Effect of sulfur and hydrocarbon fuels on titanate/ceria SOFC anodes

Olga A Marina, Larry R Pedersen, Jeff W Stevenson
Pacific Northwest National Laboratory, Richland WA

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Outline

- Requirements / Technical Issues
- R&D Objectives and Approach
- Applicability to SOFC Developers
- Results to Date
  - Review of previous progress
  - Sulfur Tolerance
  - Hydrocarbon Tolerance
- Future Work

SOFC Anode Requirements

- **Requirements:**
  - **Phase stability in fuel environment**
  - **High electronic conductivity**
  - **Excellent electrocatalytic activity for fuel oxidation**
  - **Adequate porosity for gas transport;**
  - **Chemical and physical compatibility with electrolyte, interconnect and/or contact materials**
  - **Long-term dimensional and microstructural stability**
  - **Ease of fabrication**
  - **Low cost**

Applicability to SOFC Developers

- At present, Ni-based anodes are state-of-the-art
  - High electronic conductivity
  - Excellent activity for hydrogen and clean reformed fuels
  - Chemically and physically compatible with YSZ electrolyte
  - Relatively inexpensive
- Most developers acknowledge anode limitations which impose constraints:
  - Anode protection (inert or reducing gas) during thermal cycling (system startup, shutdown)
  - Sulfur-free fuel
  - Limited amount of hydrocarbons in fuel
- Removal of some or all of these constraints would significantly reduce system complexity and cost

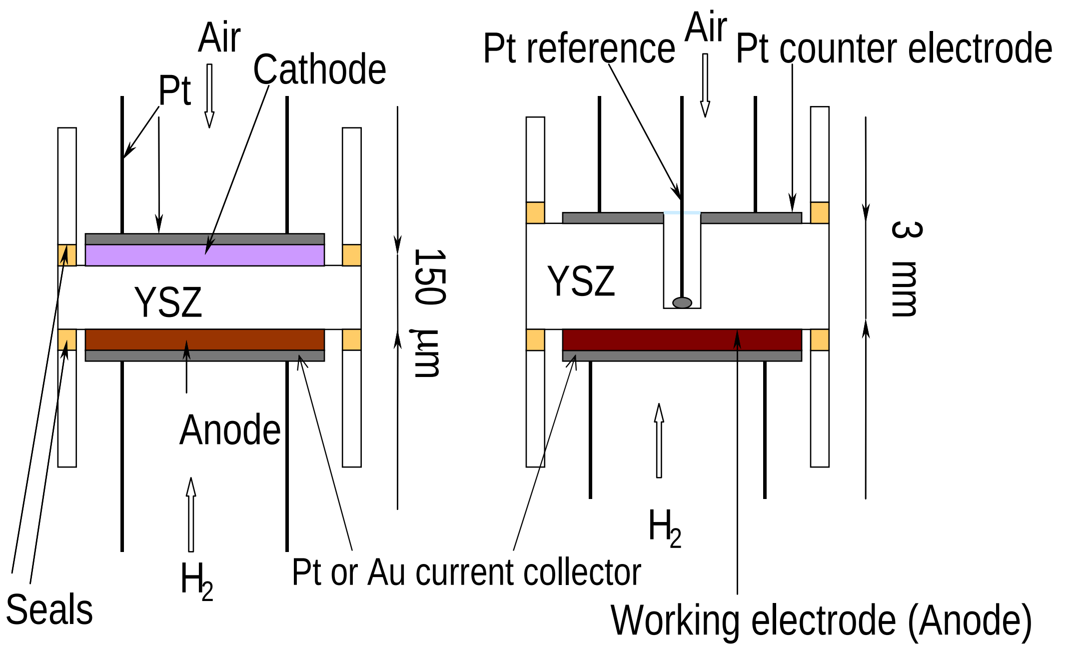
R&D Objectives

- Overall:
  - ***Develop low-cost, high-performance anodes that offer low polarization resistance as well as improved tolerance for nonidealities in anode environment such as redox cycles, sulfer and other poisons, and hydrocarbons***
- Specific:
  - ***Develop and evaluate ceramic anodes***
    - ***2 phase Sr(La)$TiO_{3-\delta}$– Ce(La)$O_{2-\delta}$ composites***
    - ***Electronic conductivity provided by doped strontium titanate.***
    - ***Activity towards fuel oxidation provided by ceria.***

R&D Approach

- Preparation of oxides
  - Glycine-nitrate synthesis
  - Calcination
  - XRD analysis
  - Attrition milling
- Evaluation of electrical and thermomechanical properties
- Anode fabrication
  - Electrode ink prep
  - Screen printing on YSZ
  - Sintering at 900-1000°C
- 2- and 3-electrode cell tests

2-electrode and 3-electrode configuration



Composite $Sr(La)TiO_{3-\delta}$ – $Ce(La)O_{2-\delta}$ anodes

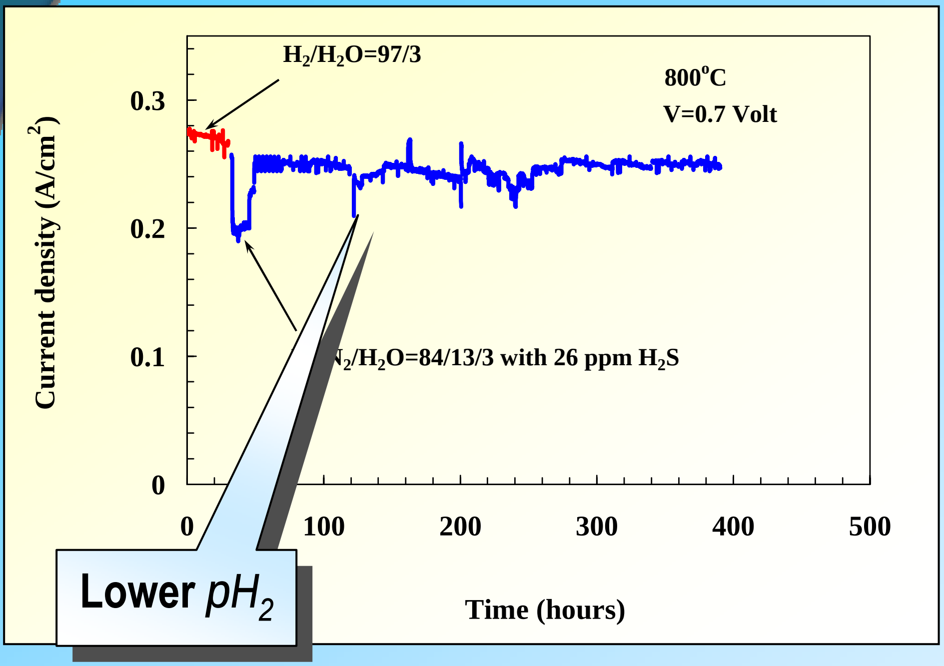
Pros

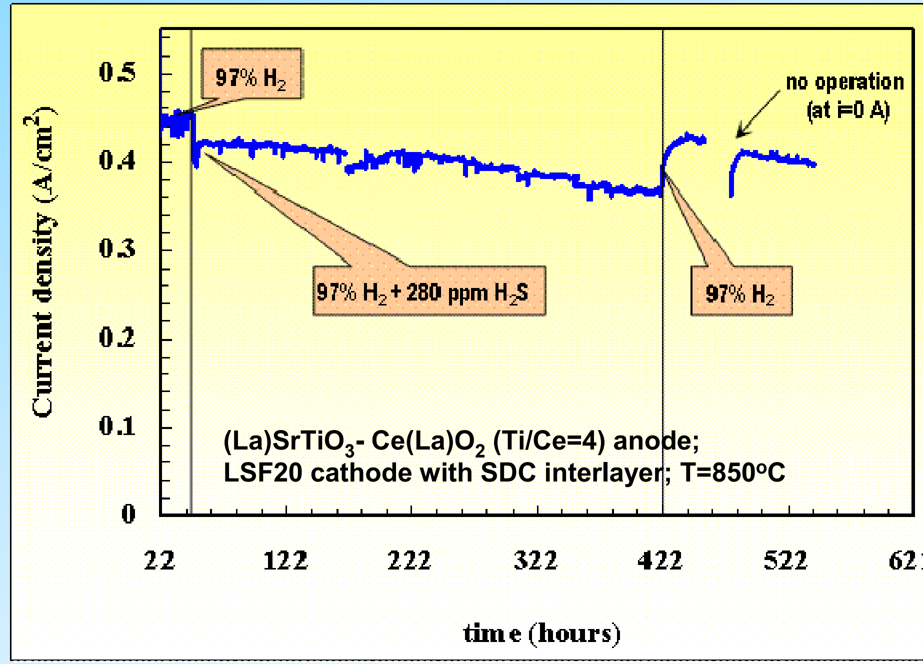
- Excellent activity for H_2 oxidation - comparable to that of Ni-YSZ
- Dimensional, chemical and electro-chemical stability under multiple red-ox cycling
- Tolerance to sulfur impurities
- Resistance to carbon formation in hydrocarbon fuels
- Good TEC compatibility with other cell components
- Good adhesion to YSZ at relatively low temperatures

Cons

- Low electrical conductivity for use as self-support
- Potential reactivity with the YSZ electrolyte at high processing temperatures (above 1300^{o}C)
- Loss of electrocatalytic activity following high processing temperatures

Task I: Effect of H_2S
Performances of YSZ electrolyte-supported cells

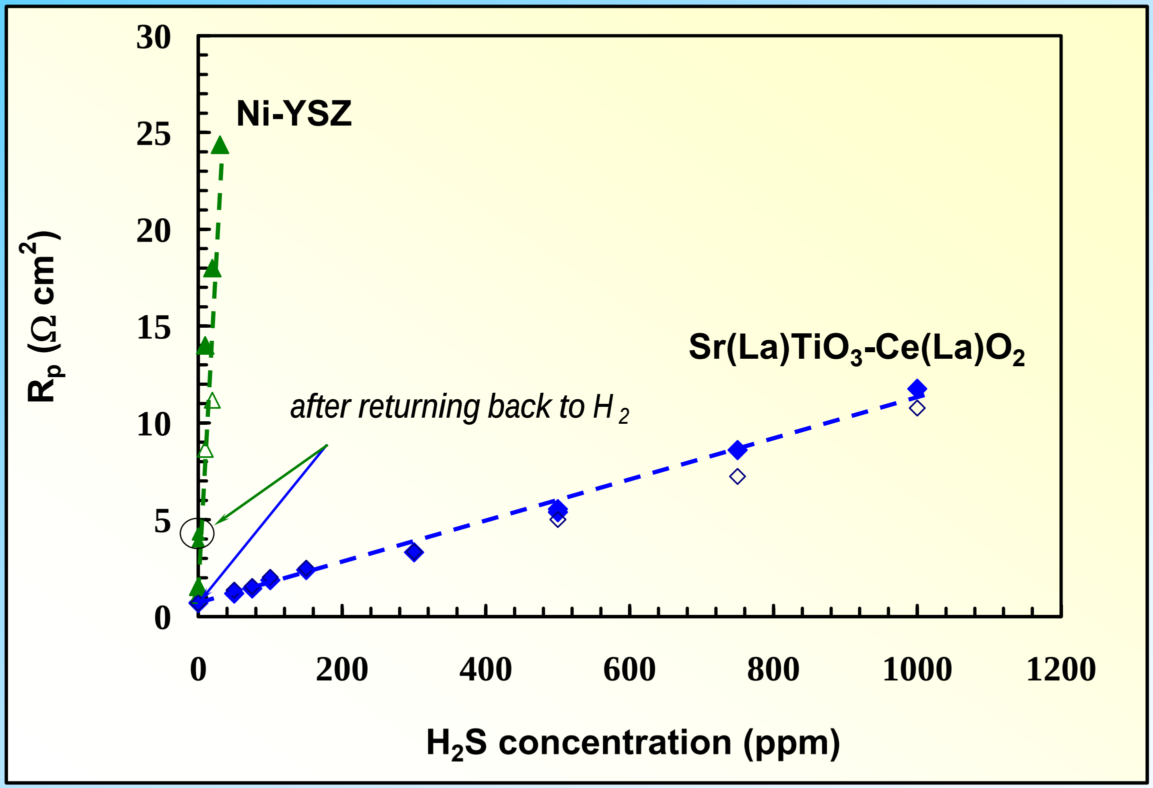




Only minor change in performance after operating for 400 h in the presence of 26 ppm H_2S

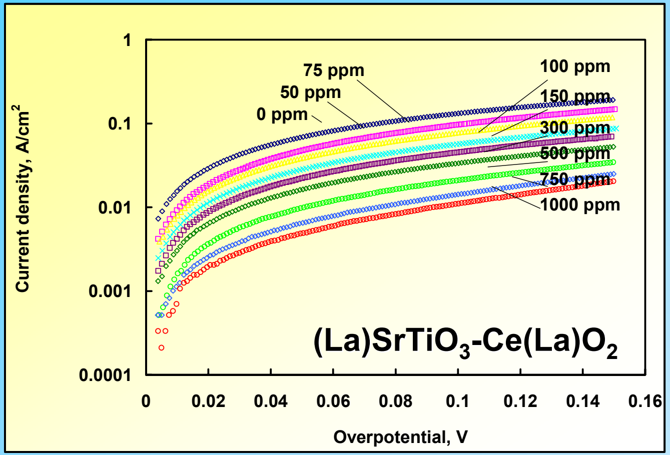
Ca. 20% drop in performance over 370 hours in the presence of 280 ppm of H_2S.

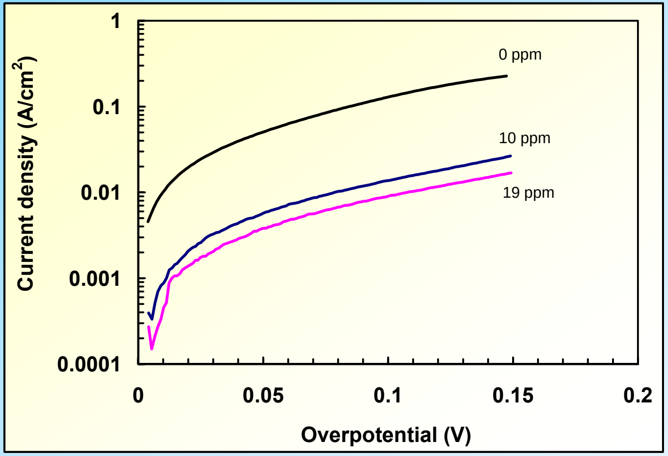
Effect of H_2S on polarization resistances of ceramic and Ni-YSZ anodes

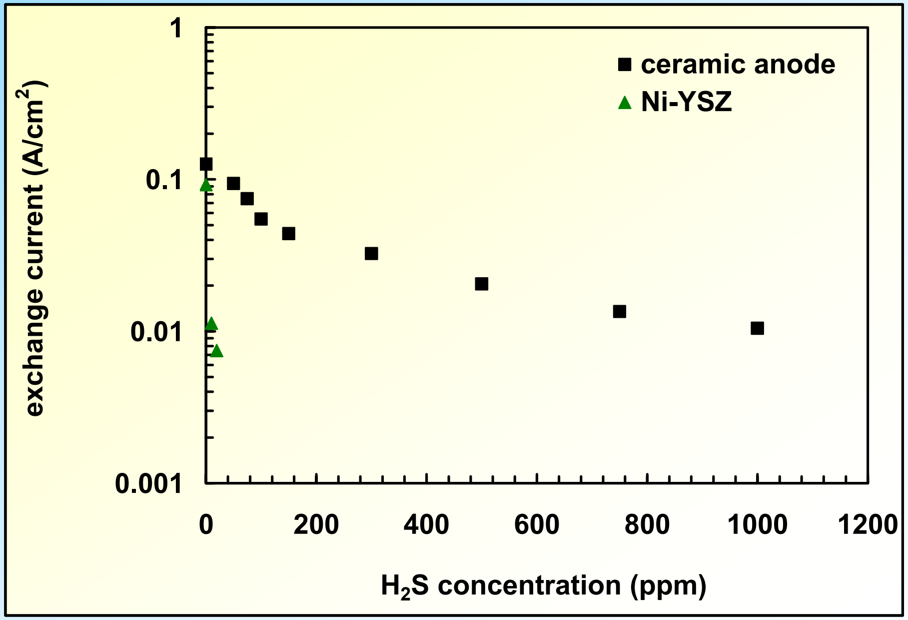


Polarization resistances of $(La)SrTiO_3$-$Ce(La)O_2$ and Ni-YSZ anodes as functions of H_2S concentration obtained via half-cell measurements using EIS (closed symbols) and dc current interrupt (open symbols). T=850^{o}C

Dependence of current density on overpotential and exchange current densities of ceramic and Ni-YSZ anodes as functions of H_2S concentration

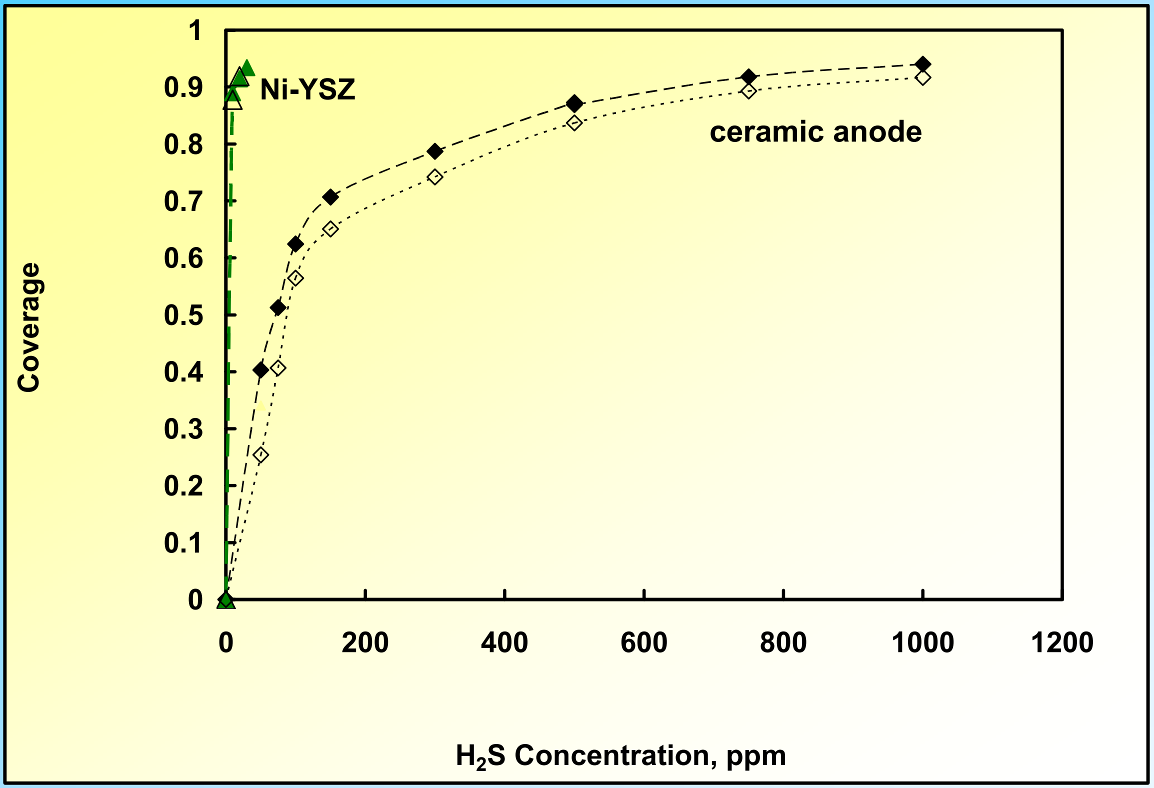






Exchange current densities calculated from the Tafel plots (left) as functions of H_2S concentration at 850°C.

Estimated sulfur coverage on ceramic and Ni-YSZ anodes at different H_2S concentration



For the titanate/ceria composite the coverage is 0.5 at 75 ppm of H_2S and 0.9 in the presence of 750 ppm.

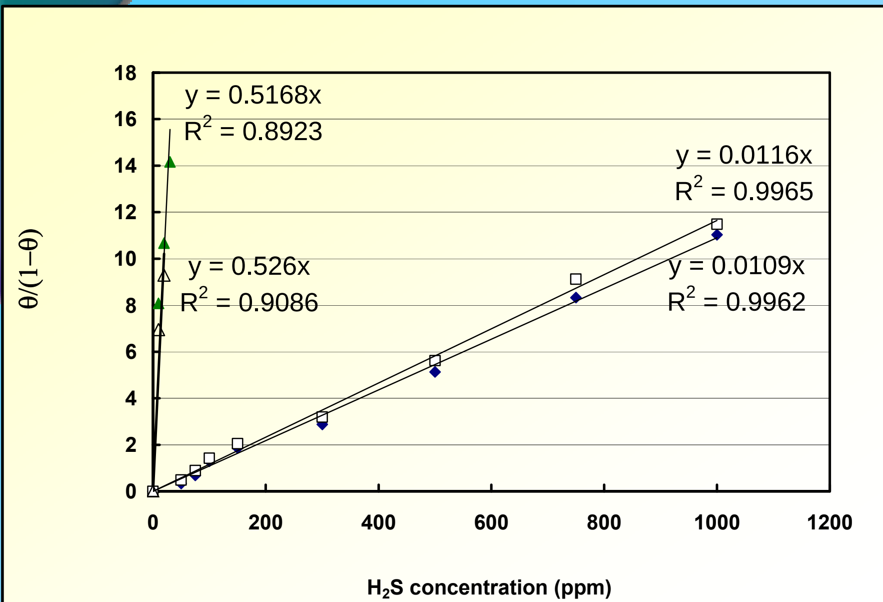
Much stronger interaction between S and Ni.

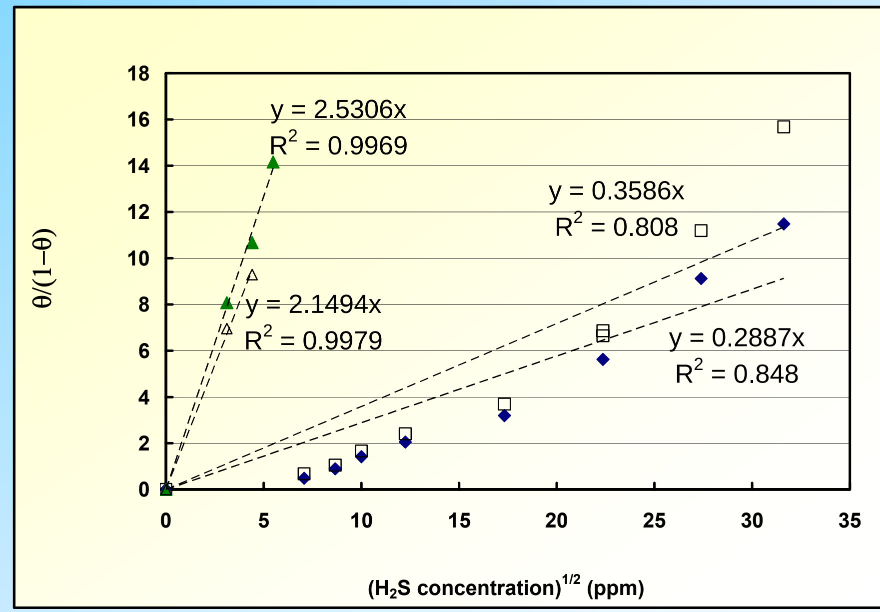
This can explain the hysterias in H_2S desorption.

The coverage is 0.9 at pH_2S>20 ppm under no current conditions.

$$\theta = 1 - \frac{i_o^{H_2S}}{i_o^{H_2}}$$, where 1 is a total number of sites.

Langmuir Isotherm Fit





Adsorption reaction:

S + M ↔ M-S

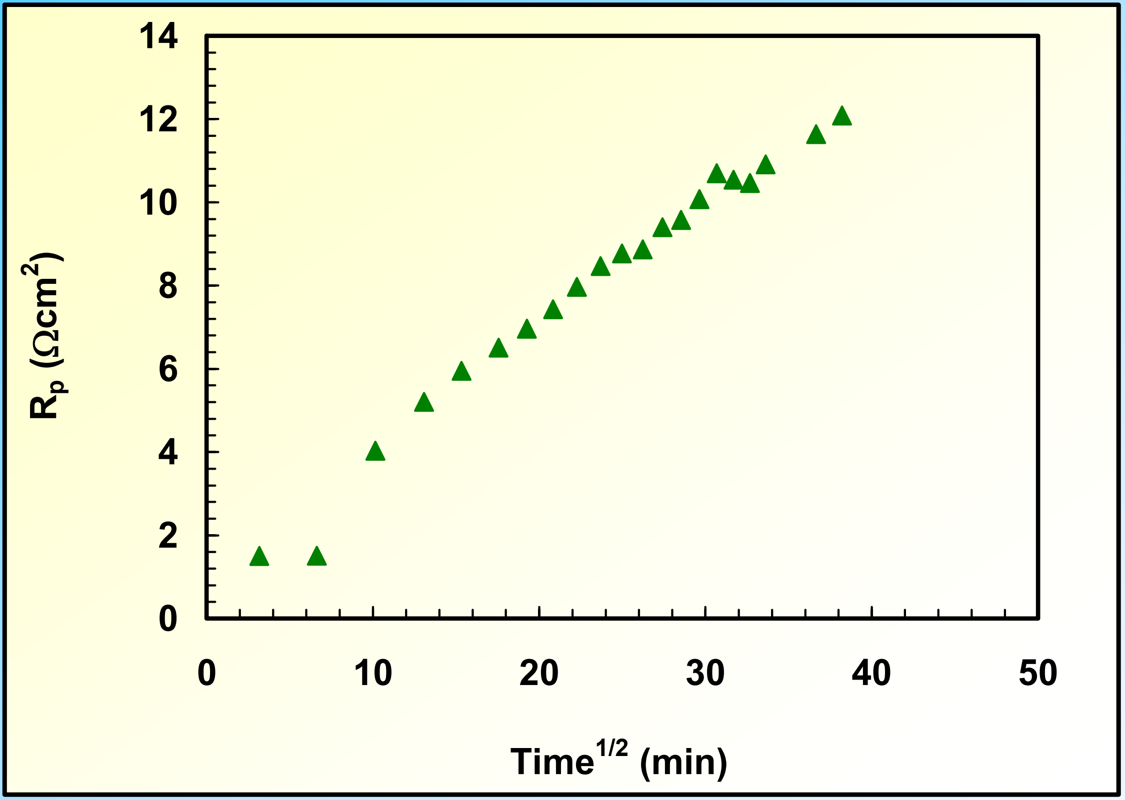
$$\theta = \frac{kP}{1+kP}$$

S + 2M ↔ M–S–M (S bridging two M)

$$\theta = \frac{\sqrt{kP}}{1+\sqrt{kP}}$$

- **H_2S apparently affects 1 site of ceria**
- **Less certain for Ni (fewer experimental data)**
  - **Formation of surface sulfide is likely, thus blocking the active sites**
    J. R. Rostrup-Nielsen, K. Pedersen, J. Catal., 59 (1979) 395
  - **Possibility of multiple occupation**

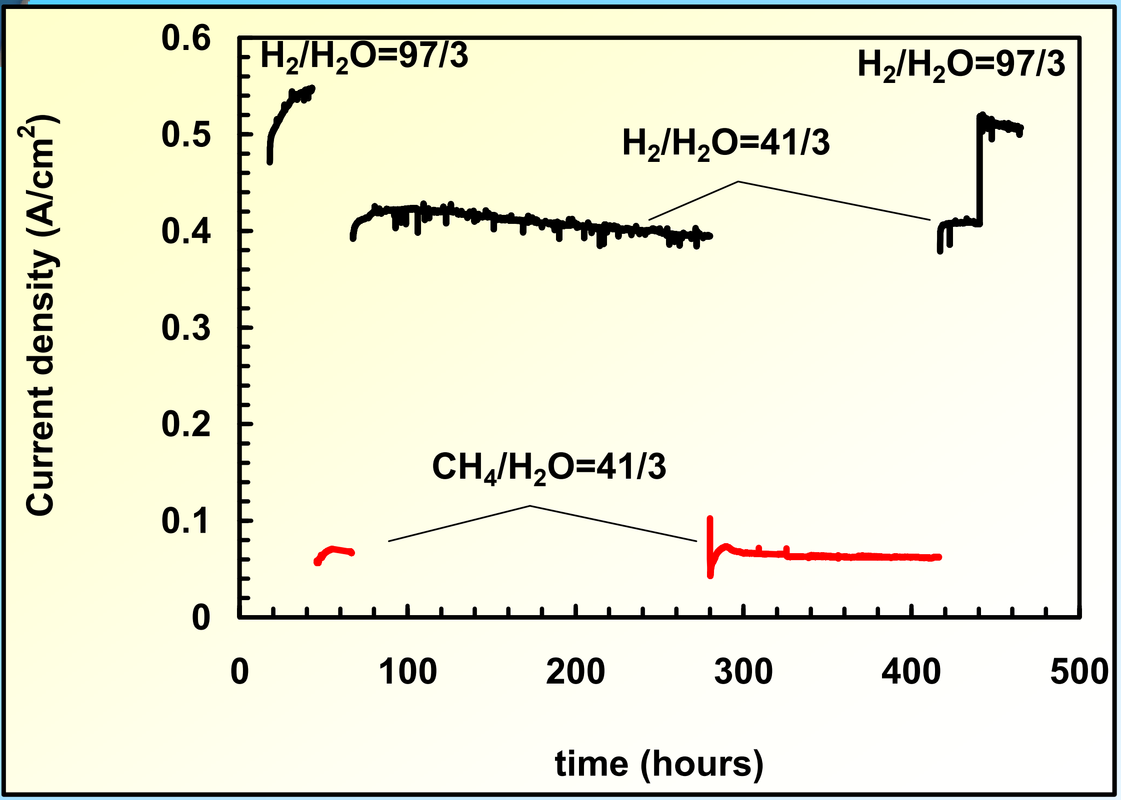
Polarization resistance of Ni-YSZ anode after exposure to 10 ppm of H_2S at 850°C



Change in polarization resistance is diffusion limited.

Unlikely simple adsorption.

Task II: Hydrocarbon fuels
Cell operation on methane

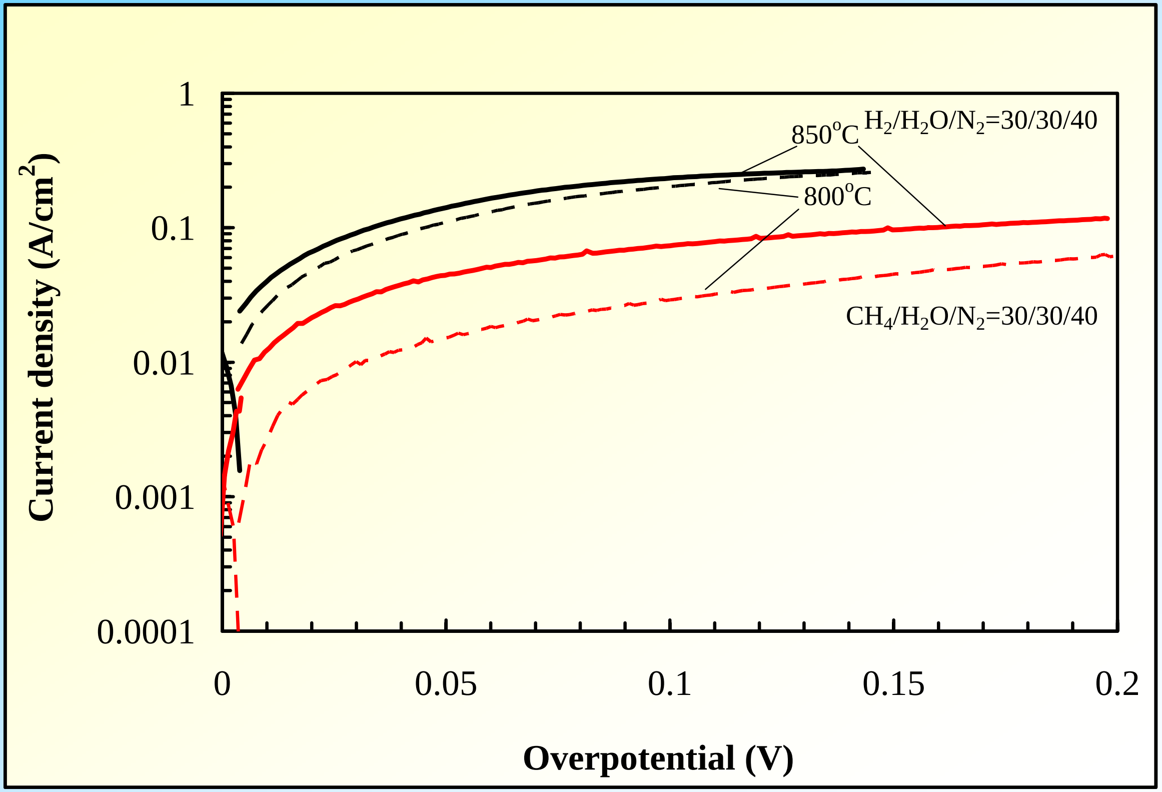


- Exhibited 6 times lower performance in CH_4 compared to that in H_2
- Operated steadily in moist methane for 1 week
- After returning to wet H_2, exhibited performance similar to the initial
- Visually, no carbon deposits seen on the anode surface after cooling in H_2
- Carbon, graphite-like, deposits were found on the gold seal rim and at the end of the alumina tube

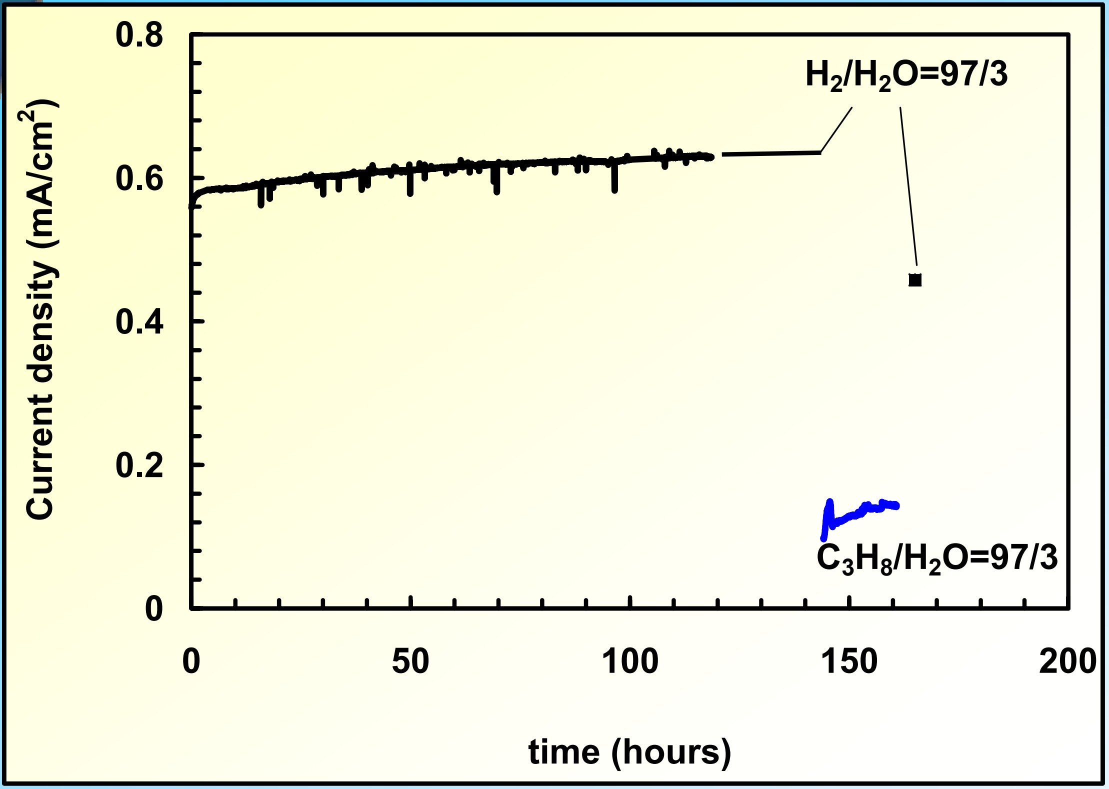
<u>Experimental conditions</u>

160 µm YSZ electrolyte-supported cell;
(La,Sr)TiO_3- Ce(La)O_2 anode
LSF20 cathode with SDC interlayer; T=850°C; Cell voltage =0.5 Volt

Polarization curves obtained on titanate/ceria composite electrode in H_2 and CH_4 at 800 and 850°C



Cell operation on propane

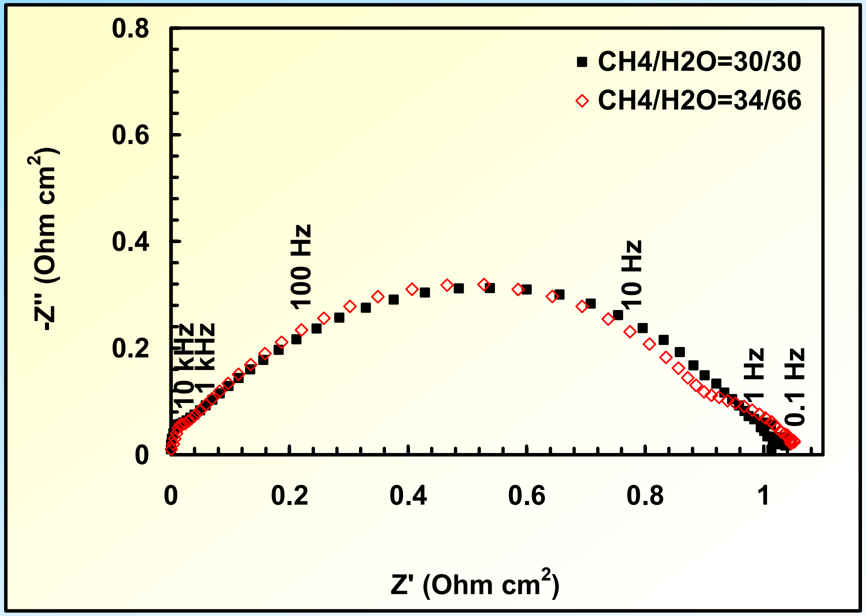


- Cell operated in moist propane for 21 hours
- Exhibited 4 times lower performance in C_3H_8 compared to that in H_2 and 1.5 times better performance than in CH_4
- After returning to wet H_2, cell did not return to the initial performance
- Tar was found on the anode, in all exhaust tubes and at the outlet

<u>Experimental conditions</u>
160 µm YSZ electrolyte-supported cell;
(La,Sr)TiO_3- Ce(La)O_2 anode
LSF20 cathode with SDC interlayer; T=850°C; Cell voltage =0.5 Volt

Mechanism considerations

- Direct electrochemical oxidation of HC is unlikely:
  - Low activity of CeO_2 for C-H bond breaking
  - Good for not coking the anode
- Steam reforming is slow:
  - Almost no effect of H_2O on the polarization resistance
  - Independent catalytic activity test (D. King)
- Thermal cracking of HC to hydrogen and carbon followed by either electrochemical oxidation of both, or H_2 only and removing carbon with steam
- CO can be utilized as fuel via electrochemical oxidation (slower) or water gas-shift (faster)



Complex impedance spectra obtained on titanate/ceria composite anode at 850°C vs Pt/air in $CH_4/H_2O/N_2$=1/1 and CH_4/H_2O=1/2.

Summary

- Interactions between H_2S and Ni and CeO_2 are different:
  - Ceramic anode shows much smaller change in the performance in the presence of H_2S and more quickly recoverable.
  - Ni-YSZ anode is more affected and recovers slowly.
  - Assumption that H_2S blocks 1 site on ceria is in agreement with experimental data (Langmuir isotherm).
  - Possibility of multiple site occupation on Ni consistent with Langmuir isotherm.
- Direct methane oxidation on the titanate/ceria anode is unlikely.
- Activity for internal on-anode steam reforming of methane is low.
- Ceramic composites are not susceptible to coking in methane; thus, there is no need for CH_4 removal from the reformate.
- The direct use of heavier hydrocarbons is unlikely due to the thermal pyrolysis issues.

Future work

- Test anodes in reformate.
- Continued optimization of ceramic anode (dopants, microstructure, thickness) to achieve performance and reliability at a level acceptable for commercial operation.
- Develop contact materials for the ceramic anode to maximize current collection between anode and metallic interconnect to achieve reliable and thermally cycable SOFCs:
  - Materials selection
  - Degradation mechanisms
  - Performance limits under high power density and during thermal and redox cycling.