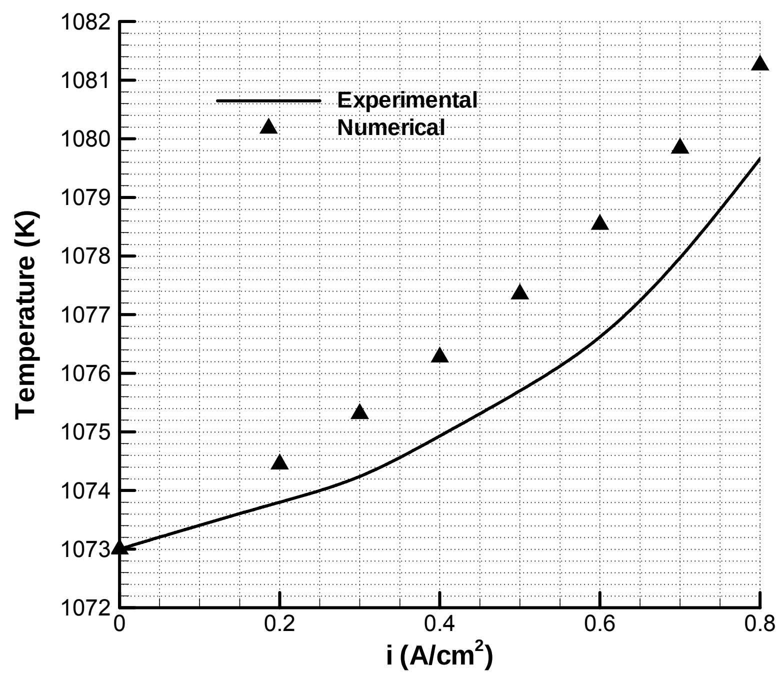
- Developed 3-D anode-supported SOFC model which includes conservation of mass, charge and energy, multi-component mass transfer, surface and gas phase reactions, simultaneous oxidation of hydrogen and CO.
- Refined parameters by fitting VI curves to experimental data.
- Equilibrium calculations for stable forms in the presence of selected contaminants.
- Phenomenological model for degradation.

Continuum Modeling

- Developed a detailed 3D model for syngas SOFCs that gives comprehensive information on various constitutive processes.



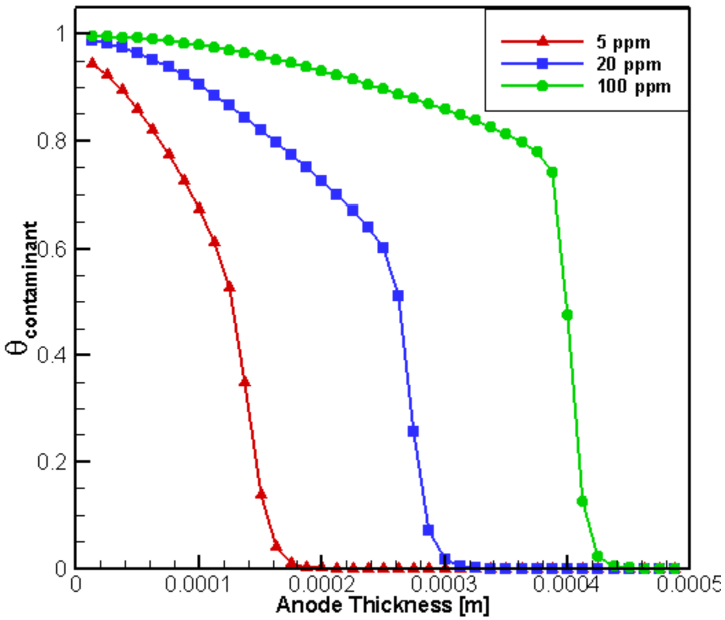
Predicted performance of button cells operating on various fuel compositions



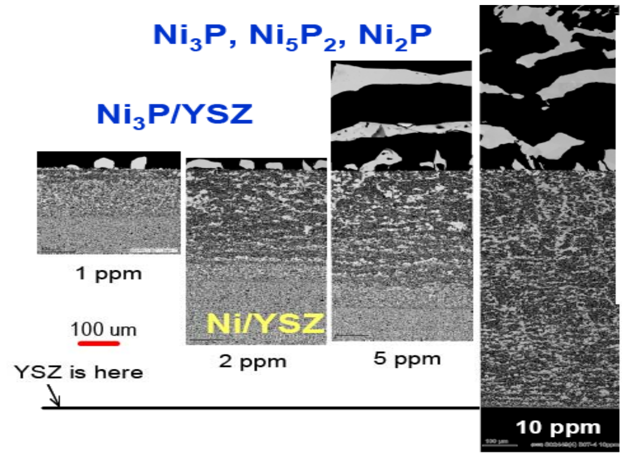
Surface temperature of a button cell operating on coal syngas at 1073 K: Comparison between experiments and simulations

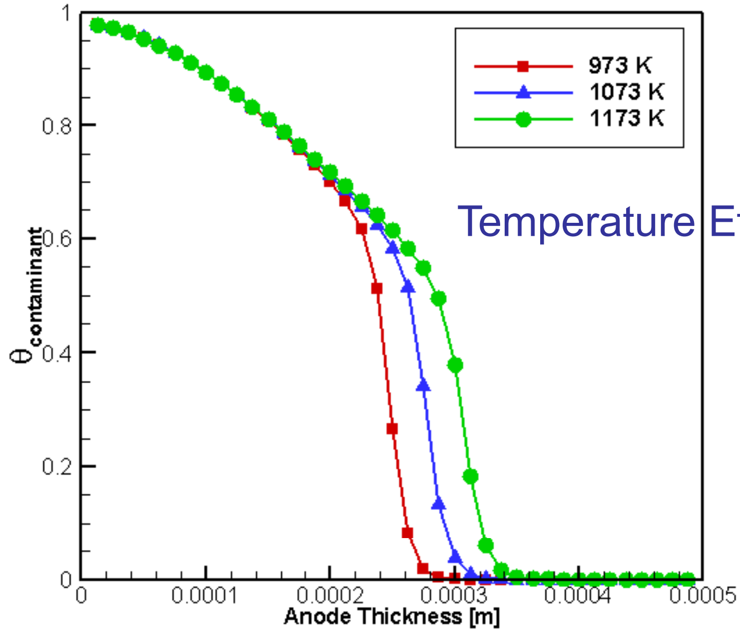
Degradation Modeling

- phenomenological model to simulate the typical poisoning effect of the impurities.



Concentration Effect





Temperature Effect

Conclusions

- PH_3 poses a significant threat to long term operation of Ni anodes in SOFCs. Once losses appear, they are irreversible.
- Possible mechanisms include nickel migration and blocking of nickel surfaces in the active layer.
- An oxidation catalyst (La-doped ceria) delays onset of degradation by H_2S. Can that strategy be applied to PH_3?
- Over 100 hours, 100 ppm HCl does not significantly affect performance or resistances in the anode, despite visible structural changes.
- More in-situ methods are needed. Optical temperature and strain measurements are promising.
- Computational methods will help understand local chemical conditions and provide predictions of failure.