Sulfur-Tolerant Anodes for SOFCs

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Outline

- **Technical Issues Addressed**
- **Objectives & Approach**
- **Recent Progress (Since Oct 2004)**
  - The H_2S 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 H_2S Poisoning Effect**
- Thermodynamic Analysis
- QM Calculations
- Exploration of New Sulfur-Tolerant Anode Materials

H_2S Poisoning of Ni-YSZ

Impedance Spectra

of a symmetrical cell

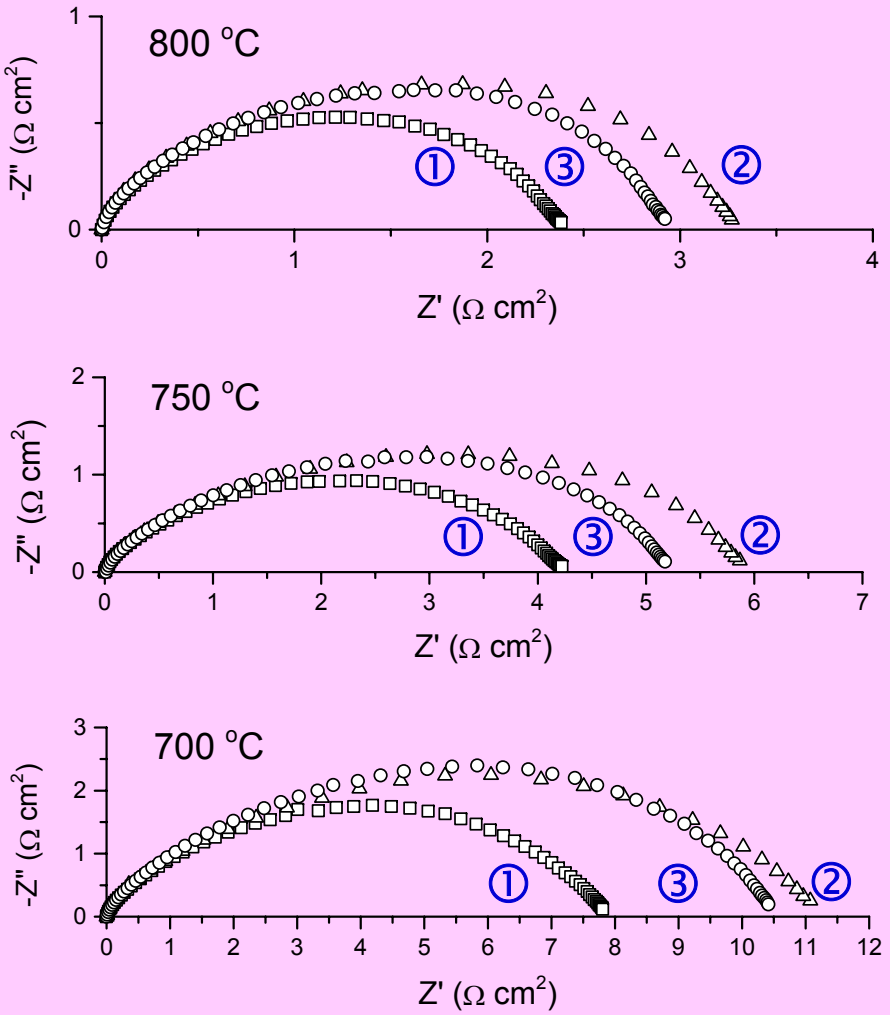
Ni-YSZ/YSZ/Ni-YSZ

immersed in

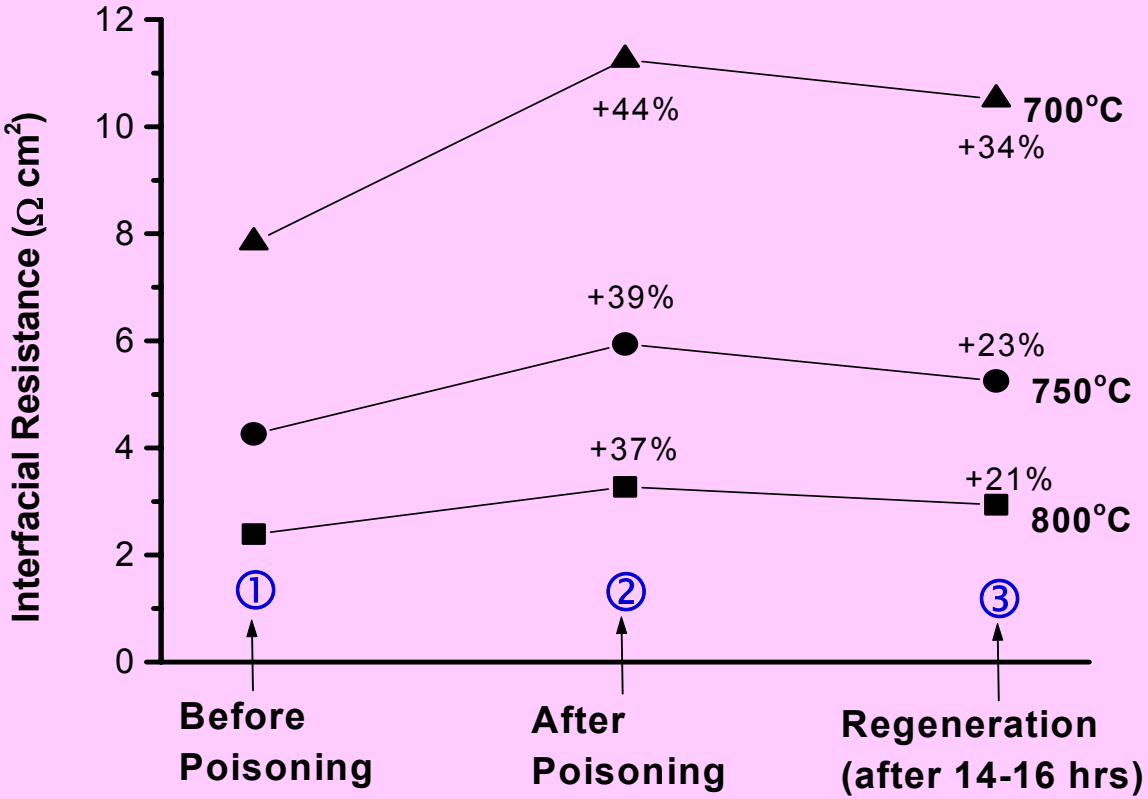
① Humidified H_2 for 3 days

② 50 ppm H_2S (50v%H_2 & 50% N_2) for 3 hours

③ Humidified H_2 (Regeneration) for 14-16 hours



Summary: Effect of H_2S on Rp

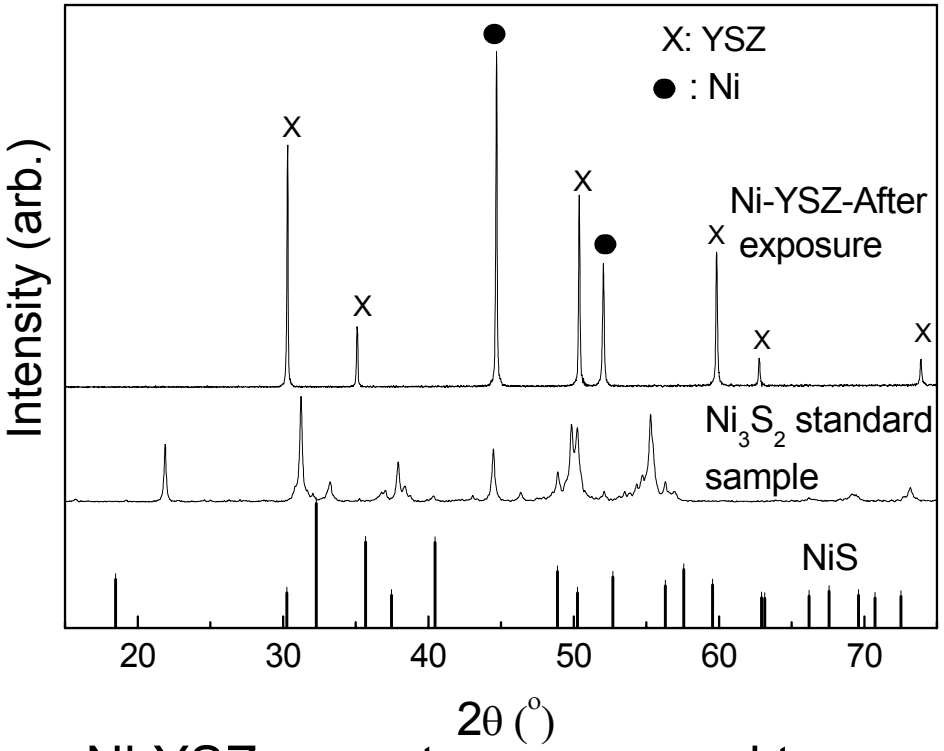


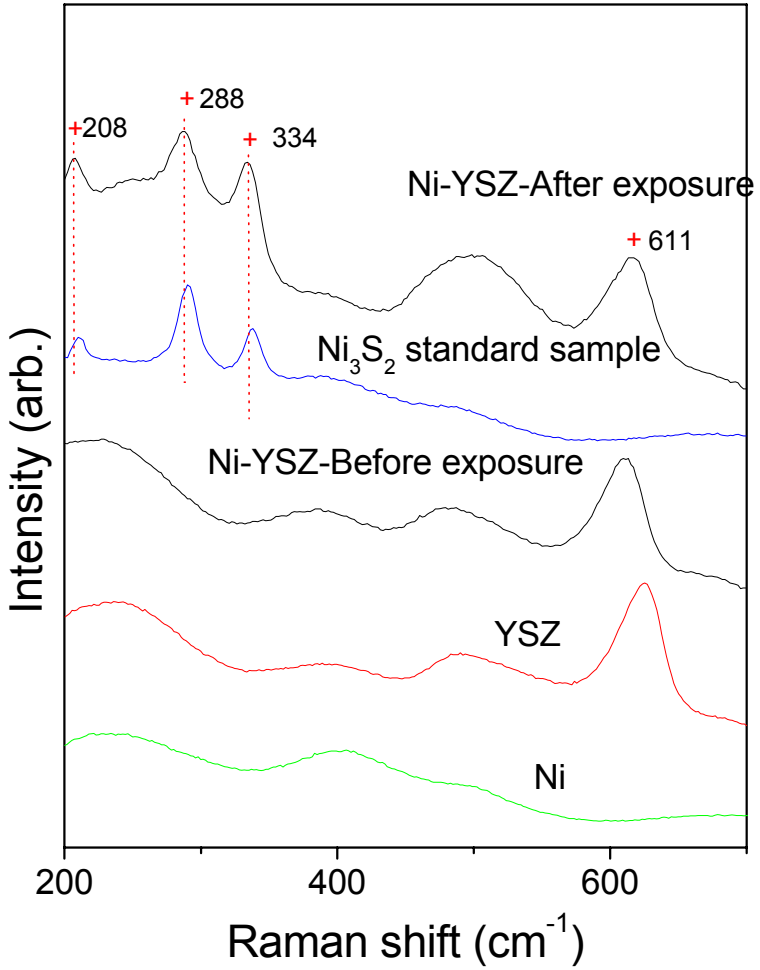
At lower temperature

- **Poisoning occurs faster and the effect is stronger**
- **Recovery is slower and more difficult**

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_2S.

XRD and Raman Study of S-Ni Interactions





Ni-YSZ cermet was exposed to humidified hydrogen containing 100 ppm H_2S at 727°C for 5 days.

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

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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.**

Question

What are the conditions under which nickel sulfides are expected?

Recent Progress: Since Oct 2004

- The H_2S Poisoning Effect
- **Thermodynamic Analysis**
- QM Calculations
- Exploration of New Sulfur-Tolerant Anode Materials

Thermodynamic Stability of Ni in 50 ppm H_2S

- Possible reactions between H_2S and Ni (bulk-phase):

$$0.5\ Ni + H_2S \rightarrow 0.5\ NiS_2 + H_2$$

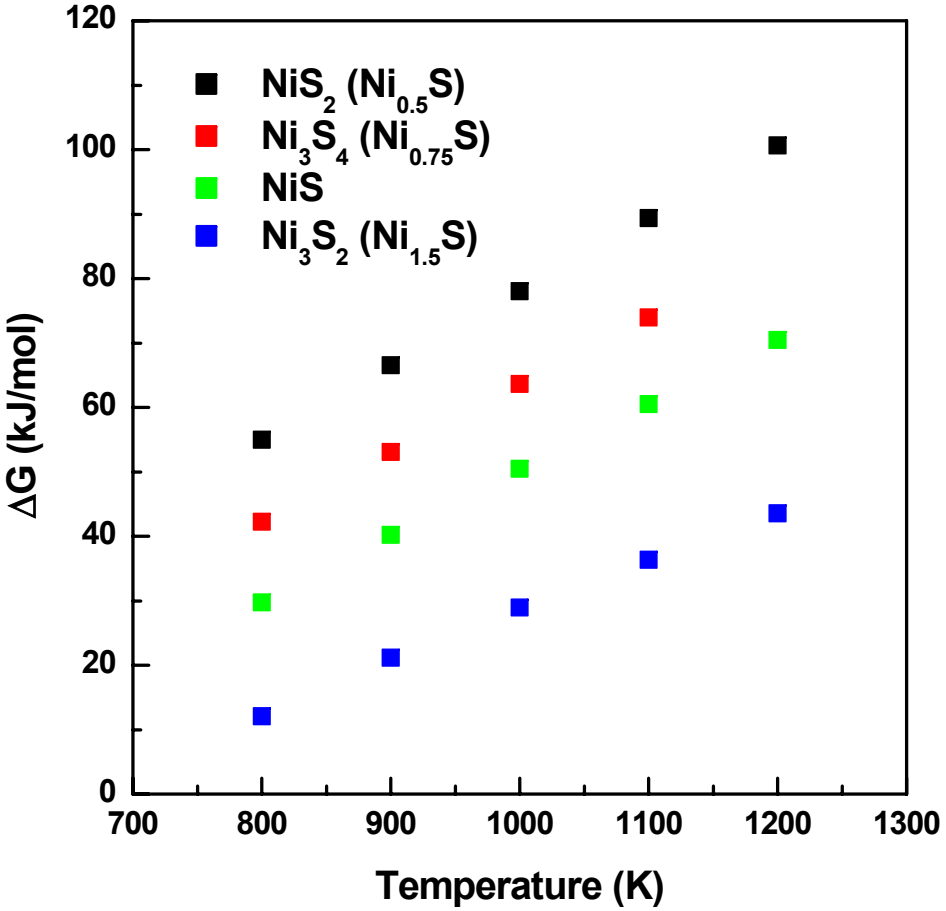
$$0.75\ Ni + H_2S \rightarrow 0.25\ Ni_3S_4 + H_2$$

$$Ni + H_2S \rightarrow NiS + H_2$$

$$1.5\ Ni + H_2S \rightarrow 0.5\ Ni_3S_2 + H_2$$

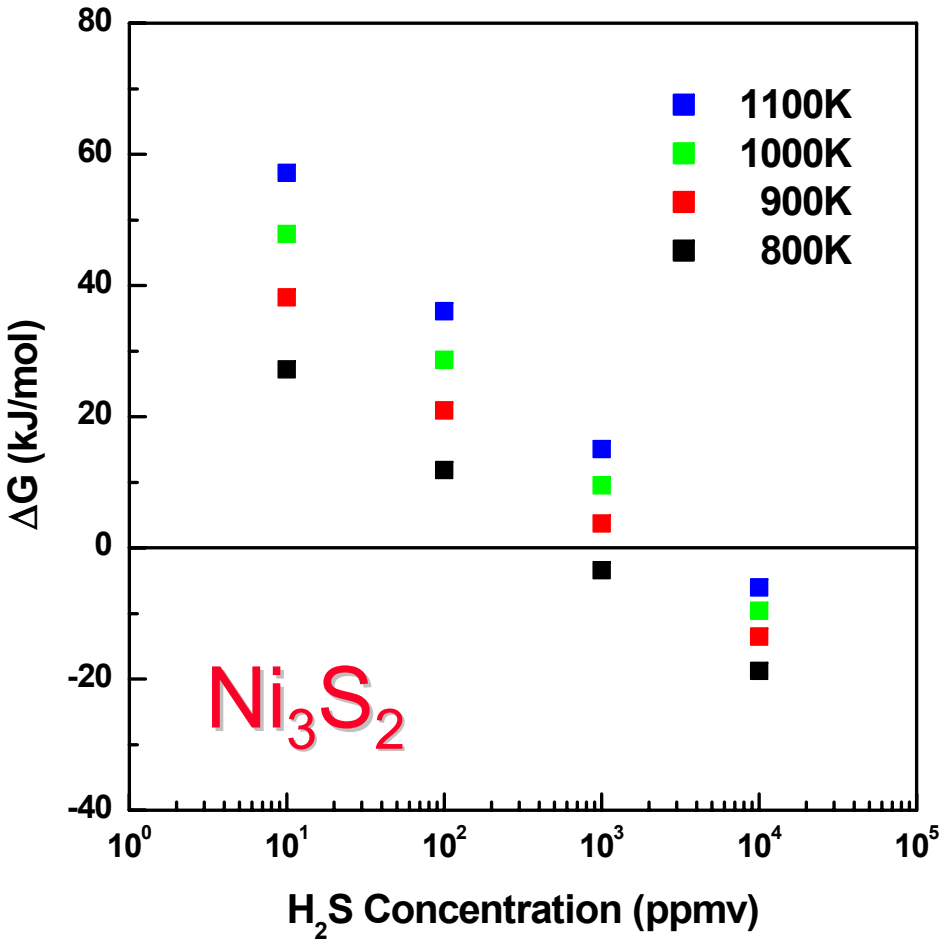
Thermodynamics predicts that (bulk-phase) Nickel is stable (or sulfide Ni_xS_y is unstable) in 50 ppm H_2S at elevated temperatures

The stability of Ni_xS_y increases with Ni to S ratio; Ni_3S_2 detected



Reaction Gibbs free energy change for several possible reactions between Ni and 50 ppmv H_2S in 50%H_2/1.5%H_2O/48.5%N_2 at elevated temperatures

Effect of H_2S Concentration



Dependence on H_2S concentration of the reaction Gibbs free energy for the formation of Ni_3S_2 from the reaction between Ni and H_2S in 97%H_2/3%H_2O

- The stability of (bulk-phase) Ni sulfide increases with H_2S concentration but decreases with temperature
- Ni sulfide (bulk-phase) will form only at relatively high concentration of H_2S at low temperatures

  e.g., Ni_3S_2 is stable only when $[H_2S] > 10^3$ ppmv at T < 800K

Conclusion

- Thermodynamics predicts that Ni-YSZ are stable in 50 ppm H_2S at >700C.

- The thermodynamic analysis does not seem to be helpful in understanding what is happened to Ni exposed to 50 ppmv H_2S.

Speculation/Hypothesis

- It was suspected that the adsorption energy for sulfur on Ni is significantly higher (more negative) than the bonding energy in a Ni_xS_y crystal*.

- It appears that sulfur adsorption on Ni surface

$$H_2S_{(g)} \rightarrow S_{(ad)} + H_{2\,(g)}$$

  is energetically favorable in low concentration of H_2S even when the formation of sulfides is unfavorable.

* C. H. Bartholomew, P. K. Agrawal, J. R. Katzer, "Sulfur Poisoning of Metals," *Advances in Catalysis*, Vol. 31 (1982), p 135.

Recent Progress: Since Oct 2004

- The H_2S Poisoning Effect
- Thermodynamic Analysis
- **QM Calculations**
- Exploration of New Sulfur-Tolerant Anode Materials

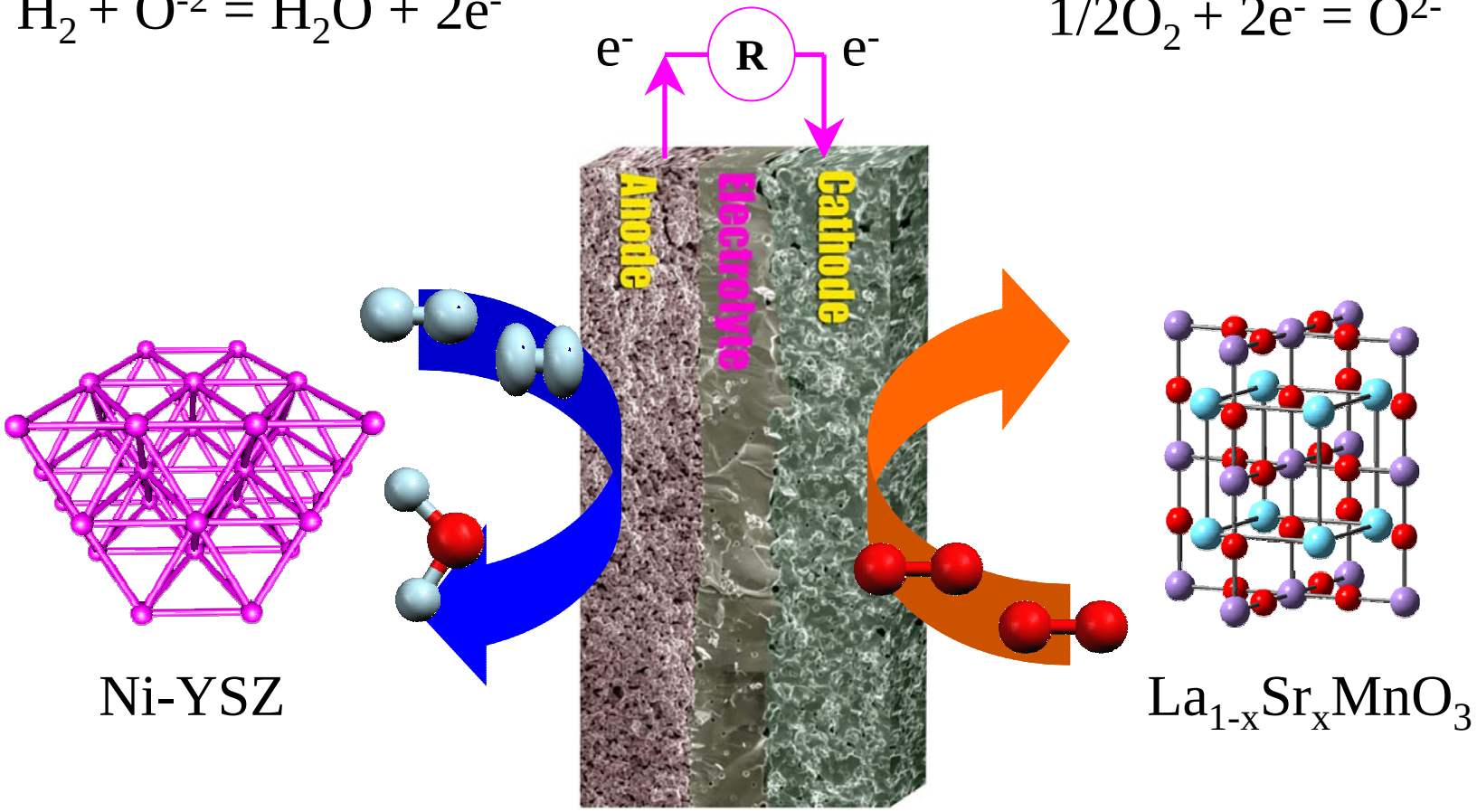
Schematic of an SOFC in the molecular level

Fuel oxidation

$H_2 + O^{-2} = H_2O + 2e^-$

Oxygen reduction

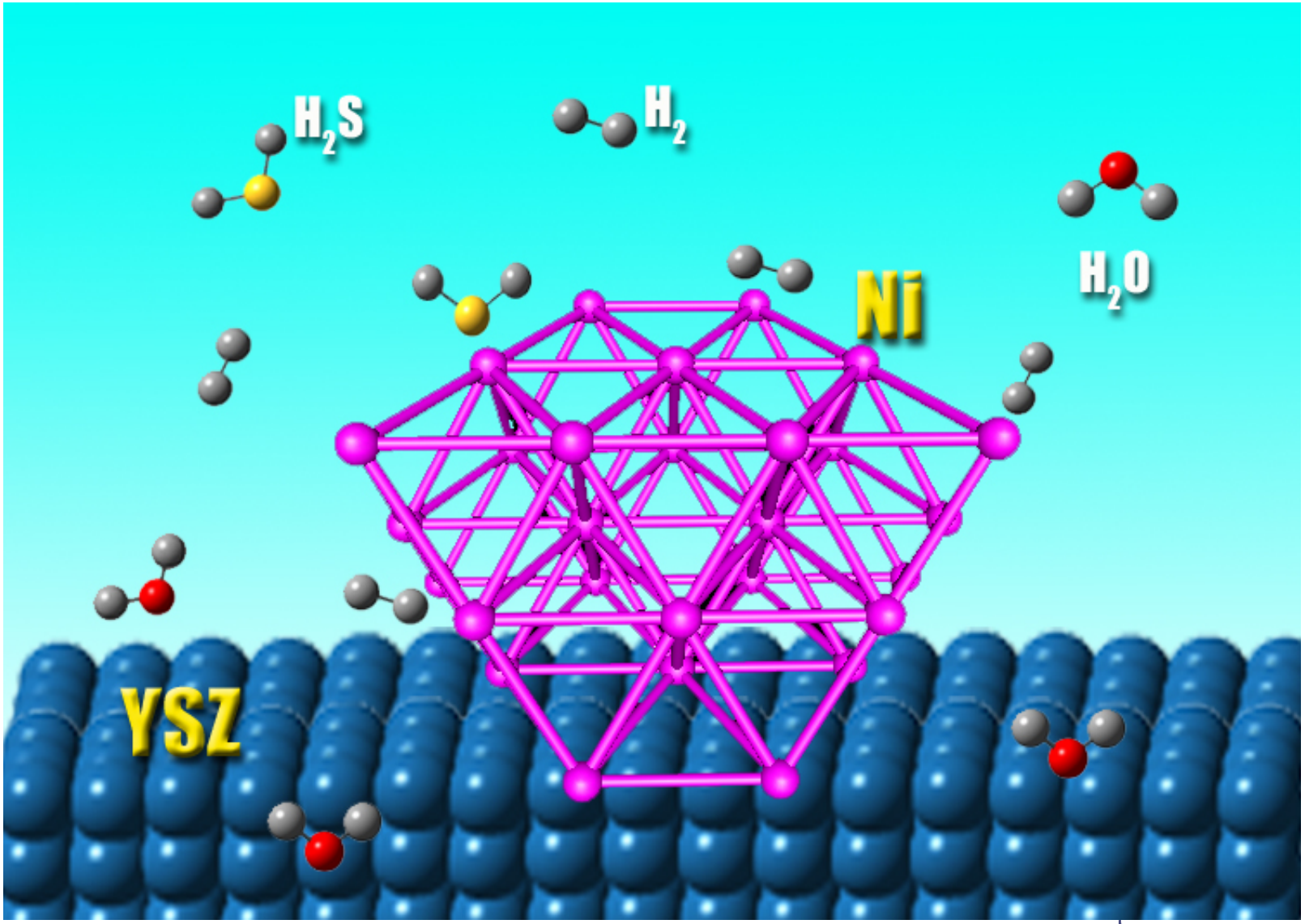
$1/2O_2 + 2e^- = O^{2-}$



Ni-YSZ

$La_{1-x}Sr_xMnO_3$

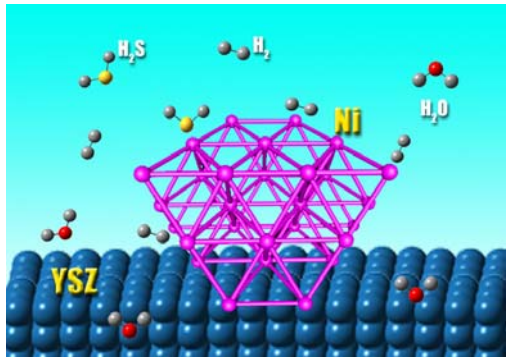
QM Calculation of H_2S–Ni Interactions



Computational Approach

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

$$H\Psi = E\Psi$$



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

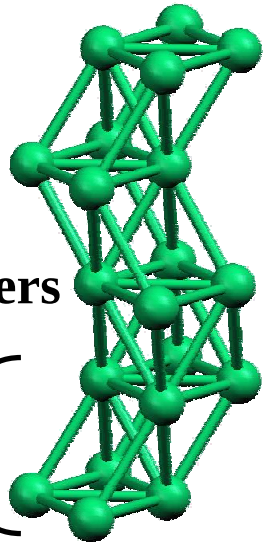
Energetics → **Energy for ads., dissociation, favorable reaction pathways**

Vibrations → **FTIR/Raman Spectroscopy**

Computational Method

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

Side view

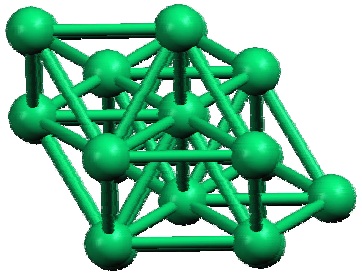


Coordinates are relaxed

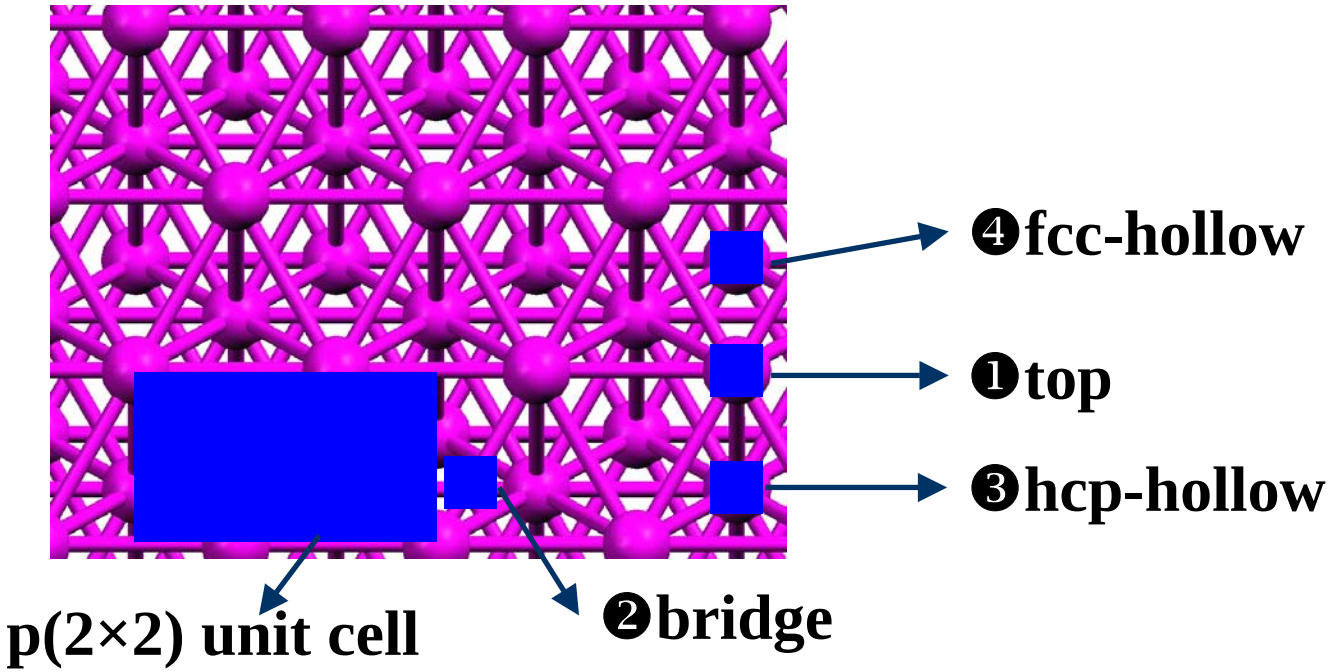
Fixed layers (bulk)

Super cell

Top view



(111) Surface and Adsorption Sites

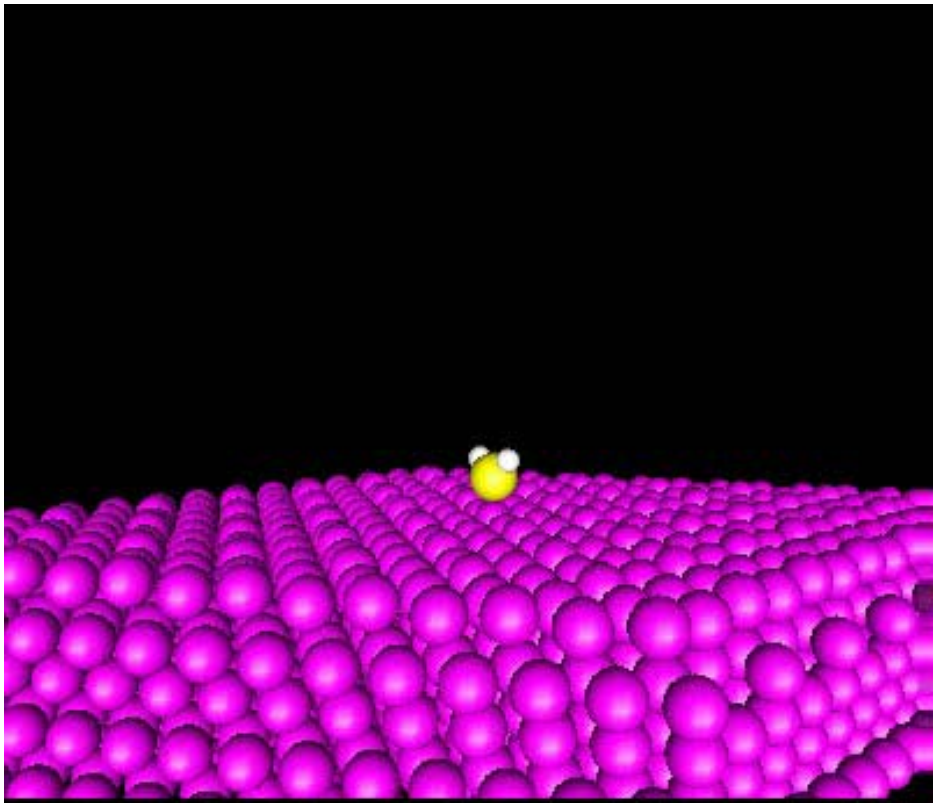


Adsorption energy in kcal/mol

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

$= E[\text{surface + adsorbate}] - E[\text{surface}] - E[\text{adsorbate}]$

Molecular Dynamics for H_2S Dissociation

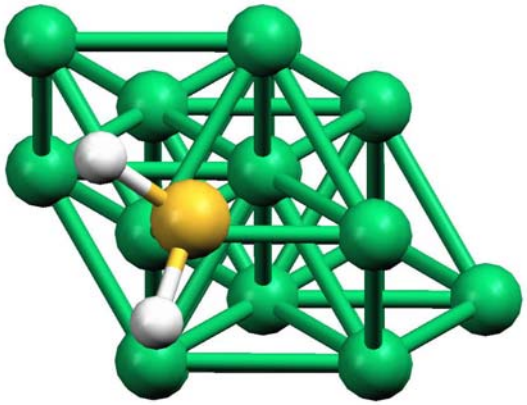


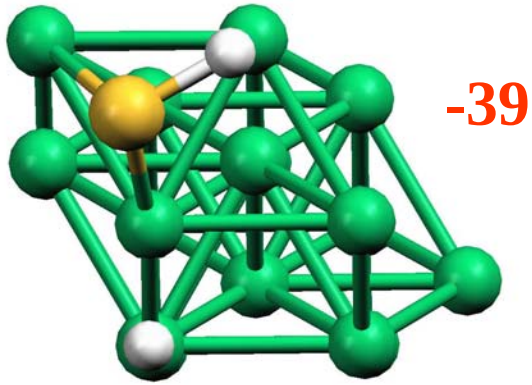
- H_2S decomposition forming sulfur adsorption on Ni anode surface can occur in approximately **110 fs** under SOFC operating condition at 700°C.

H_2S Decomposition on Ni(111) Surface

H_2S Adsorption

Dissociative H_2S adsorption



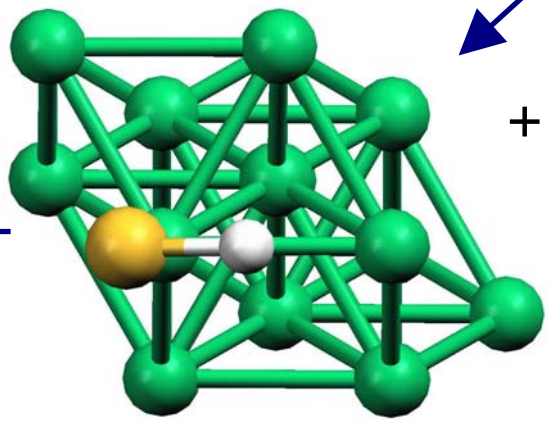


-39.8 kcal/mol

-13.1 kcal/mol

SH + H

+ H



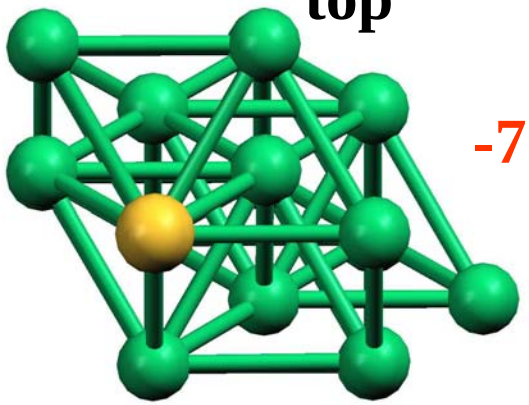
Ni(111)-S + 2H

-15.7 kcal/mol

- **Energies are relative to Ni(111) + H_2S**

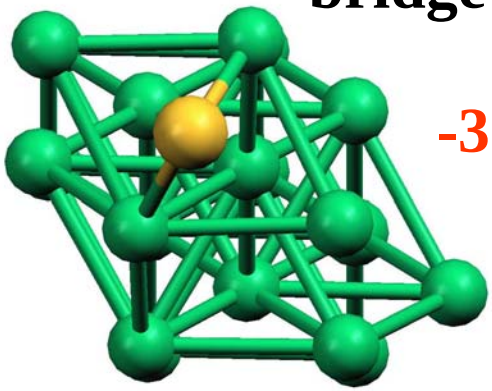
Adsorption on Ni(111) Surface

top



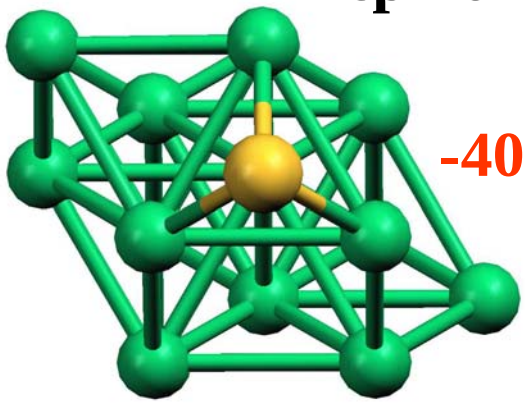
-7.1 [-90.8]

bridge



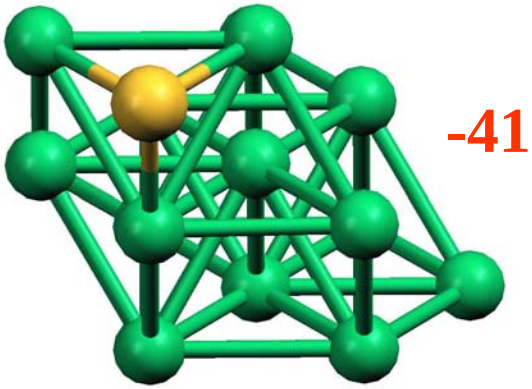
-36.3 [-119.9]

hcp hollow



-40.7 [-124.3]

fcc hollow

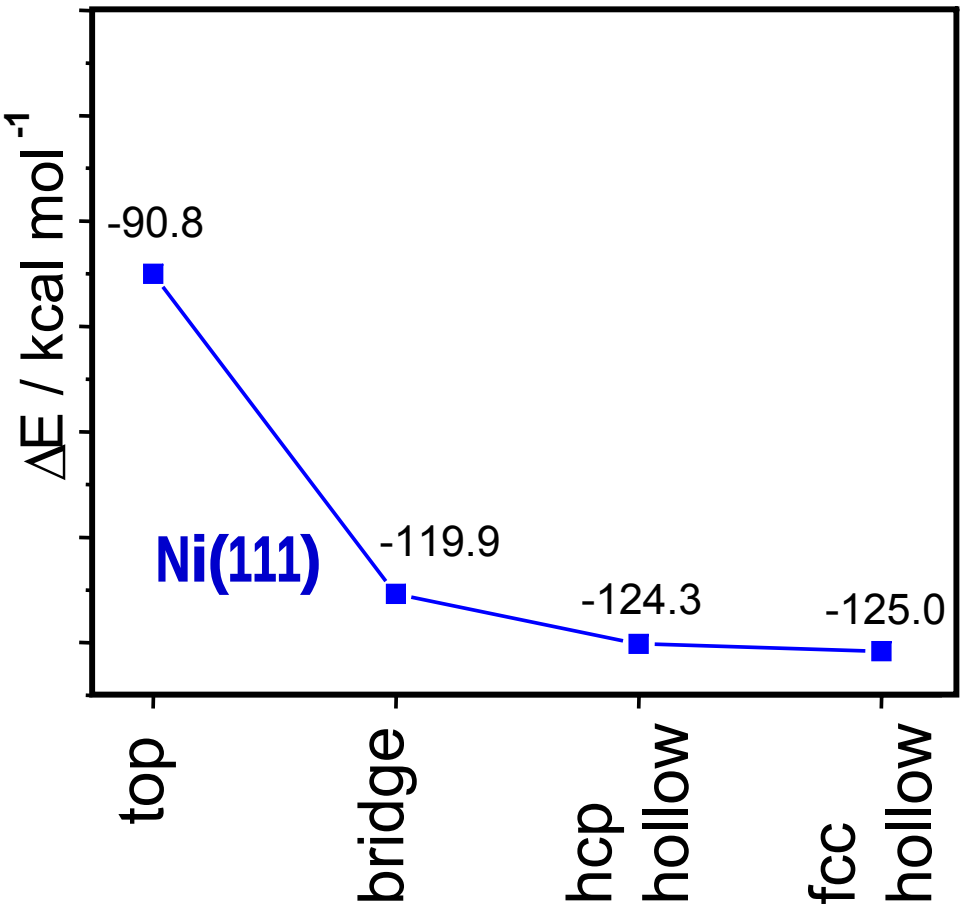


-41.3 [-125.0]

- **Energies in brackets are relative to Ni(111) + S**

Adsorption Energy on Ni (111) Surface

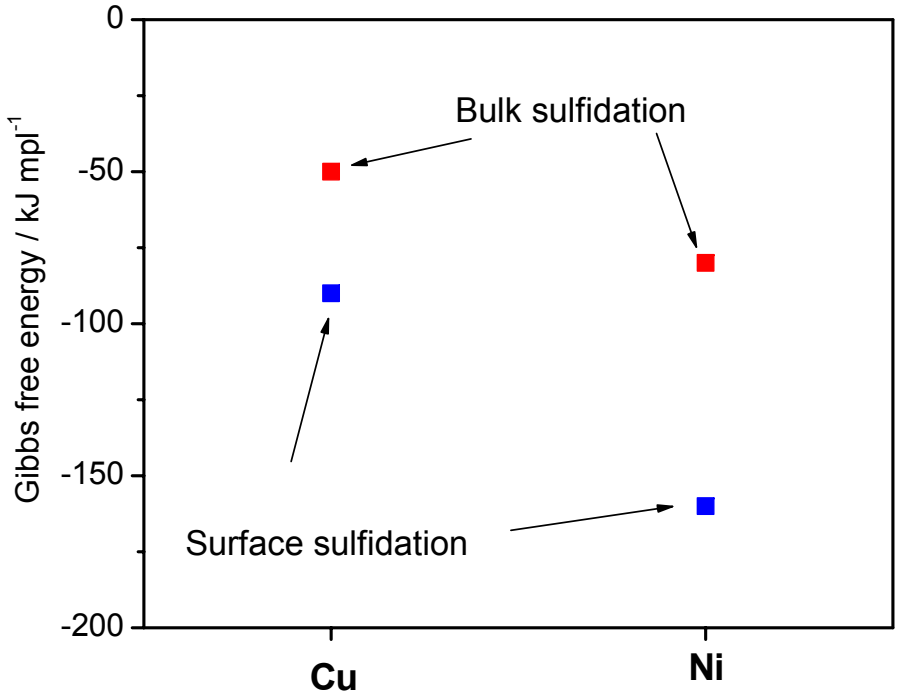
- 1/4 monolayer (ML)



- 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

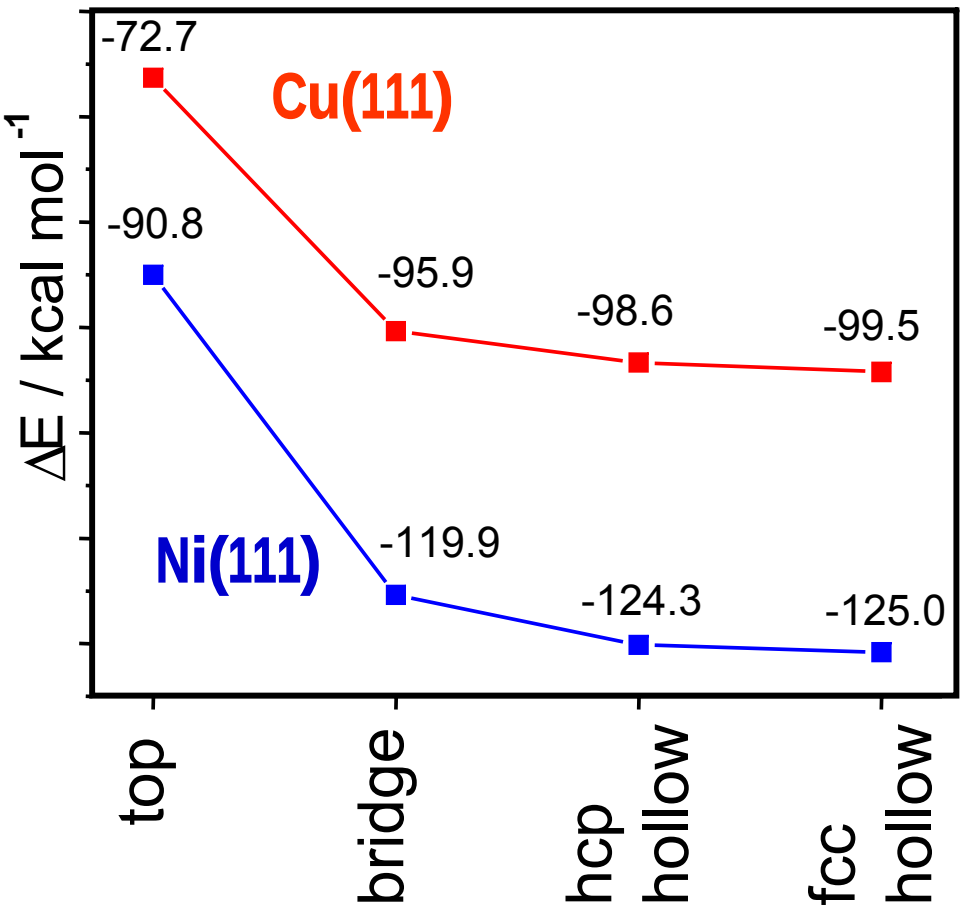


- The formation of bulk and surface sulfide on nickel is easier than on copper
- Surface sulfide is far more stable than bulk sulfide

- C. H. Bartholomew et al., *Advanced in Catalysis*, Vol. 31, pp. 166-170, **1982**.
- L. G. Marianowski et al., Eur. Patent, 88810131.8, **1988**.

Sulfur Tolerance of Ni and Cu

- 1/4 monolayer (ML)



- 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 H_2S decomposition on Ni(111) surface, which is in-line with XRD and Raman studies

Implications

- 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 H_2S 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**,…)

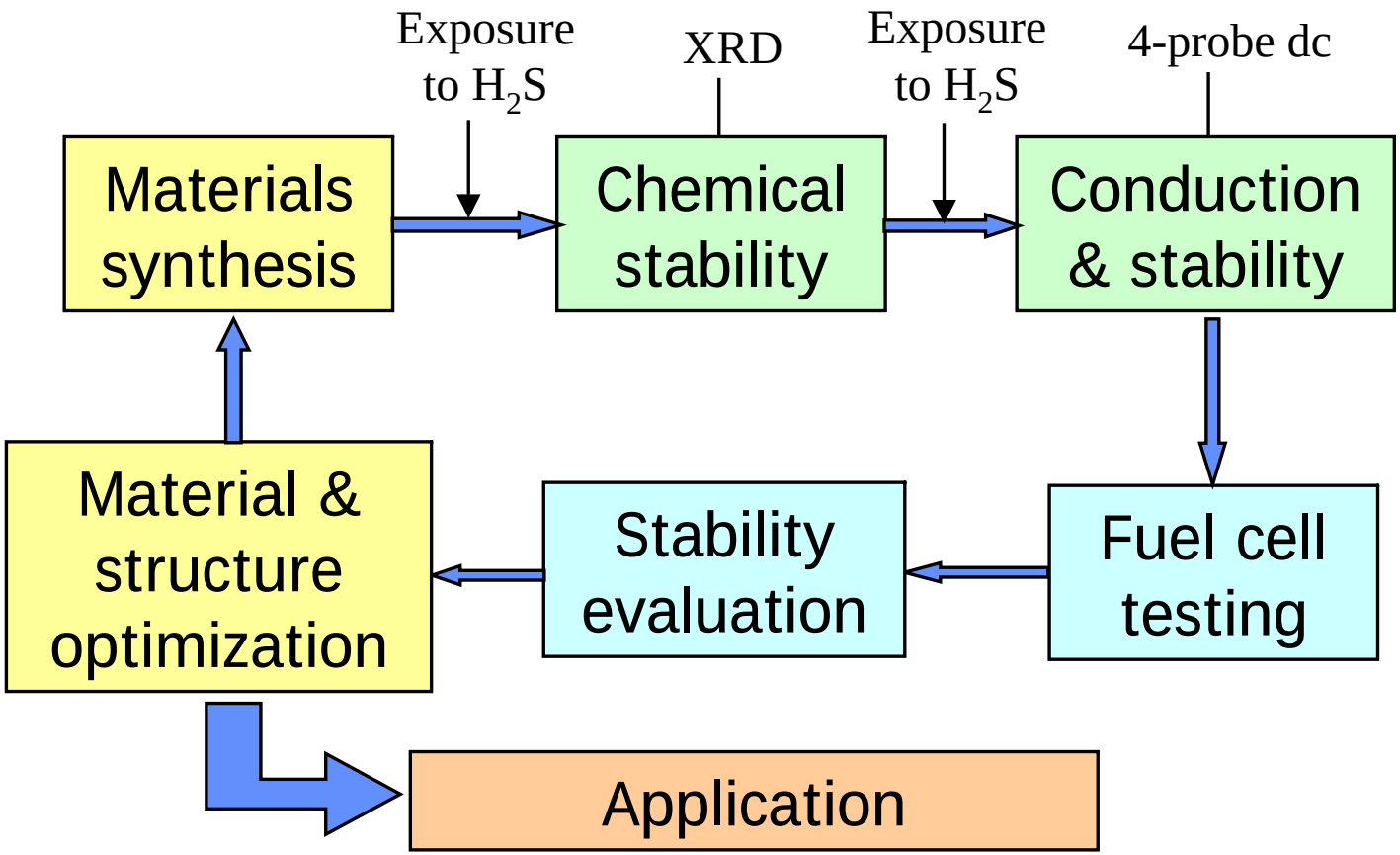
* For modification/decoration of Ni or Cu surfaces

Other Desirable Properties

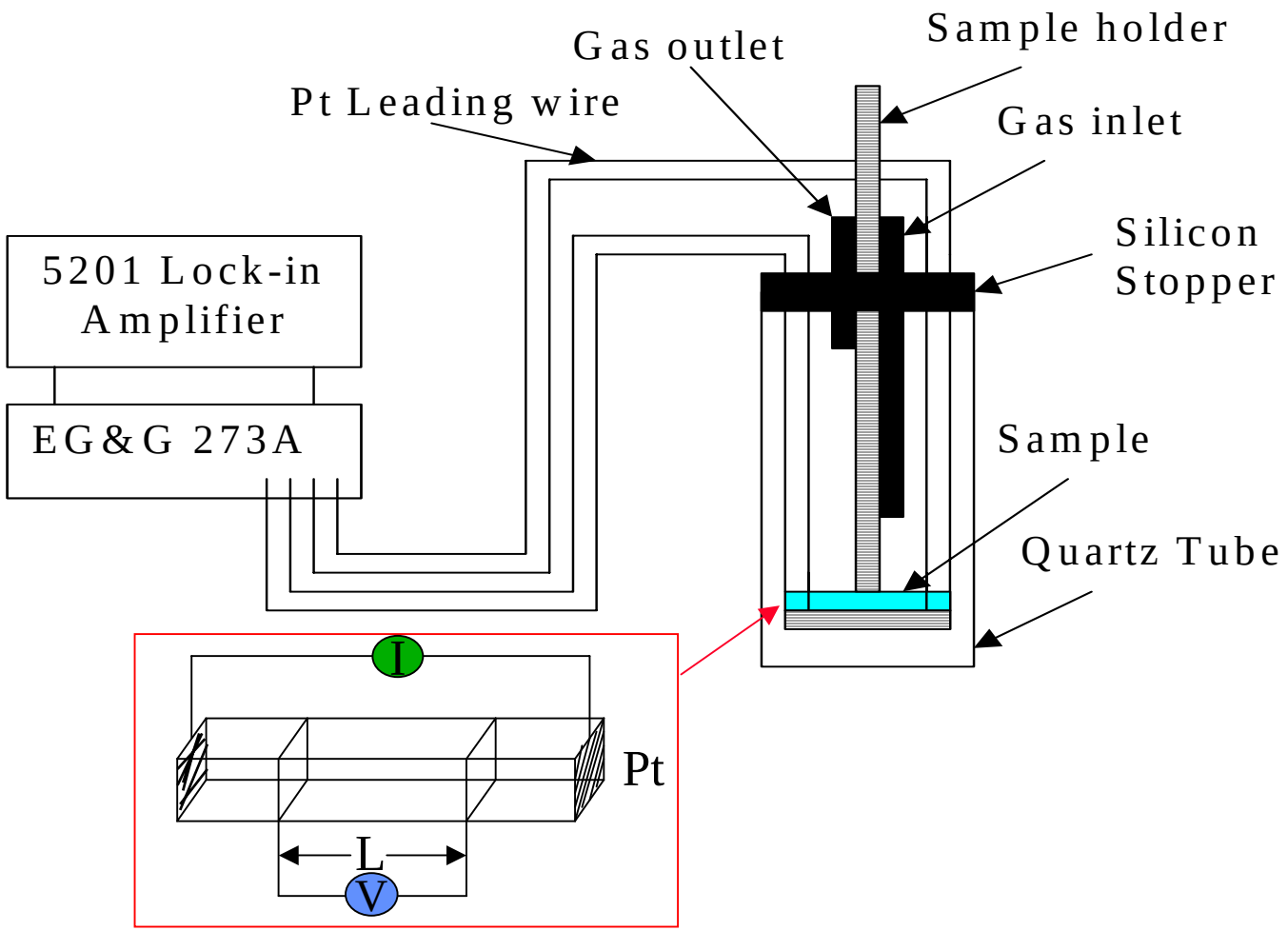
- Sufficient Electrical conductivity
- Adequate compatibility with Electrolyte/Interconnect
- Resistance to Oxidation

* For Replacement of Ni-Based anode

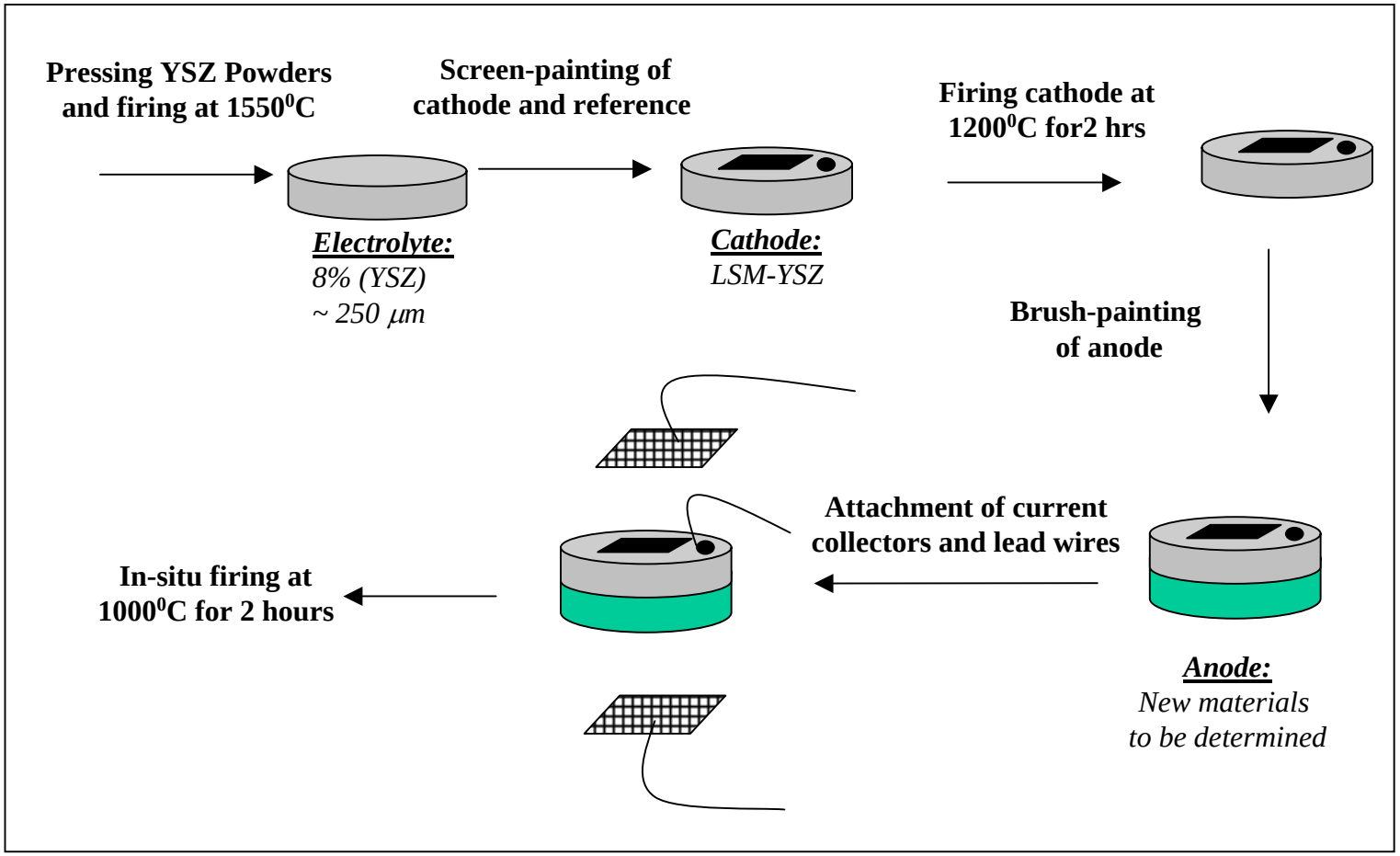
Development of New Anode Materials



Conductivity Measurement



Fuel Cell Fabrication Procedures



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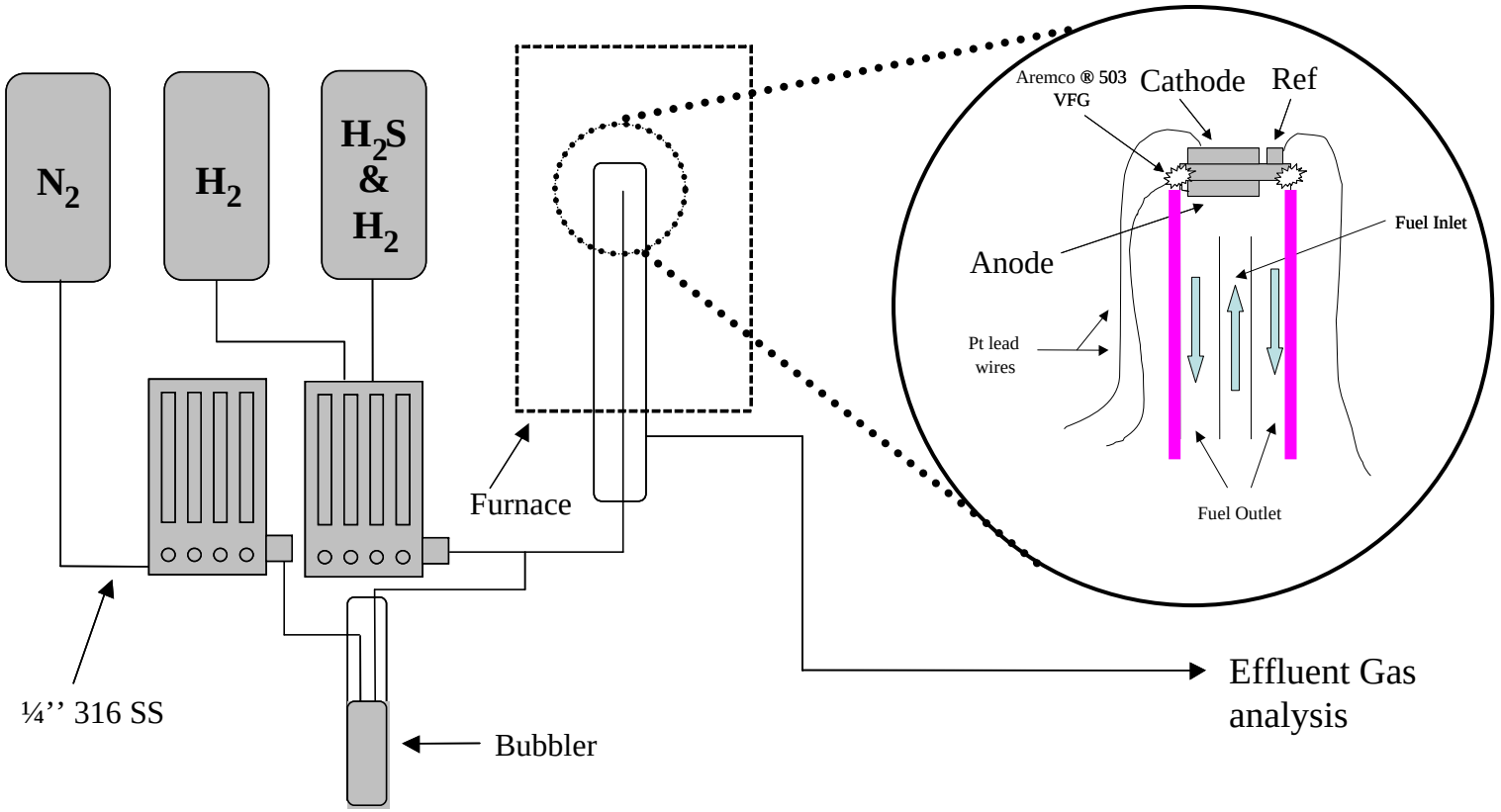
Testing of SOFCs in a H_2S Containing Fuel



Experiment setup for testing of SOFC in H_2S containing fuel

Candidate Anode Materials

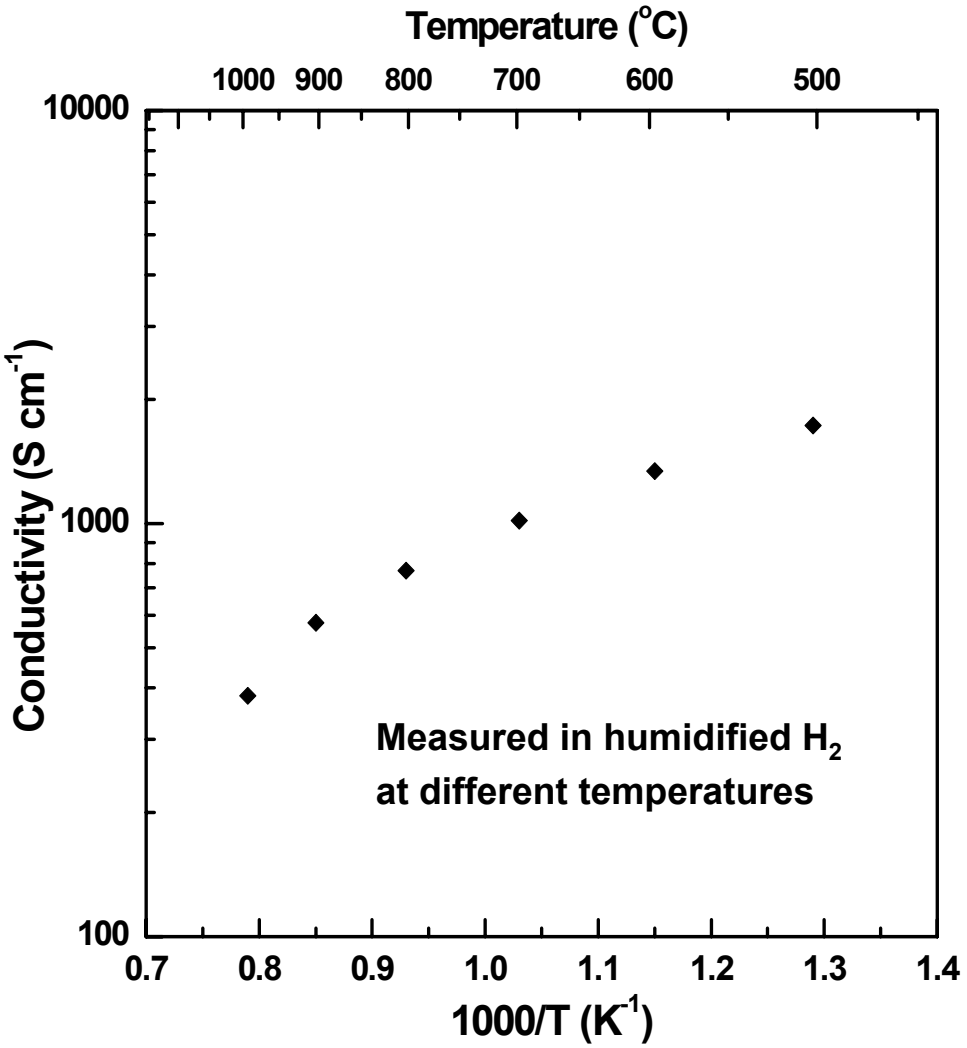
Complex oxides (e.g., ABO_3, $A_2B_2O_7$, etc.)

- 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

Material for example	σ at 800°C (S cm^{-1})	CTE (10^{-6} K^{-1})	R_p at 800 °C (Ω cm^2)	Chemical stability
$La_{0.35}Sr_{0.65}TiO_3$ (LST) [a, b, c]	600	11-12	9	Excellent
$La_{0.7}Sr_{0.3}VO_3$ (LSV) [a]	140	10-12	4	Fair
$La_{1-x}Sr_xCr_{1-y}Mn_yO_3$ (LSCM) [a, b, c]	1.5	10-11	-	Excellent
$Gd_2Ti_{1-x}Mo_xO_7$ (GTMO) [a]	1	10.8	3	Fair
$SrVO_3$ [a]	800	-	1	Fair

[a] for GTFC, [b] for PNNL, [c] for Los Alamos

Vanadium-Based Perovskites: $SrVO_3$



- **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: σ = 1000S/cm @ 700°C, comparable to that for Ni/YSZ cermet**

Resistance to H_2S

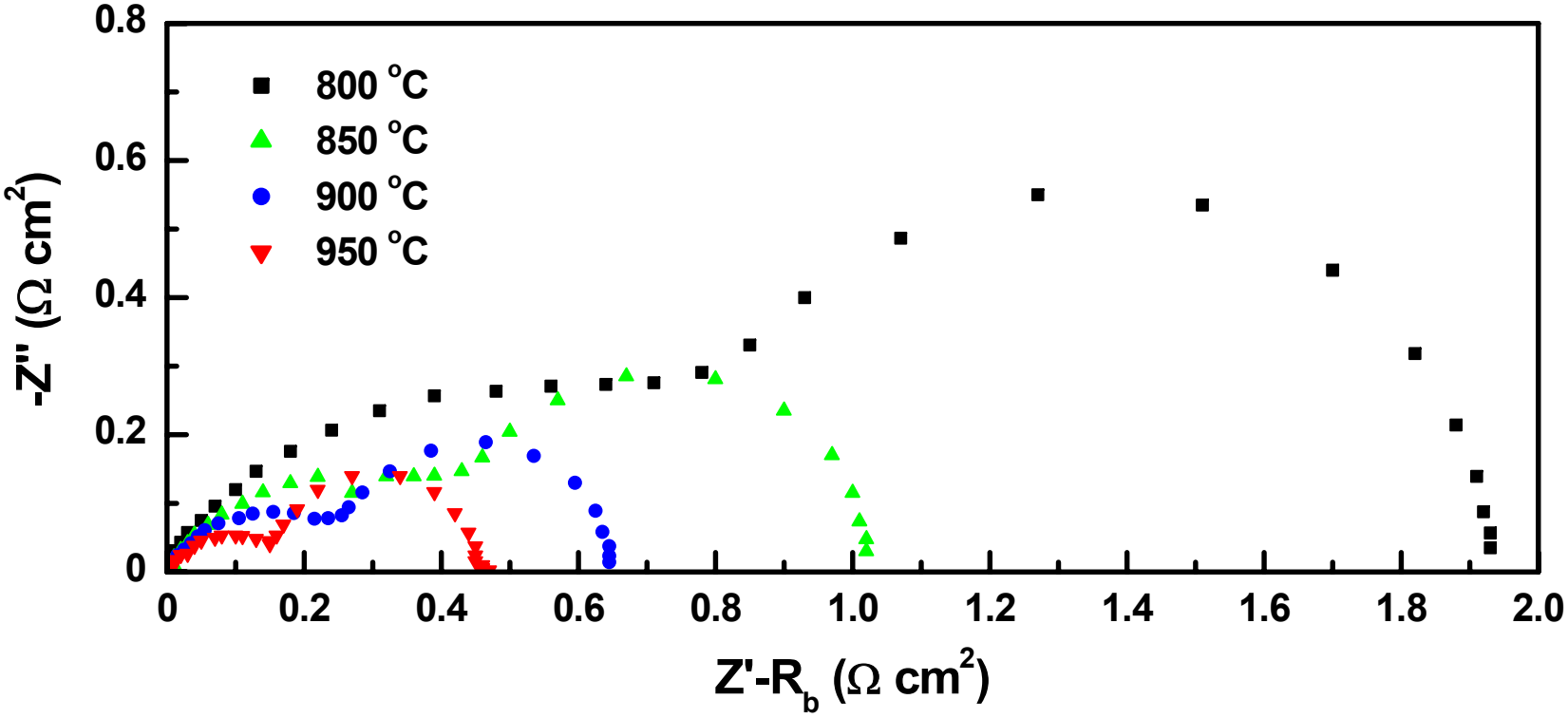
- Thermodynamic analysis indicated that $SrVO_3$ is chemically stable in 100 ppm H_2S at elevated temperature.

- Under condition of 1000K, 100 ppm H_2S/3%H_2O/97%H_2, the free energy change for the following sulfidation reaction:

  $SrVO_{3\,(s)} + H_2S_{\,(g)} + 0.5\,H_{2\,(g)} \rightarrow SrS_{\,(s)} + 0.5\,V_2O_{3\,(s)} + 1.5\,H_2O_{\,(g)}$

  is: $\Delta G \approx +37$ kJ/mol, i.e., this material is thermodynamically stable against low concentration of H_2S.

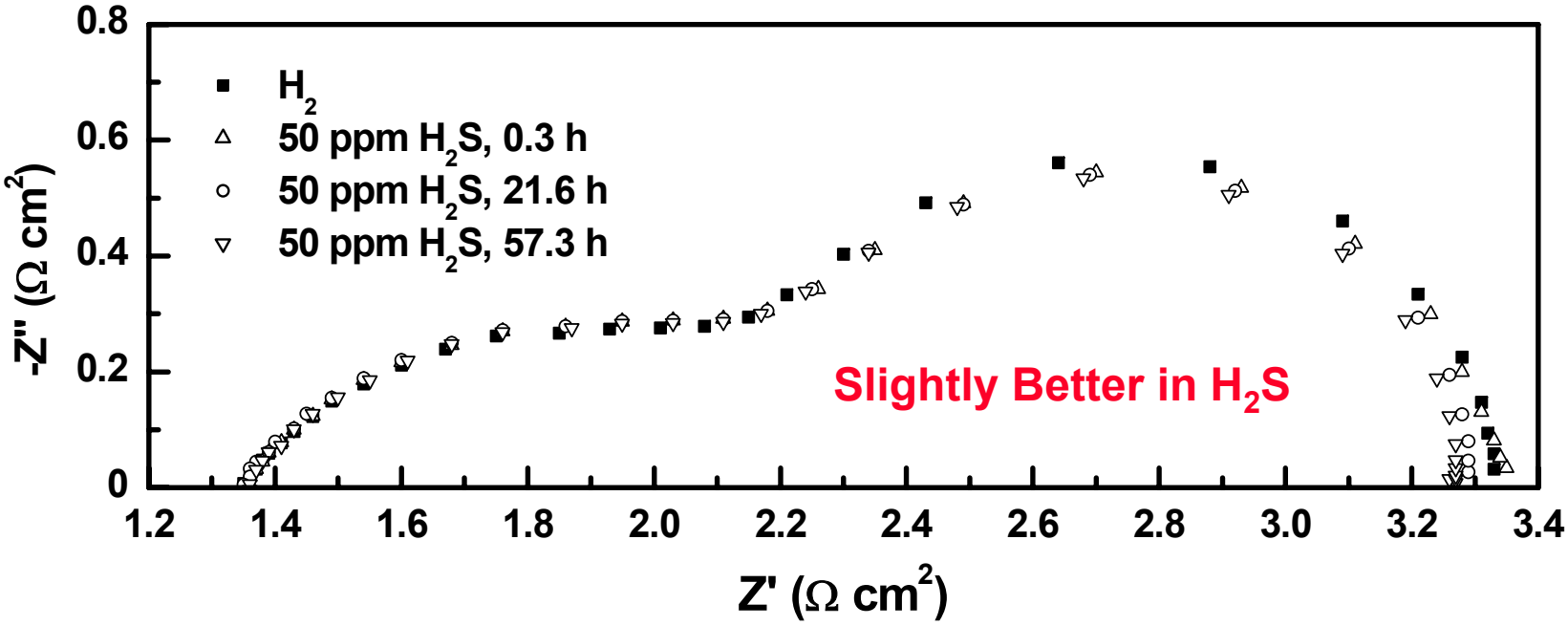
Polarization Resistance - $SrVO_3$



Impedance spectra for a $SrVO_3$/YSZ/ $SrVO_3$ symmetrical cell in 50%H_2/1.5%H_2O/48.5%N_2.

- $SrVO_3$ has decent activity for H_2 oxidation in fuel environment (0.25 Ω cm^2 @ 950°C); similar to Ni-YSZ

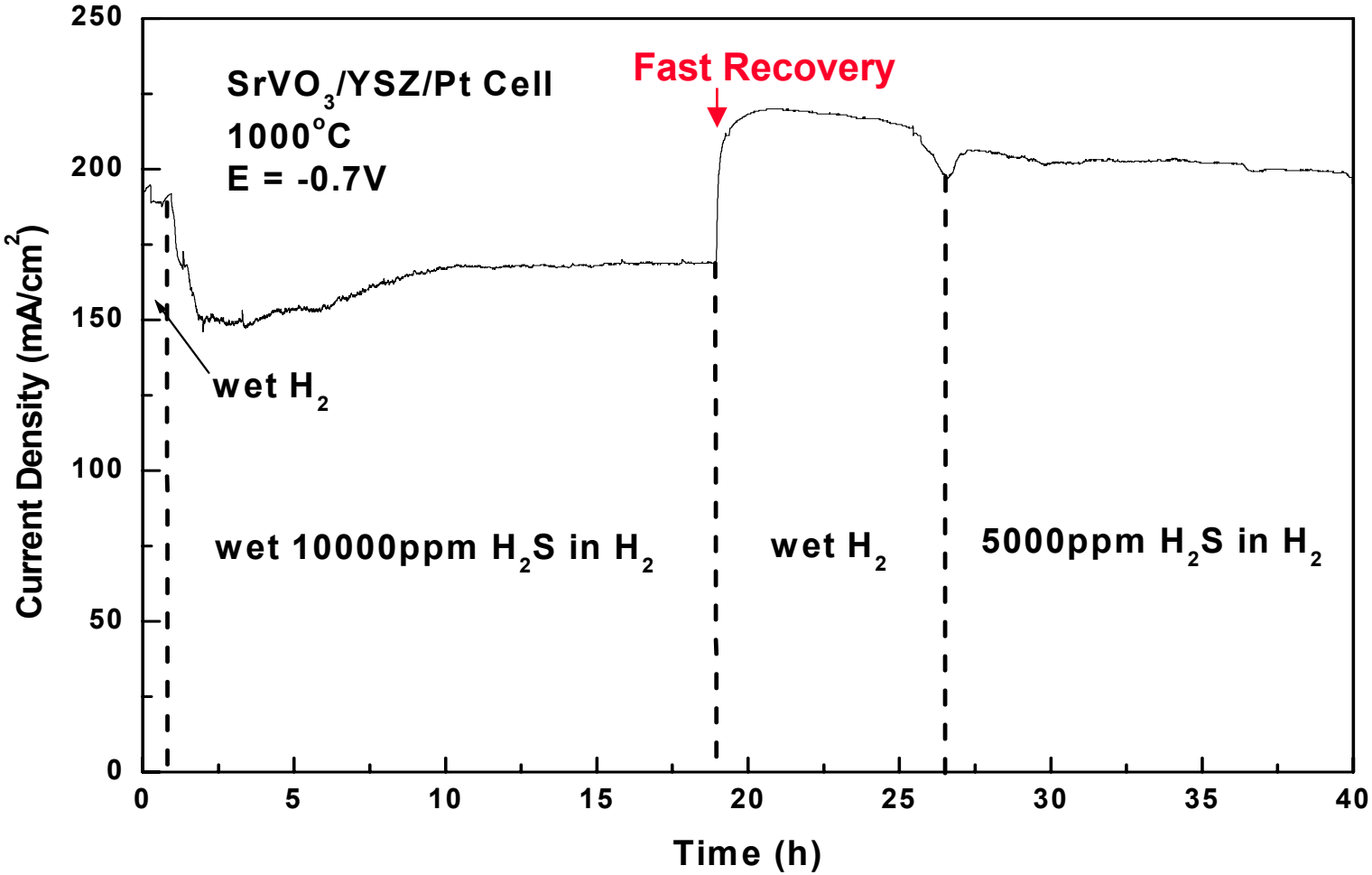
Effect of 50 ppmv H_2S on $SrVO_3$



Impedance spectra for a $SrVO_3$/YSZ/ $SrVO_3$ symmetrical cell when 50ppm H2S is introduced to a fuel of 50%H_2/1.5%H_2O/48.5%N_2

- The interfacial resistance for $SrVO_3$ anode showed no degradation in 50ppm H_2S for ~60 h.

Stability of $SrVO_3$-Based SOFC in H_2S/H_2



The result of cell stability test under much harsher condition (i.e., 1000°C, 5000-10,000ppm H_2S) suggested that the performance loss for $SrVO_3$ anode might be reversible up to 10,000 ppm of H_2S.

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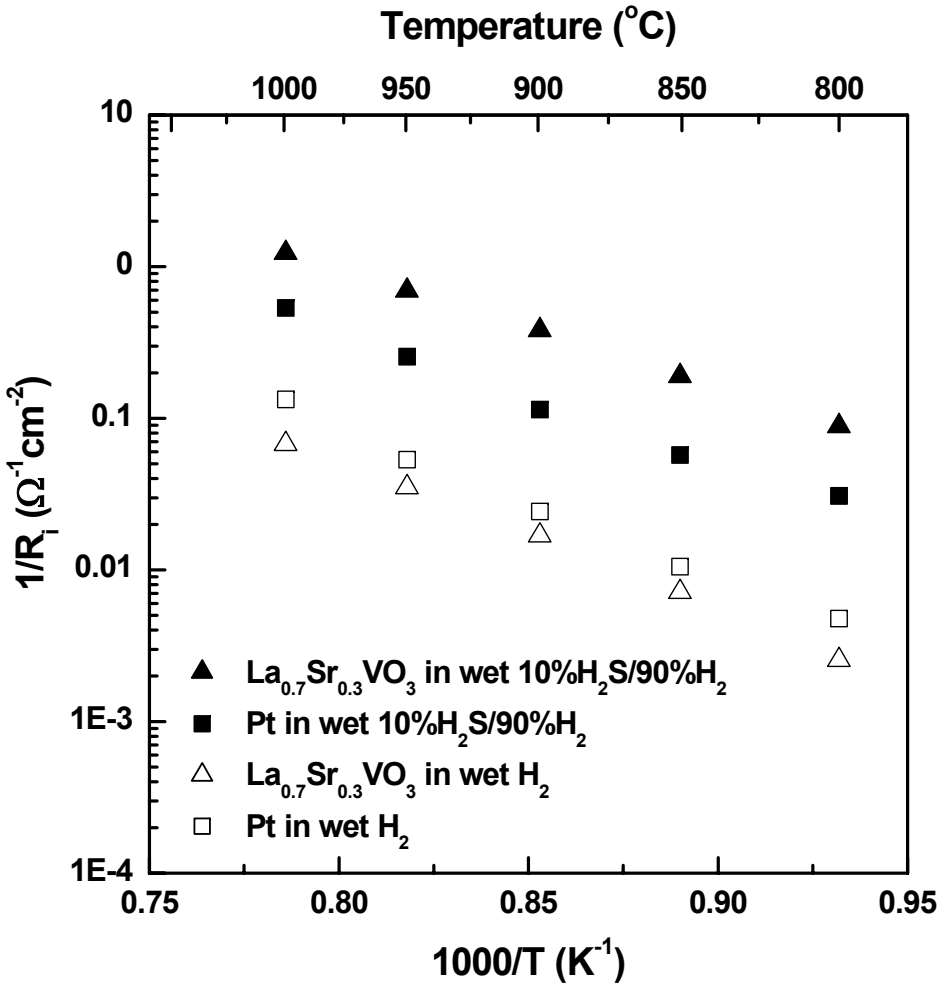
Other Vanadium-Based Oxides: LSV

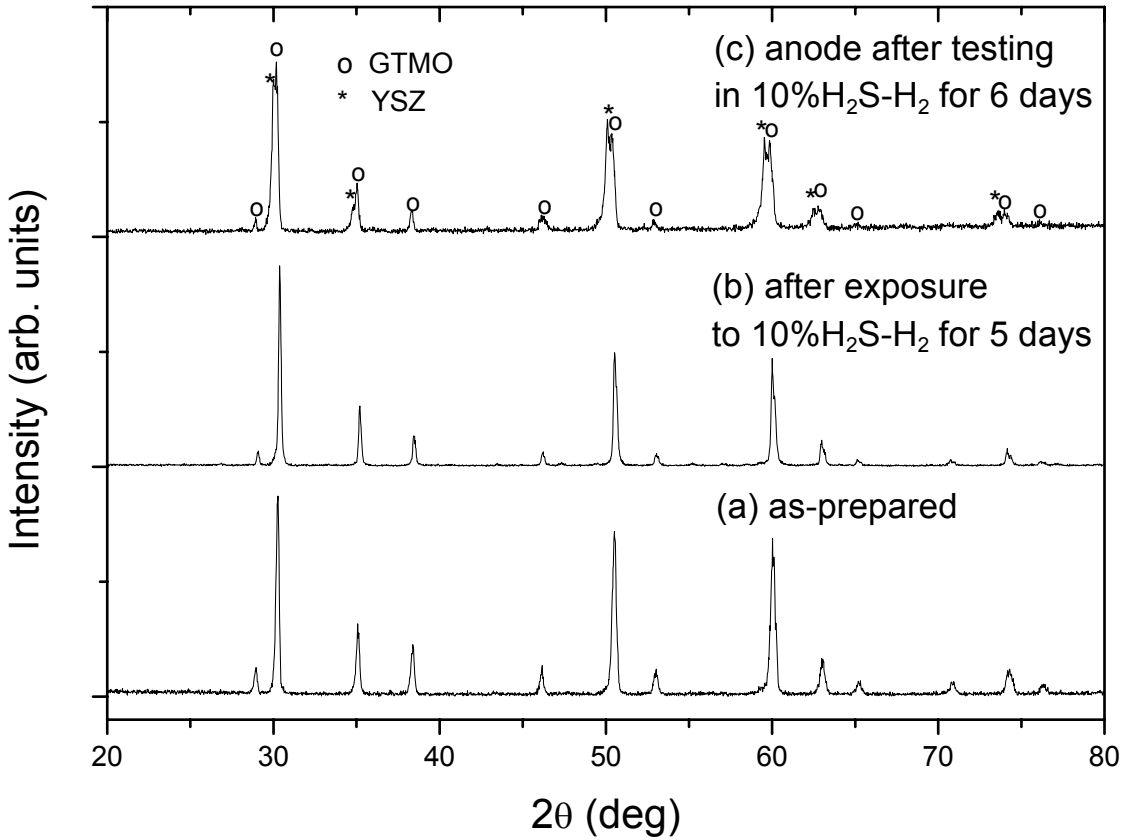


Inverse interfacial resistance vs. inverse temperature for LSV/YSZ/LSV and Pt/YSZ/Pt symmetrical cells at different temperatures

- $La_{0.7}Sr_{0.3}VO_3$ 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

$Gd_2Ti_{1.4}Mo_{0.6}O_7$ (GTMO)

Phase Stability in H_2S

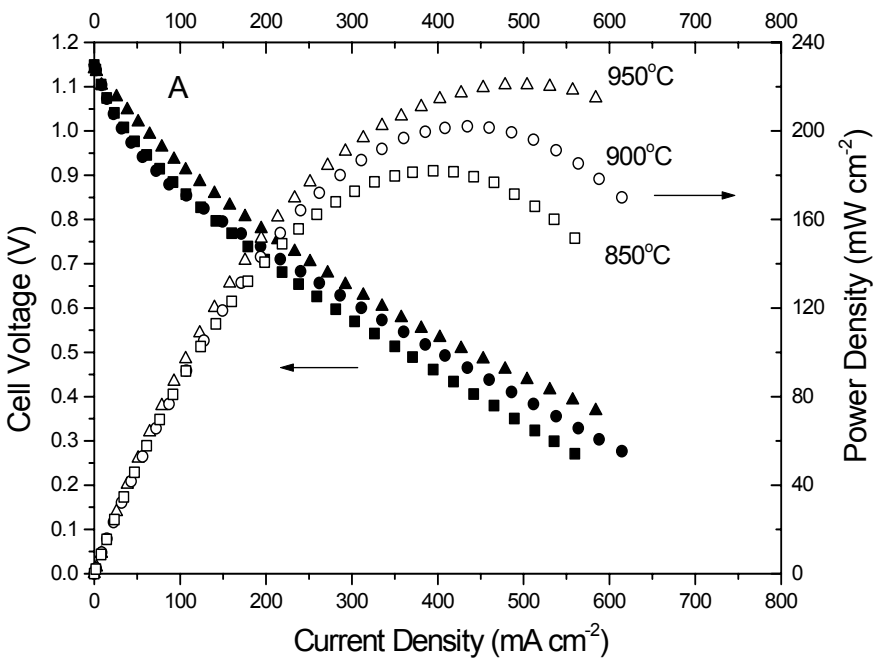


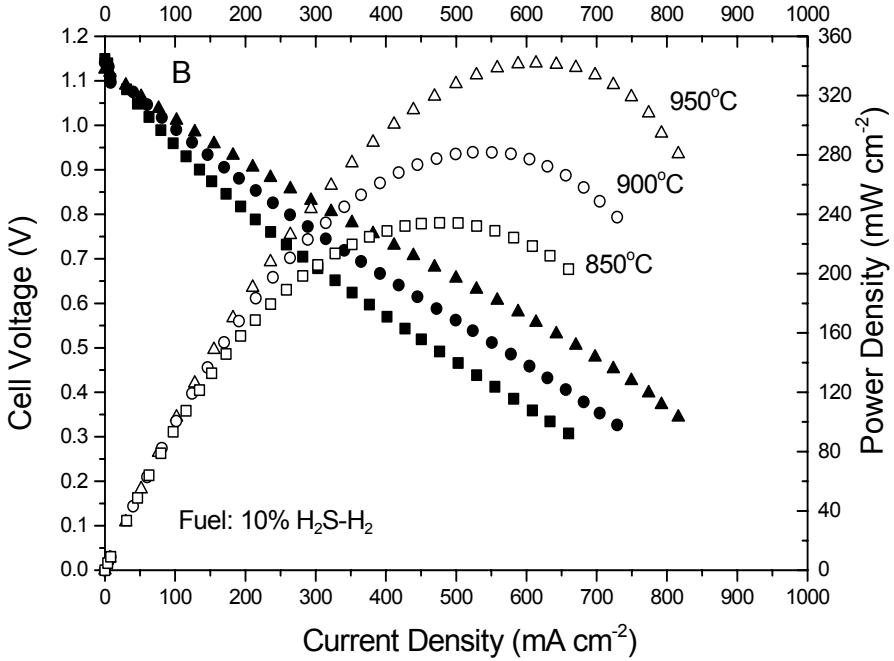
- Pyrochlore
- Phase stable under anodic conditions
- No reaction with H_2S

Note: Exposure & FC testing temperature: 950°C

Performance of GTMO Anode in an SOFC

Fuel cell: $Gd_2Ti_{1.4}Mo_{0.6}O_7$/YSZ (0.25 mm)/LSCM



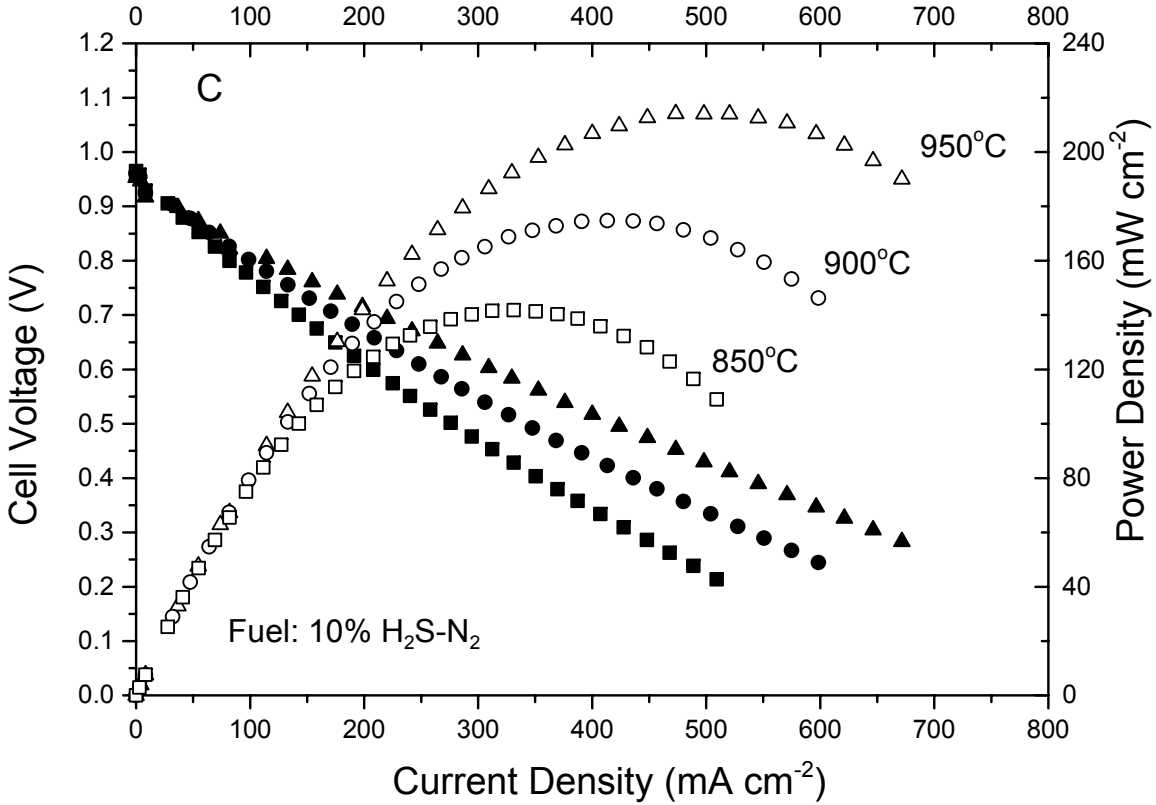


Fuel: H_2, 28 ml min^{-1}

Fuel: 10%H_2S-90%H_2, 20 ml min^{-1}

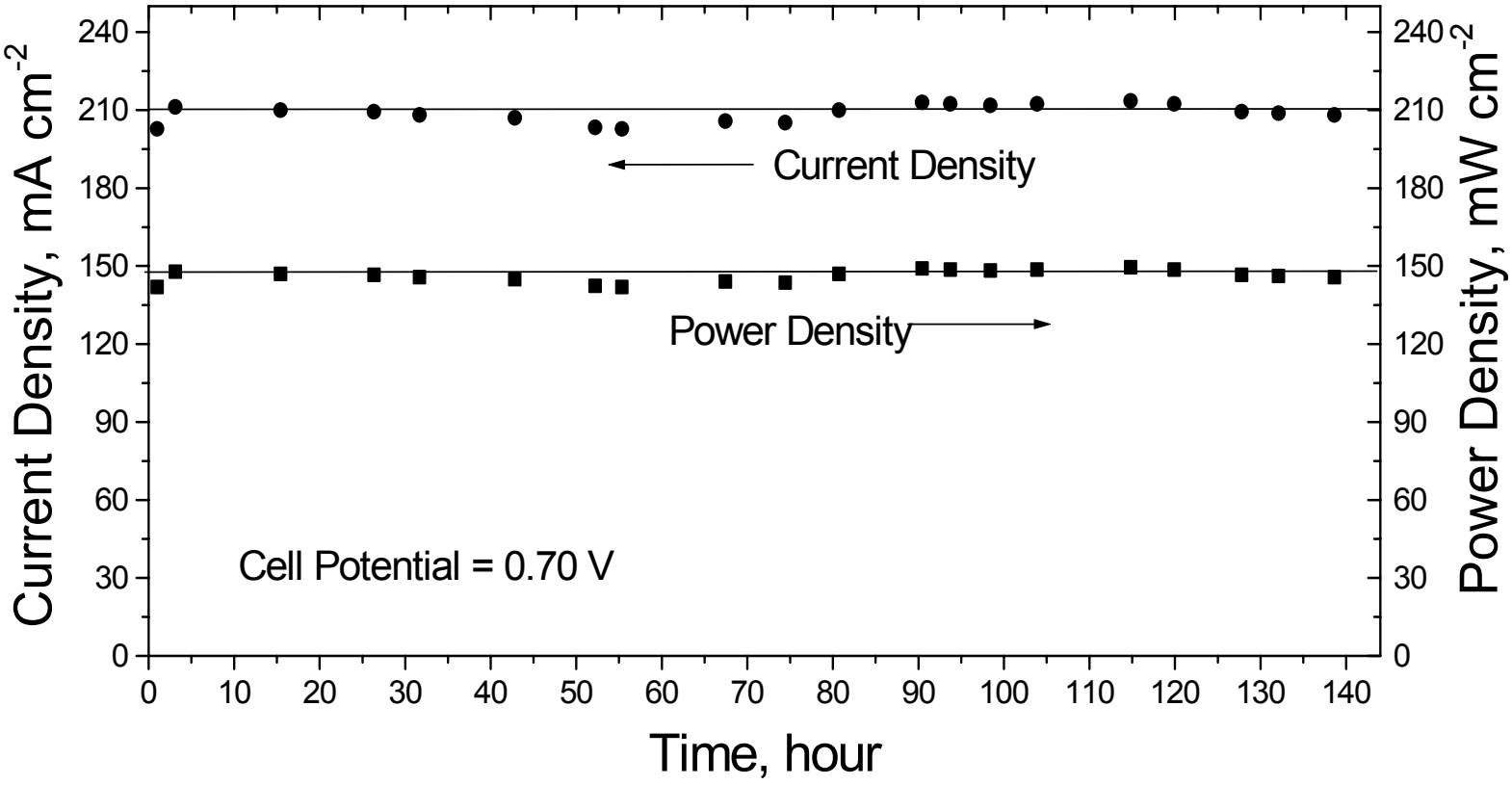
Performance of GTMO in H_2S

Fuel cell: $Gd_2Ti_{1.4}Mo_{0.6}O_7$/YSZ (0.25 mm)/LSCM



Fuel: 10%H_2S in N_2, 12 ml min^{-1}

Performance Stability of GTMO Anode

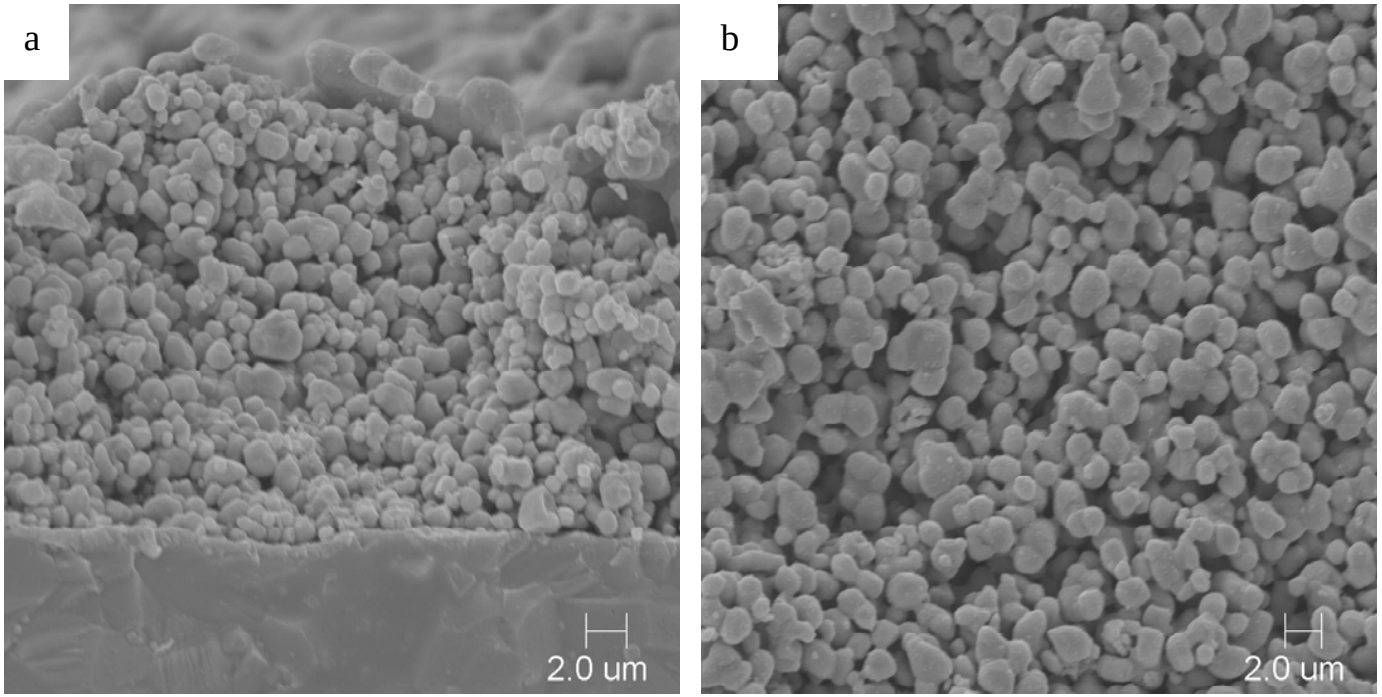


Stability testing (6 days) of a fuel cell operated on 10% H_2S-H_2 at 950 ^oC at a constant cell terminal voltage of 0.70 V. Cathode: Pt

Microstructure of $Gd_2Ti_{1.4}Mo_{0.6}O_7$ Anode

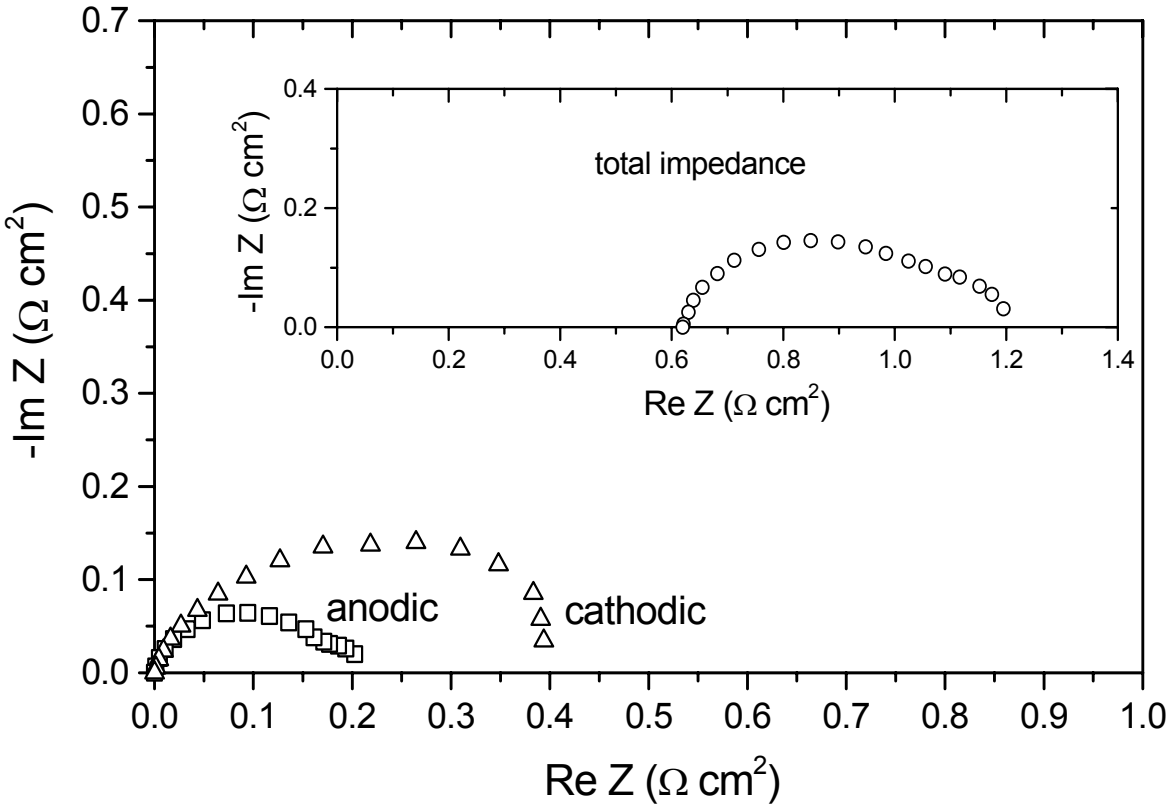
Cross-Section

Top View



SEM images of the $Gd_2Ti_{1.4}Mo_{0.6}O_7$ anode after fuel cell testing

Impedance Spectra of GTMO



YSZ bulk R:

0.6 Ω cm²

Cathode/YSZ:

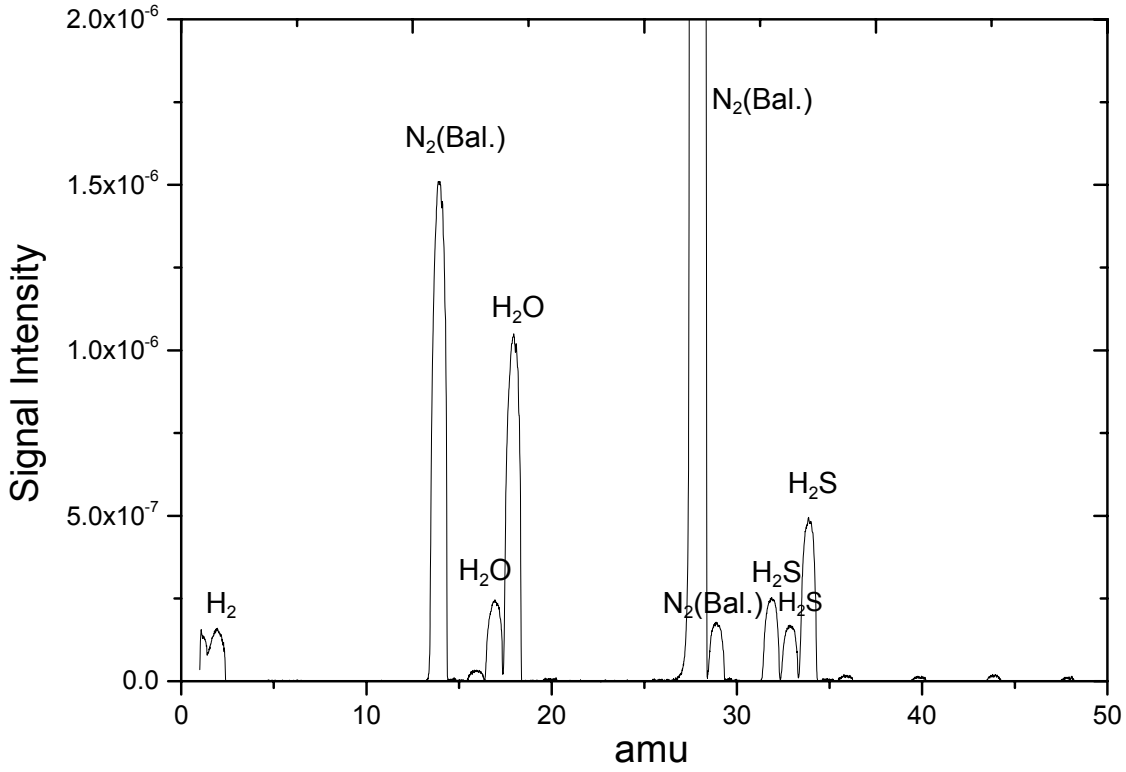
0.4 Ω cm²

Anode/YSZ

0.2 Ω cm²

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%H_2S-90%H_2, Cathode: air

Effluent Gas Analysis



Effluent gas compositions:

H_2O, small amount H_2, unreacted H_2S,

and

element S (condensed in the gas line)

Mass spectrum of the effluent gas when the anode was fed on 10% H_2S (N_2 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}.

Conclusions

- Vanadium based compounds demonstrated excellent S-tolerance and high catalytic activity in H_2S-containing fuels and thus are possible candidates for modifying the surface of Ni/YSZ anode.
- Pyrochlore $Gd_2Ti_{1.4}Mo_{0.6}O_7$ (GTMO) also showed excellent sulfur tolerance and catalytic activity towards electrochemical oxidation of H_2S.

Activities for the Next 6-12 Months

- To elucidation 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

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