Sulfur-Tolerant Anodes for SOFCs

Project Manager: Lane Wilson, NETL/DoE

S. Zha, Z. Cheng, Y. Choi, and M. Liu
Center for Innovative Fuel Cell and Battery Technologies
School of Materials Science and Engineering
Georgia Institute of Technology

April 18-21, 2005
Monterey, CA
Outline

• Technical Issues Addressed

• Objectives & Approach

• Recent Progress (Since Oct 2004)
  – The H₂S Poisoning Effect
  – Thermodynamic Analysis
  – QM Calculations
  – Exploration of New Sulfur-Tolerant Anode Materials
  – Mechanisms of Sulfur-Anode Interactions

• Activities for the next 6-12 Months
Critical Issues

• What are the impacts of sulfur poisoning?
• How to study the interactions between sulfur and anodes?
• What is the mechanism of sulfur poisoning?
• What is required to achieve the sulfur tolerance needed for the SECA program?
• How to design new materials with required sulfur tolerance?
Objectives

• To characterize the effect of sulfur-poisoning on fuel cell performance under various operating conditions

• To investigate the detailed mechanisms of sulfur-poisoning

• To develop strategies for achieving both sulfur-tolerance and high performance

• To explore new sulfur-tolerant materials to meet SECA Program objectives
Technical Approach

• Phenomenological Characterization of Sulfur Poisoning Effect
  – Impedance spectroscopy (I.S.)
  – Cell performance and anode over-potential

• Understanding Sulfur Poisoning Mechanism
  – ex-situ examination of the anode via XRD, Raman, etc
  – in-situ Raman spectroscopy coupled with I.S.
  – Thermodynamic/kinetic analysis
  – MD and QM calculations

• Design of New Anode Materials/New Structure
  – For modification/decoration of Ni-YSZ Surface
  – For replacement of Ni-YSZ anode
Recent Progress: Since Oct 2004

• The $\text{H}_2\text{S}$ Poisoning Effect

• Thermodynamic Analysis

• QM Calculations

• Exploration of New Sulfur-Tolerant Anode Materials
Impedance Spectra
of a symmetrical cell
Ni-YSZ/YSZ/Ni-YSZ

immersed in

① Humidified H₂ for 3 days
② 50 ppm H₂S (50v%H₂ & 50% N₂) for 3 hours
③ Humidified H₂ (Regeneration) for 14-16 hours
Summary: Effect of H$_2$S on Rp

Note: The percentage adjacent to each data point represents the increase in Rp after poisoning or regeneration compared to the initial value before exposure to H$_2$S.

At lower temperature:
- Poisoning occurs faster and the effect is stronger
- Recovery is slower and more difficult

Interfacial Resistance (Ω cm$^2$)

- Before Poisoning
- After Poisoning
- Regeneration (after 14-16 hrs)

Sulfur-Tolerant Anodes
Ni-YSZ cermet was exposed to humidified hydrogen containing 100 ppm H₂S at 727°C for 5 days.

**Bulk sulfides are not detected by XRD; yet S-Ni vibration are identified by Raman**
Implications

• The surface sulfur is most likely responsible to the observed degradation in performance.

• While XRD is insensitive to sulfur poisoning, Raman spectroscopy could be used for probing and mapping of NiSx under in-situ conditions and hence for elucidating the sulfur-poisoning mechanism.
What are the conditions under which nickel sulfides are expected?
Recent Progress: Since Oct 2004

• The H$_2$S Poisoning Effect

• Thermodynamic Analysis

• QM Calculations

• Exploration of New Sulfur-Tolerant Anode Materials
Thermodynamic Stability of Ni in 50 ppm H₂S

- Possible reactions between H₂S and Ni (bulk-phase):
  
  \[
  0.5 \text{Ni} + \text{H}_2\text{S} \rightarrow 0.5 \text{NiS}_2 + \text{H}_2
  \]
  
  \[
  0.75 \text{Ni} + \text{H}_2\text{S} \rightarrow 0.25 \text{Ni}_3\text{S}_4 + \text{H}_2
  \]
  
  \[
  \text{Ni} + \text{H}_2\text{S} \rightarrow \text{NiS} + \text{H}_2
  \]
  
  \[
  1.5 \text{Ni} + \text{H}_2\text{S} \rightarrow 0.5 \text{Ni}_3\text{S}_2 + \text{H}_2
  \]

Thermodynamics predicts that (bulk-phase) Nickel is stable (or sulfide NiₓSᵧ is unstable) in 50 ppm H₂S at elevated temperatures.

The stability of NiₓSᵧ increases with Ni to S ratio; Ni₃S₂ detected.

Reaction Gibbs free energy change for several possible reactions between Ni and 50 ppmv H₂S in 50%H₂/1.5%H₂O/48.5%N₂ at elevated temperatures.
The stability of (bulk-phase) Ni sulfide increases with H$_2$S concentration but decreases with temperature.

Ni sulfide (bulk-phase) will form only at relatively high concentration of H$_2$S at low temperatures.

e.g., Ni$_3$S$_2$ is stable only when [H$_2$S] $> 10^3$ ppmv at T $< 800$K.
Conclusion

• Thermodynamics predicts that Ni-YSZ are stable in 50 ppm H₂S at >700°C.

• The thermodynamic analysis does not seem to be helpful in understanding what is happened to Ni exposed to 50 ppmv H₂S.
• It was suspected that the adsorption energy for sulfur on Ni is significantly higher (more negative) than the bonding energy in a Ni$_x$S$_y$ crystal*.

• It appears that sulfur adsorption on Ni surface

\[ \text{H}_2\text{S (g)} \rightarrow \text{S (ad)} + \text{H}_2 \ (\text{g}) \]

is energetically favorable in low concentration of H$_2$S even when the formation of sulfides is unfavorable.

Recent Progress: Since Oct 2004

- The H$_2$S Poisoning Effect
- Thermodynamic Analysis
- QM Calculations
- Exploration of New Sulfur-Tolerant Anode Materials
**Fuel oxidation**

\[ \text{H}_2 + \text{O}^{-2} = \text{H}_2\text{O} + 2e^- \]

**Oxygen reduction**

\[ \frac{1}{2}\text{O}_2 + 2e^- = \text{O}^{2-} \]

- **Ni-YSZ**
- **La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3}**
QM Calculation of $\text{H}_2\text{S}$–$\text{Ni}$ Interactions
Computational Approach

To Predict the Most Energetically Favorable Surface Configuration
for reactants, intermediates, and products

- Molecular properties of the gas molecules
- Properties of (e.g. crystal structure) of the solids
- Defect structures: vacancy, Interstitials, impurities

\[ H \Psi = E \Psi \]

Energetics
- Energy for ads., dissociation, favorable reaction pathways

Vibrations
- FTIR/Raman Spectroscopy
**Computational Method**

- **VASP (Vienna Ab initio Simulation Package)**
  - Supercell: Five layer \([p(2\times2)]\) units
  - DFT: LDA with PW91 (GGA) correction
  - Core pseudopotential
  - Cut-off energy: 400 eV
  - Vacuum space: \(\sim 10.0\ \text{Å}\)

---

**Side view**

**Top view**

Coordinates are relaxed

Fixed layers (bulk)
(111) Surface and Adsorption Sites

Adsorption energy in kcal/mol

\[ \Delta E_{ad} = \Sigma E[\text{products}] - \Sigma E[\text{reactants}] \]

\[ = E[\text{surface + adsorbate}] - E[\text{surface}] - E[\text{adsorbate}] \]
• $\text{H}_2\text{S}$ decomposition forming sulfur adsorption on Ni anode surface can occur in approximately $110 \text{ fs}$ under SOFC operating condition at $700^\circ\text{C}$. 
H$_2$S Decomposition on Ni(111) Surface

**H$_2$S Adsorption**

-13.1 kcal/mol

Ni(111)-S + 2H

**Dissociative H$_2$S adsorption**

-39.8 kcal/mol

SH + H

-15.7 kcal/mol

*Energies are relative to Ni(111) + H$_2$S*
Adsorption on Ni(111) Surface

-7.1 [-90.8]  
-36.3 [-119.9]  
-40.7 [-124.3]  
-41.3 [-125.0]

• Energies in brackets are relative to Ni(111) + S
Sulfur-Tolerant Anodes

Adsorption Energy on Ni (111) Surface

1/4 monolayer (ML)

Surface adsorption energy is very large

Sulfur is very stable on Ni surface, difficult to remove
Free Energies of Sulfide Formation on Ni & Cu

- Free energy change for sulfidation reaction at about 650°C

The formation of bulk and surface sulfide on nickel is easier than on copper.

- Surface sulfide is far more stable than bulk sulfide

Sulfur Tolerance of Ni and Cu

The results are in good agreement with data reported in literature.

Cu-based anodes is more sulfur-tolerant than Ni-based anodes.
Summary

- Constructed Ni(111) surface for the slab model calculations
- Predicted adsorption energies of S on the Ni(111) and Cu(111) surfaces, suggesting that fcc hollow site is the most stable
- Predicted step-wise reaction mechanism of \( \text{H}_2\text{S} \) decomposition on Ni(111) surface, which is in-line with XRD and Raman studies
While bulk sulfides may not be formed, sulfur strongly adsorbed on Ni or Cu surface blocks active sites for fuel oxidation, leading to performance degradation (poisoning effect).

Surface adsorbed sulfur is difficult to remove, implying that Ni or Cu surfaces will have difficulty to get around sulfur poisoning effect.

New materials must be developed to achieve sulfur tolerance.
Recent Progress: Since Oct 2004

- The H₂S Poisoning Effect
- Thermodynamic Analysis
- QM Calculations
- Exploration of New Sulfur-Tolerant Anode Materials
Requirements for S-Tolerant Anode Materials

Two primary requirements
- Small Sulfur Adsorption Energy
- High Catalytic Activity for Fuel Oxidation (H, C, S, …)
  * For modification/decoration of Ni or Cu surfaces

Other Desirable Properties
- Sufficient Electrical conductivity
- Adequate compatibility with Electrolyte/Interconnect
- Resistance to Oxidation
  * For Replacement of Ni-Based anode
Development of New Anode Materials

Materials synthesis

Material & structure optimization

Chemical stability

Exposure to H₂S

XRD

Conduction & stability

Exposure to H₂S

4-probe dc

Stability evaluation

Fuel cell testing

Application

Sulfur-Tolerant Anodes
Conductivity Measurement

- 5201 Lock-in Amplifier
- EG&G 273A
- Pt Leading wire
- Gas outlet
- Sample holder
- Gas inlet
- Silicon Stopper
- Sample
- Quartz Tube

Sulfur-Tolerant Anodes
Fuel Cell Fabrication Procedures

Pressing YSZ Powders and firing at 1550ºC

Screen-painting of cathode and reference

Firing cathode at 1200ºC for 2 hrs

Brush-painting of anode

Electrolyte: 8% (YSZ) ~ 250 µm

Cathode: LSM-YSZ

In-situ firing at 1000ºC for 2 hours

Attachment of current collectors and lead wires

Anode: New materials to be determined

Sulfur-Tolerant Anodes
Testing of SOFCs in a H$_2$S Containing Fuel

Experiment setup for testing of SOFC in H$_2$S containing fuel
# Complex oxides (e.g., $\text{ABO}_3$, $\text{A}_2\text{B}_2\text{O}_7$, etc.)

- **Sufficient conductivity** due to delocalized $d$ electron and/or doping-induced electronic defects
- **Good thermal match** with YSZ due to their relatively open structure
- **Good chemical stability** due to stabilized cations by the complex structure
- **Decent catalytic activity** due to the transition metal ions in the structure

<table>
<thead>
<tr>
<th>Material for example</th>
<th>$\sigma$ at 800°C (S cm$^{-1}$)</th>
<th>CTE (10$^{-6}$ K$^{-1}$)</th>
<th>$R_p$ at 800 °C (Ω cm$^2$)</th>
<th>Chemical stability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{La}<em>{0.35}\text{Sr}</em>{0.65}\text{TiO}_3$ (LST) $^a$, $^b$, $^c$</td>
<td>600</td>
<td>11-12</td>
<td>9</td>
<td>Excellent</td>
</tr>
<tr>
<td>$\text{La}<em>{0.7}\text{Sr}</em>{0.3}\text{VO}_3$ (LSV) $^a$</td>
<td>140</td>
<td>10-12</td>
<td>4</td>
<td>Fair</td>
</tr>
<tr>
<td>$\text{La}_{1-x}\text{Sr}<em>x\text{Cr}</em>{1-y}\text{Mn}_y\text{O}_3$ (LSCM) $^a$, $^b$, $^c$</td>
<td>1.5</td>
<td>10-11</td>
<td>-</td>
<td>Excellent</td>
</tr>
<tr>
<td>$\text{Gd}<em>2\text{Ti}</em>{1-x}\text{Mo}_x\text{O}_7$ (GTMO) $^a$</td>
<td>1</td>
<td>10.8</td>
<td>3</td>
<td>Fair</td>
</tr>
<tr>
<td>$\text{SrVO}_3$ $^a$</td>
<td>800</td>
<td>-</td>
<td>1</td>
<td>Fair</td>
</tr>
</tbody>
</table>

$^a$ for GTFC, $^b$ for PNNL, $^c$ for Los Alamos
Vanadium-based oxide has good catalytic activity towards sulfur, e.g., $V_2O_5$ is used for $SO_2$ oxidation.

- $SrVO_3$ has high electrical conductivity: $\sigma = 1000 \text{S/cm} @ 700^\circ\text{C}$, comparable to that for Ni/YSZ cermet.
Resistance to H₂S

• Thermodynamic analysis indicated that SrVO₃ is chemically stable in 100 ppm H₂S at elevated temperature.

• Under condition of 1000K, 100 ppm H₂S/3%H₂O/97%H₂, the free energy change for the following sulfidation reaction:

\[
\text{SrVO}_3 (s) + \text{H}_2\text{S} (g) + 0.5 \text{H}_2 (g) \rightarrow \text{SrS} (s) + 0.5 \text{V}_2\text{O}_3 (s) + 1.5 \text{H}_2\text{O} (g)
\]

is: \(\Delta G \approx + 37 \text{ kJ/mol}\), i.e., this material is thermodynamically stable against low concentration of H₂S.
• SrVO$_3$ has decent activity for $\text{H}_2$ oxidation in fuel environment (0.25 $\Omega$ cm$^2$ @ 950°C); similar to Ni-YSZ
The interfacial resistance for SrVO₃ anode showed no degradation in 50ppm H₂S for ~60 h.
Stability of SrVO₃-Based SOFC in H₂S/H₂

The result of cell stability test under much harsher condition (i.e., 1000°C, 5000-10,000ppm H₂S) suggested that the performance loss for SrVO₃ anode might be reversible up to 10,000 ppm of H₂S.

SrVO₃/YSZ/Pt Cell
1000°C
E = -0.7V

Fast Recovery
Sulfur-Tolerant Anodes

- La_{0.7}Sr_{0.3}VO_3 show even better activity in H_2S than in pure H_2

- The activity of LSV is better than Pt in high H_2S content

- Possible candidate for modifying the surface of Ni/YSZ anode
Sulfur-Tolerant Anodes

**Gd₂Ti₁.₄Mo₀.₆O₇ (GTMO)**

- Pyrochlore
- Phase stable under anodic conditions
- No reaction with H₂S

**Phase Stability in H₂S**

- (a) as-prepared
- (b) after exposure to 10%H₂S-H₂ for 5 days
- (c) anode after testing in 10%H₂S-H₂ for 6 days

Note: Exposure & FC testing temperature: 950°C
Performance of GTMO Anode in an SOFC

Fuel cell: $\text{Gd}_2\text{Ti}_{1.4}\text{Mo}_{0.6}\text{O}_7$/YSZ (0.25 mm)/LSCM

- **Fuel:** $\text{H}_2$, 28 ml min$^{-1}$
- **Fuel:** 10%$\text{H}_2\text{S}$-90%$\text{H}_2$, 20 ml min$^{-1}$
Performance of GTMO in H$_2$S

Fuel cell: Gd$_{2}$Ti$_{1.4}$Mo$_{0.6}$O$_{7}$/YSZ (0.25 mm)/LSCM

Fuel: 10% H$_2$S-N$_2$, 12 ml min$^{-1}$
Stability testing (6 days) of a fuel cell operated on 10% H₂S-H₂ at 950 °C at a constant cell terminal voltage of 0.70 V. Cathode: Pt
Microstructure of $\text{Gd}_2\text{Ti}_{1.4}\text{Mo}_{0.6}\text{O}_7$ Anode

SEM images of the $\text{Gd}_2\text{Ti}_{1.4}\text{Mo}_{0.6}\text{O}_7$ anode after fuel cell testing
Impedance spectra measured at 950 °C under open circuit conditions using a three-electrode configuration. Inset is the total impedance of the fuel cell. Anode: 10%H₂S-90%H₂, Cathode: air.

- YSZ bulk R: 0.6 Ω cm²
- Cathode/YSZ: 0.4 Ω cm²
- Anode/YSZ: 0.2 Ω cm²
Effluent Gas Analysis

Mass spectrum of the effluent gas when the anode was fed on 10% H₂S (N₂ balanced) at 950°C. The fuel cell was operated at a constant current density of 400 mA cm⁻². The fuel flow rate: 12 ml min⁻¹.

Effluent gas compositions:

H₂O, small amount H₂, unreacted H₂S, and element S (condensed in the gas line)
Conclusions

- Vanadium based compounds demonstrated excellent S-tolerance and high catalytic activity in H₂S-containing fuels and thus are possible candidates for modifying the surface of Ni/YSZ anode.

- Pyrochlore Gd₂Ti₁.₄Mo₀.₆O₇ (GTMO) also showed excellent sulfur tolerance and catalytic activity towards electrochemical oxidation of H₂S.
Activities for the Next 6-12 Months

• To elucidate the mechanism for $H_2S$ adsorption, decomposition, and interaction with oxide materials using in-situ characterization techniques in order to achieve intelligent design of new anode materials with sulfur tolerance

• Further exploration of other potential sulfur-tolerant materials

• Evaluation of catalytic activities towards oxidation of other sulfur compounds/contaminants

• Long-term stability evaluation and strategies

• Surface and structure modification of conventional Ni-based anode to tolerate 50 ppm $H_2S$
  ✓ sputtering
  ✓ solution infiltration
  ✓ suspension infiltration
Acknowledgement

Lane Wilson, NETL/DoE

SECA Core Technology Program
Dept of Energy/National Energy Tech Laboratory

Equipment funded by DURIP/ARO
Center for Innovative Fuel Cell and Battery Technologies, Georgia Tech