Cost-Effective Manufacturing and Morphological Stabilization of Nanostructured Cathodes for Commercial Solid Oxide Fuel Cells

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Project Organization and Structure

Penn

1) Develop “manufacturable” infiltration process to make composite electrodes

USC

2) Develop methods for stabilization of electrode nanostructure.

FCE

3) Demonstrate that the results from 1) and 2) can be incorporated into larger cells and stacks.

Project period: 10/01/14 - 09/30/17
Electrode Fabrication by Infiltration:

1) Make porous scaffold of electrolyte
2) Infiltrate catalysts and electronic conductor

Advantages for cathode fabrication:

A) Separate firing temperatures for YSZ and perovskite.
B) Composite structure is not random; perovskite coats pores.
   → High conductivity with low perovskite loading
   → CTE is that of the scaffold
C) High-performance is possible.

Problems with Infiltration:

1) Difficult to Manufacture:
   → Need 35-wt% (20-vol%) perovskite phase for conductivity
   → To get this loading requires many steps.

2) Long-term stability – nanoparticles coarsen.
Approach 1: Electrodeposit Cathode:

Step 1: Make scaffold conductive: Coat pores with carbon (pyrolysis of butane).

Step 2: Electrodeposit Mn & Co; then heat in air to 800°C to form MnCo$_2$O$_4$:

\[ \sigma(40\text{-wt\% MCO}) = 11 \text{ S/cm @ 700°C} \]

Issues:

1) Electrodeposition is single-step but slow:
   → Need to deposit slowly to prepare uniform coverages

2) Very difficult to electrodeposit Rare Earths:

3) Performance is just okay:
Approach 2: Prepare a Conducting Scaffold

1) LSF (La\(_{1-x}\)Sr\(_x\)FeO\(_3\)) is relatively unreactive with YSZ:


2) Make LSF-YSZ Scaffold for Conductivity; add LSCF for Catalytic Activity
Single-step infiltration into a conducting scaffold could simplify fabrication:

1) Co-fire NiO-YSZ/YSZ (1350°C)  
2) Deposit GDC interlayer; fire (1150°C)  
3) Screen-print cathode; fire (1150°C)  

Conventional Cell Fabrication

- LSCF
- GDC
- YSZ
- NiO/YSZ

One-Step Infiltration

- LSCF in LSF-YSZ
- YSZ
- NiO-YSZ

1) Co-fire NiO-YSZ/YSZ/LSF-YSZ (1350°C)  
2) Infiltrate LSCF; fire to operating temperature.
Symmetric Cell - 700°C in air

LSF/YSZ composite scaffold with infiltrated LSCF

Scaffold provides conductivity.
Infiltration decreases non-ohmic losses.

Fuel-cell performance consistent with cathode ASR:

Temperature: 973 K
Fuel: 97% H₂ - 3% H₂O
Electrolyte: 80 µm YSZ
Cathode: LSCF (2 cycles) in LSF-YSZ scaffold
Anode: Sr-doped LaVO₃/Pd/CeO₂
Need improved conductivity of LSF-YSZ composites:

1) Upon calcination, there is Zr doping of LSF phase.
2) Zr-doped LSF has a lower conductivity.
3) Level of doping depends on Sr content.
Conductivity of dense, 50% LSF-YSZ mixtures:

1) Conductivity of LSF increases with Sr:La ratio.
2) Loss of conductivity depends on level of Zr doping.
3) Optimum Sr:La ratio minimizes reaction, maximizes conductivity.
Scaffold cannot be pure LSF:

1) Ohmic losses cannot be completely removed by infiltration of pure LSF scaffold.
2) Likely due to poor interfacial contact.
Good YSZ/LSF-YSZ Interface Is Essential:

1) Need to optimize porosity.
2) Improve pore size distribution.
Technology Transfer to FuelCell Energy:

50:50 LSF-YSZ composite (co-fired at 1350°C)
Infiltrated with LSCo.
Initial Cell Test

Base cell with standard GDC/Cathode

Infiltrated cathode
Stabilization of Nanostructure

Possible reason for stabilization:

Crystallite size of CeO$_2$ powder as a function of calcination temperature, with and without 0.5-nm film of ZrO$_2$.
LSCF Electrode with 5-nm ZrO$_2$ ALD:

- ALD with ZrO$_2$ lowers performance, but slows degradation
- Incorporating Co helps mitigate the negative effect of the ZrO$_2$, but compromises stability
Possible Solution:
Make ALD film of catalytically active materials

MgAl₂O₄, 120 m²/g.
1-nm ALD film of LaFeO₃ on MgAl₂O₄.

MgAl₂O₄, 120 m²/g.

Perovskite peaks are shown in gray.
Future Research

1. Investigate ways to improve conductivity and performance with the LSF-YSZ scaffolds (modify porosity, composition, and fabrication conditions).

2. Study Coating of the cells with a conformal layer of the selected oxides using ALD process.

3. Continue validation of the materials set and one-step fabrication process in button cells.

4. Validate the down-selected materials sets and process parameters in 100 cm² active area cells.

5. Investigate scale up the one-step fabrication process to commercially-relevant sizes.