Progress in Coal Syngas Contaminants Study at West Virginia University

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- The results presented here are the outcomes of the combined efforts of these researchers:

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Outline

- Introduction
- Objectives
- Methodology
- Characterization of Impurity Effects on SOFC's
- Remedies for Impurity Poisoning
- Modeling
- Conclusions

Introduction

- Coal syngas contains numerous contaminants and trace elements: As, P, Hg, Cd, Zn, Sb, Pb, Bi, Na, K, Fe etc.
- Small amounts of contaminants (1-5 ppm) cause significant degradation in SOFC performance.
- The effect of some trace elements is not well established.
- It is expensive to completely remove the contaminants, hence Lifetime prediction of the SOFCs exposed to low levels of fuel impurities is critical for design considerations.
- Remedies are needed for contaminant poisoning.

Objectives

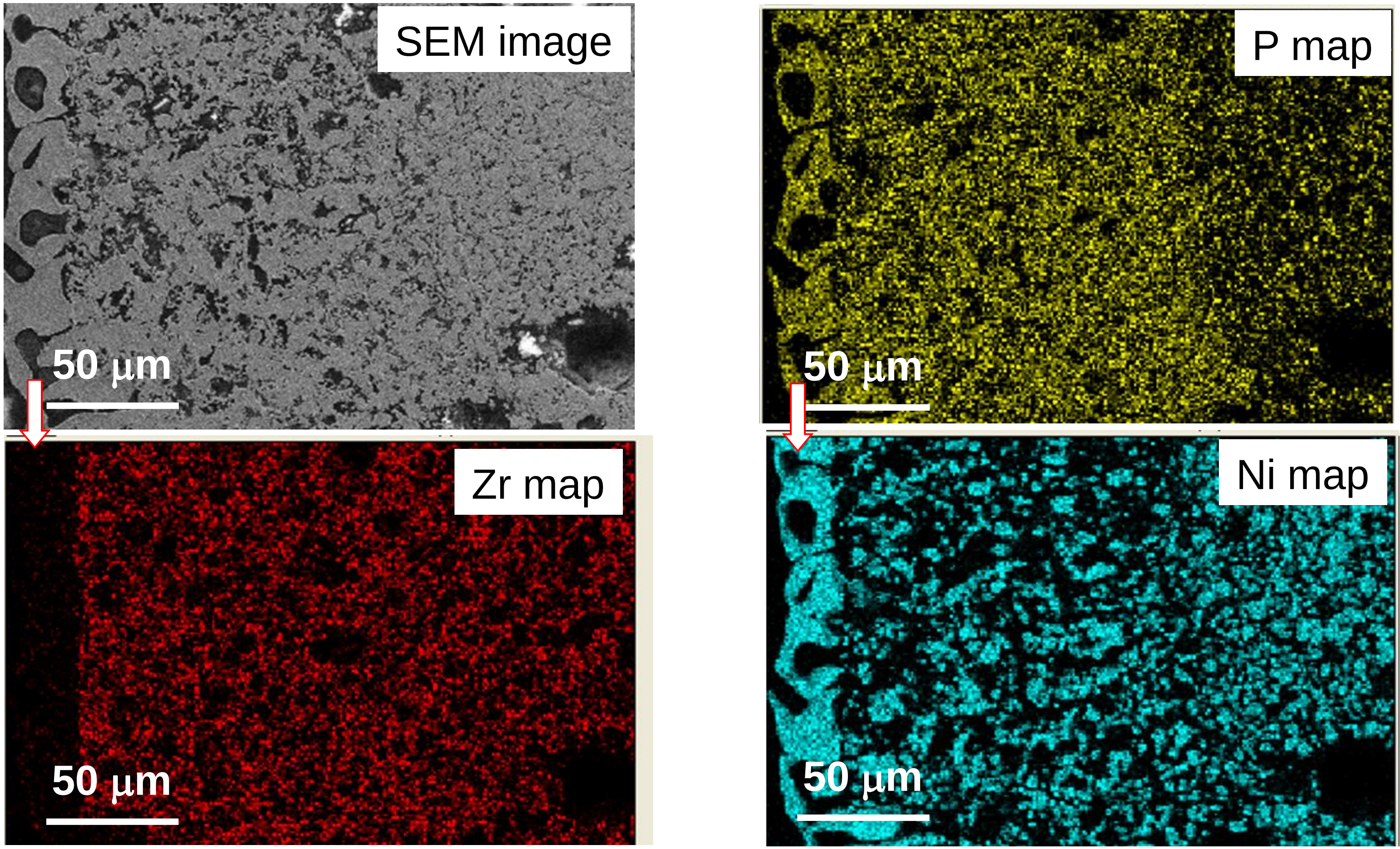
- Characterize degradation mechanisms for coal syngas trace contaminants.
- Develop novel anode materials for improving performance of SOFCs operating on coal-Syngas.
- Predict lifetime and durability of cell and stacks.

Methodology

- Multi-scale, multidisciplinary approach.
- In-house cell manufacturing using novel materials and techniques.
- Electrode and cell level testing in simulated syngas with contaminants.
  - SEM, XPS, XRD, TEM, Raman, EDAX
  - EIS, CV, ESEM, MS, Van Der Pauw, In-situ temperature and deformation measurement
- Continuum level modeling for cell and system level performance analysis.
- Phenomenological modeling based on accelerated laboratory tests to predict long term slow degradation rates and lifetime.

Effect of PH_3 on the Microstructure

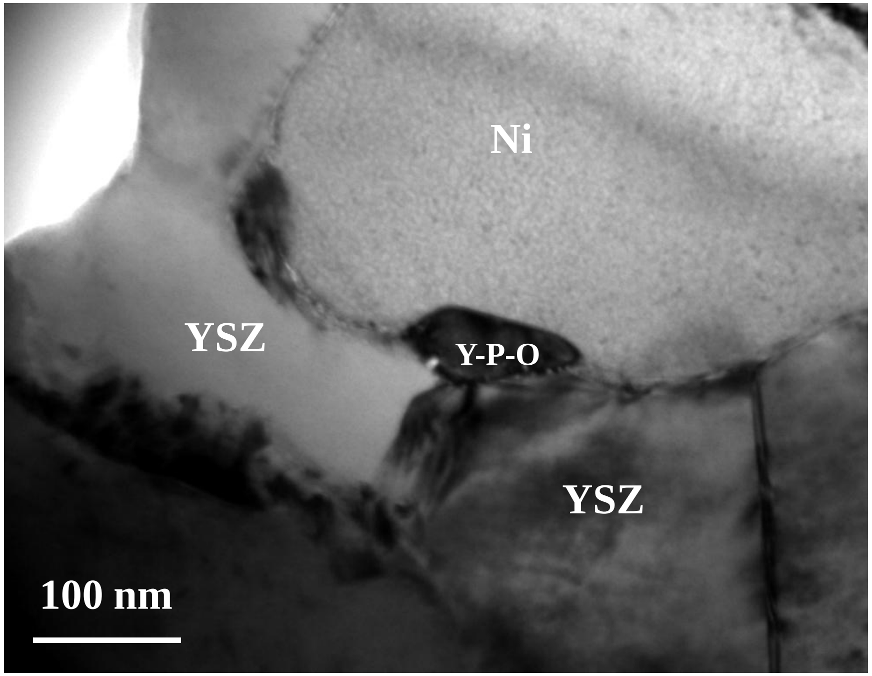
SOFC operated in syngas with 10ppm PH_3 for 250 h

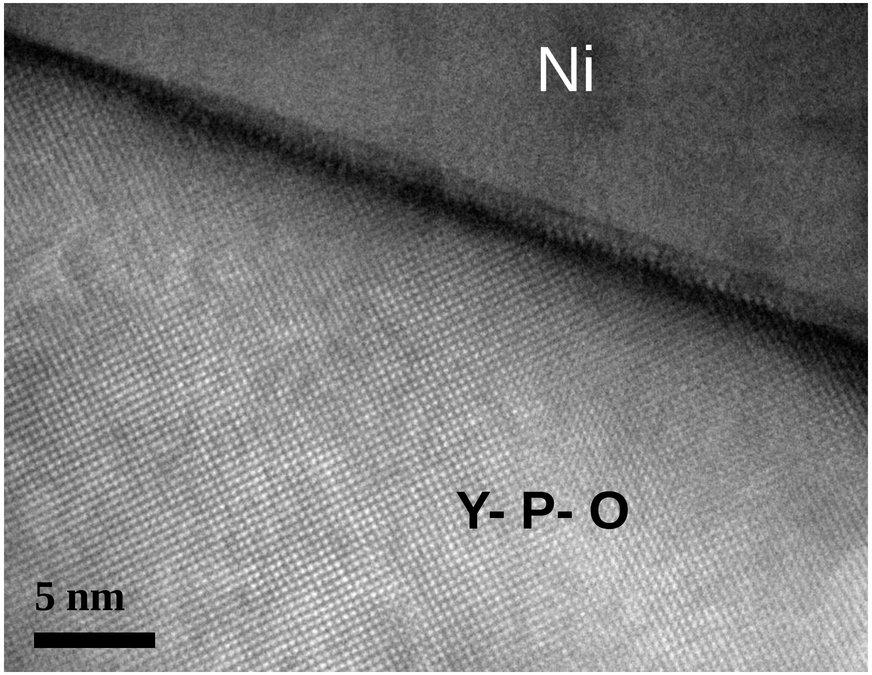


(I). Formation of Ni-P outer layer

Effect of PH_3 on the Microstructure (TEM)

SOFC operated in syngas with 10ppm PH_3 for 100 h





(II). Formation of Y-P-O phase at Ni/YSZ interface

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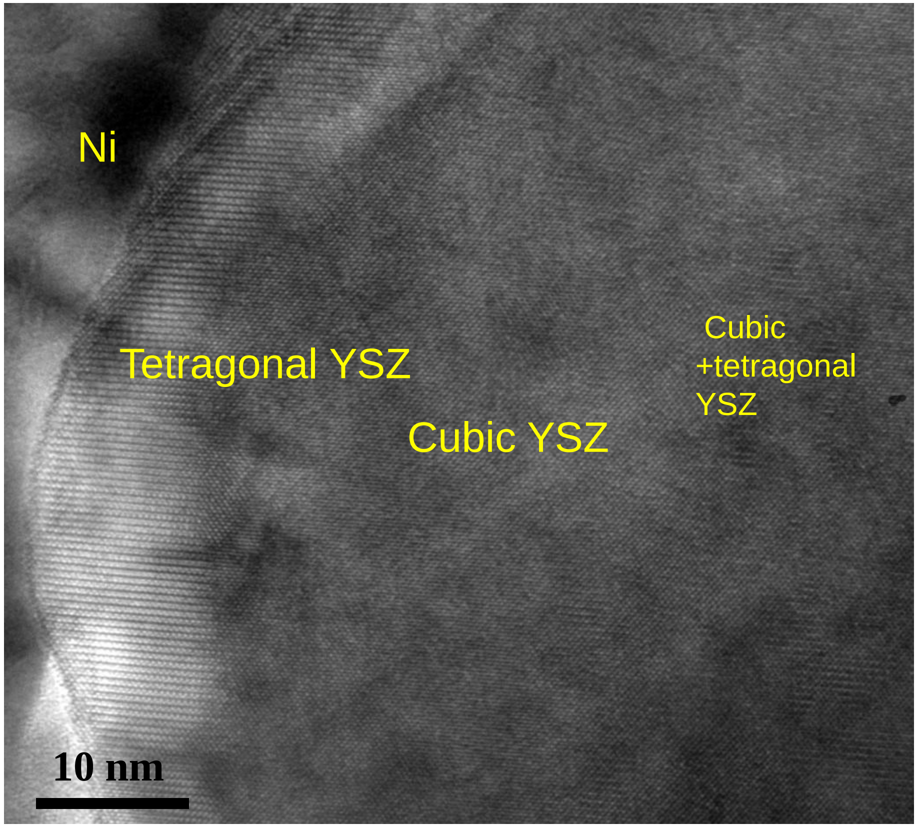
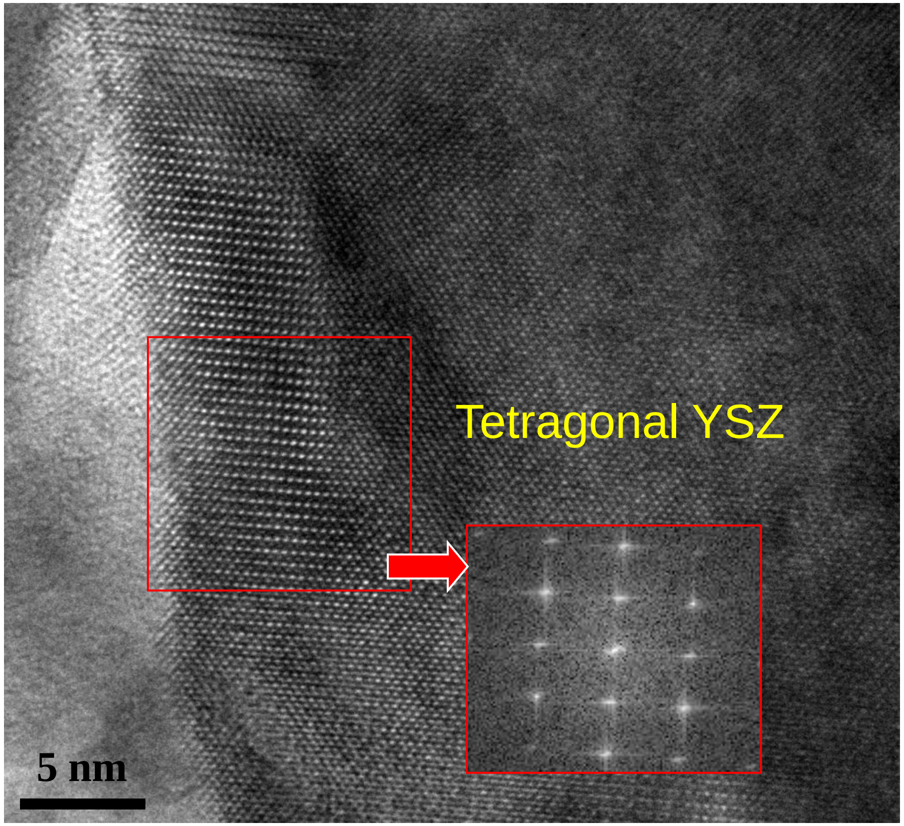
Effect of PH_3 on the Microstructure (TEM)

SOFC operated in syngas with 10ppm PH_3 for 100 h





(III). Formation of tetragonal YSZ layer(5-10nm) at Ni/YSZ interface

Effect of PH_3 on the Microstructure

SOFC operated in syngas with 10ppm PH_3 for over 100 h:

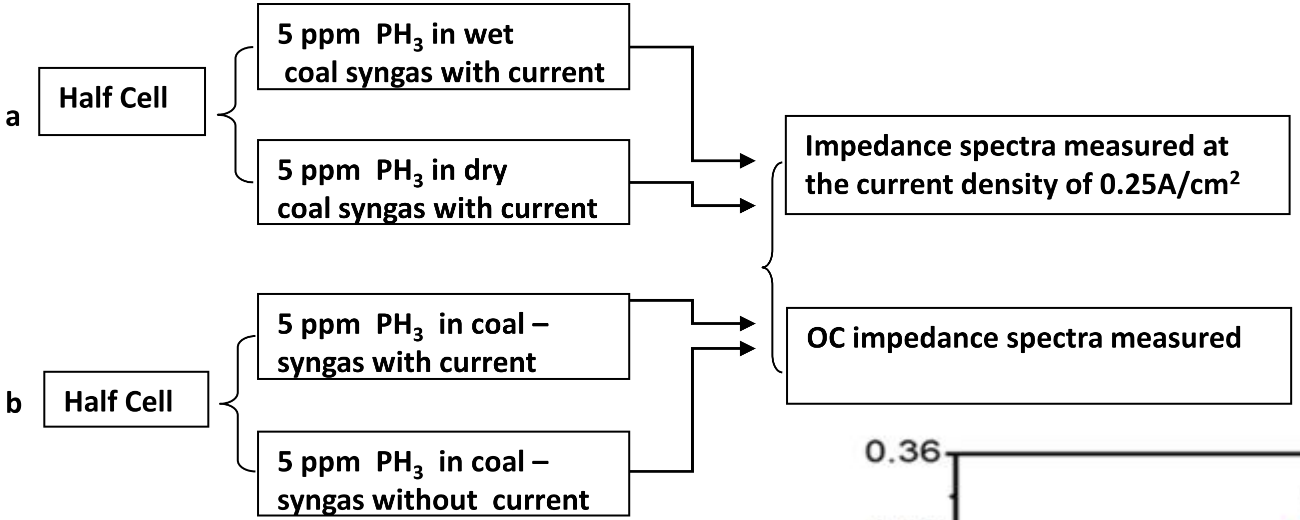
(I). PH_3 reacts with Ni and forms a thick layer of Ni-P phase at the outer layer of anode.

(II). PH_3 also reacts with YSZ and forms a Y-P-O phase at the interface of Ni/YSZ.

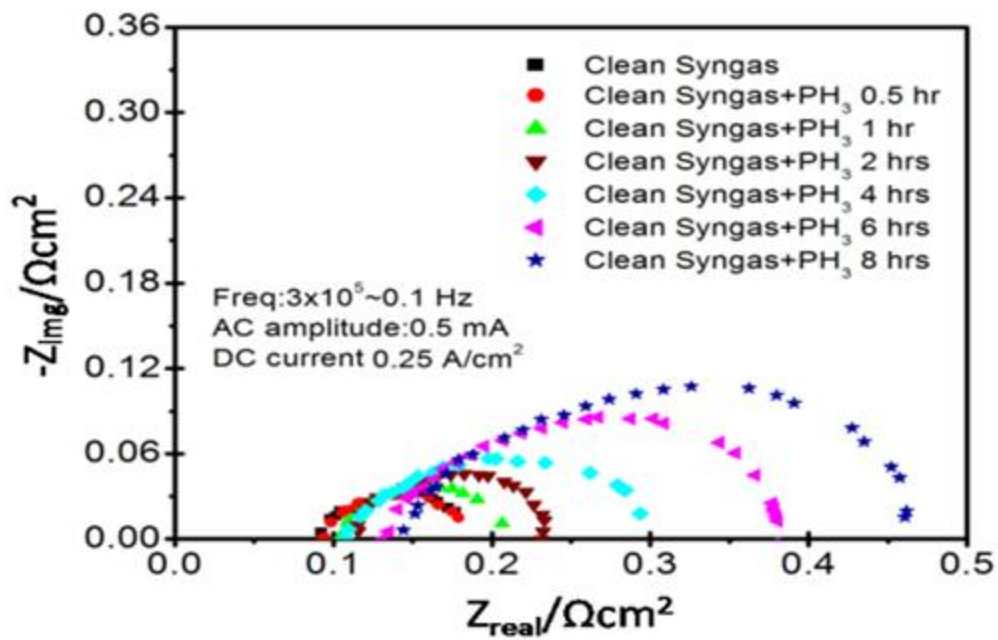
(III). PH_3 contamination causes Y deficiency in the YSZ at the Ni/YSZ interface, which consequently forms a tetragonal YSZ interface layer.

Conclusion: PH_3 reacts with both Ni and YSZ from the anode of the SOFC.

Performance Degradation due to PH_3



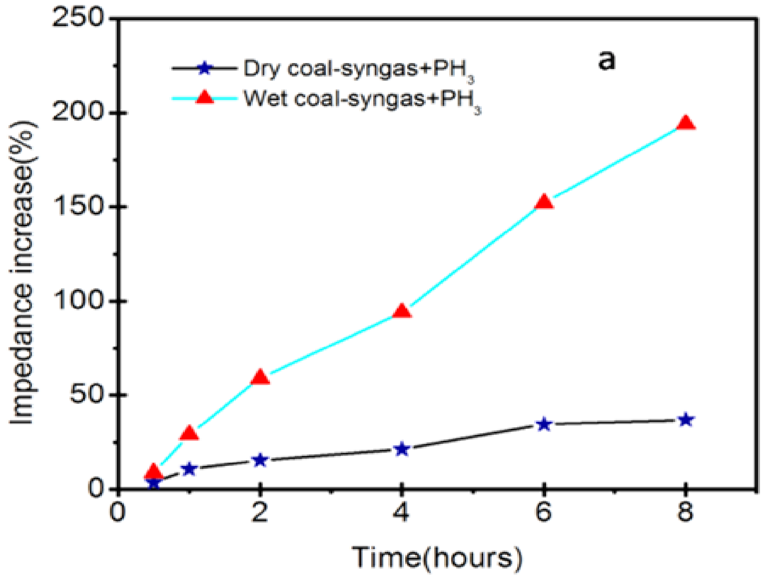
Anode half-cell test: (a) in dry and water containing condition; (b) with and without current loading; T = 800 ^oC



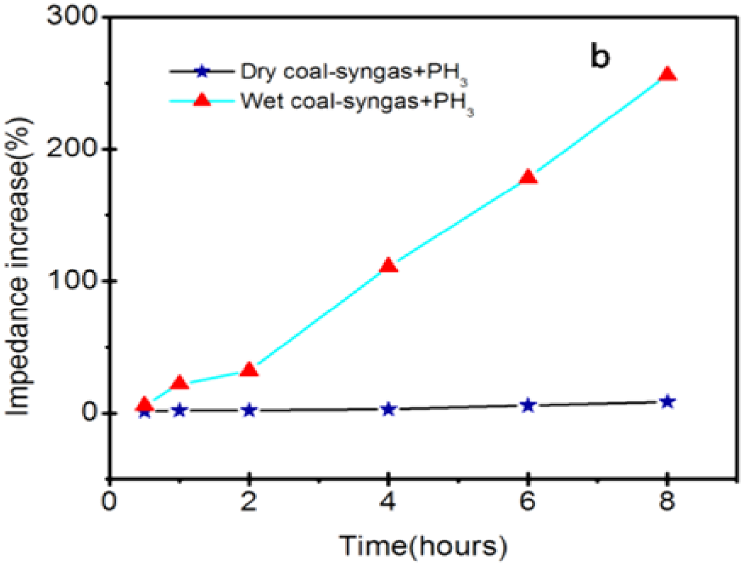
Example impedance spectrum taken from a half cell operated at 0.25A/cm^2 in wet coal-syngas with 5 ppm PH_3.

Performance Degradation due to PH_3

Cell operation in dry and wet syngas



a) Impedance with at 0.25 A/cm[2] bias measured at different times

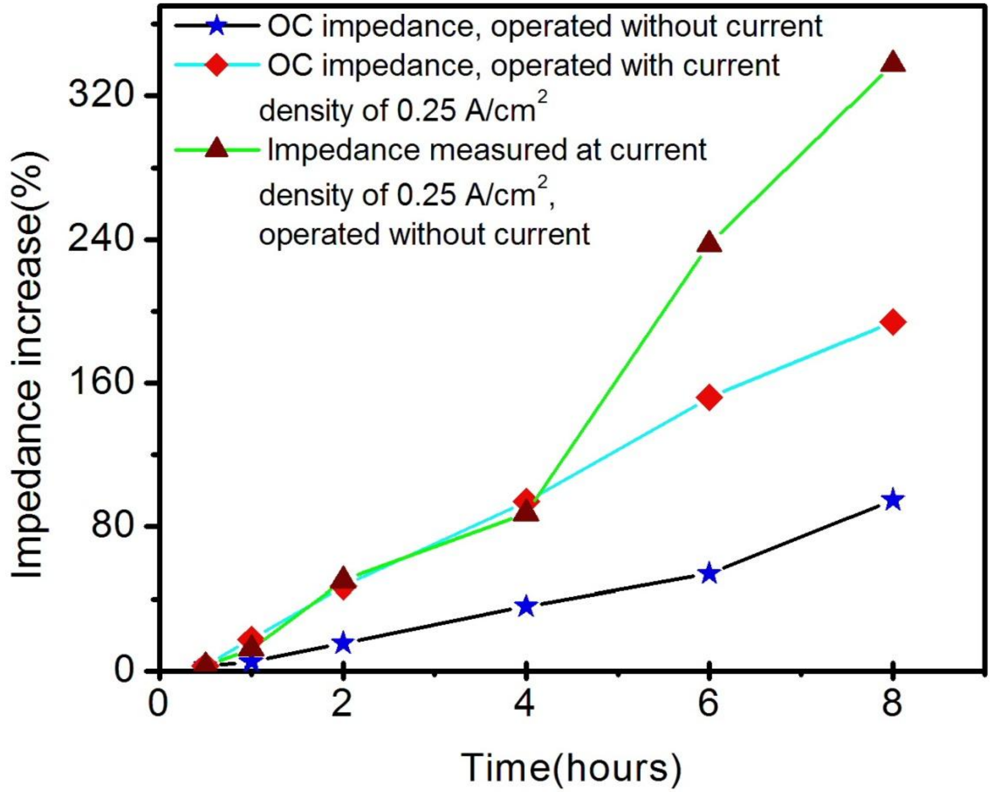


b) OC impedance measured at different times

The increase in the polarization resistances measured for the cell operated in dry coal-syngas with 5 ppm PH_3 is ambiguous, while that measured for the cell in wet coal-syngas with 5 ppm PH_3 is significant.

Performance Degradation due to PH_3

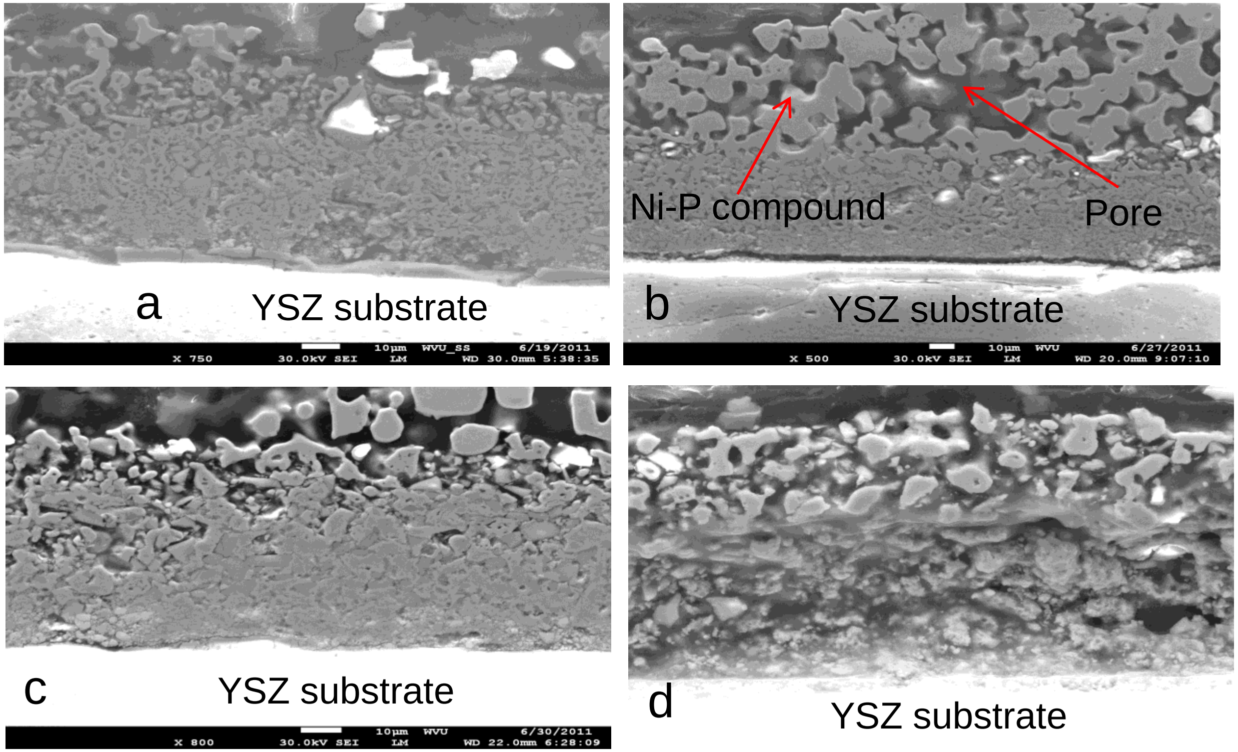
Cell operation with and without current in wet syngas



The increase in activation polarization impedance is larger with current loading than that without current loading.

Performance Degradation due to PH_3

Ni-YSZ anode after being exposed to PH_3 in various conditions



a. Clean syngas,

b. 5 ppm PH_3 for 24 hrs with current density of 0.25A/cm^2,

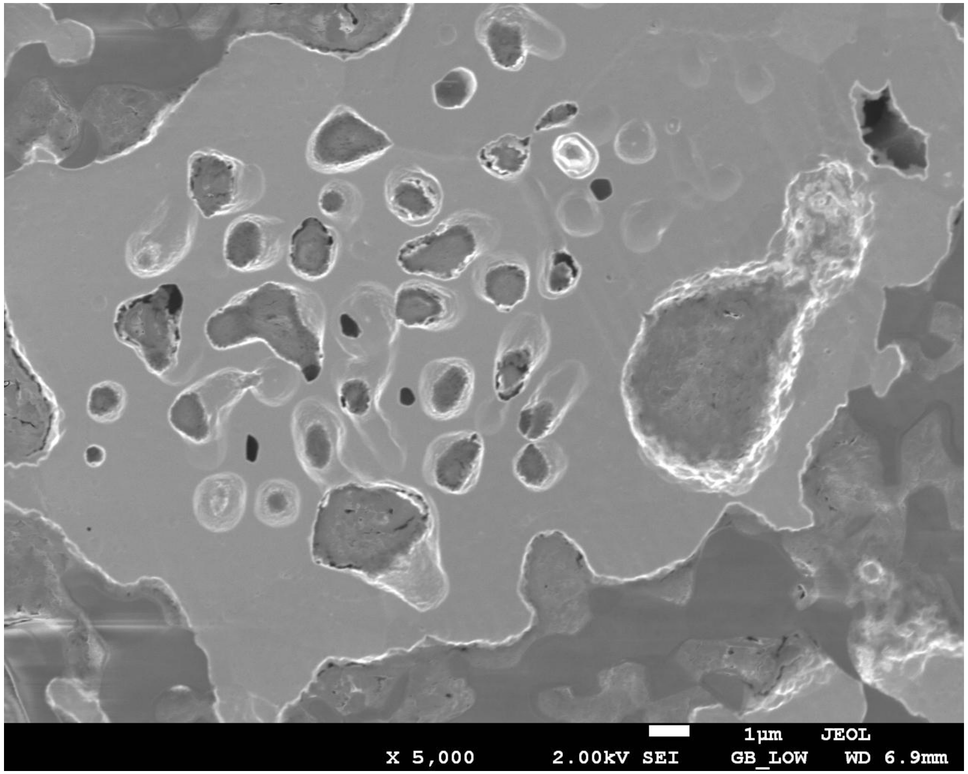
c. 5 ppm PH_3 for 24 hrs without current loading,

d. 5 ppm PH_3 for 24 hrs dry syngas

- *The half-cell operated with current loading shows (Fig.5b&c) more aggregates to big particles compared to cell w/o current.*
- *The anode operated with 5 ppm PH3 in dry coal syngas exhibits more severe agglomeration compared to wet syngas.*

Effect of PH_3 on Microstructure

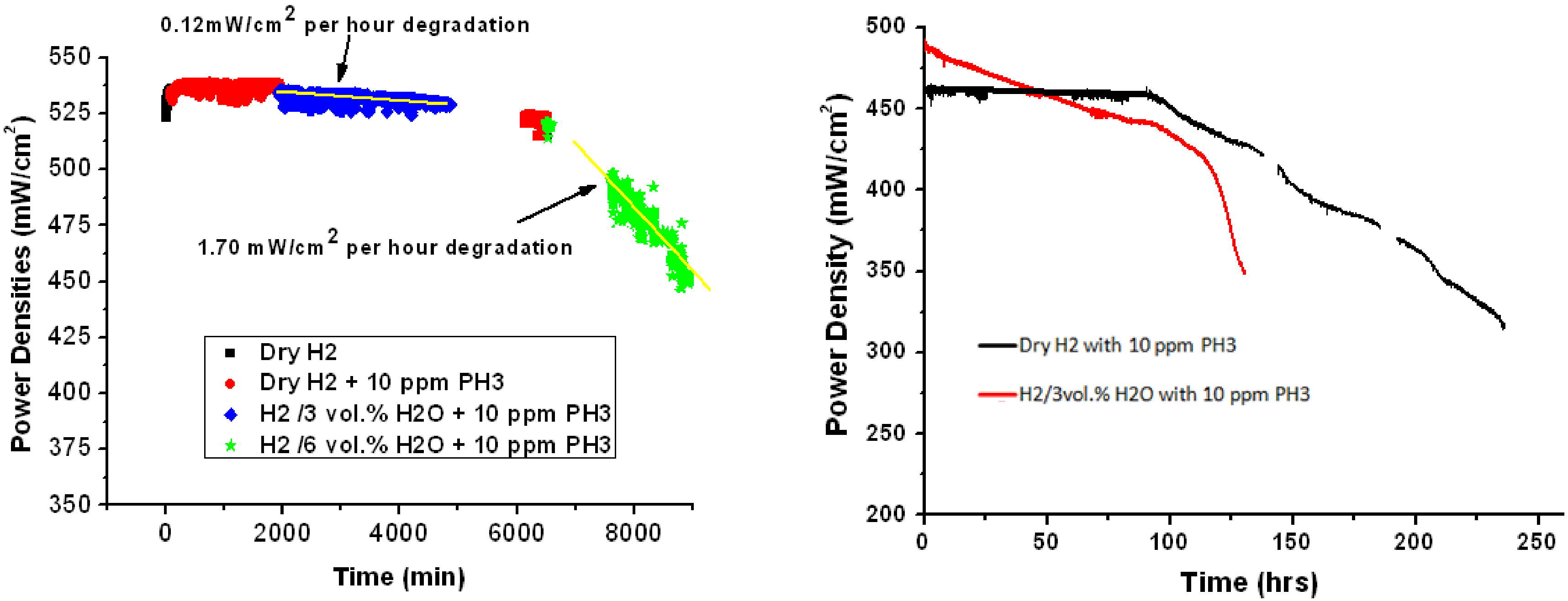
SEM analysis of SOFC anode after exposure to syngas plus 10 ppm phosphine for 250 hrs at 0.5 A/cm^2. Sample impregnated with polymer, cut and polished.



The nickel phase (the lighter gray area in the center) exhibits considerable pitting. Ni, C, P, and O elements detected in the pits.

PH3 Effects on SOFC Performance: Fuel Cell

Dry vs. Wet Conditions



Power density history under dry and wet H_2 + PH_3

- *Cell degrades immediately in H_2+3%H_2O with 10ppm of PH_3*
- *Cell performance remains stable in dry H_2+10ppm of PH_3 for about 4 days and then degrades slowly due to the formation of nickel phosphate*
- *The rapid failure at the later stage might be caused by substantial internal stresses in the Ni-free YSZ matrix due to the Ni migration and secondary phase stratification.*

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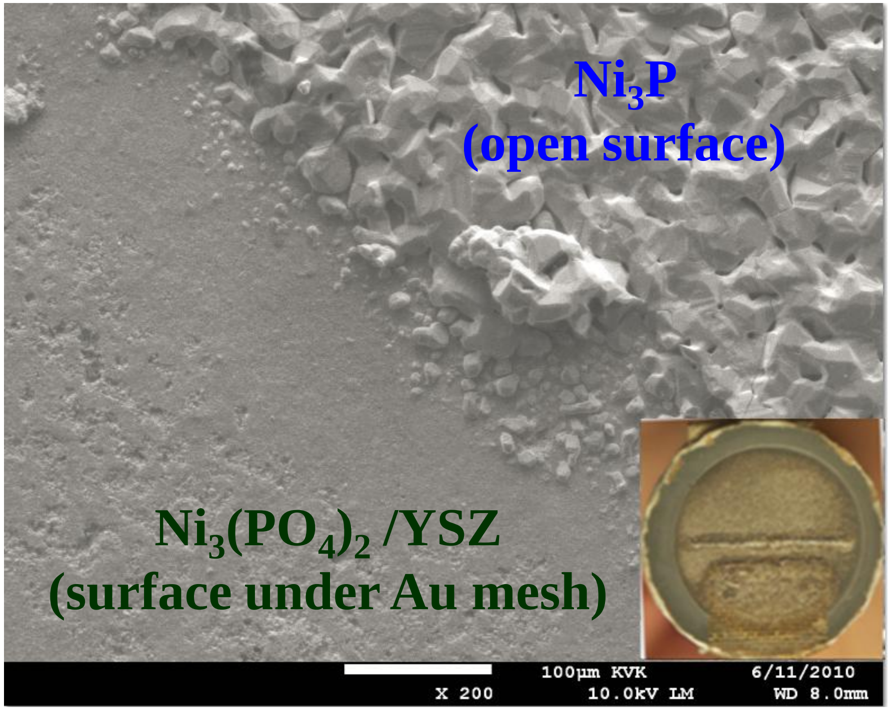
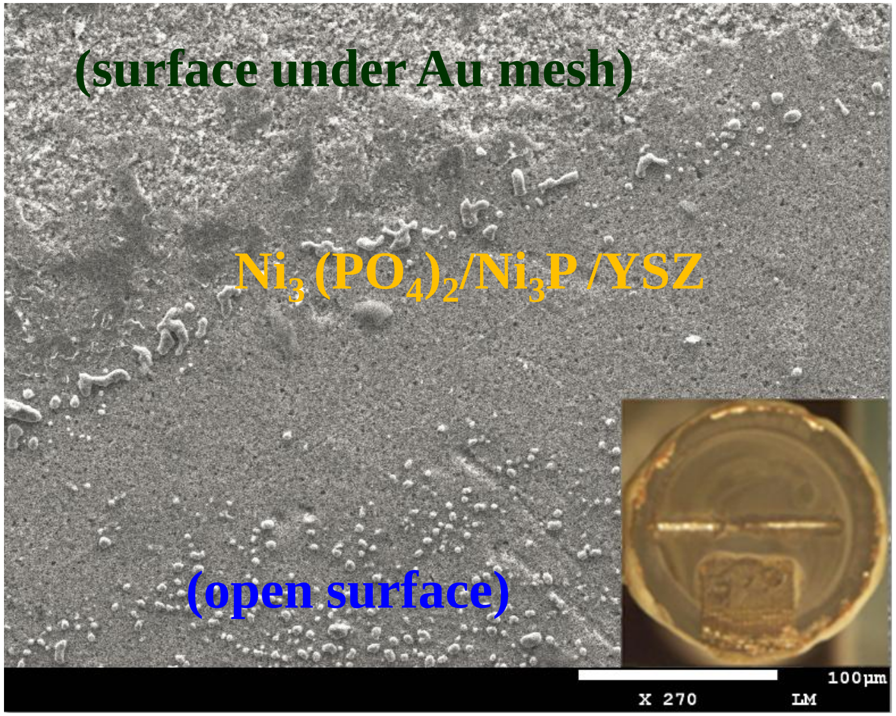
Surface Morphology Changes due to PH_3



PH_3+H_2/3 vol.%H_2O for 9 days



PH_3 + dry H_2 for 11 days

Steam accelerates the migration of Ni to the surface and reaction with Phosphorous

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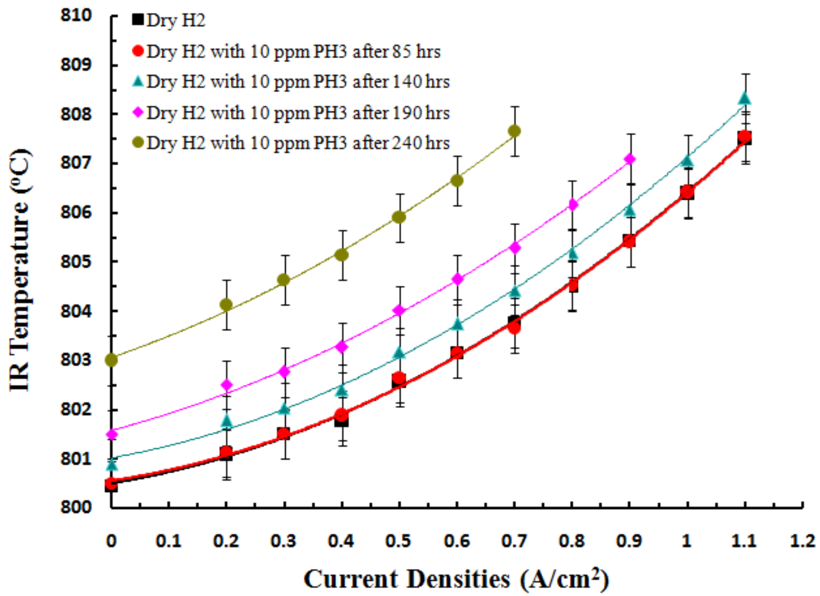
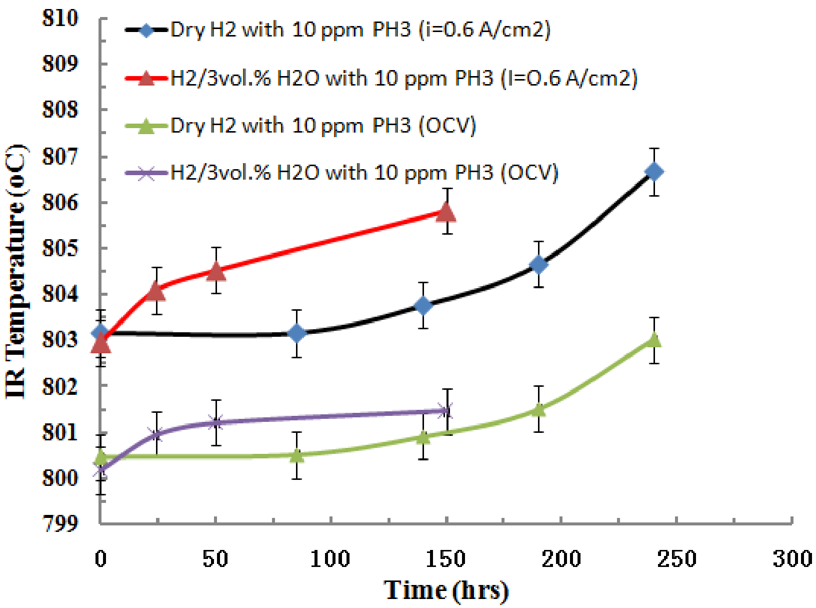
In-Situ Temperature Measuments

Temperature: Variation due to PH_3 Effects



Surface IR Emission Variation as a function of current density

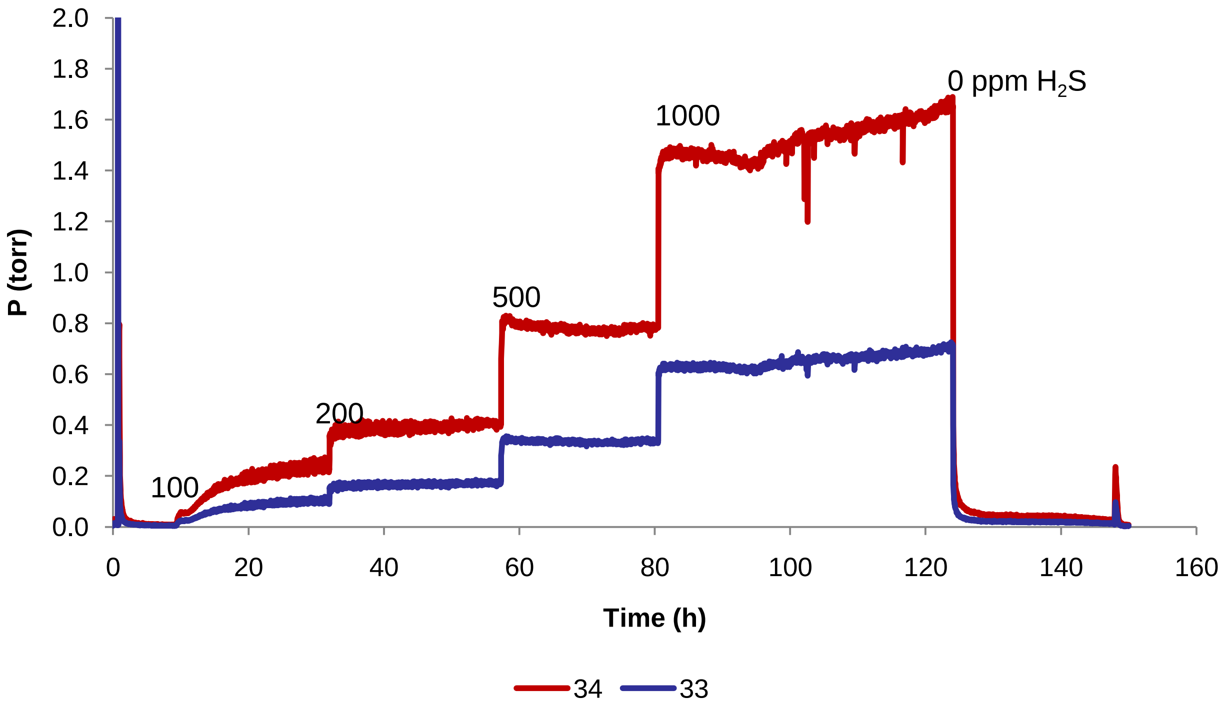


Surface IR Emission Variation under different test conditions

- *Analogous to the performance degradation history surface temperature remained stable initially and then increased with the polarization as the cell degraded.*
- *The button cell exposed to 10 ppm PH_3 in H_2/3 vol.% H_2O showed higher surface temperature, which may be attributed to its more severe secondary phase formation and cell electrochemical degradation.*
- *These results also support model validation efforts.*

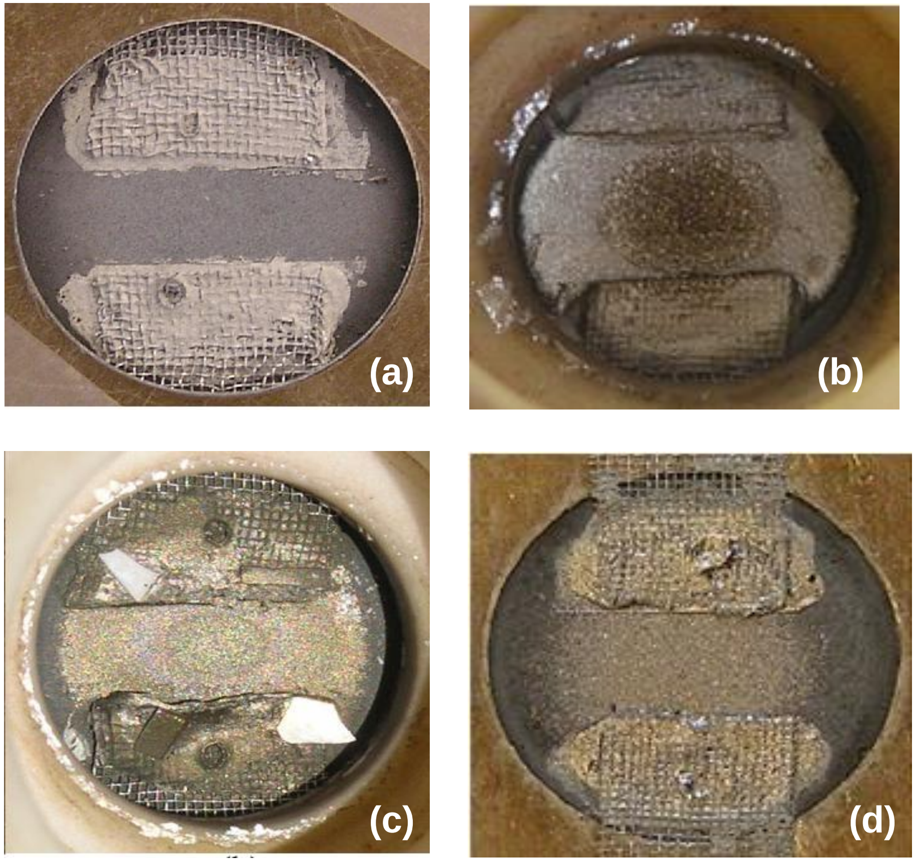
In-Situ Concentration Measurements

- Monitored inlet and exhaust gas stream with the mass spectrometer.
- Can track concentration changes in H_2S at the 10 – 1000 ppm level.
- Initial slow rise at low concentrations indicates adsorption of H_2S in the system.



Mass 34 (H_2S) and mass 33 (HS) track gas concentrations.

Poisoning effect of 10 ppm PH_3 in syngas fuel on Ni-YSZ anode



Post-mortem (a) clean syngas; PH3 poisoned cell anodes at (b) 750°C (c) 800°C and (d) 850°C.

The visible anode diameter is 2 cm. Ni phosphide was produced on the anode surface.

$$2PH_3\,(g) + 5Ni(s) = Ni_5P_2\,(s) + 3H_2\,(g)$$

$$\Delta G(1073\ K) = -\ 495.07\ kJ/mol$$

$$10PH_3\,(g) + 24Ni(s) = 2Ni_{12}P_5\,(s) + 15H_2(g)$$

*These experiments indicate that a **nickel-based filter** in front of the cell anode could reduce the PH_3 concentration on the Ni-YSZ anode surface and postpone its degradation.*

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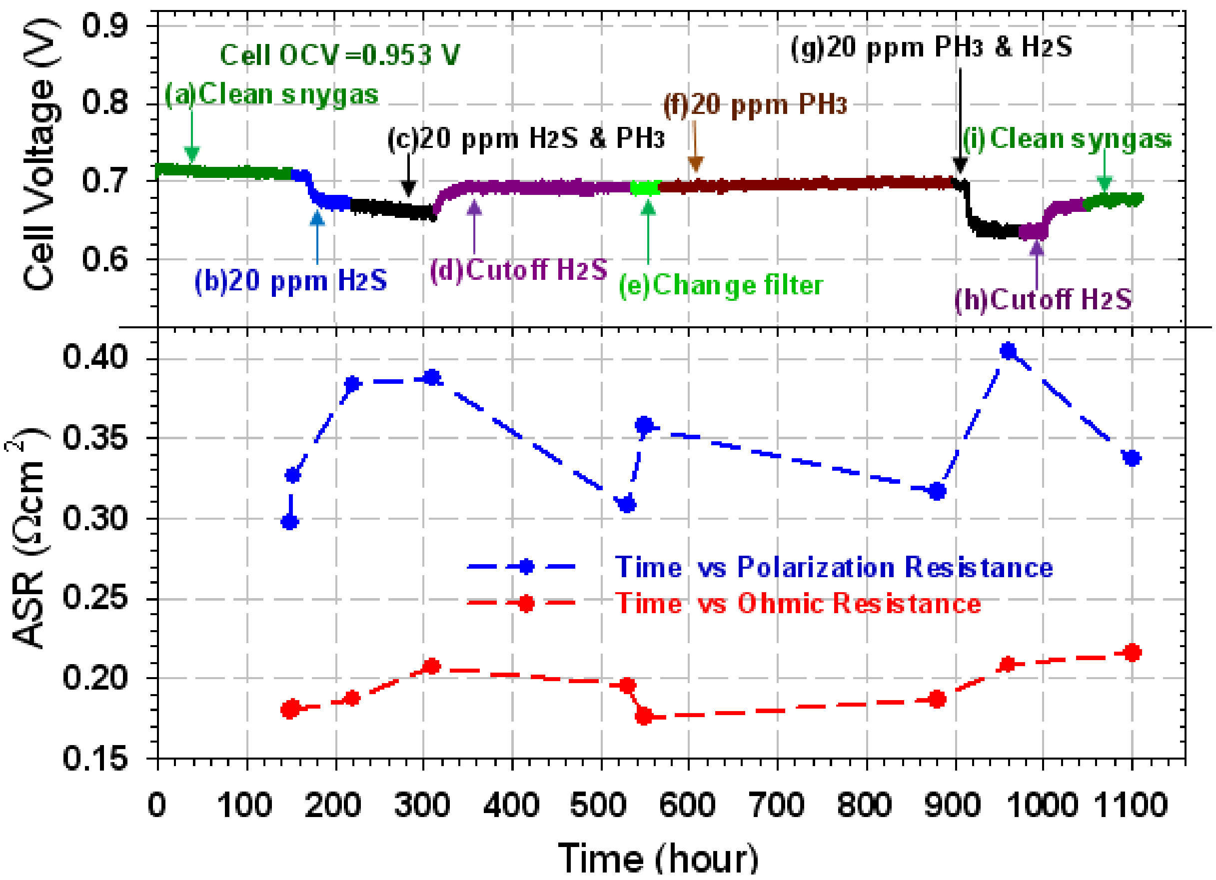
Ni and Ni/Fe Based Pre-filter for both H_2S and PH_3



1)Does H2S poison the PH3 filter?
Answer: No!

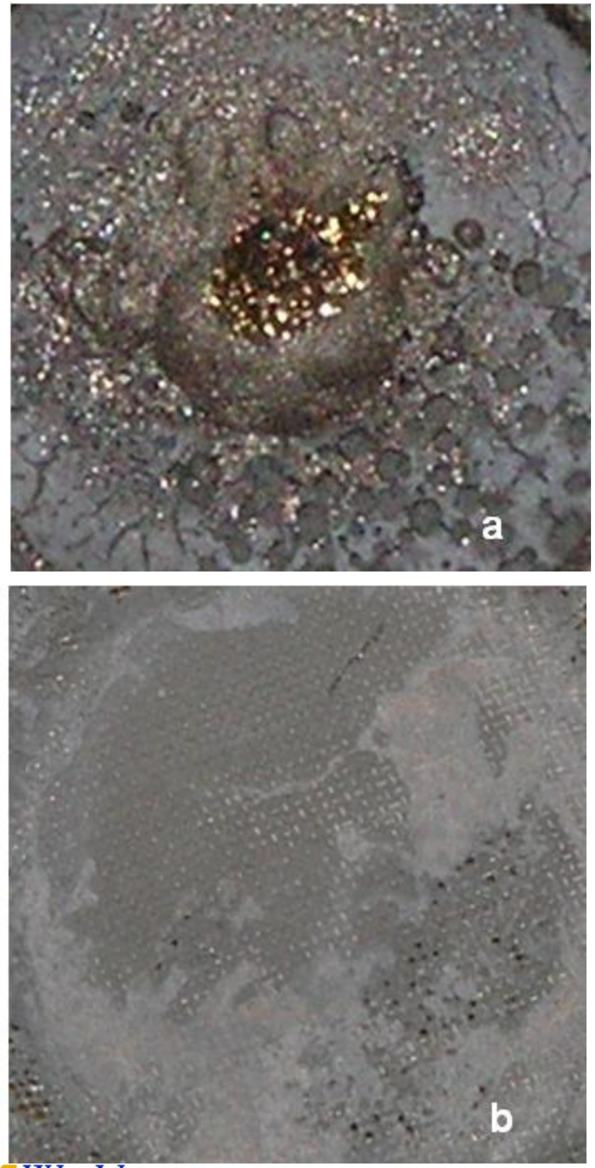
2) Does H2S poison the cell with the PH3 filter?
Answer: Yes!

3*) Solution:*
Develop an H2S tolerant anode.

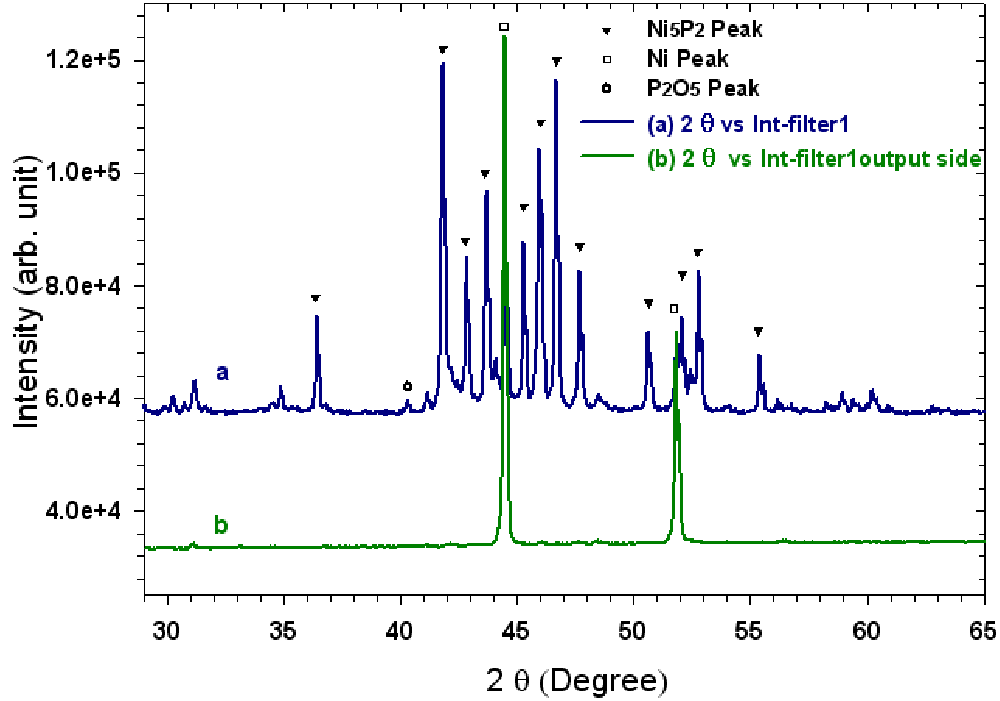
4*) The PH3 filter is also expected to remove As and Sb impurities which have the same chemistry as P.*

Performance of Ni-YSZ anode supported cell and its area specific resistances (ASR) in syngas with PH_3 and H_2S impurities. Current load = 0.5 A/cm^2

Characterization of PH_3 Poisoned Ni Based Pre-filter



(a) A photograph of the front face of the filter which was exposed to syngas with 10 ppm PH_3 for 200 h and (b) the backside of the same filter.



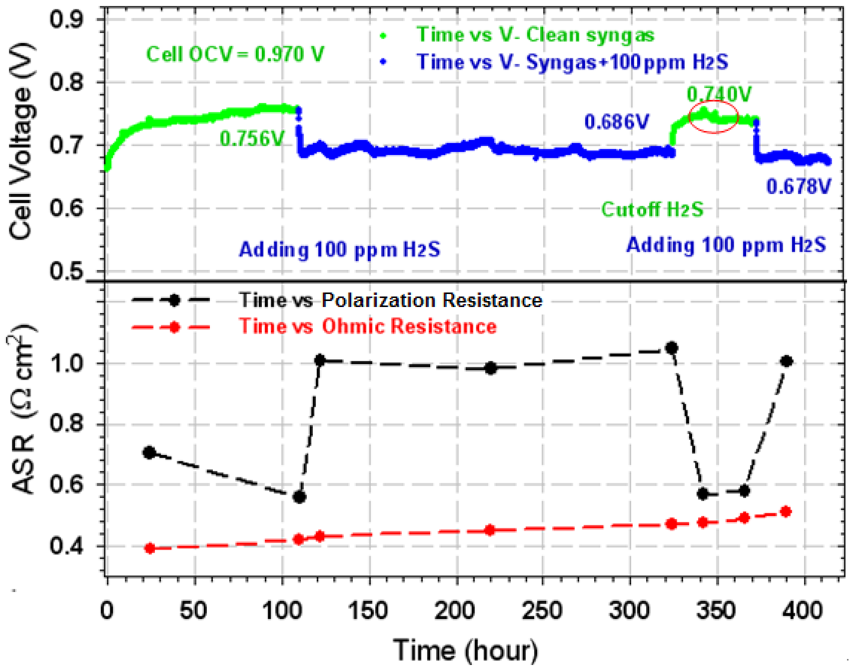
XRD spectra of the PH_3 poisoned filter (a) exposed surface and (b) backside.

Sulfur and Tolerant Anodes

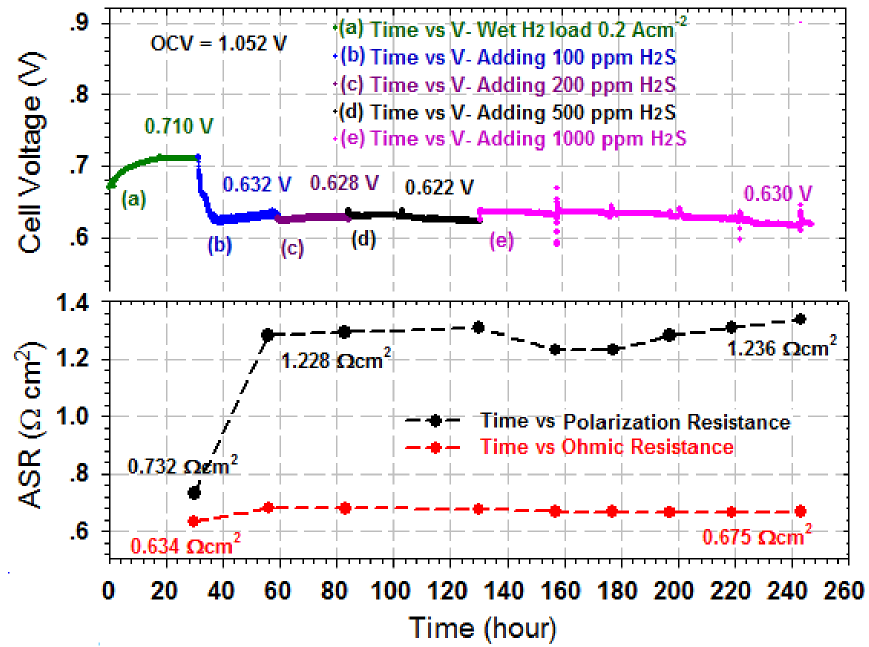
- Four strategies were explored for sulfur tolerant anodes
  - Ni-GDC anodes
  - SMM-GDC anodes
  - LDC impregnated Ni-YSZ anodes
  - LaO impregnated Ni-YSZ anodes

Sulfur tolerant Ni-GDC anode with a GDC barrier layer-1

Ni-GDC anodes showed tolerance to up to 1000 ppm H_2S for over 200 hours.

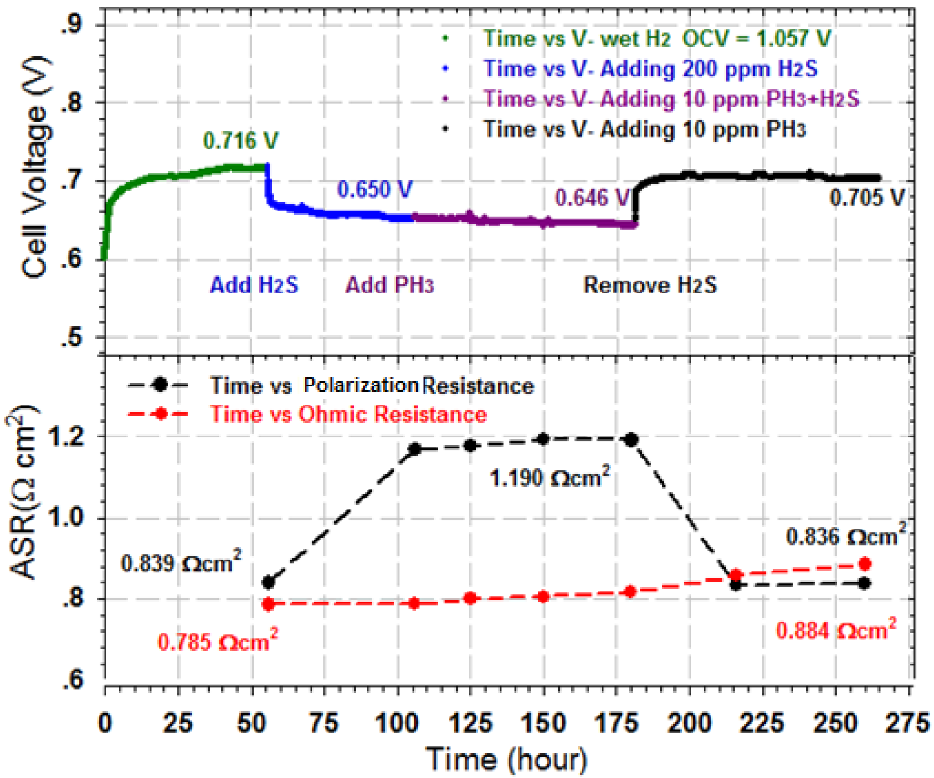


Performance of cell with Ni-GDC and GDC-10 barrier and ASR in clean syngas and syngas with 100 ppm H_2S.



Performance of cell with **Ni-GDC** and GDC-20 barrier and its ASR in H2+3% H_2O adding upto1000 ppm H_2S.

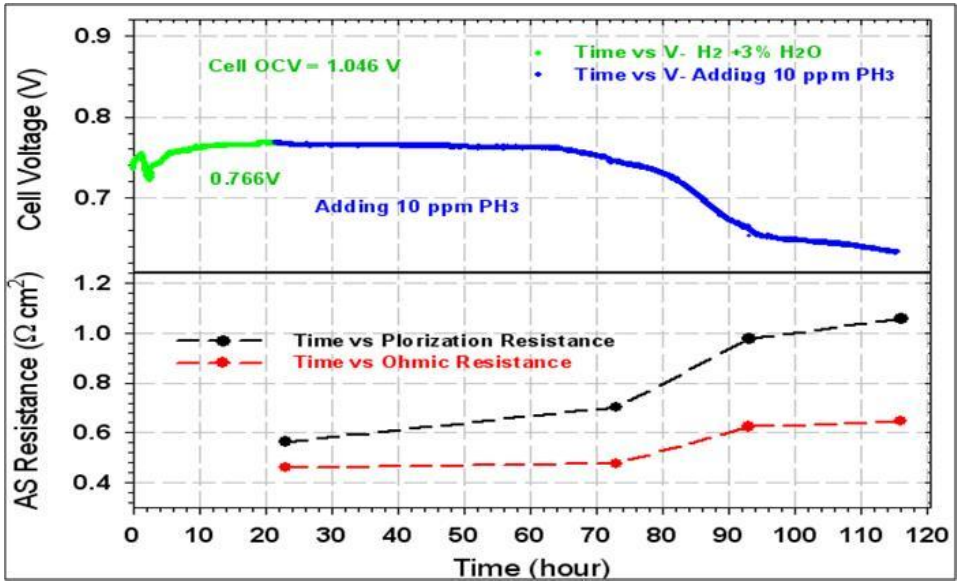
Combined H_2S and PH_3 tolerance test

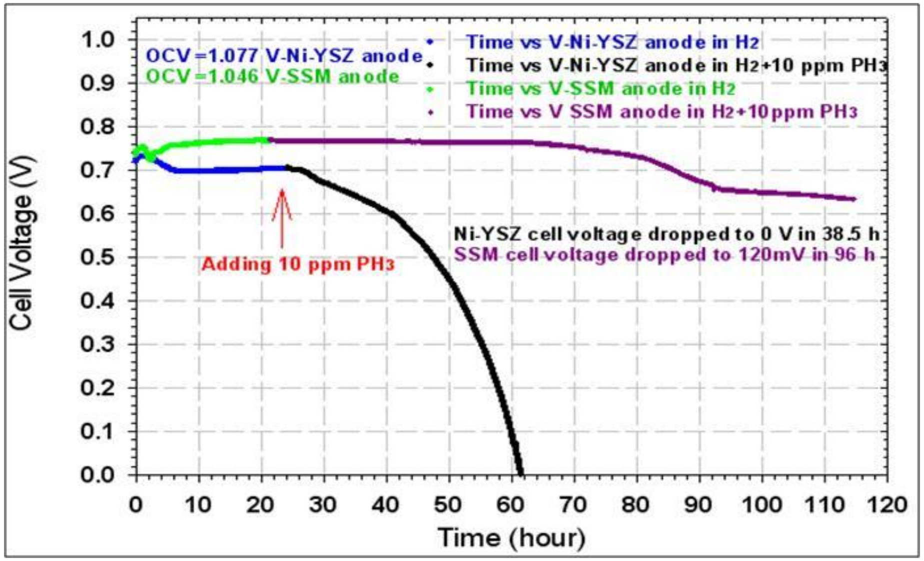


Performance and ASR of the Ni-GDC anode with a GDC barrier:

Filter H_2S (200 ppm) and PH_3 (10 ppm) in wet H_2. The filter prevented PH_3 attack and the anode resisted H_2S poisoning.

$Sr_2MgMoO_{6-\delta}$/GDC Anode in H_2 /10 ppm PH_3

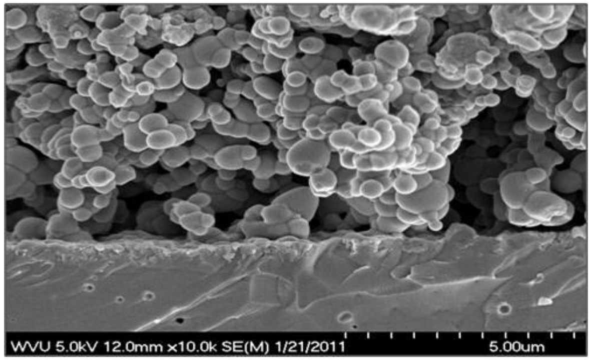


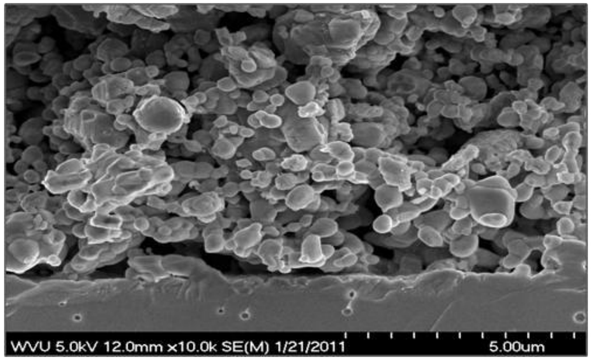


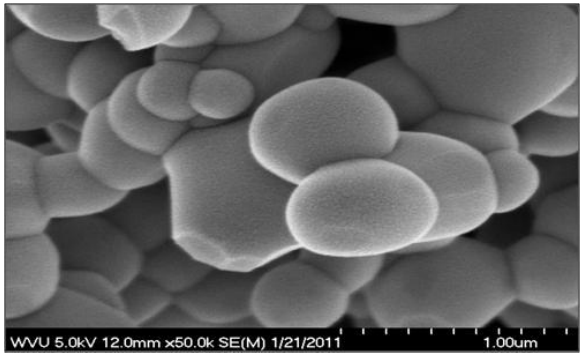
- *SMM/GDC anode exhibits better tolerance to PH_3 than the standard Ni/YSZ anode.*
- *Decrease in cell performance of almost 46% resulted from this long term exposure.*
- *SMM/GDC composite showed initial tolerance of 10 ppm PH_3 for upwards of 50 hours before a decrease in potential is observed.*

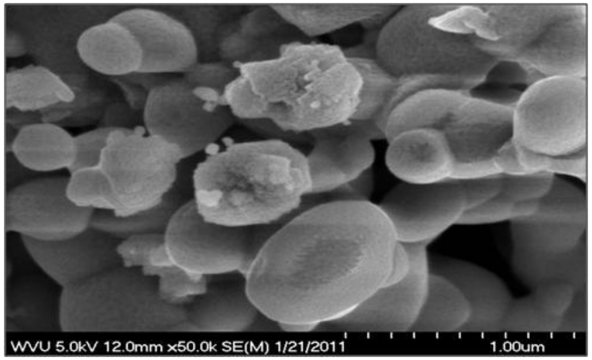
Post-Mortem Analysis of $Sr_2MgMoO_{6-\delta}$/GDC Anode-1

H_2 | H_2 w/ 10 ppm PH_3



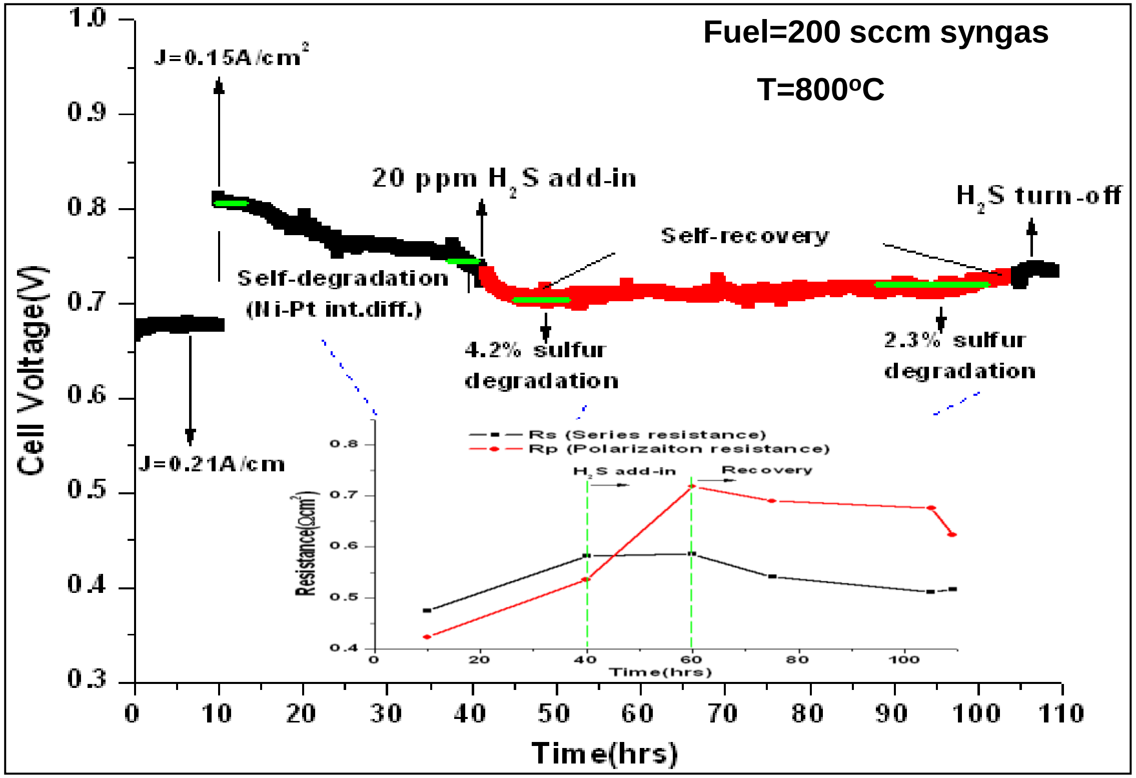






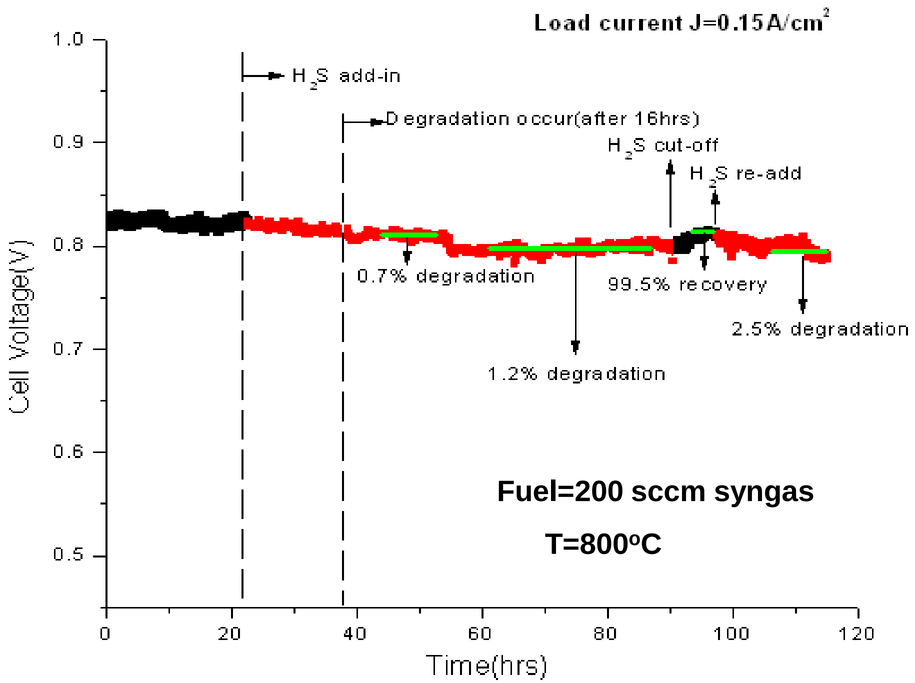
- *Changes to the microstructure before and after operation in PH_3 are minimal.*
- *Neither Densification of the electrode nor reaction of phosphorus with the anode or electrolyte constituents are apparent.*
- *The initial test in syngas shows stability for 20 hours which is promising for future studies.*

Sulfur tolerance of LDC impregnated Ni-YSZ anode



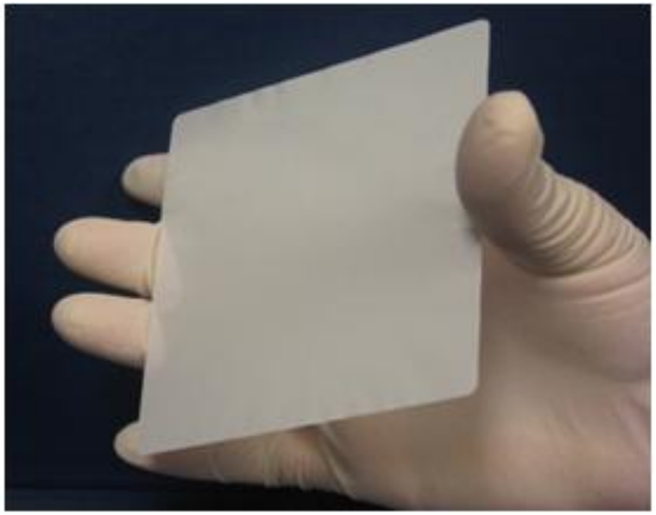
- *LDC exhibited resistance to H_2S for over 50 hours. The material shows promise for a sulfur tolerant anode*

Improve of sulfur tolerance with La-doped Ni-YSZ anode



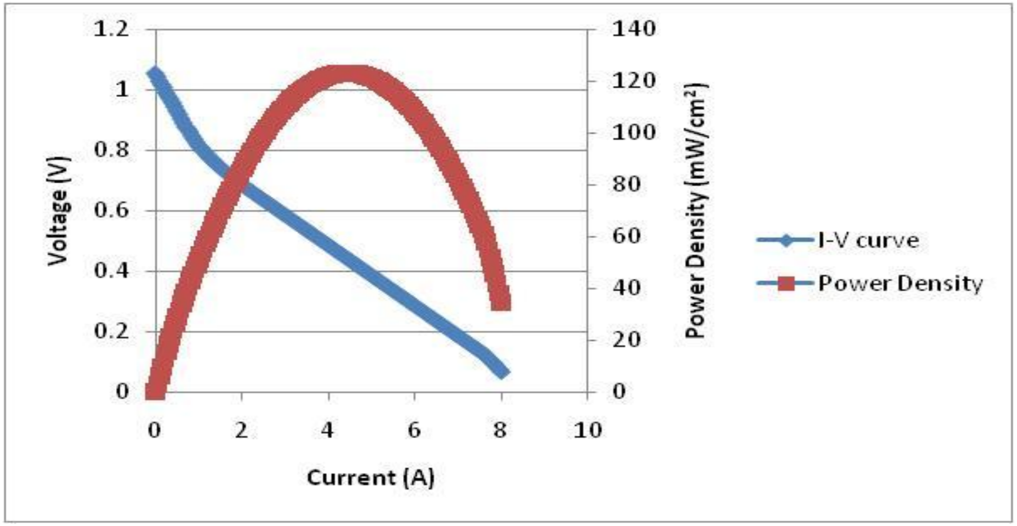
Pure La_2O_3-impregnated Ni anode showed less initial potential drop and slower degradation rate than LDC-impregnated anode

Testing Planar SOFCs in H_2S and PH_3 Laden Fuels



100 cm² electrolyte-supported SOFC fabricated at WVU

Ceramic and Haynes 242 Compressive Manifolds for 100 cm² Testing



Initial test in H_2 fuel at 750 C of a 16 cm² planar electrolyte-supported SOFCS fabricated at WVU

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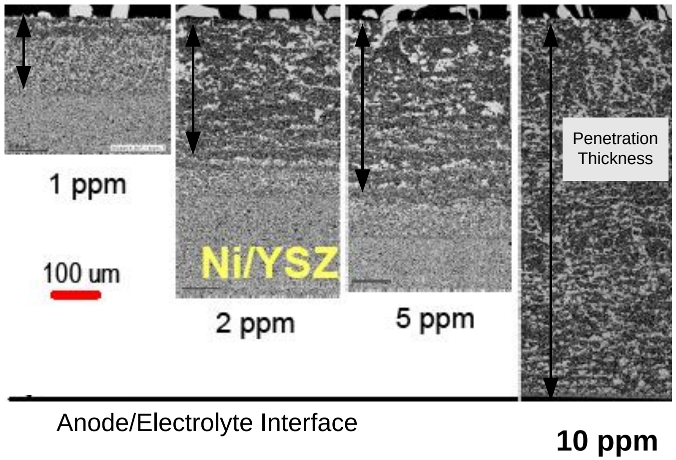
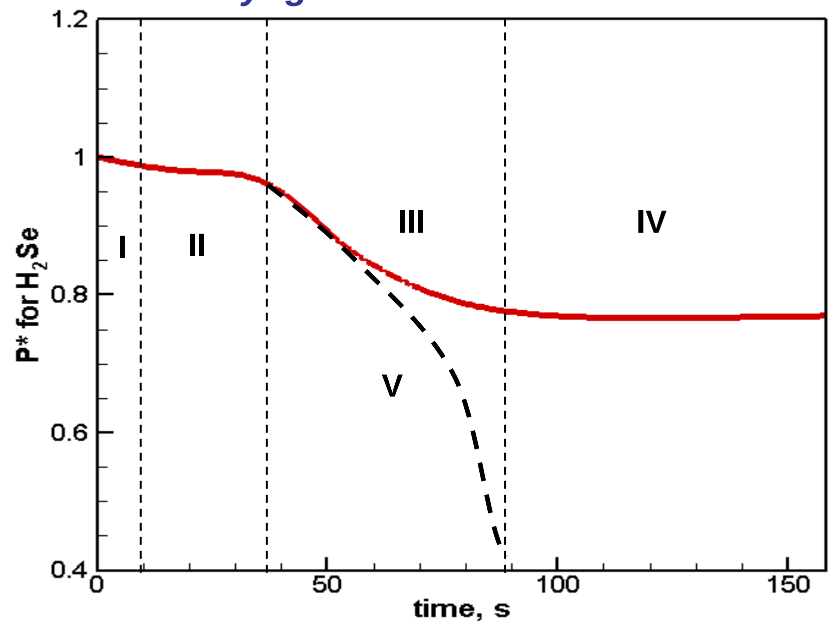
Contaminant Degradation Model

Penetration thickness after 990 h of exposure to PH_3 in coal syngas (PNNL)



Deposition starts near F/A interface and slowly moves toward the A/E interface

Typical degradation curve for 1 ppm H_2Se in coal syngas at 700 ℃



- **1-D Transport Equation for θ Propagation :**

$$\frac{\partial \theta_i}{\partial t} = D_\theta \frac{\partial^2 \theta_i}{\partial z^2} + \omega_{\theta_i}$$

θ_i **: progress variable**

D_θ **: transport coefficient**

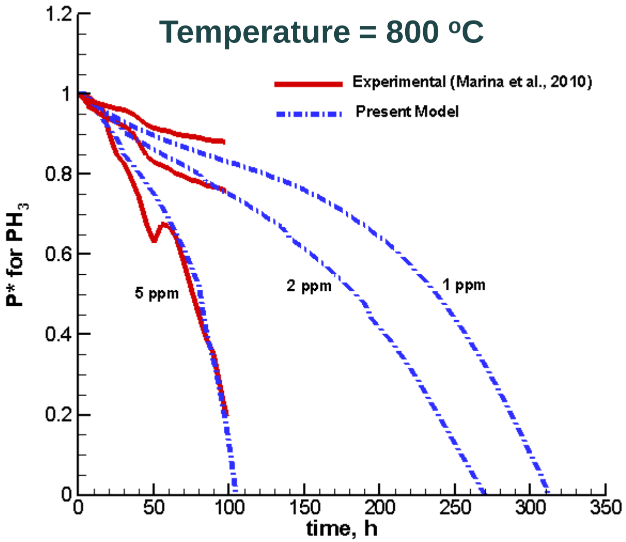
ω_{θ_i} **: source terms**

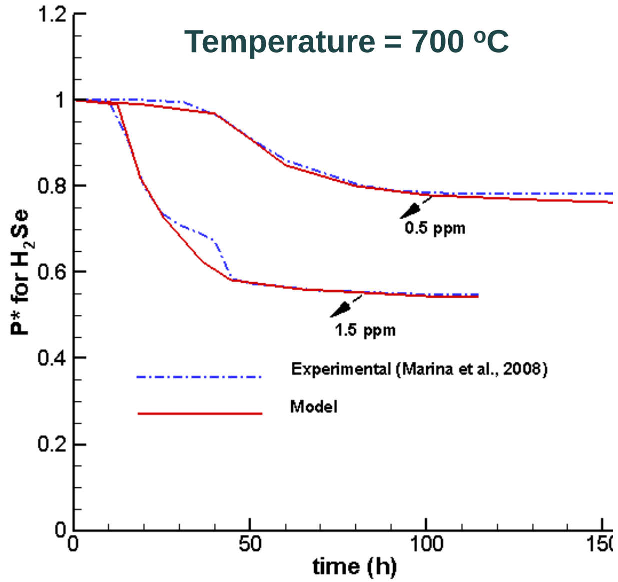
Four stages of degradation:

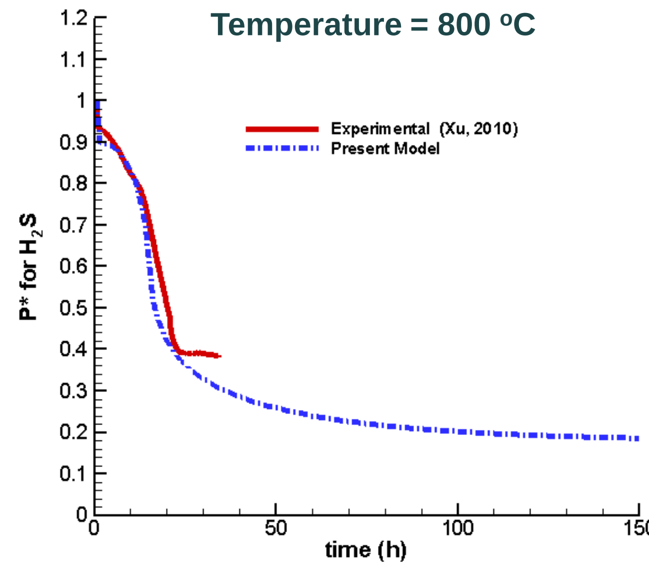
- **I** → **Initial performance drop**
- **II** → **Intermediate slow degradation**
- **III** → **Second fast degradation**
- **IV** → **Final slow degradation**
- **V** → **Structural failure and/or rapid degradation**

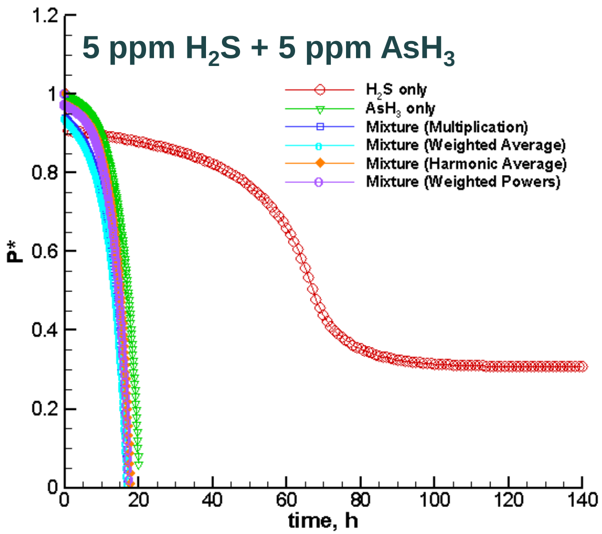
Degradation stages correspond to extent of impurity Penetration !

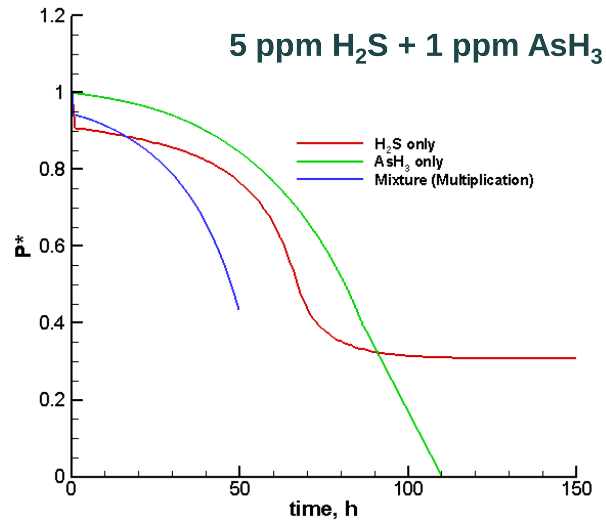
Model Predictions





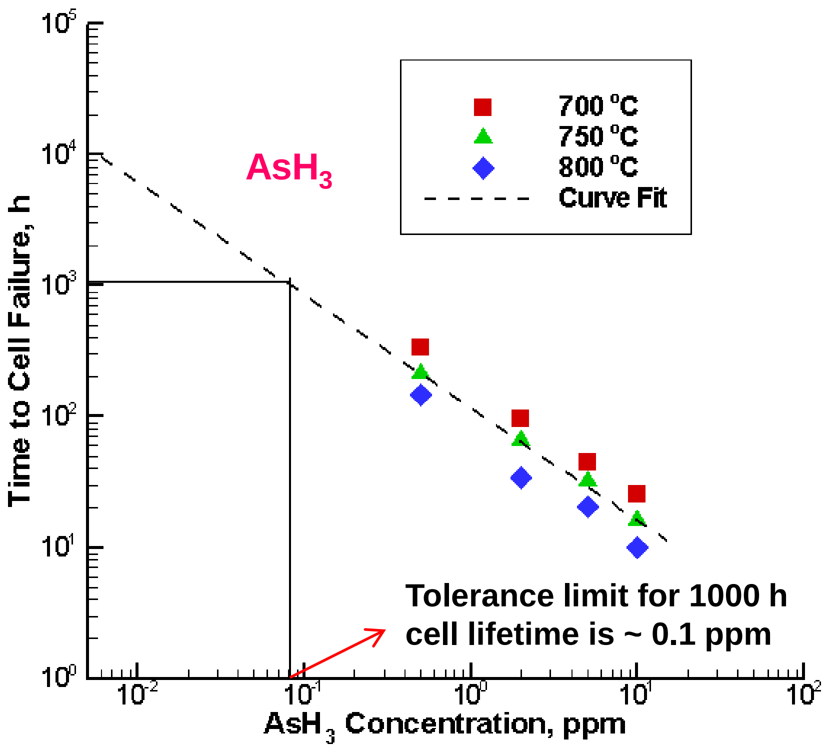


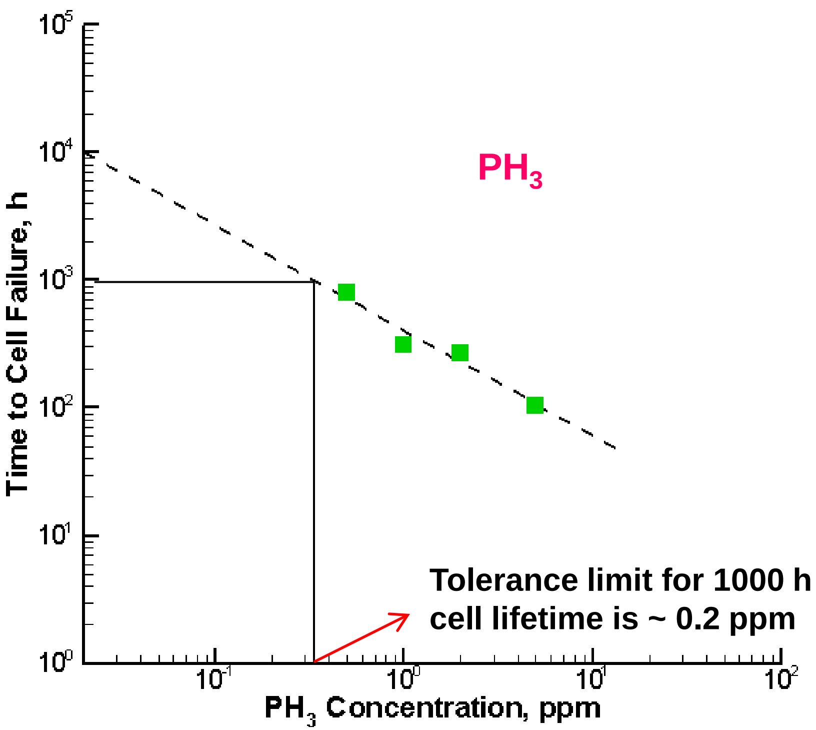




Modeling: Cell Lifetime and Tolerance Limits

Cell failure is taken as when performance reduces by 60%





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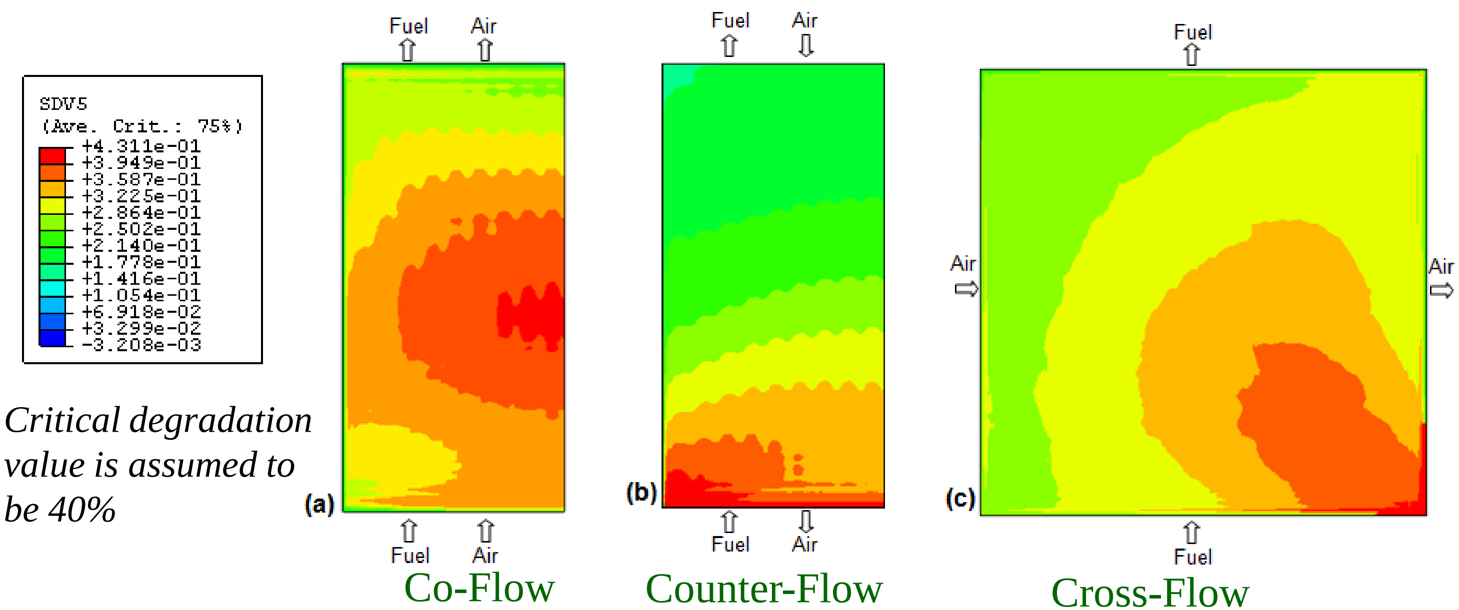
Structural Degradation: Effect of Impurities

Planar-SOFC Anode Structure Failure Locations



Critical degradation value is assumed to be 40%

Anode structural degradation in anode under 5ppm of PH_3, inlet temp. 800^{o}C and 20 A (a) 19,917 h (b) 16,310 h (c) 1,8450 h

Co-flow arrangement yields longest anode structural life prediction as compared to the other two configurations under similar operating conditions

At low impurity concentrations structural degradation may be more important than electrochemical degradation

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Conclusions – 1

- TEM characterization revealed new nano-scale phenomena in the SOFC anodes exposed to impurities.
- Determined that 10 ppm PH_3 in wet H_2 fuel leads to faster degradation when compared to dry fuel condition.
- Measured surface temperature of button cells under different operating conditions using new in-situ technique.
- A mass spectrometer was used to monitor in-situ forms of impurity species and their concentrations, before and after passing through the furnace.
- Ni and Fe based filters are shown to remove PH_3 impurity effectively from syngas.
- The mechanism responsible for sulfur tolerance of LDC impregnated anodes was studied and Ni/GDC anode was shown to be a suitable material for syngas contaminated with H_2S.

Conclusions – 2

- New SMM/GDC anodes were prepared in-house and are shown to be tolerant to PH_3 in syngas.
- Numerical simulations showed that the co-flow arrangement in a planar SOFC resulted in longest structural life compared to counter-flow and cross-flow arrangements.
- Model results revealed that, at low PH_3 levels, the anode structural degradation may be as significant as electrochemical degradation.
- A new phenomenological degradation model was developed and used to study cell lifetimes and tolerance limits for impurities.
- The synergistic effects of multiple impurities were simulated including H_2S, AsH_3 and PH_3.
- The in-house SOFC code was modified to simulate button cells operating on biogas.

Thank you

Recent Publications

1. H. Guo, G. Iqbal, and B. S. Kang (2011) “Effects of PH3 Contaminant on SOFC Performance and Related Anode Surface Temperature Measurements,” International Journal of Applied Ceramic Technology, v. 8, p. 68-73.
2. D. Ding, M. Gong, C. Xu, N. Baxter, Y. Li , J. Zondlo, K. Gerdes, X. Liu (2011) "Electrochemical Characteristics of Samaria-Doped Ceria Infiltrated Strontium-Doped LaMnO3 Cathodes with Varied Thickness for Yttria-Stabilized Zirconia Electrolytes” Journal of Power Sources, v. 196, 2551-2557.
3. C. Xu, J. Zondlo, M. Gong, F. Elizalde-Blancas, X. Liu, I.B. Celik (2010) “Tolerance Tests of H2S-laden Biogas Fuel on Solid Oxide Fuel Cells” Journal of Power Sources v.195 , p. 4583-4592.
4. C. Xu, J. Zondlo, M. Gong, X.Liu, (2011) "Effects of PH3 poisoning on a Ni-YSZ anode-supported SOFC under various operation conditions”, Journal of Power Sources, v. 196, p. 116-125.
5. Fatma N. Cayan , Suryanarayana R. Pakalapati, Ismail Celik, Chunchuan Xu and John Zondlo (2011) "A Degradation Model for Solid Oxide Fuel Cell Anodes due to Impurities in Coal Syngas: Part I. Theory and Validation", submitted to Fuel Cells.
6. Chunchuan Xu, John Zondlo, Edward Sabolsky, “A prefilter for mitigating PH3 contamination of a Ni-YSZ anode” Journal of Power Sources, accepted for publication.
7. Huang Guo, Gulfam Iqbal, and Bruce S. Kang, “Investigation of Secondary Phases Formation due to PH3 Interaction with SOFC Anode,” American Society Ceramics Transaction, accepted for publication.
8. Gulfam Iqbal, Raju Pakalapati, Huang Guo, Ismail Celik, and Bruce Kang, “PEN Structure Thermal Stress Analysis for Planar-SOFC Configurations,” American Society Ceramics Transaction, accepted for publication.
9. Gulfam Iqbal, and B.S. Kang, “Elastic Brittle Damage Model for Ni-YSZ and Predicted Stress-Strain Relations as a Function of Temperature and Porosity,” ASME Journal of Fuel Cell Sciences and Technology, Accepted for publication (2011)
10. F. Elizalde-Blancas, S. R. Pakalapati, F. N. Cayan, C. Xu, I. B. Celik, H. O. Finklea, J. W. Zondlo, "A Computational Model for SOFC Running on Syngas” submitted to Journal of Power Sources.
11. Y. Chen, S. Chen, H. Finklea, X. Song, G. Hackett, K. Gerdes, “Microstructure and chemistry evolution of triple phase boundaries in the anode of solid oxide fuel cells”, submitted to Solid State Ionic.

Supplementary Slides

Performance Degradation due to PH_3

Ni-YSZ anode after being exposed to PH_3 in various conditions

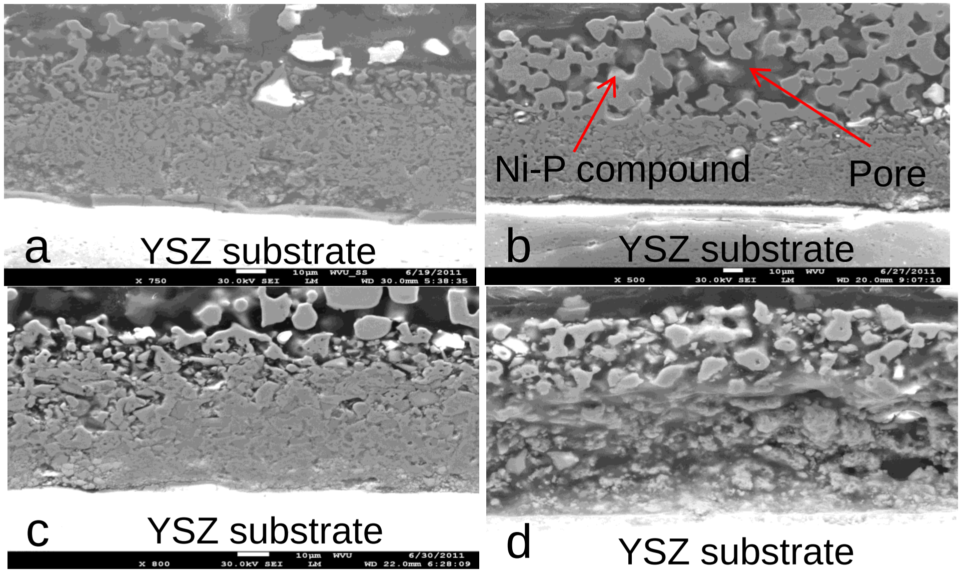


Fig.5. SEM images of the Ni-YSZ working electrode cross section

a. Clean syngas,

b. 5 ppm PH_3 for 24 hrs with current density of 0.25A/cm^2,

c. 5 ppm PH_3 for 24 hrs without current loading,

d. 5 ppm PH_3 for 24 hrs dry syngas

- *The half-cell operated with current loading shows (Fig.5b&c) more aggregates to big particles compared to cell w/o curremt.*
- *The anode operated with 5 ppm PH3 in dry coal syngas exhibits more severe agglomeration.*

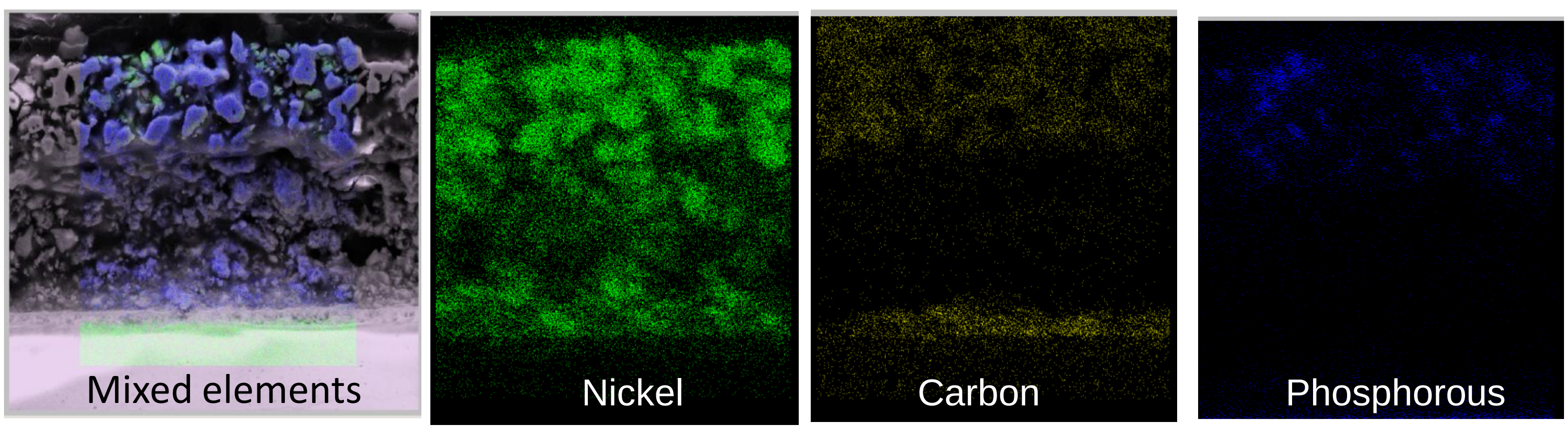
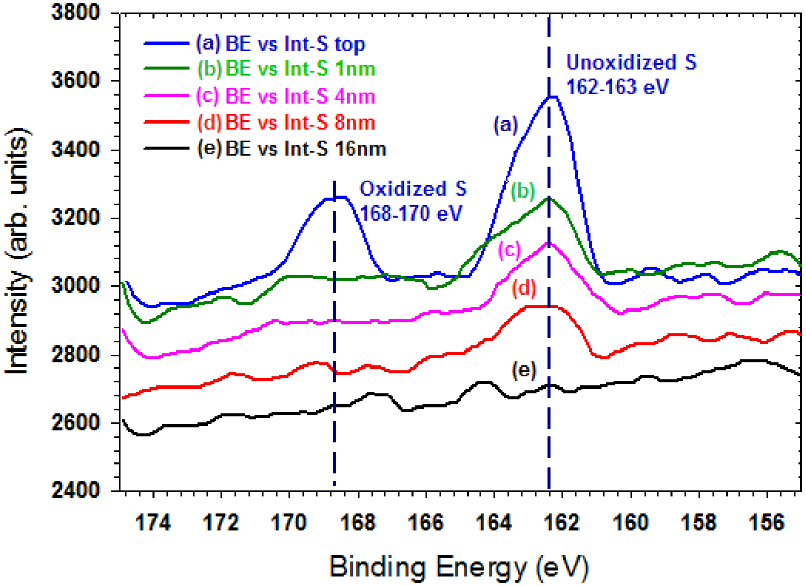


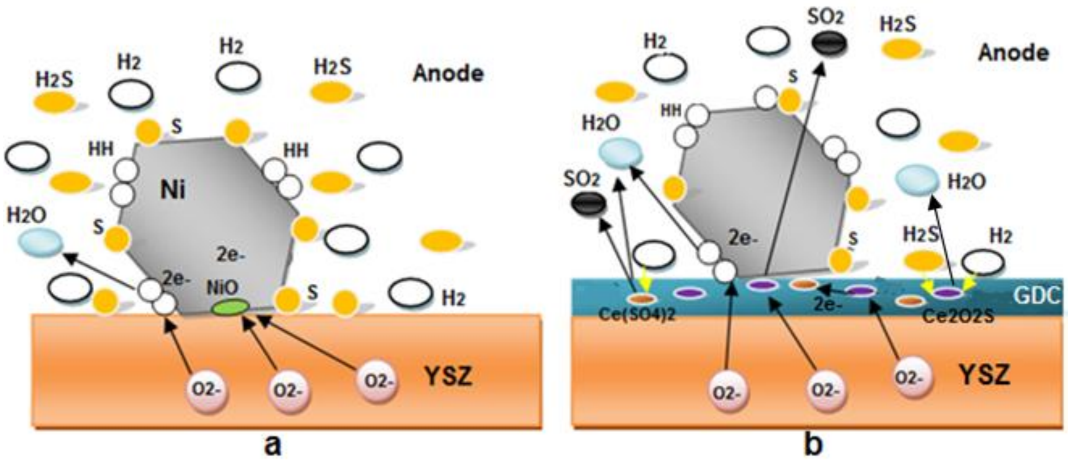
Fig.5. EDS mapping on the cross section of the Ni/YSZ anode after being exposed to 5 ppm PH_3 for 24 hrs without steam

Sulfur tolerant Ni-GDC anode with a GDC barrier layer-2



The depth profile of XPS spectra on the Ni surface of the H_2S poisoned cell.

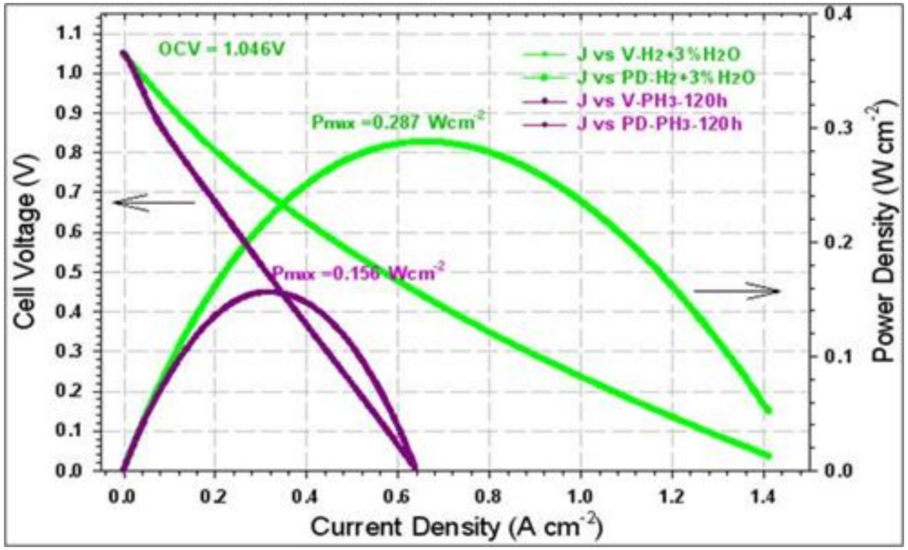
The oxidized S peak at 169-170 eV is only significant on the top Ni surface. The unoxidized S peak is detectable at 8 nm depth from the Ni surface.

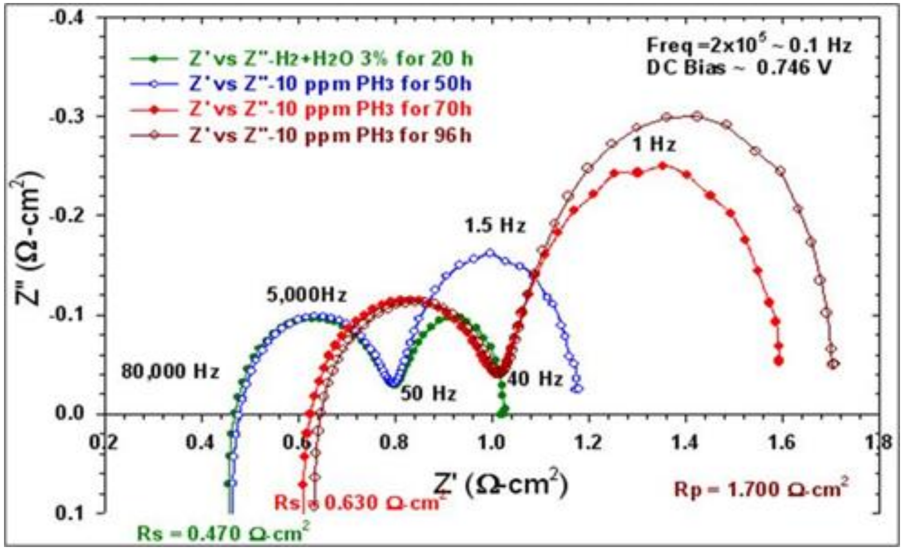


A conceptualization of the cell anode and electrolyte active interface

(a) The Ni is slowly oxidized by O^{2-} at the active interface and
(b) The GDC layer is suppressing the NiO formation at the active interface.

$Sr_2MgMoO_{6-\delta}$/GDC Anode in H_2 /10 ppm PH_3

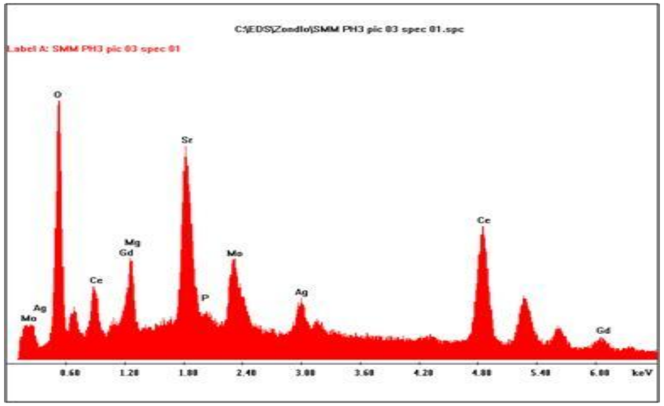


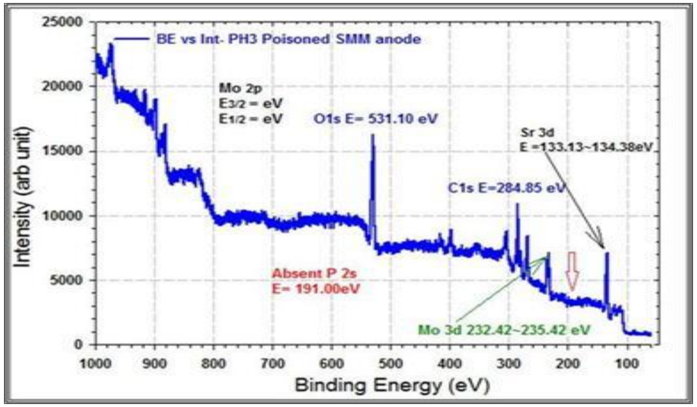


- Results show promise for development of a H_2S and PH_3 tolerant anode.
- Better understanding of interaction of H_2/PH_3 fuel at various loadings is required for further development.

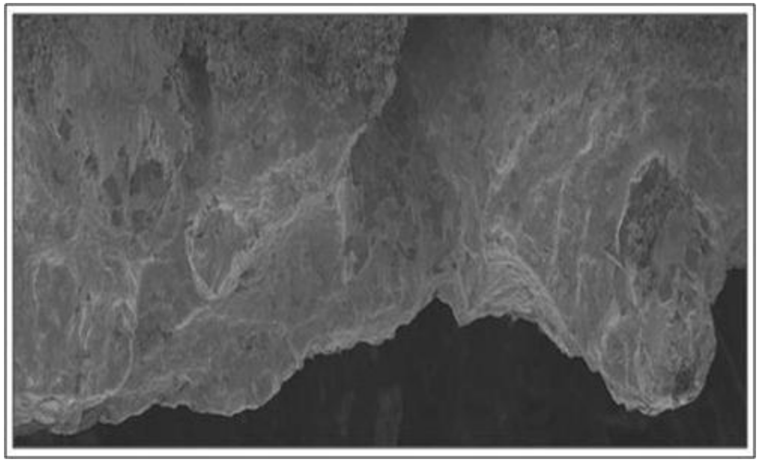
- No change in Ohmic resistance after 50 hours.
- Ohmic and polarization resistance increases after 100 hours.
- Failure of Pt interconnection is one key issue.

Post-Mortem Analysis of $Sr_2MgMoO_{6-\delta}$/GDC Anode-2





- EDS analysis detected a slight presence of phosphorus at the interface.

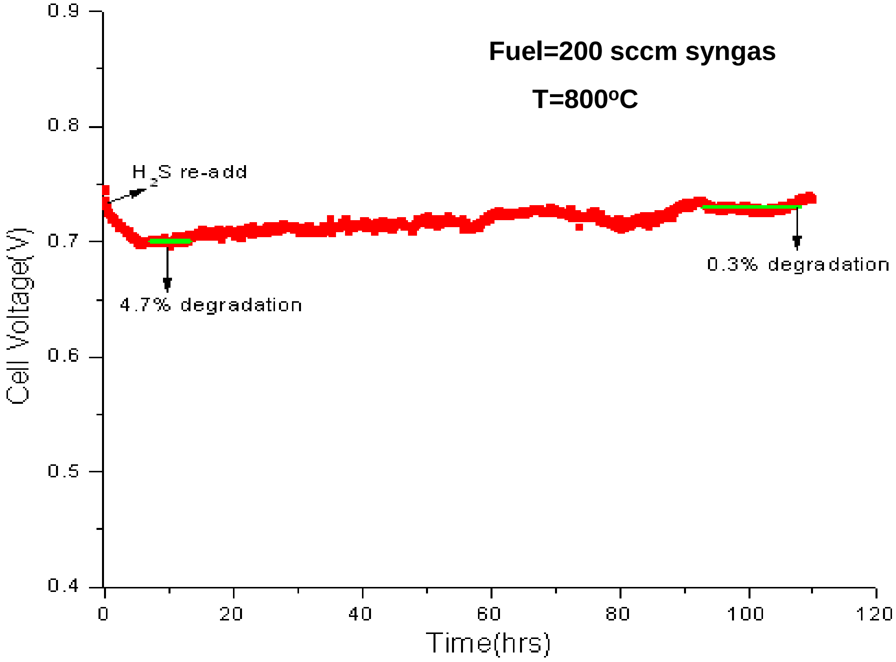


SEM image of the Pt paste

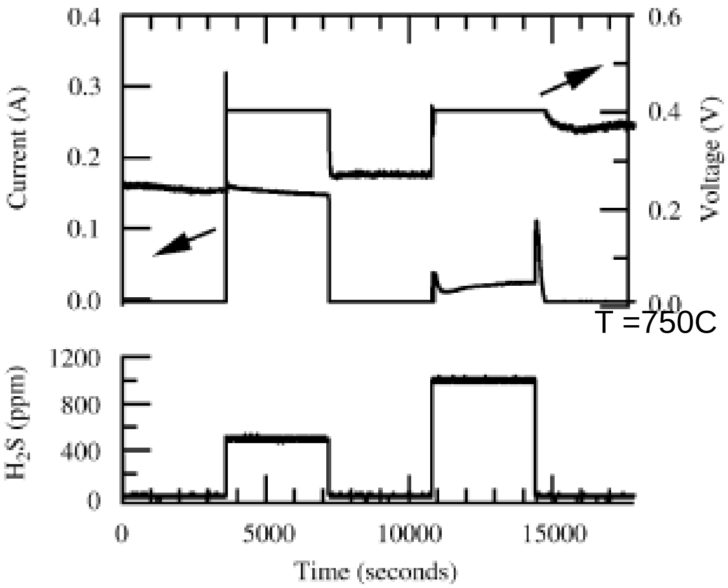
•Pt densification may be the cause for increase in cell polarization.

Recovery of LDC impregnated Ni-YSZ anode

Verification of recovery mechanism with Ni-GDC anode and further sulfur exposure



Our results with LDC impregnation

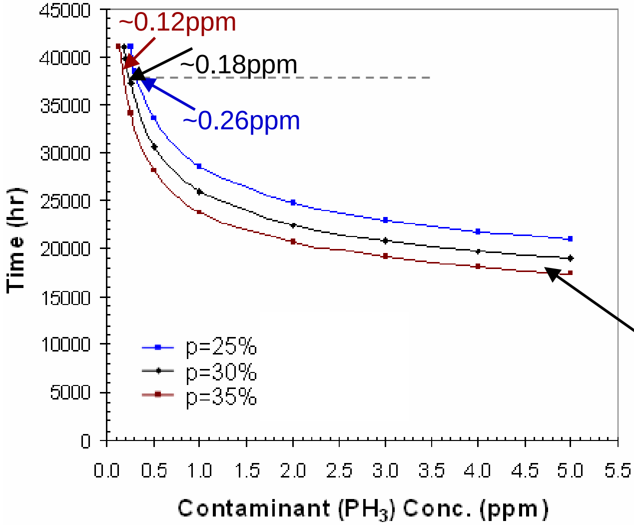


A.Lussier, S.Soffier,J.Dvorak, Y.Idzerda. Int.J.Hydr.Energy,2008

Literature data with GDC impregnation

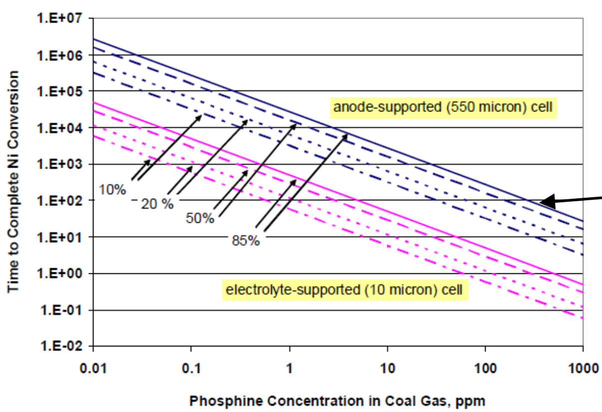
Structural Degradation: Effect of Impurities

Anode Structural Life: Electrochemical vs. Structural Degradation

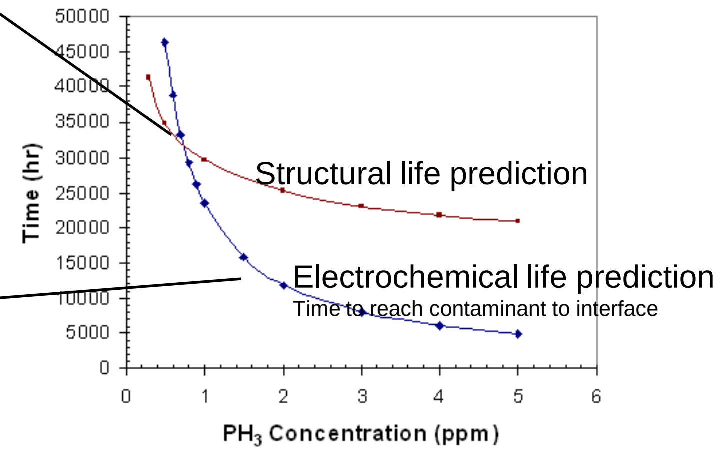


Acceptable limit of PH_3 contaminant for specified anode structural life

- *Anode structural life increases exponentially with the decrease in the contaminant concentration*
- *Under lower concentration of contaminant, the anode structural degradation may be significant as compared to electrochemical degradation*



Penetration depth of PH_3 under different concentration[1]



Comparison of predicted anode structural life and time required the contaminant reached the interface

[1] O.A. Marina et al. 9th Annual SECA Workshop, August 2008, Pittsburgh, PA