Progress in Coal Syngas Contaminants Study at West Virginia University

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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 PH₃ on the Microstructure (TEM)

SOFC operated in syngas with 10ppm PH₃ for 100 h

(II). Formation of Y-P-O phase at Ni/YSZ interface
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.
Anode half-cell test: (a) in dry and water containing condition; (b) with and without current loading; T = 800 °C

Example impedance spectrum taken from a half cell operated at 0.25A/cm² in wet coal-syngas with 5 ppm PH₃.
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.
The increase in activation polarization impedance is larger with current loading than that without current loading.

**Performance Degradation due to PH$_3$**

Cell operation with and without current in wet syngas

- OC impedance, operated without current
- OC impedance, operated with current
- Impedance measured at current

Density of 0.25 A/cm$^2$, operated without current
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 $\text{PH}_3$ 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

**Cell degrades immediately in** \( H_2 + 3\% H_2O \) **with 10ppm of PH3**

**Cell performance remains stable in** dry \( H_2 + 10\text{ppm of PH}_3 \) **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.**
Surface Morphology Changes due to PH$_3$

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

PH$_3$ + H$_2$/3 vol.% H$_2$O for 9 days

PH$_3$ + dry H$_2$ for 11 days
Surface IR Emission Variation as a function of current density

- 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$_2$O 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$_2$S at the 10 – 1000 ppm level.
- Initial slow rise at low concentrations indicates adsorption of H$_2$S in the system.

Mass 34 (H$_2$S) 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; PH$_3$ 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.

\[
2 \text{PH}_3 (g) + 5 \text{Ni(s)} = \text{Ni}_5 \text{P}_2 (s) +3 \text{H}_2 (g) \\
\Delta G(1073 \text{ K}) = - 495.07 \text{ kJ/mol} \\
10 \text{PH}_3 (g) +24 \text{Ni(s)} = 2\text{Ni}_{12}\text{P}_5 (s) +15\text{H}_2(g)
\]

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.
1) Does H$_2$S poison the PH$_3$ filter?
   Answer: No!

2) Does H$_2$S poison the cell with the PH$_3$ filter?
   Answer: Yes!

3) **Solution:**
   Develop an H$_2$S tolerant anode.

4) The PH$_3$ 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$_2$S 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$_2$S 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$_2$S.

Performance of cell with Ni-GDC and GDC-20 barrier and its ASR in H$_2$+3% H$_2$O adding up to 1000 ppm H$_2$S.
Performance and ASR of the Ni-GDC anode with a GDC barrier:

*Filter H₂S (200 ppm) and PH₃ (10 ppm) in wet H₂. The filter prevented PH₃ attack and the anode resisted H₂S poisoning.*
Sr$_2$MgMoO$_{6-\delta}$/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$_2$MgMoO$_{6-\delta}$/GDC Anode-1

- 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 $\text{H}_2\text{S}$ for over 50 hours. The material shows promise for a sulfur tolerant anode.
Improve of sulfur tolerance with La-doped Ni-YSZ anode

Fuel=200 sccm syngas

T=800°C

Load current J=0.15A/cm²

Fuel=200 sccm syngas

T=800°C

Pure La₂O₃-impregnated Ni anode showed less initial potential drop and slower degradation rate than LDC-impregnated anode
Testing Planar SOFCs in H₂S and PH₃ Laden Fuels

100 cm² electrolyte-supported SOFC fabricated at WVU

Ceramic and Haynes 242 Compressive Manifolds for 100 cm² Testing

Initial test in H₂ fuel at 750 C of a 16 cm² planar electrolyte-supported SOFCs fabricated at WVU
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

- 1-D Transport Equation for $\theta$ Propagation:

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

$\theta_i$: progress variable

$D_\theta$: transport coefficient

$\omega_{\theta_i}$: source terms

Degradation stages correspond to extent of impurity Penetration!

Typical degradation curve for 1 ppm H$_2$Se in coal syngas at 700 °C

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
Temperature = 800 °C

5 ppm H₂S + 5 ppm AsH₃

5 ppm H₂S + 1 ppm AsH₃
Cell failure is taken as when performance reduces by 60%.

**AsH\(_3\)**
- Tolerance limit for 1000 h cell lifetime is ~ 0.1 ppm

**PH\(_3\)**
- Tolerance limit for 1000 h cell lifetime is ~ 0.2 ppm
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.

Anode structural degradation in anode under 5ppm of PH$_3$, inlet temp. 800°C and 20 A

(a) 19,917 h  
(b) 16,310 h  
(c) 1,8450 h

Critical degradation value is assumed to be 40%
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$_2$S.
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$_2$S, AsH$_3$ and PH$_3$.
• The in-house SOFC code was modified to simulate button cells operating on biogas.
Thank you
Recent Publications


7. Huang Guo, Gulam Iqbal, and Bruce S. Kang, “Investigation of Secondary Phases Formation due to PH3 Interaction with SOFC Anode,” American Society Ceramics Transaction, accepted for publication.


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 current.
- The anode operated with 5 ppm PH$_3$ 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$_2$S 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) 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$_2$MgMoO$_6$-δ/GDC Anode in H$_2$/10 ppm PH$_3$

- Results show promise for development of a H$_2$S 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 $\text{Sr}_2\text{MgMoO}_{6-\delta}/\text{GDC}$ Anode-2

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

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

SEM image of the Pt paste
Recovery of LDC impregnated Ni-YSZ anode

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

Fuel=200 sccm syngas

T=800°C

Our results with LDC impregnation

Literature data with GDC impregnation


T=750°C
Structural Degradation: Effect of Impurities

Anode Structural Life: Electrochemical vs. Structural Degradation

- 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.

Acceptable limit of PH$_3$ contaminant for specified anode structural life.

Penetration depth of PH$_3$ under different concentration$^1$

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