Lanthanum Ferrite
Cathode Development at PNNL

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Study Objectives

- Decreased cathode polarization (↑ electrochemical activity) from 600-800°C.

- Long-term cathode stability (with thermal cycling).

- To achieve the above properties, two materials’ systems are being studied.

  - Cells utilizing a ceria interlayer between the YSZ electrolyte and the \( \text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3 \) (LSF-20) cathode.

  - Cells in which a chemically modified LSF cathode is applied directly to YSZ.
Test Configuration

Button Cells –25 mm diameter
Anode-supported thin film YSZ
  - Ni-YSZ anode 500 µm thick
  - YSZ electrolyte <10 µm thick
All subsequent layers are screen-printed
Pt mesh cathode current collector
Ni mesh anode current collector
H₂ fuel with 3% H₂O
4 point measurement with Arbin BT2000
1st Approach - LSF Cathodes Utilizing SDC Interlayers

The use of a screen-printed Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ (SDC-20) interlayer (~5 µm) between the YSZ and LSF-20 cathode results in ~50% performance enhancement.

Power at 0.7V and 750°C
With ceria ~950 mW/cm$^2$
Without ceria ~675 mW/cm$^2$
Long-Term Stability

- LSF-20 cathodes (+ SDC interlayer) have consistently indicated 0.8-0.9 W/cm² at 0.7V/750°C and reasonable performance stability.

- Cathode is subject to a burn-in period (~200 hours) qualitative adhesion analysis indicates improved cathode adherence after testing – burn-in rate possibly enhanced by temperature and current density?

![Graph showing power density over time.](image)

Data recorded at 750°C/0.7V
Further Cathode Optimization

- At present the LSF-20/SDC-20 combination appears to be the most promising materials’ set at PNNL.

- Other cathodes (e.g. LSC, LSCF, LSM, LSFN and LNF) have been studied (in conjunction with the SDC interlayer) but do not appear to offer the same combination of power density and longevity.

- Previous investigations at PNNL have sought to establish optimum material and processing conditions for LSF-20 ➔ particle size, porosity, adherence.

- Current studies are addressing optimizing interfaces relevant to the LSF-SDC cathode.
Further Cathode Optimization

- **LSF-SDC Interface** - processing textured ceria interlayers ➔ increased LSF-SDC contact area.
Textured SDC Interlayer

Two methods currently under investigation both utilize screen-printing as the application technique, and involve composition and organic binder manipulations to achieve the textured effect.
SDC-YSZ Interface

- Even at 1200°C SDC and 8-YSZ react to form an equi-molar Ce-Zr solid solution ($\sigma_{\text{ionic}} \rightarrow 1$ order of magnitude lower than YSZ or SDC).

- Reactivity is apparently reduced with higher Y-contents $\Rightarrow$ use of 10-YSZ as the thin-film electrolyte may be a preferable option.
  - 10-YSZ conductivity only slightly lower than 8-YSZ.
  - 10-YSZ should also provide improved electrolyte phase stability.
2nd Approach - Negating the Need of the SDC Interlayer

- LSF and YSZ interact above ~950°C – Zr$^{4+}$ migrates to the LSF B-site.
  - Fixed-valence Zr$^{4+}$ cations act as blocking sites to electron migration.
  - Electron holes formed by acceptor doping of Sr$^{2+}$ cations may be negated by the donor doping with Zr$^{4+}$ cations.

<table>
<thead>
<tr>
<th>Conductivity at 750°C (S/cm)</th>
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<tbody>
<tr>
<td>LSF-20</td>
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<tr>
<td>10 mol.% Zr</td>
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<tr>
<td>20 mol.% Zr</td>
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Low-Temperature Sintering LSF

- Adding 2 mol. Cu to the B-site and reducing the A/B cation ratio to 0.98 significantly enhances sintering below 1000°C.

- LSFCu cathode applied directly on 8-YSZ at 950°C yields ~1.5-2 times typical LSF-SDC performance.
1000 Hour LSFCu Data

- 1000 hour testing reveals 4 distinct regions:
  - Exaggerated burn-in (5-6 times performance improvement)
  - Stable performance (~200 hours)
  - Rapid degradation
  - Some degree of re-stabilization

Data at 750°C/0.7V
Possible Cause of Burn-In

Cross-sectional TEM/EDX of pre-tested samples indicates SrZrO$_3$ formation – also verified with powder XRD.

Line Scan: LSFCu-YSZ Interface

Sr K$_\alpha$ Elemental Map

Analysis Point (0.05 µm increments)
Post Burn-In TEM

- SrZrO$_3$ re-absorbed after testing at 750°C/0.7V for ~150 hours.

- Re-absorption of La$_2$Zr$_2$O$_7$ has been observed in several studies on LSM-YSZ combinations – lower pO$_2$ at interface during testing?
**LSFCu Degradation**

- 2 identical cells processed – (1) not tested, (2) tested for 1000 hours (cell degradation).

- SEM indicates some evidence of microstructural coarsening (loss of fine porosity) ➔ 750°C operating temperature may be too close to 950°C sintering temperature.

- Pt migration from the cathode current collector to the LSFCu-YSZ interface.
Degradation from Pt Migration

- Pt migration mechanism ➔ formation of Pt-oxides on the current collector surface, vapor phase transport to the YSZ interface, and reduction back to Pt metal.

- Our intention is to negate the need for Pt current collectors with modified compressive loading cell fixtures ➔ more analogous to “real world” SOFC stacks, and should impart better long-term stability of our cathodes.
The Influence of the YSZ Electrolyte on LSFCu/Cell Stability

- Preliminary data indicates improved long-term stability with an in-house synthesized 8-YSZ electrolyte compared to commercial powders when utilized with an LSFCu cathode.

In-house YSZ produced with high purity (99.9%) nitrates (low Si and Hf contents).

Low Y-content in commercial 8-YSZ - actually closer to 7-YSZ.
Conclusions

- LSF-SDC interlayer combination still offers the most attractive combination of power and stability ➔ hence a significant portion of future work will be directed towards further optimization of this configuration.

- Low-temperature LSFCu cathodes have shown very high performances but they are subject to:
  - Reactivity with YSZ (forming Sr-zirconate phases – re-absorbed??).
  - Poor long-term stability – signs of microstructure coarsening and Pt migration – YSZ composition may affect stability?
  - Performance and reactivity is extremely sensitive to calcination and sintering temperatures – optimum performance achieved for 950-975°C sintering range – very narrow processing window.
Future Work

- Investigation of the cathode burn-in phenomenon predominantly observed for LSF-based cathodes, and takes ~200 hours what materials’, processing and test variables affect the burn-in rate??

- Continued study of direct application of LSF-based cathode onto YSZ – considering cathode modifications that will physically inhibit the incorporation of Zr cations at sintering temperatures of 1100-1200°C.

- After screening with button cell tests, alternative experimental fixtures will be used with the ability to analyze:
  1. Larger cell areas.
  2. Cells incorporating compressive contacts and no Pt.
  3. The effects of different connection materials between cathode and interconnect.
  4. Thermal cycling capabilities of both cathode and various seal materials.