Development of advanced SOFC anodes

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Existing Technology: Nickel-YSZ Anode

Pros

- High electronic conductivity
- Excellent activity for clean reformed fuels
- Chemically and physically compatible with YSZ electrolyte
- Relatively inexpensive

Cons

- Sintering / agglomeration during operation
- Sensitive to oxygen
- Too high activity towards steam reforming
- Coking in hydrocarbons
- Easy poisoning by sulfur
- Toxic

Objective: Develop a high-performance anode that offers higher tolerance to <u>oxidizing, hydrocarbon-containing and sulfur-containing</u> environments

Composite $Sr(La)TiO_3$ – $Ce(La)O_{2-\delta}$ anodes

Pros

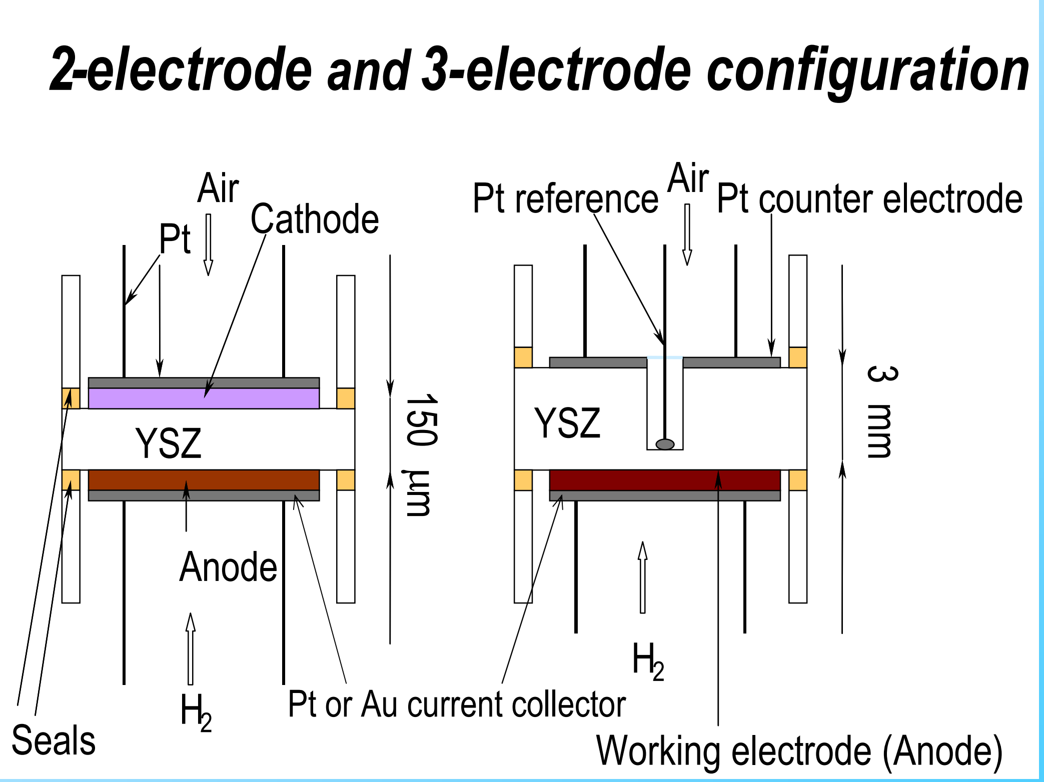
- Excellent activity for H_2 oxidation - comparable to that of Ni-YSZ
- Dimensional, chemical and electro-chemical stability under multiple red-ox cycling
- Tolerance to sulfur impurities
- Resistance to carbon formation in hydrocarbon fuels
- Good TEC compatibility with other cell components
- Good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

Approach

- Synthesis and characterization of oxides
  - Glycine-nitrite synthesis
    - Simultaneously co-synthesized
    - Separately synthesized and mixed
  - Calcination at 1200°C
  - XRD analysis
  - Attrition milling
  - Electrode ink
  - Screen printing on YSZ
  - Sintering at 900-1000°C
- 2- and 3-electrode cell tests
- Evaluation of the electrical, thermal and thermo-mechanical properties



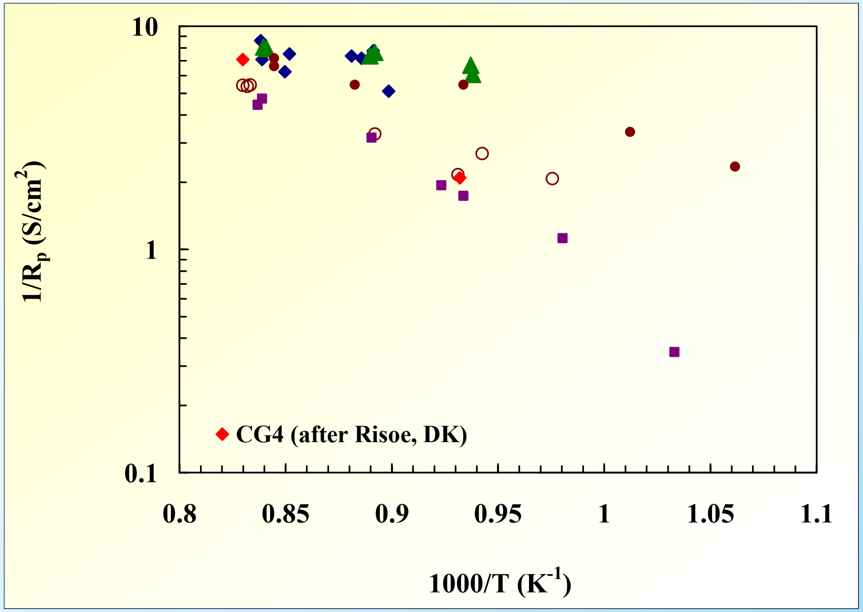
Recent Highlights

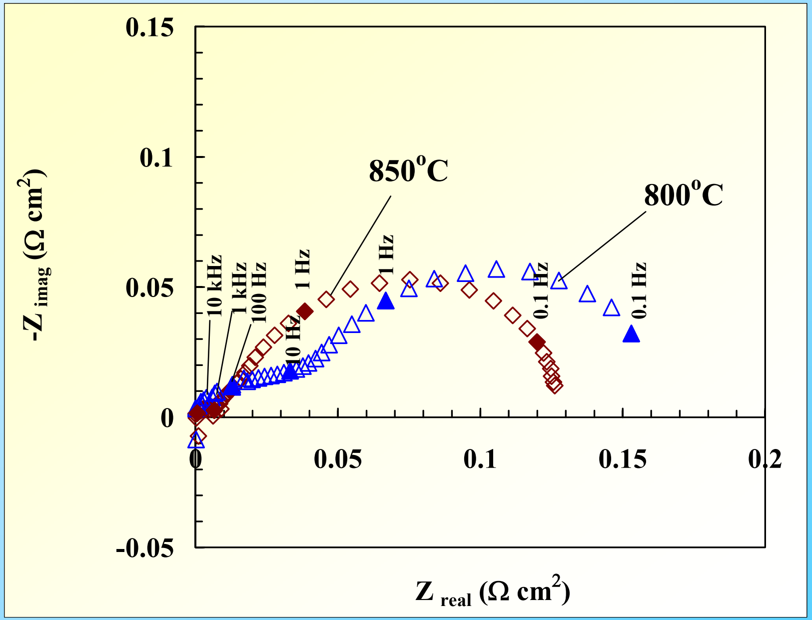
- Evaluated different anode compositions
- Investigated properties of alternative dopants in the ceria phase
- Alternative dopants led to the improved activity for hydrogen oxidation
- Evaluated effects of sulfur (H_2S) on anode performance
- Implemented a deconvolution method to facilitate impedance data analysis

Optimization of anode compositions

- Evaluated different mixtures of $Sr_{1-x}La_xTiO_3$ + $Ce_{1-y}La_yO_{2-0.5y}$ to identify the most electrochemically active composition
- Activity for hydrogen oxidation is mainly determined by the composition and amount of the ceria phase rather than the titanate phase; samples containing $Sr_{0.75}La_{0.25}TiO_3$-doped ceria and $Sr_{0.65}La_{0.35}TiO_3$-doped ceria showed similar activity
- Increasing La content in the ceria phase ($Ce_{0.7}La_{0.3}O_{1.85}$, $Ce_{0.6}La_{0.4}O_{1.8}$ and $Ce_{0.5}La_{0.5}O_{1.75}$) led to an electrocatalytic activity increase

Doped ceria phase optimization

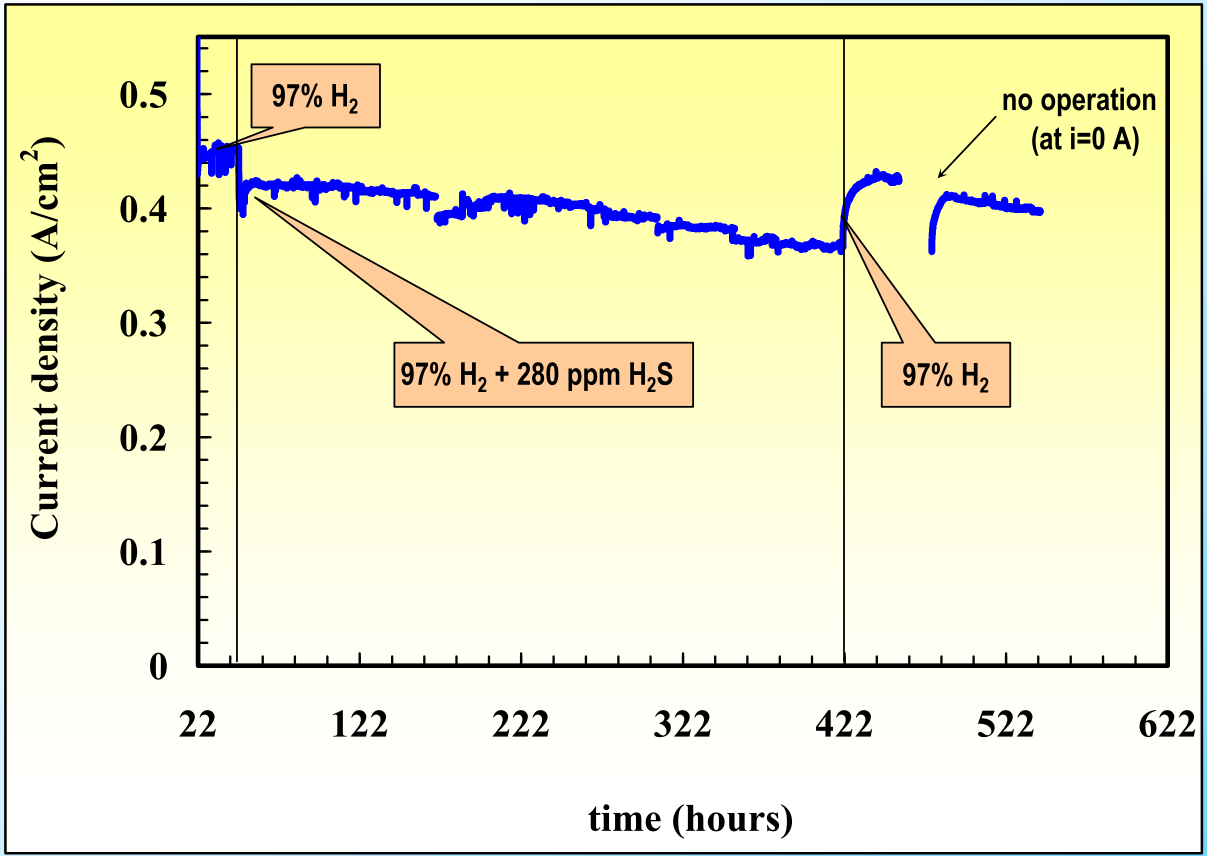




Alternative dopants appear to give slightly better performance compared to La_2O_3 and Gd_2O_3 dopants

Impedance spectra of doped ceria in H_2/H_2O=97/3 vs. Pt/air

Effect of gaseous sulfur additives (280 ppm H_2S) on cell performance



Results

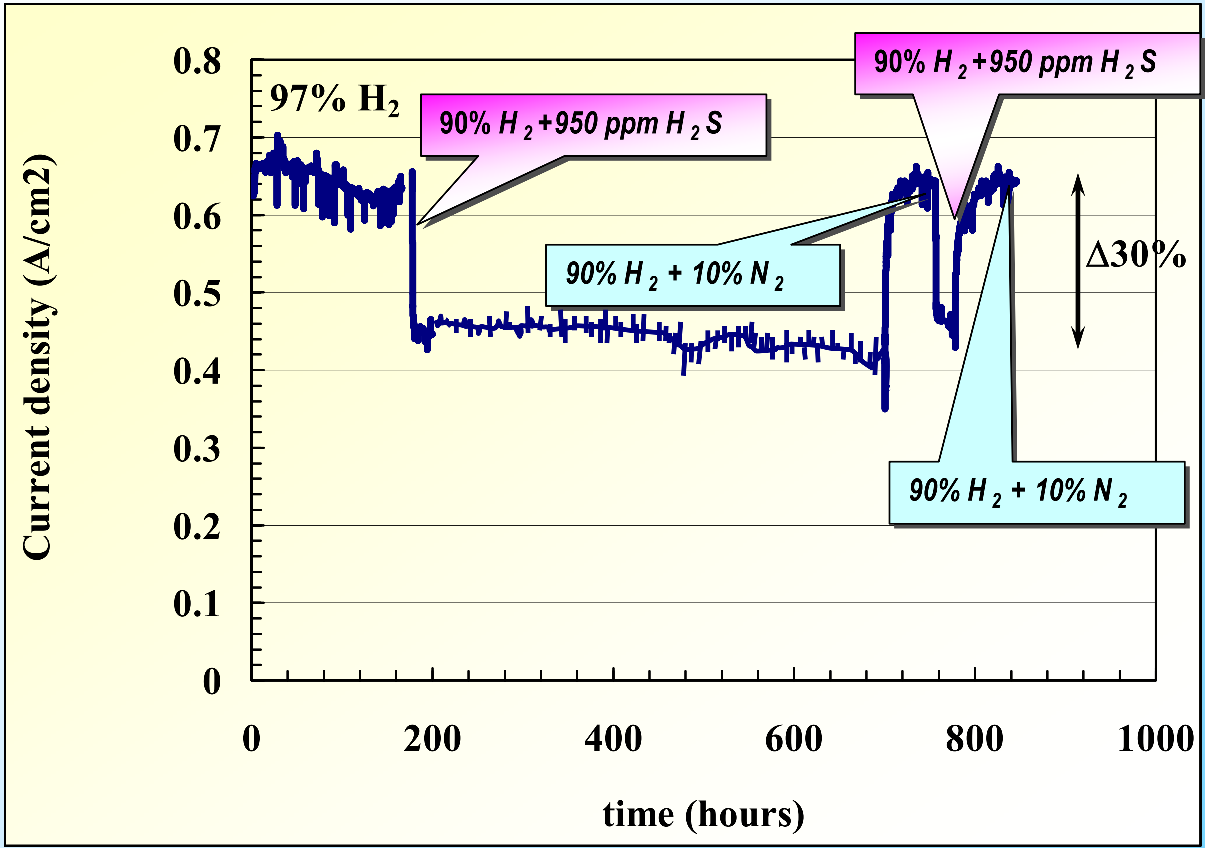
- 7% initial performance drop in the presence of 280 ppm H_2S
- Further 12% drop over 370 hours
- Anode full self-recovery after shutting H_2S down
- Visually, no sulfur deposits found on the anode after cooling in H_2
- Further degradation in H_2
- Anode degrading with time was not observed in half-cell measurements

Experimental conditions

160 μm YSZ electrolyte-supported cell; (La)$SrTiO_3$- Ce(La)O_2 (Ti/Ce=4) anode; LSF20 cathode with SDC interlayer; T=850°C; Cell voltage =0.3 Volt

Battelle

Effect of gaseous sulfur additives (950 ppm H_2S) on cell performance



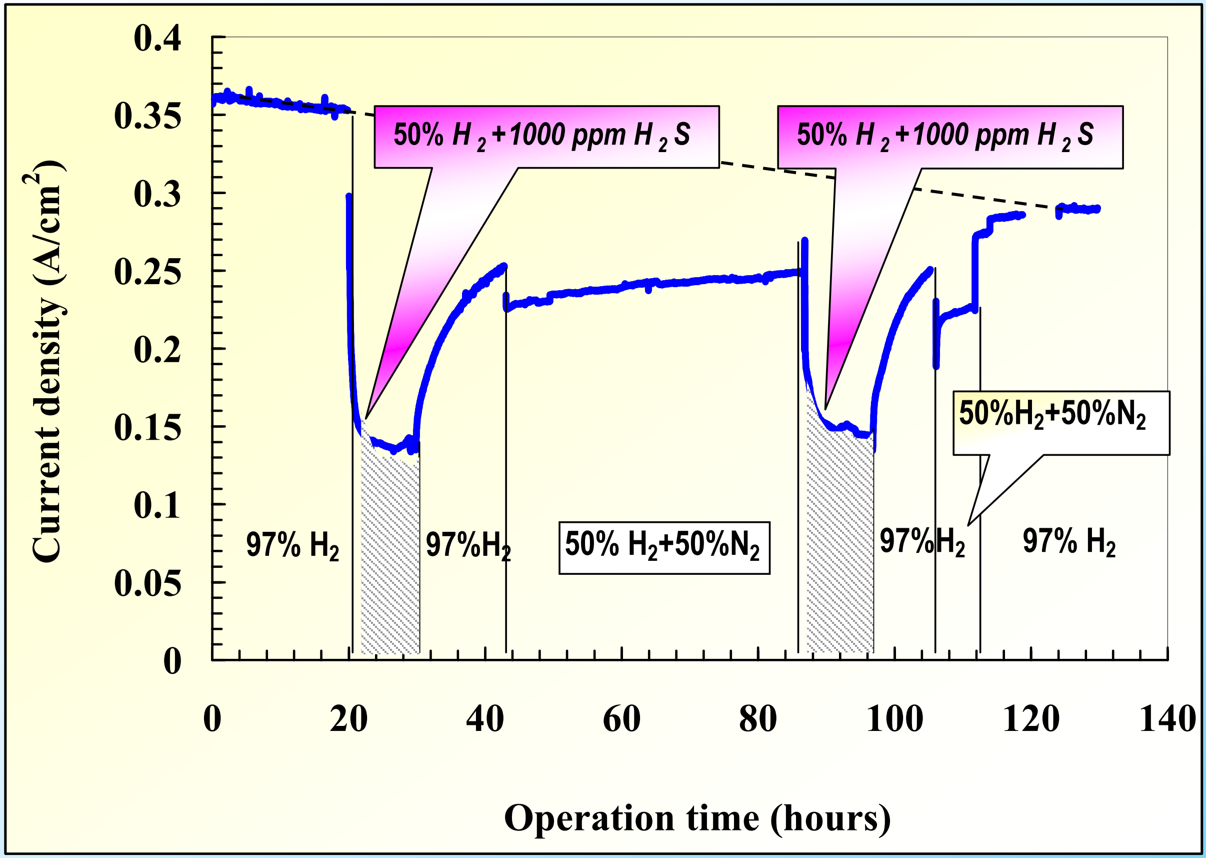
Results

- After initial 160 hours of operating in wet hydrogen, the cell ran for 500 hours on 90% hydrogen with 950 ppm H_2S
- Performance dropped by 30% in the presence of H_2S
- Self-recovered after turning H_2S off (repeated twice)
- No air required to the anode for sulfur removal

Experimental conditions

160 μm YSZ electrolyte-supported cell;
$La_{0.35}Sr_{0.65}TiO_3$- $Ce_{0.7}La_{0.3}O_2$ (7:3 mol%);
LSF20 cathode with SDC interlayer; T=850^{o}C; Cell voltage =0.3 Volt

Effect of gaseous sulfur additives (1000 ppm H_2S) on cell performance



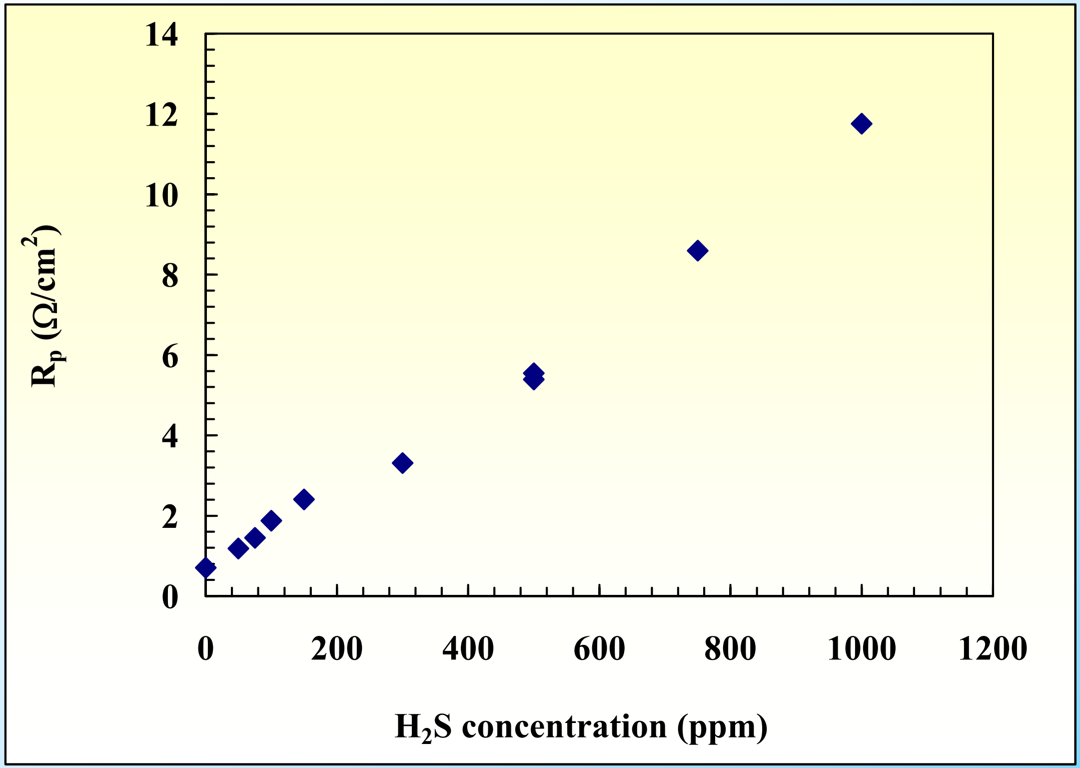
Experimental conditions

160 μm YSZ electrolyte-supported cell; (La)$SrTiO_3$- Ce(La)O_2 (Ti/Ce=4) anode; LSF20 cathode with SDC interlayer; T=850°C ; Cell voltage =0.7 Volt

Results

- 40% performance drop in the presence of 1000 ppm H_2S
- Anode self-recovery after shutting H_2S down (repeated twice)
- No air or hot steam required for sulfur removal
- Visually, no sulfur deposits found on the anode after cooling in H_2
- Sulfur found on the alumina sample holder
- Final performance decrease of 18% may be related to (i) anode degradation in the presence of H_2S; (ii) cathode degradation with time; (iii) observed Pt current collector delamination from the anode; (iv) Pt poisoning by sulfur..

Effect of H_2S on the anode polarization resistance



Experimental conditions

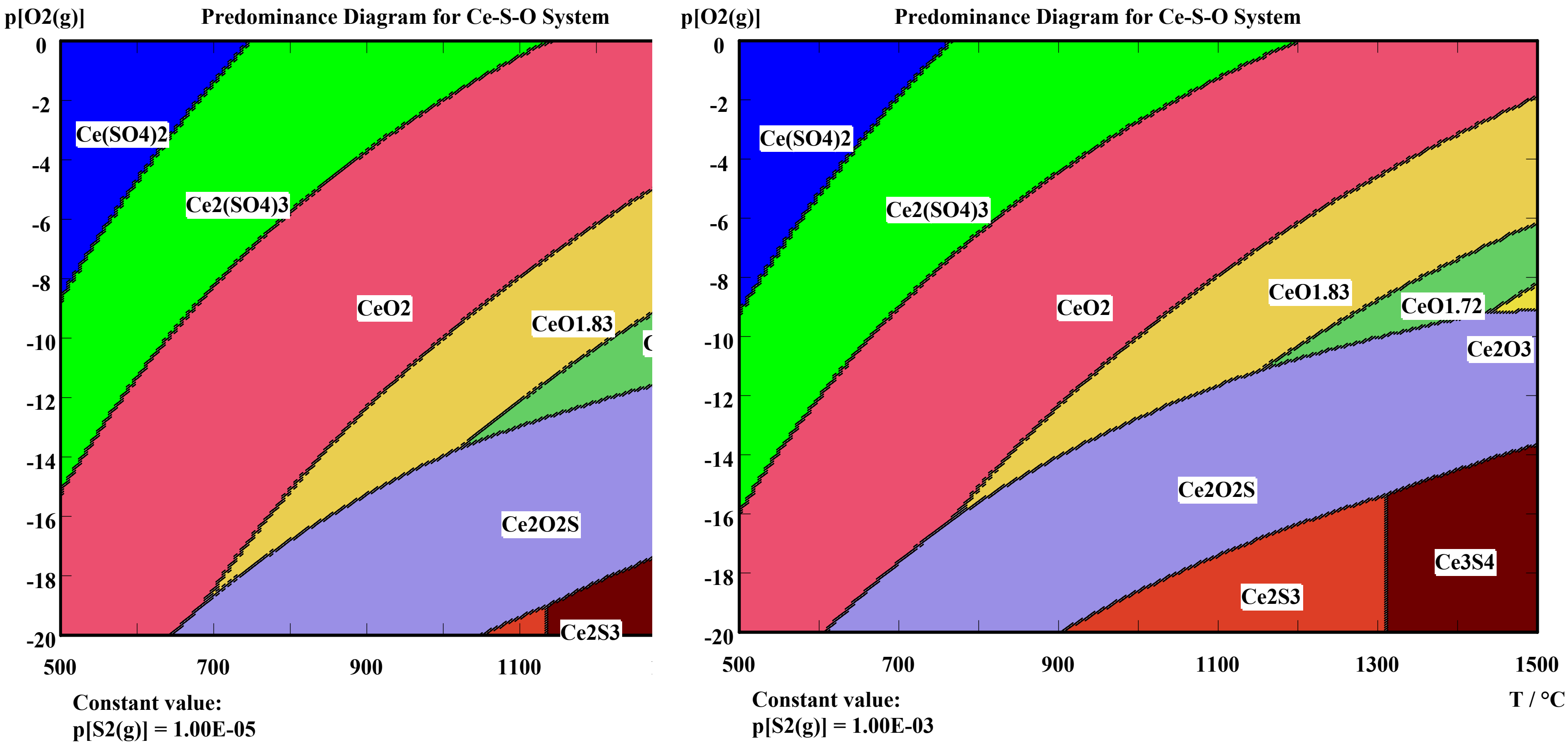
Half-cell measurements

$La_{0.35}Sr_{0.65}TiO_3$- $Ce_{0.7}La_{0.3}O_2$ (7:3 mol%)

T=850°C

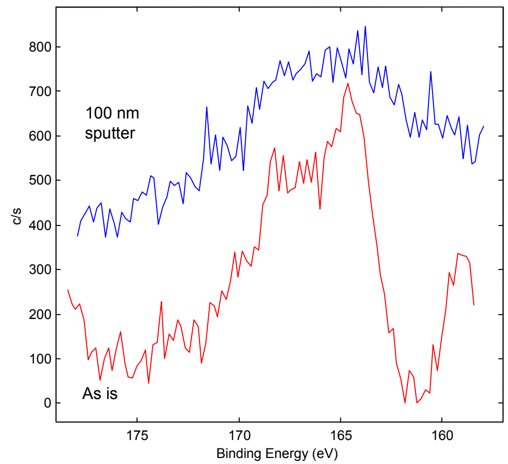
12-24 hours at each pH_2S to reach steady-state

Predominance diagrams for Ce-S-O system

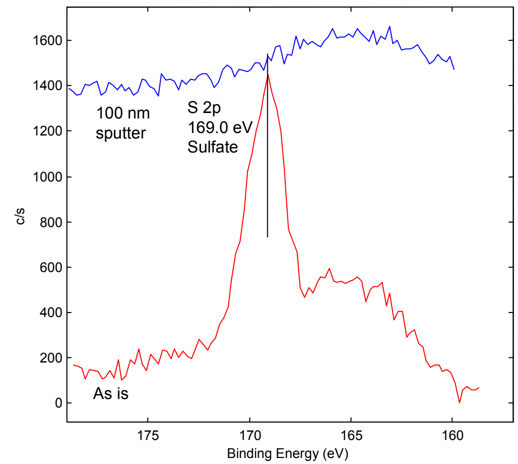


S_2 partial pressure is 10 and 1000 ppm;
Variables are T and pO_2

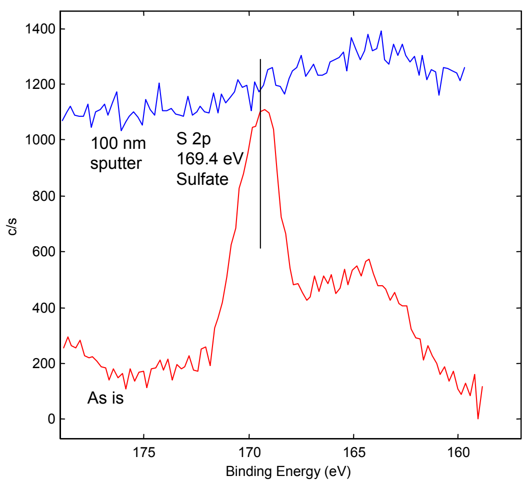
XPS photoemission spectra of the S 2p region



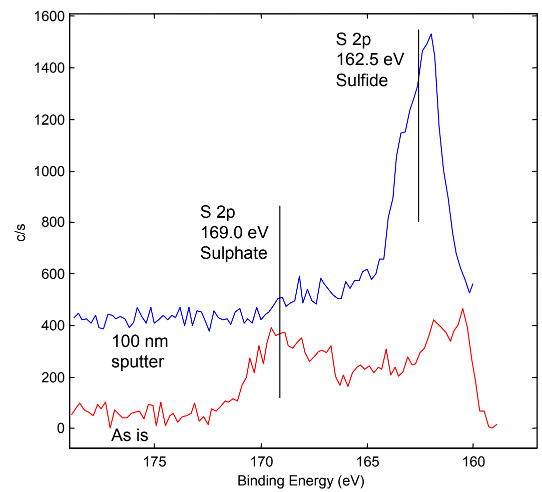
Control sample (tested in H_2)



#1 (tested in 950ppm H_2S)



#2 (tested in 1000ppm H_2S)



#3 (exposed to 950 ppm H_2S at i=0 A)

Red – as it is

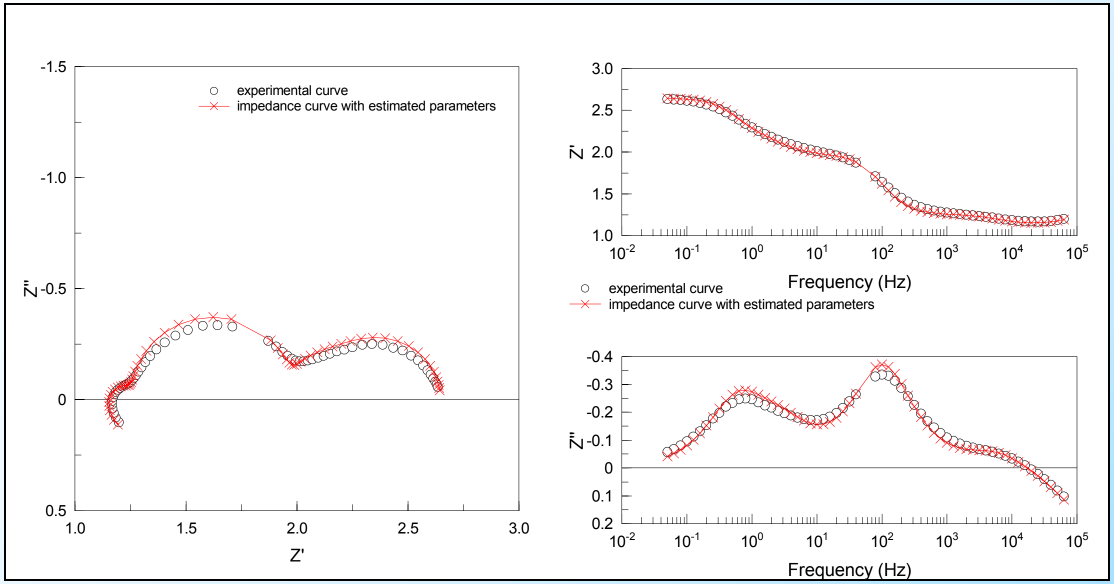
Blue - after 4 kV Ar+ ion sputter ~100 nm

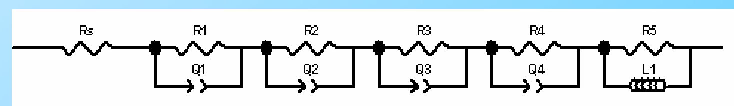
- Control sample was tested in H_2 only and showed no sulfides.
- Samples #1 and 2 tested in H_2-H_2S contained surface sulfates. It is likely due to sulfides converted to sulfates in air. No bulk sulfides or elemental sulfur was found.
- Sample #3 contained surface sulfides and sulfates as well as bulk sulfides.

Deconvolution of impedance spectra for the identification of the electrode reaction mechanism

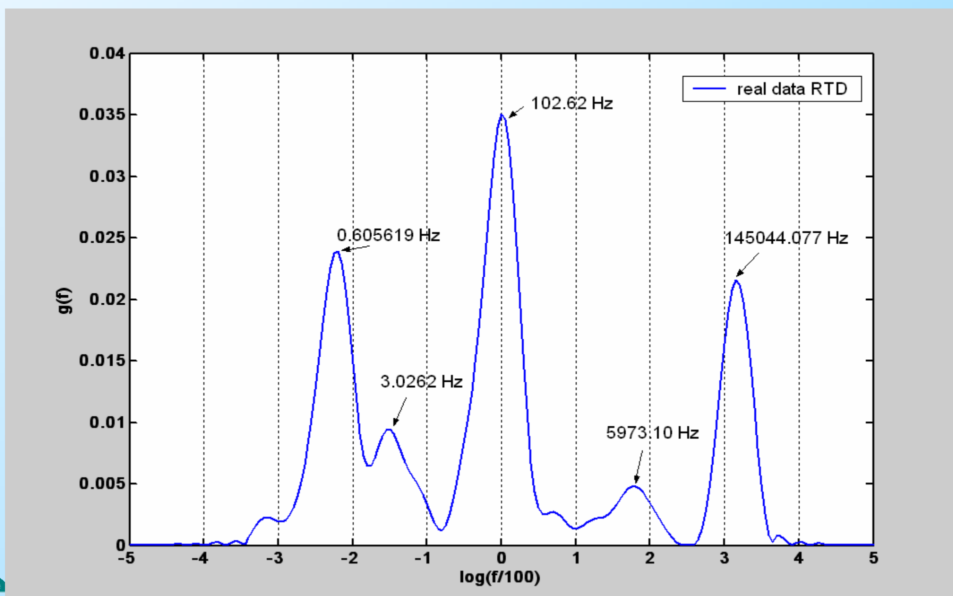
- Impedance spectra can be described by the equivalent circuit series $LR_s(RQ)_1(RQ)_2\ldots(RQ)_n$.
- Due to the high complexity of the system it is difficult to separate the individual processes by conventional semi-empirical equivalent circuit models.
- A deconvolution method is being implemented to calculate the relaxation distributions related to the physical processes [Schichlein et al., University of Karlsruhe]. With that it should be possible to recognize the different processes without *a priori* knowledge.
- Each peak on the distribution of relaxation times will correspond to a process.
- Estimating R_n and calculating C_n one can find all (R_nC_n), suggest an equivalent circuit and using the nonlinear least square algorithm fit the experimental impedance spectrum.

Example of the relaxation time distribution





χ^2	2.42E-07
Sum-Sqr	2.54E-05
Rs(Ω)	1.141
R1(Ω)	0.53721
Y1	0.53101
n1	0.87979
R2(Ω)	0.11771
Y2	0.32308
n2	0.96722
R3(Ω)	0.73155
Y3	0.003626
n3	0.91493
R4(Ω)	0.12234
Y4	0.001124
n4	0.84598
R5(Ω)	0.32691
L1(H)	3.59E-07



Summary

- Anode composition was being optimized by
  - Varying the La dopant in the titanate phase to increase the electronic conductivity;
  - Varying the La dopant amount in the ceria phase to increase the catalytic activity;
  - Using alternative dopants in the ceria phase to improve the activity.
- Cell performance was evaluated in fuels containing potential impurities (sulfur).
- Long-term performance test revealed relative tolerance of ceramic composites to H_2S:
  - No performance loss was seen in fuels with H_2S lower than 30 ppm.
  - Degradation in 50-1000 ppm of H_2S was reversible.
  - XPS analysis of anodes operated in H_2-H_2S did not show the bulk sulfide formation.
- Electrode reaction mechanisms are being elucidated using a deconvolution of impedance spectra approach.

Future work

- Long-term anode testing for carbon tolerance
- Anode tests in a variety of hydrocarbon fuels
- Scale-up testing to include larger dimension cells
- Further optimization of anode materials and microstructures
- Improvement of mechanistic understanding of effects of sulfur and carbon on anode performance

Acknowledgements

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<u>Contributors</u>
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