Improvement of SOFC Electrodes through Catalyst Infiltration & Control of Cr volatilization from FeCr components

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Motivation for LBNL Work

- Use of metal interconnects introduces problems of $\text{Cr}_2\text{O}_3$ scale growth and Cr volatilization on cathode side.
- Lower temperature operation reduces scale growth problem.
- Lower temperature operation permits the use of TEC matched braze seals under development at LBNL.
- Lower temperature operation reduces electrode performance, however, performance can be significantly improved by catalyst infiltration.
- Single-step electrode infiltration under development at LBNL allows novel cell manufacture.
Cr Volatilization Measurements

P = 1 x 10^4 Pa (100 mb)

Cr sample temperature = 700°C to 900°C

Time of exposure = 86.4 ks (24 hours)

After test, all glass parts rinsed in dilute HNO₃

Cr containing solutions analyzed by ICPMS (<ppb)

Surface and X-section of samples analyzed by SEM and EDS
Sample Preparation

- Baseline tests done with 99.8% Cr$_2$O$_3$
- Cr$_2$O$_3$ samples 10 x 10 x 6 mm, ground and polished with 0.5 µm diamond paste
- 430 SS (Fe-16Cr) 15 x 14 x 0.6 mm, ground and polished with 0.5 µm diamond paste
- Some SS alloys samples coated with LSM (La$_{0.65}$Sr$_{0.3}$MnO$_{3-x}$) or MnCo$_2$O$_4$
- Coated and uncoated alloy samples pre-oxidized at 800 °C for 50 hours
Protective Coatings

LSM (Praxair) or
MnCo$_2$O$_4$ (glycine nitrate)
Attritor milled, dispersed with polymer binders, samples dip-coated

800 °C for 50 hours
Cr transport as a function of Carrier Gas Flow Rate (Cr$_2$O$_3$)

Gas-flow rate independent
Temperature Dependence of Chromium Vaporization for $\text{Cr}_2\text{O}_3$ Exposed to Moist Air

Thermodynamic values

Order of magnitude lower
Control of Cr Vaporization

(a) 430

(b) 430 + LSM

(c) 430 + MnCo$_2$O$_4$
Asymmetric Scale Growth Under Current

Toshio Maruyama, Tokyo Institute of Technology, “High Temperature Oxidation and Hydrogen Permeation of Alloys for Interconnects of SOFC”


Non-uniform current distribution

H₂/H₂O → O₂/H₂O → Mn₂O₄ coating
Infiltration Approach

- Precursor Solution
- Heat Treatment

- A low-temperature processing technique
- Allows use of electrode materials unsuitable for high-temp fabrication
- Create nano-structured features
I. Improving LSM-YSZ Cathode Performance With Nano Sm$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (SSC) Particles
Introducing nano oxide electrocatalyst into LSM-YSZ cathodes enhances the oxygen reduction reaction and reduces cathode polarization at low temperatures.
Materials Selection

**Sm$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ – Superior Electrocatalyst**

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**Graph:**

- **Temperature (°C):**
  - 700
  - 500
  - 500

- **Oxygen Surface Exchange Coefficient ($k$ (cm/s))**
  - $10^{-3}$
  - $10^{-6}$
  - $10^{-9}$
  - $10^{-11}$

- **Graph Lines:**
  - $Sm_{0.6}Sr_{0.4}CoO_{3-\delta}$
  - $La_{0.5}Sr_{0.5}MnO_{3-\delta}$
  - YSZ

- **Legend:**
  - $K$: Oxygen Surface Exchange Coefficient

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Synthesis of SSC at Low Temperatures

800°C; 2h

Urea+Nitrate

Nitrate
SEM Images of Fractured LSM-YSZ-SSC Cathodes

Nano SSC particles

700°C
750h

100nm
WD 6.4mm

NCEM SEI 5.0kV X30,000 100nm
SSC Reduces Cathode Polarization Resistance

Symmetric cell

Temperature: 600°C

Graph showing comparison of different materials:
- LSM-YSZ
- LSM-YSZ with infiltrated LSM
- LSM-YSZ with infiltrated SSC

Graph parameters:
- ImZ (ohm·cm²)
- ReZ (ohm·cm²)

2R_p: Cathode Polarization Resistance
SSC Particles Enhance Cell Performance

- LSM-YSZ
- LSM-YSZ-SSC

Cathode: YSZ
Ni-YSZ

600°C, 97%H₂ + 3%H₂O
II. Complete Infiltration of SOFC Cathodes into Porous YSZ in a Single-Step
Background

YSZ Electrolyte YSZ Electrolyte

Perovskite $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$ etc.


- Require multiple infiltration steps to add sufficient material for percolation through porous YSZ networks
- Randomly-distributed material decreases porosity and may impede gas-phase diffusion
One-step infiltration to form cost-effective electrodes
Nano-sized materials distributed in a mono-layer fashion
Need Additive

Nitrate precursor

With additive

800°C, 2h
SEM Image of a Single-Step Infiltrated LSM-YSZ Cathode

Ni-YSZ Anode

YSZ Electrolyte

LSM-YSZ Cathode
HRSEM Image of an LSM-YSZ Cathode

- YSZ Electrolyte
- LSM-YSZ Cathode
- LSM particles
- YSZ grains
Performance of SOFC with Single-step Infiltrated LSM-YSZ Cathode

650 °C Operation

Cell Voltage (V) vs. Current Density (A/cm²)
Stability of the LSM-YSZ Cathode

After 1000h @ 700°C
Ag braze seals are not thermally matched to YSZ; thermal cycling leads to cracking.

New braze seal is well matched to YSZ and stainless steel support, no evidence of cracking after 100s of thermal cycles.

Braze seal exhibits exceptional strength and is stable to oxidation.
Simplified SOFC Manufacture

Single-step electrode infiltration

Braze-seal thermally matched to YSZ & SS

SS window

Porous YSZ electrode support/YSZ thin-film/YSZ electrode
Chromium volatilization from Cr₂O₃ exposed to moist air at 700 to 900 °C is an order of magnitude lower than expected from thermodynamic calculations.

Coatings are effective physical barriers to Cr vaporization from metal interconnects exposed to moist air (factors of 3 to 30 reduction observed for porous coatings).

Incorporating nano-sized Sm₀.₆Sr₀.₄CoO₃₋δ particles into LSM-YSZ cathodes dramatically improves cathode and cell performance at low temperatures.

Due to the unique distribution of SSC particles in the cathode, they appear very resistant to coarsening at 700°C.

SOFC cathodes (e.g. LSM-YSZ) can be effectively fabricated using an single-step infiltration approach.

Single-step infiltration led to nano-sized LSM covering the surface of porous YSZ networks in a monolayer distribution; performance at low temperature was quite good.

The development of braze seals at LBNL that are thermally matched with YSZ and stainless steel look promising.

Single-step infiltration and braze seals may lead to low-cost SOFCs.