Development of Ceramic Composites as SOFC Anodes

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Existing Technology: Nickel-YSZ Anode

Advantages

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

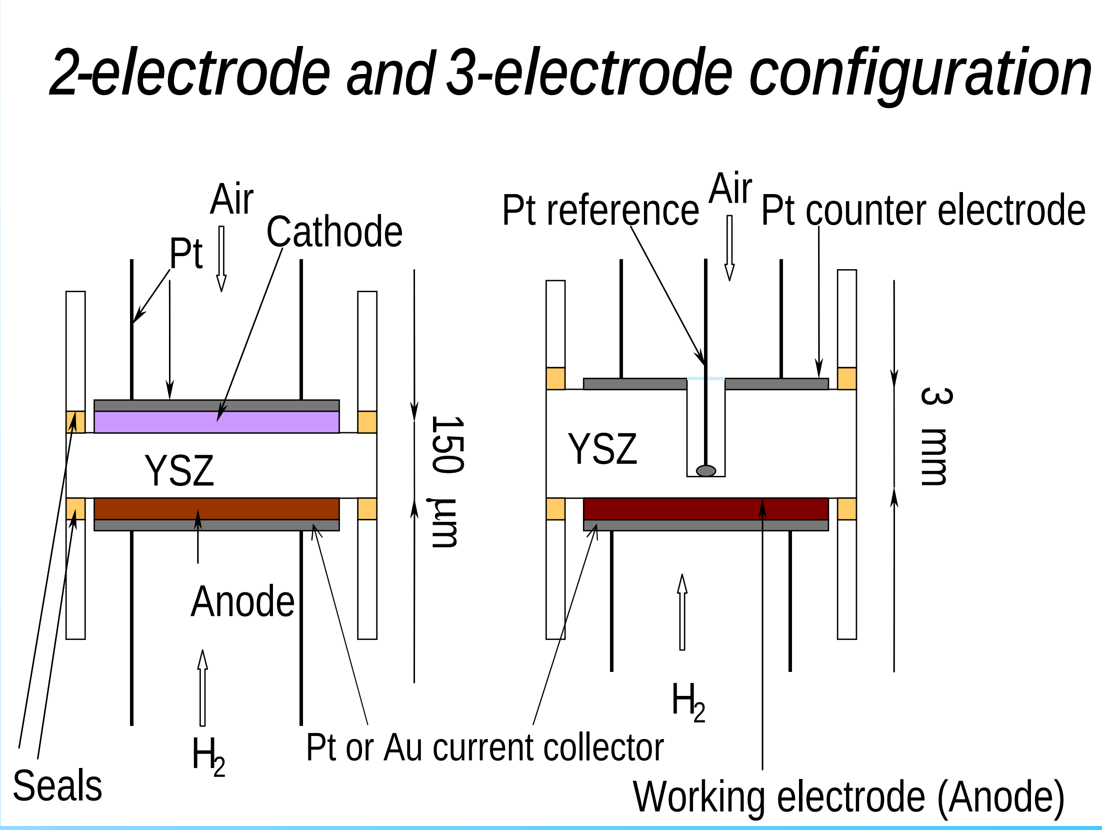
Disadvantages

- 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 oxidizing, hydrocarbon-containing and sulfur-containing environments**

Approach

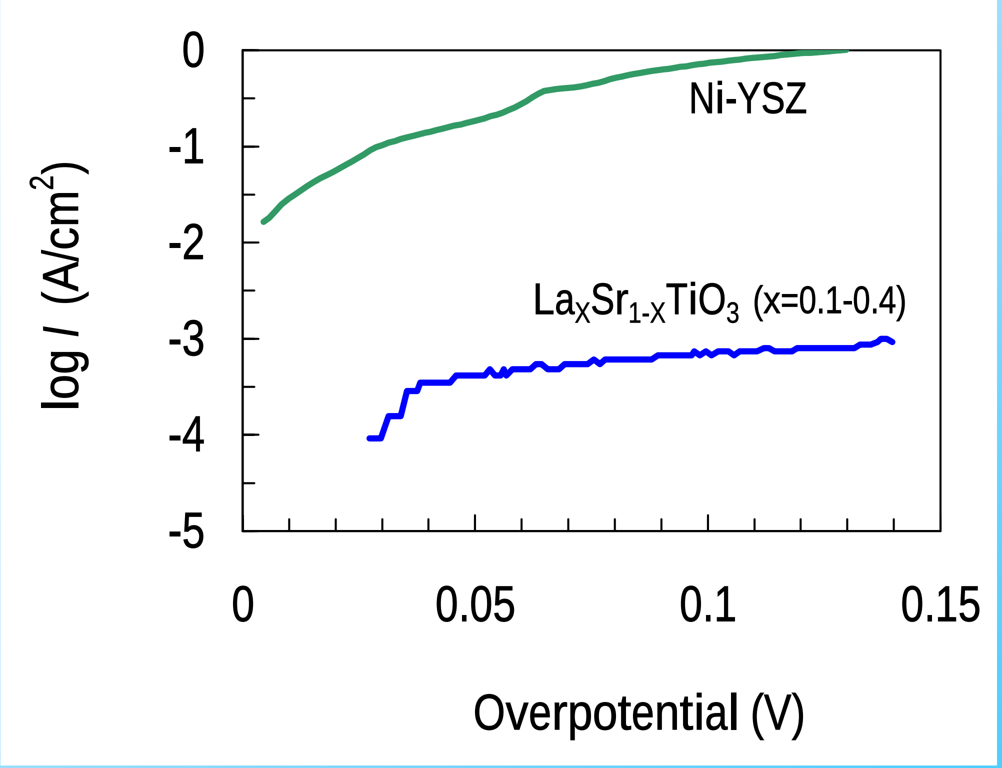
- Synthesis and characterization of candidate oxides
  - Glycine-nitrite synthesis ⇒
  - Calcination at 1200ºC ⇒
  - XRD analysis ⇒
  - Attrition milling ⇒
  - Electrode ink ⇒
  - Screen printing on YSZ ⇒
  - Sintering at 900-1200ºC
- Evaluation of the electrical, thermal and thermo-mechanical properties
- 2- and 3-electrode cell tests



Ceramic anode properties

La-doped $SrTiO_3$

- Reasonable electrical conductivity (up to 15 S/cm)
- Dimensional and chemical stability under red-ox cycling
- TEC compatibility with other cell components
- Good adhesion to YSZ at relatively low temperatures

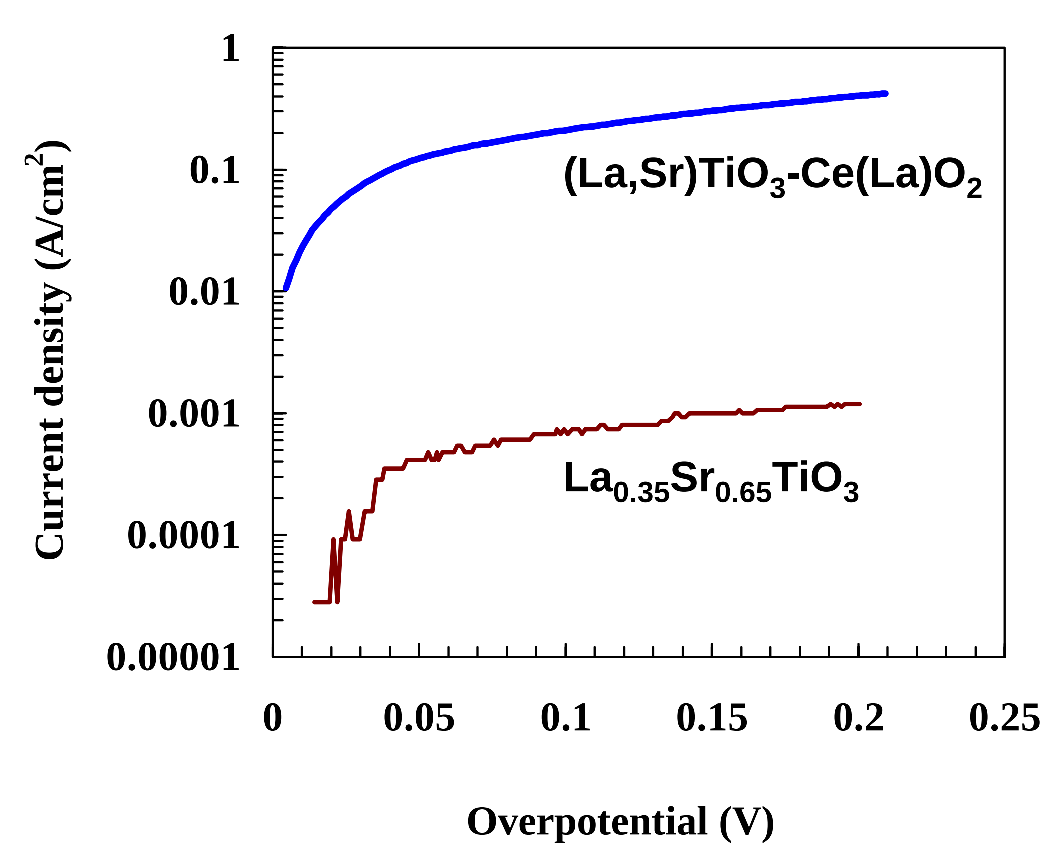


T=850ºC in wet H_2 vs. Pt/air

But....

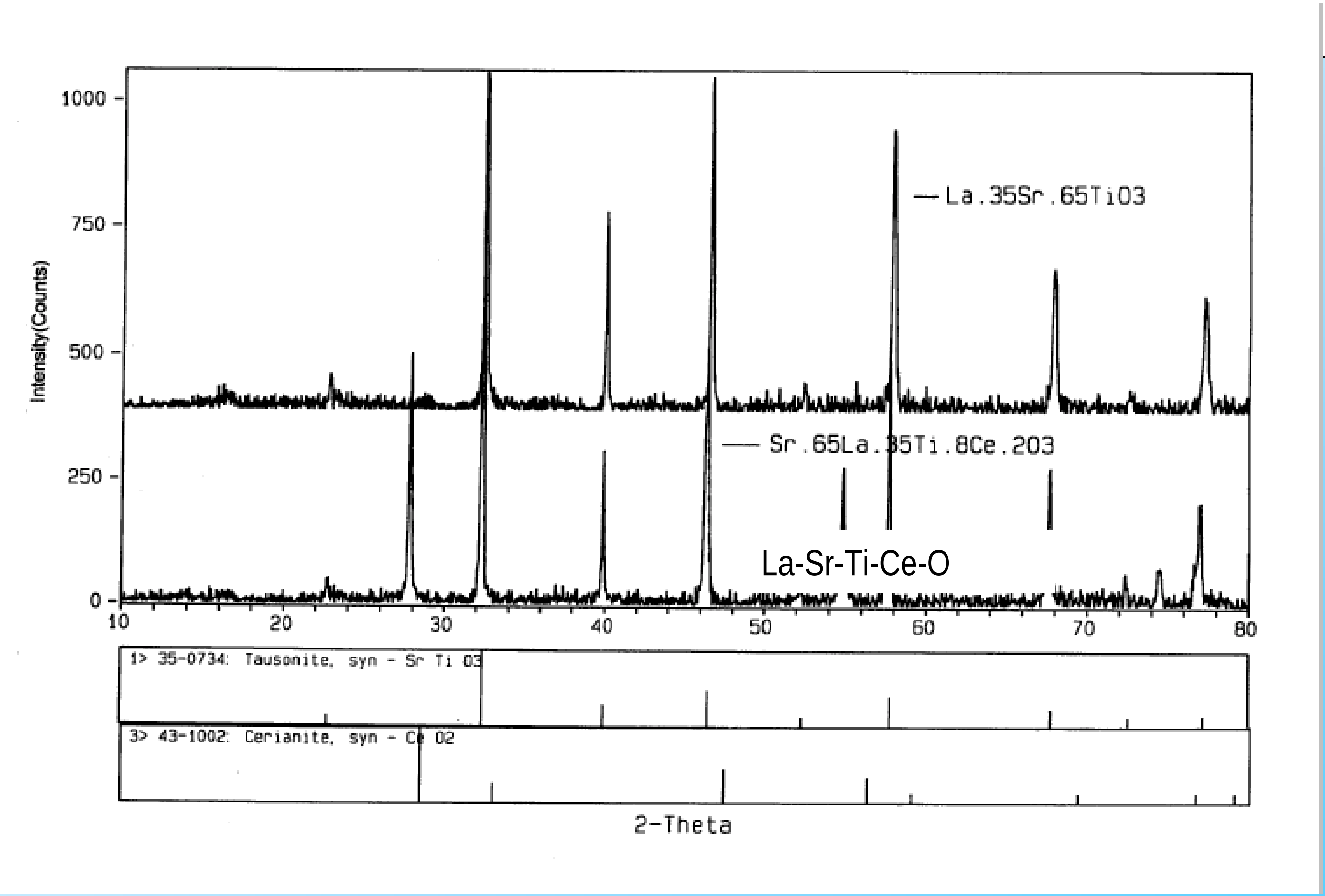
- **Low catalytic activity for hydrogen oxidation**

Effect of cerium oxide addition



T=850^{o}C in wet H_2 vs Pt/air

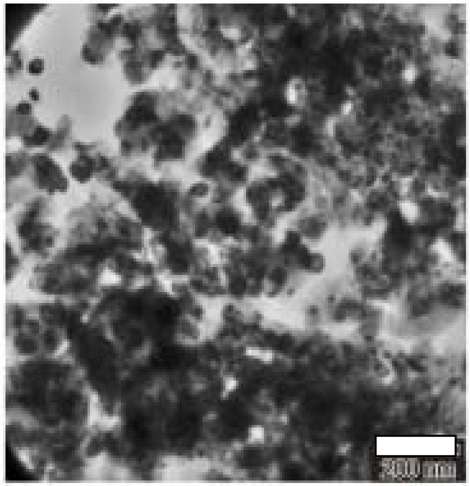
2 phase anode: Titanate/Ceria composite



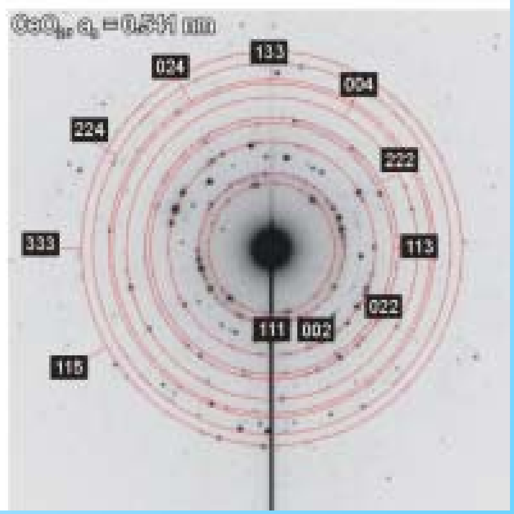
Electronic conductivity provided by doped titanate.

Activity towards fuel oxidation provided by ceria.

TEM Analysis of 2-phase ceramic anode



200 nm bar

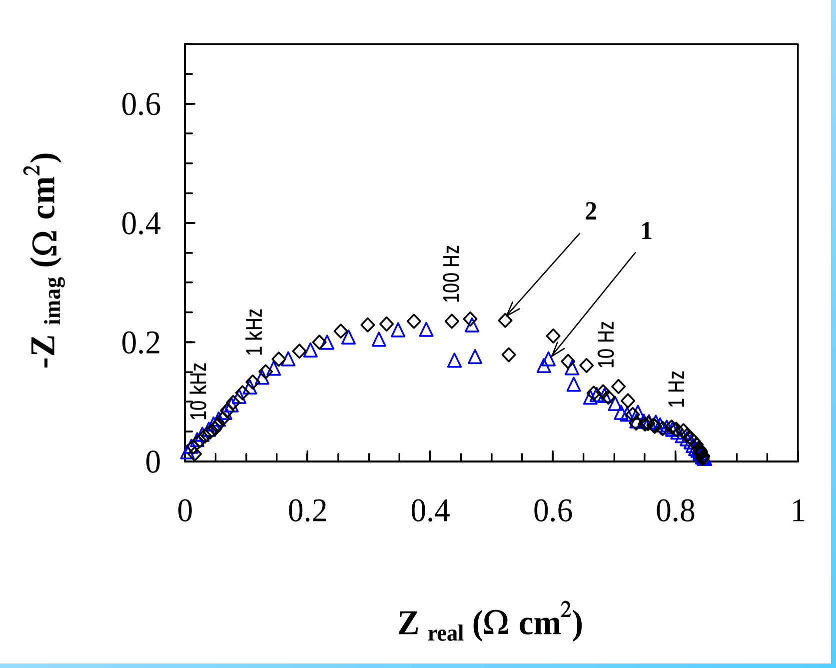


Diffraction pattern obtained from a typical "broad" area of La-Sr-Ti-Ce-O (35 mol% of La (A-site basis) and 15 mol% of Ce (B-site basis)) confirms presence of 2 phases. The $SrTiO_3$ reference pattern is superimposed in blue (bottom left) and that of CeO_2 is imposed in red (bottom right).

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

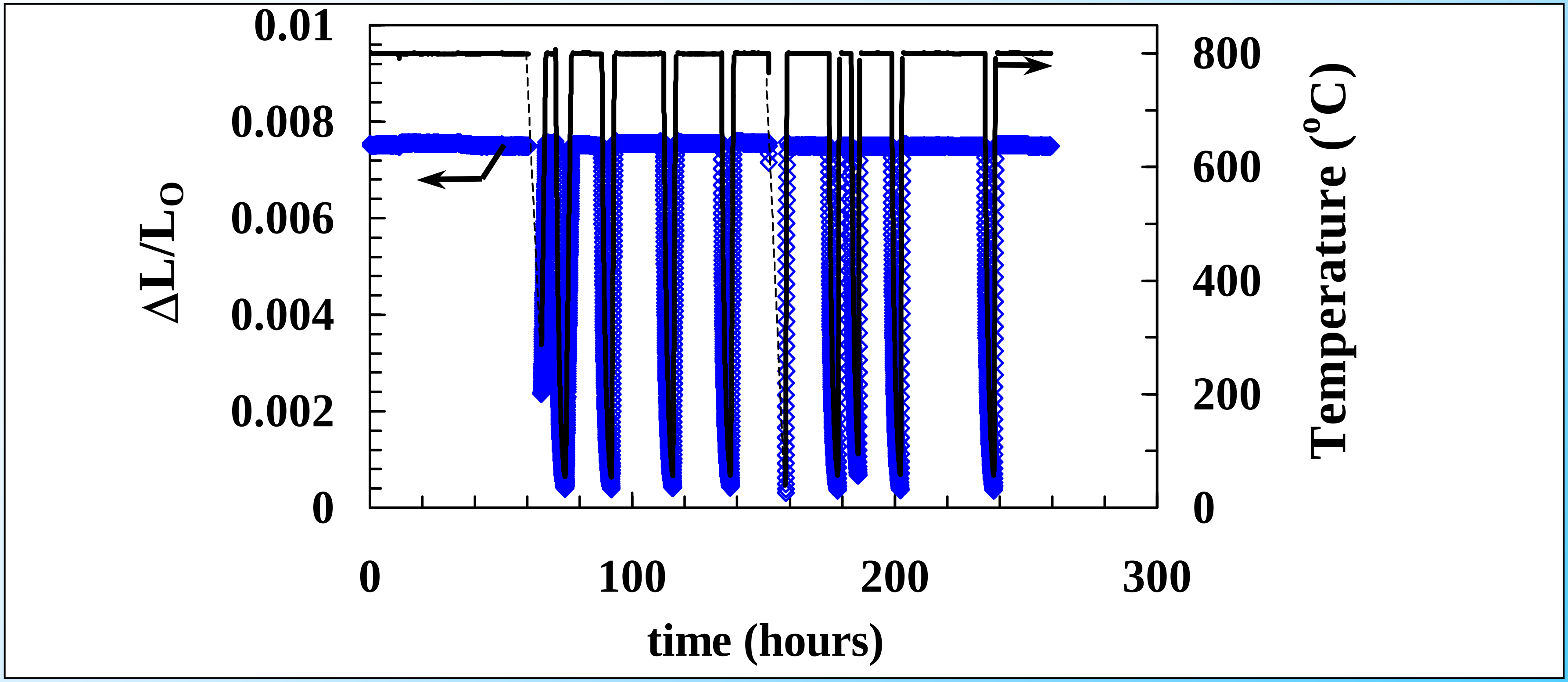
I. Single combustion synthesis

- Simultaneously co-synthesized in the same reactor vessel from an aqueous glycine/nitrate solution
- Excellent activity for electrochemical H_2 oxidation
- Withstand multiple reduction-oxidation cycles
- Tolerate exposures to hydrogen sulfide
- TEC compatibility with other cell components



T=750°C
(1) $H_2/H_2O/N_2$=77/3/20
(2) $H_2/H_2O/N_2$=77/3/20+ 6ppm H_2S

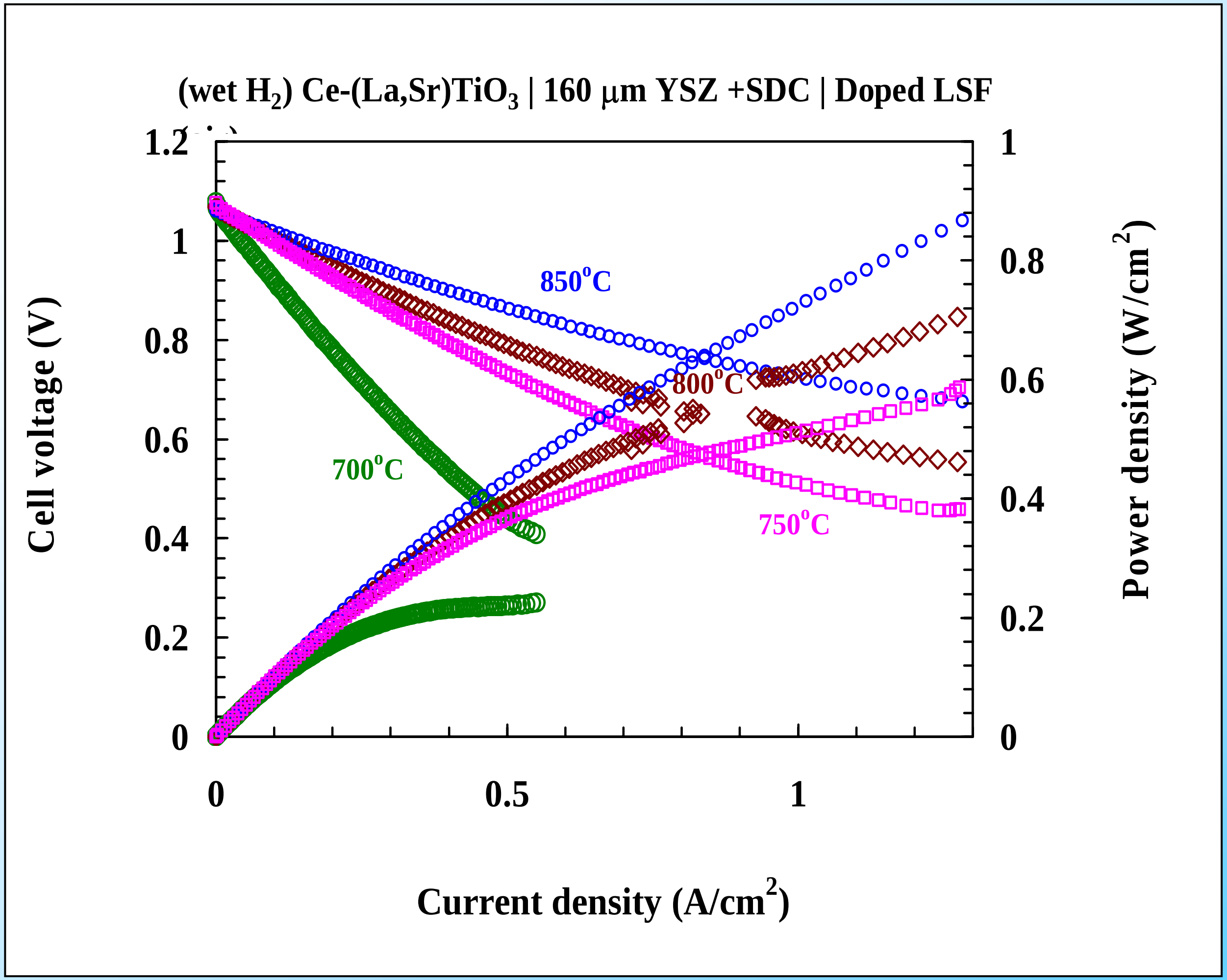
Thermal Redox Cycling



I: Exposure to reducing environment at 800ºC (corresponding to SOFC anode environment during operation)

II: Exposure to air during thermal cycling (corresponding to conditions an unprotected anode would experience during system startup and shutdown)

Composite Sr(La)TiO$_3$-Ce(La)O$_2$ anode



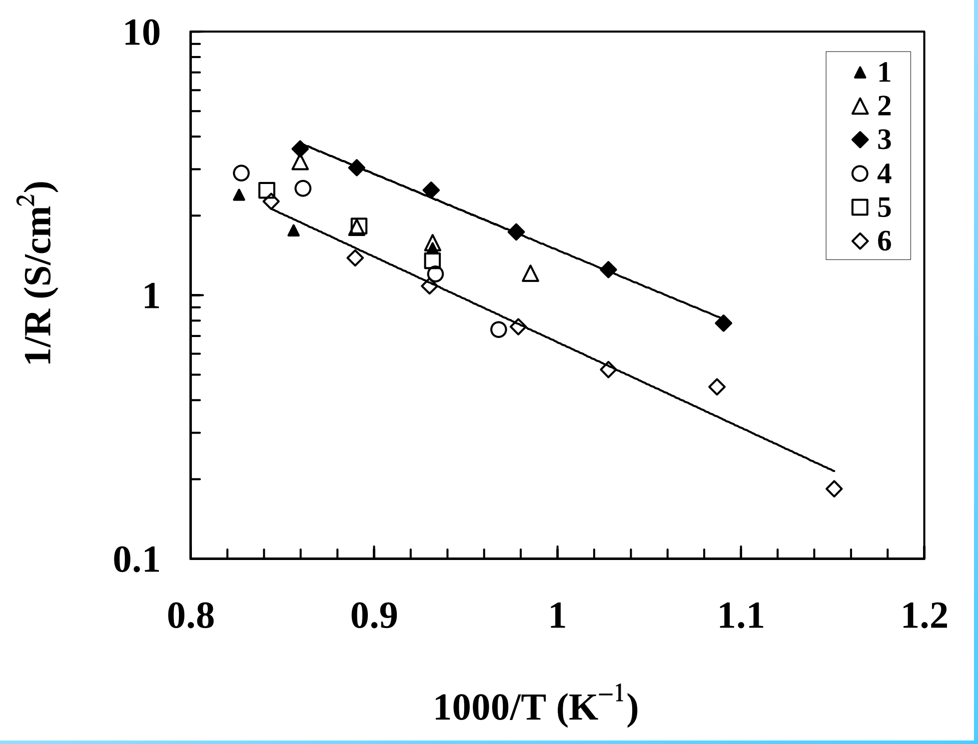
Cerium oxide addition to Sr(La)TiO$_3$ results in remarkable improvement in the performance

Electrolyte-supported cell (160 μm YSZ)
Fuel: H_2/H_2O=97/3
Oxidant: air
Electrolyte: 150 μm YSZ

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

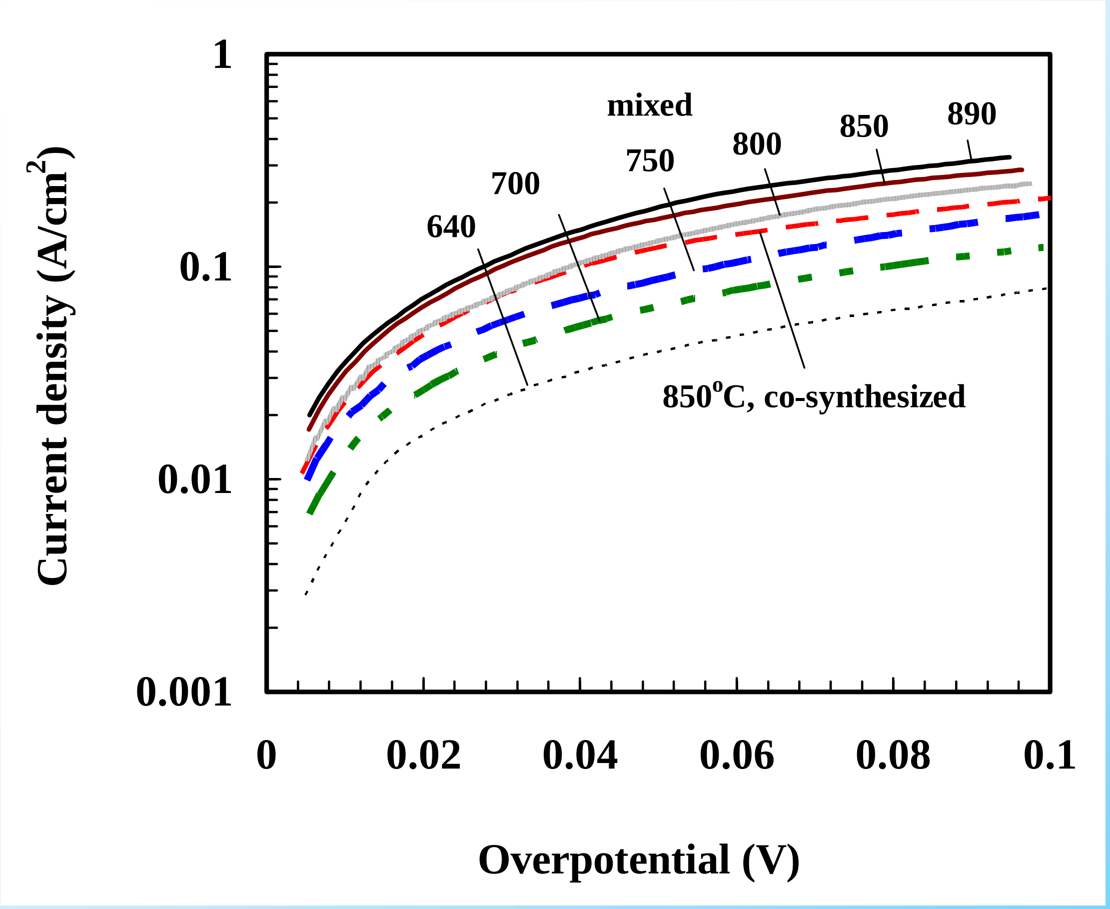
<u>II. Mixing of separately prepared powders</u>

- Tailoring of the individual phases for optimized composite performance
- Adjusting the amount of dopant in each oxide (to optimize electronic conductivity and/or mixed conductivity).
- Similar electrocatalytic activity for hydrogen oxidation in the temperature range 700-900ºC



Polarization resistances of composite anodes in H_2/H_2O=97/3.
1is x=0.25, y=0.5 (50:50); 2 - x=0.35, y=0.3 (50:50);
3 - x=0.35, y=0.5, (60:40); 4 - x=0.25, y=0.3 (50:50);
5 - x=0.25, y=0.3 (60:40), 6 - x=0.25, y=0.4 (70:30).

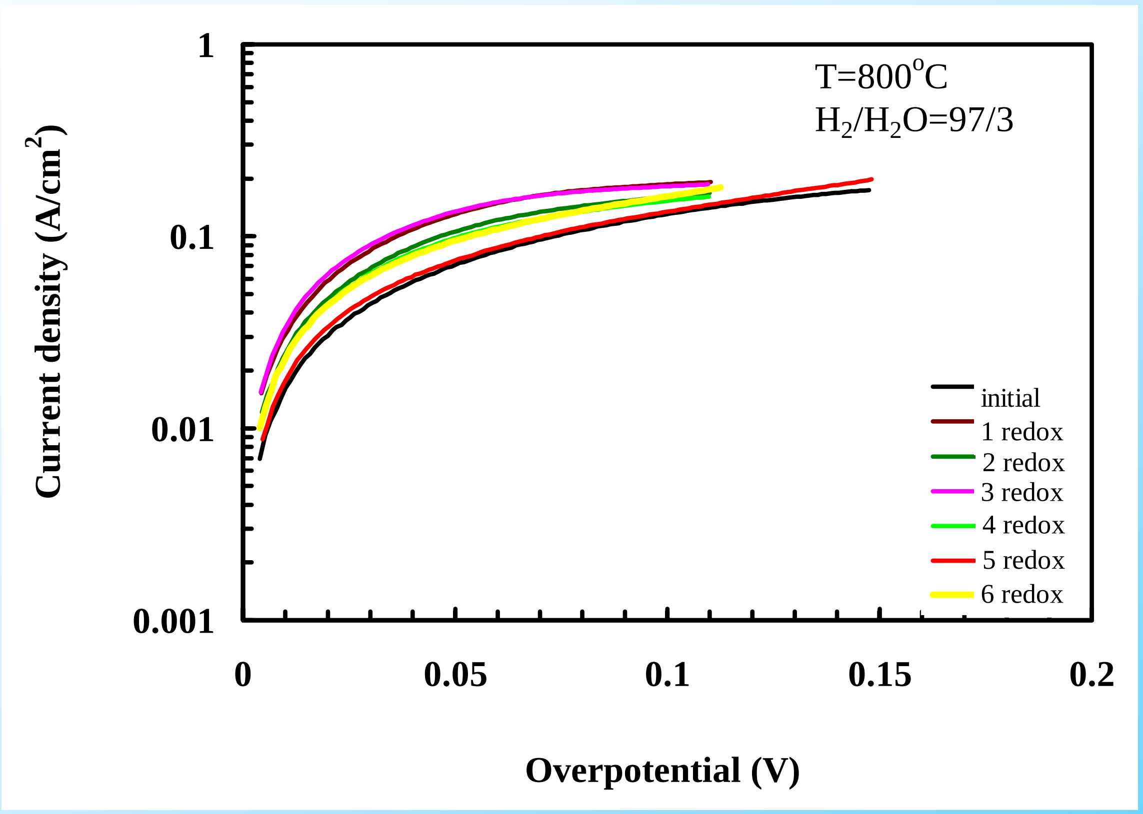
Polarization curves of composite anodes



Co-synthesized Sr(La)TiO_3-Ce(La)O_2, where Ti/Ce=9, and mixed $Sr_{0.65}La_{0.35}TiO_3$-$Ce_{0.5}La_{0.5}O_{2-\delta}$ (60:40 molar ratio) composite anodes tested vs. Pt/air at H_2/H_2O=97/3.

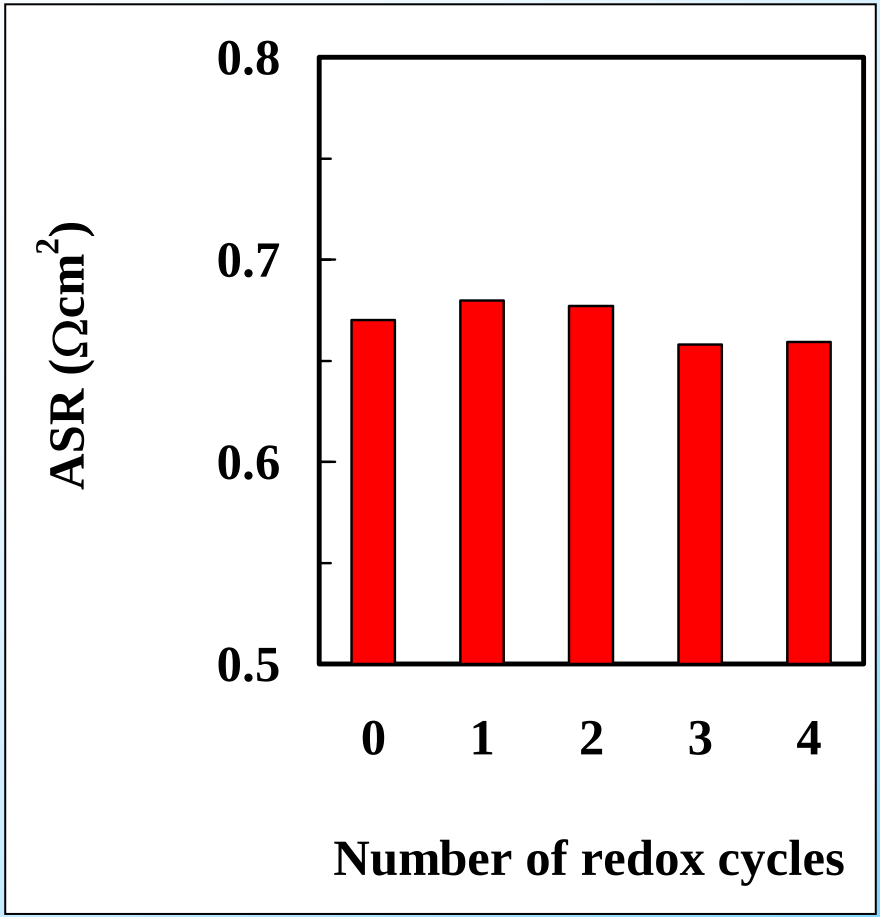
It is possible to achieve comparable or improved properties with mixed powder anodes.

Polarization curves of a composite anode in wet hydrogen vs. Pt/air after several oxidation-reduction cycles



- Half-cell test
- Oxidized by exposing to air at 800ºC
- Reduced by H_2/H_2O=97/3 at 800ºC
- No decrease in performance
- No mechanical failure

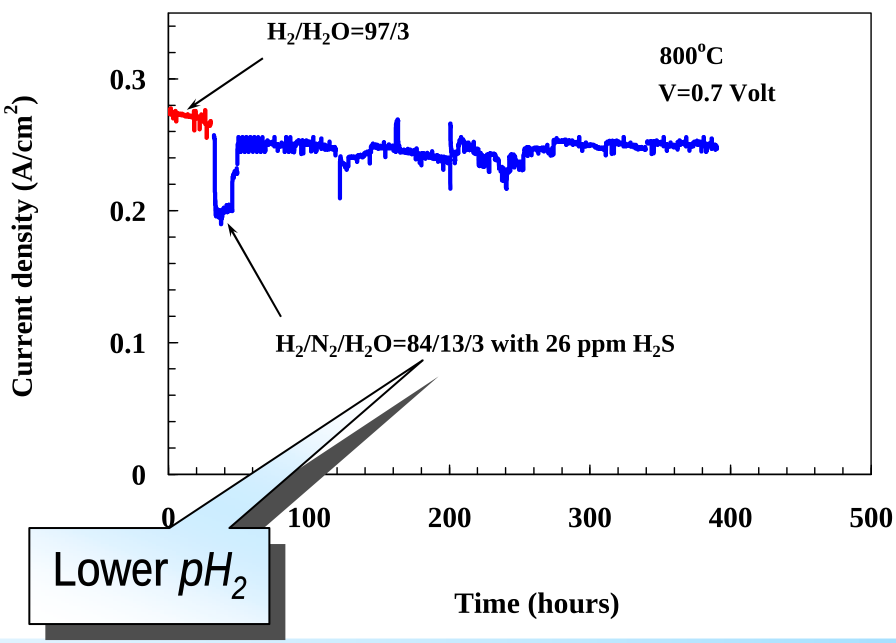
Effect of oxidation-reduction cycles on the cell area specific resistance at 0.7 V

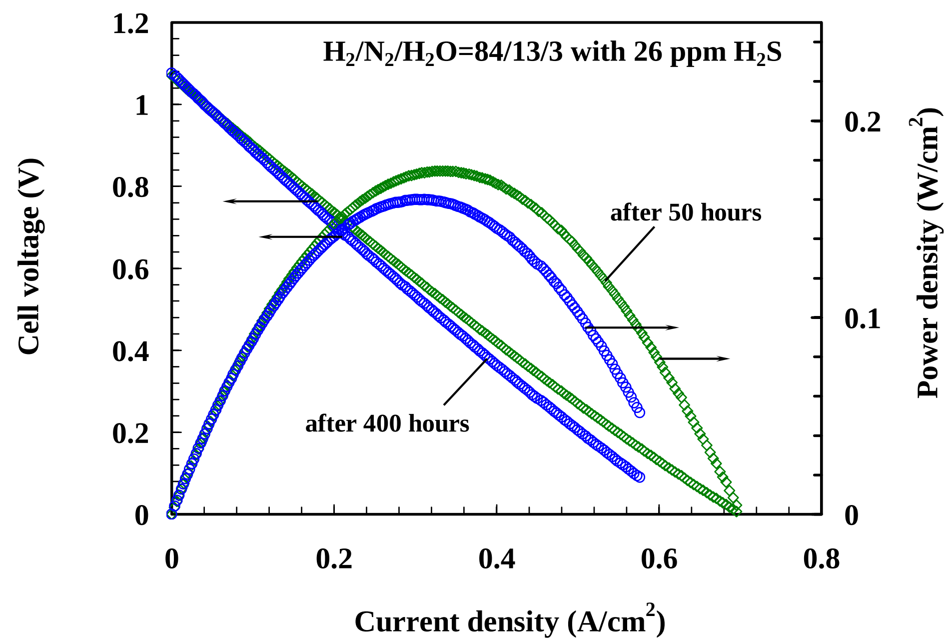


- Full cell test
- T= 800^{o}C.
- Fuel is H_2/H_2O=97/3
- Oxidant is air

- No change in cell resistance after several redox cycles
- No loss in dimensional stability

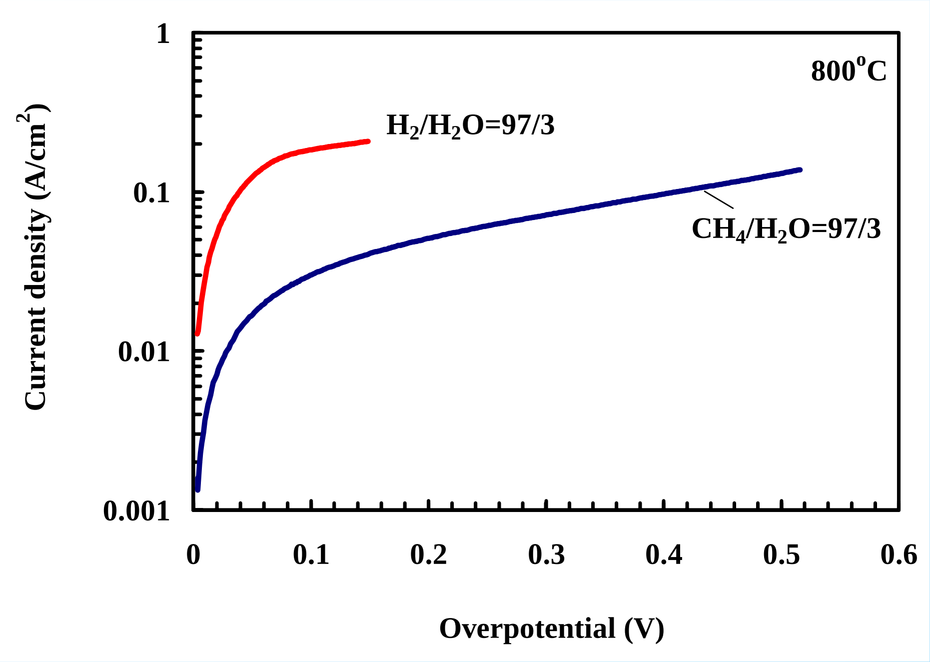
Effect of H_2S addition to the hydrogen fuel at 800°C

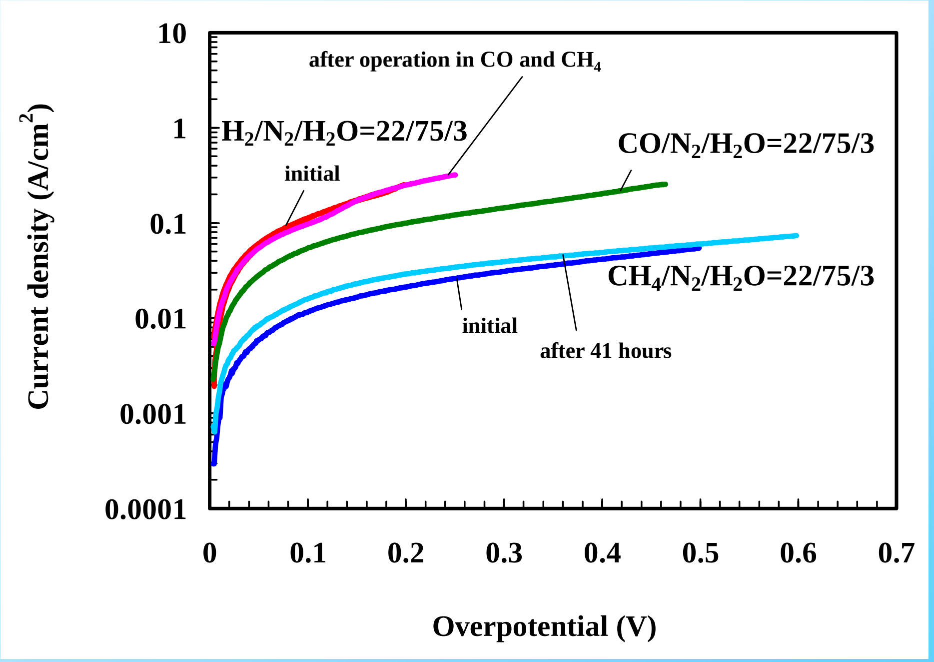




- Only minor change in performance after operating for 400 hs in the presence of 26 ppm H_2S
- Not affected by short-term exposures to 190 ppm H_2S in N_2
- No sulfur compounds detected by the post-mortem EDS/XRD examination

Methane and CO oxidation at 800°C





- Lower activity for CO and CH_4 oxidation in respect with H_2 oxidation
- No degradation in performance after testing in “dry” methane (3%H_2O) for 20 h
- No anode sooting after operating at CO/H_2O=22/3 for 120 h and CH_4/H_2O=22/3 for 41 h
- Immediate return to the initial performance if exposed to H_2

Summary

- Doped strontium titanate - doped ceria ceramic composites
  - Demonstrate excellent performance in hydrogen in the temperature range 750-850^{o}C
  - Operable in hydrogen at low temperatures (600-700^{o}C)
  - Exhibit excellent tolerance to oxidizing environments
  - Resistant to carbon deposition in “dry” methane and CO
  - Tolerant to sulfur poisoning
- All-ceramic anode shows good promise for use in SOFCs

Limitations for the practical application of the composites as SOFC anodes

- Low electrical conductivity for use as self-support
- Potential reactivity with the YSZ electrolyte at high processing temperatures
- Loss of electrocatalytic activity following high processing temperatures

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Future work

- Evaluation/optimization of two-phase anodes prepared by mixing doped titanate and ceria powders
- Long-term anode testing for sulfur and carbon tolerance
- Anode tests on a variety of hydrocarbon fuels
- Scale-up testing to include larger dimension cells

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