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 1200°C ⇒
- XRD analysis ⇒
- Attrition milling ⇒
- Electrode ink ⇒
- Screen printing on YSZ ⇒
- Sintering at 900-1200°C

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

But....
- Low catalytic activity for hydrogen oxidation

$T=850^\circ$C in wet $H_2$ vs. Pt/air
Effect of cerium oxide addition

(Ta,Sr)TiO₃-Ce(La)O₂

La₀.₃₅Sr₀.₆₅TiO₃

Current density (A/cm²)

Overpotential (V)

T=850°C in wet H₂ 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

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$_2$O/N$_2$=77/3/20
(2) H$_2$/H$_2$O/N$_2$=77/3/20 + 6ppm H$_2$S
Thermal Redox Cycling

I: Exposure to reducing environment at 800°C (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 of the cell.

Electrolyte-supported cell (160 µm YSZ)
Fuel: $\text{H}_2/\text{H}_2\text{O}=97/3$
Oxidant: air
Electrolyte: 150 µm YSZ
Composite Sr(La)TiO$_3$ – Ce(La)O$_{2-\delta}$ anodes

II. Mixing of separately prepared powders

- 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 700-900°C

![Graph showing polarization resistances of composite anodes in H$_2$/H$_2$O=97/3.](image)

1 is 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)TiO₃-Ce(La)O₂, where Ti/Ce=9, and mixed Sr₀.₆₅La₀.₃₅TiO₃-Ce₀.₅La₀.₅O₂₋δ (60:40 molar ratio) composite anodes tested vs. Pt/air at H₂/H₂O=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 800°C
- Reduced by $\text{H}_2/\text{H}_2\text{O}=97/3$ at 800°C
- 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°C.
- Fuel is H₂/H₂O=97/3
- Oxidant is air

- No change in cell resistance after several redox cycles
- No loss in dimensional stability
**Effect of H₂S addition to the hydrogen fuel at 800°C**

- Only minor change in performance after operating for 400 hs in the presence of 26 ppm H₂S
- Not affected by short-term exposures to 190 ppm H₂S in N₂
- No sulfur compounds detected by the post-mortem EDS/XRD examination
Methane and CO oxidation at 800°C

- Lower activity for CO and CH₄ oxidation in respect with H₂ oxidation
- No degradation in performance after testing in “dry” methane (3%H₂O) for 20 h
- No anode sooting after operating at CO/H₂O=22/3 for 120 h and CH₄/H₂O=22/3 for 41 h
- Immediate return to the initial performance if exposed to H₂
Summary

Doped strontium titanate - doped ceria ceramic composites

- Demonstrate excellent performance in hydrogen in the temperature range 750-850°C
- Operable in hydrogen at low temperatures (600-700°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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