Intermediate Temperature SOFC Operation Using Lanthanum Gallate Electrolyte

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### Present SOFC Electrolytes

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<th>Cathode Material and Issues</th>
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<td>Zirconia</td>
<td>Low conductivity 0.1 S/cm at 1000°C 0.02 S/cm at 800°C</td>
<td>Ni-zirconia Ni coarsening</td>
<td>La(Sr)MnO₃ zirconate formation at the interface</td>
<td>Demonstrated No electronic leak current 1000°C Operation typical; very thin electrolyte allows 800°C operation; lower than 800°C?</td>
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<td>Ceria</td>
<td>High conductivity (0.1 S/cm at 800°C)</td>
<td>Ni-ceria</td>
<td>La(Sr)CoO₃ CTE mismatch</td>
<td>Electronic short Differential expansion from air to fuel side</td>
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<tr>
<td>La gallate</td>
<td>High conductivity (&gt;0.1 S/cm at 800°C)</td>
<td>Ni-ceria Formation of La-Ni-O insulating phases</td>
<td>La(Sr)CoO₃ CTE mismatch</td>
<td>No electronic leak current CTE similar to zirconia Long term cell stability is an issue, strength, material cost</td>
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</table>
Conductivity Comparison

- Conductivity: LSGM at 650°C > YSZ at 800°C
Conductivity Comparison: LSGM and YSZ Electrolyte
Benefits of LSGM Electrolyte

- Stability in SOFC environment (air and fuel pO₂)
  - Ionic transference number ~1
- Potential for 650°C operation
  - Conductivity comparable to YSZ at 800 - 850°C
  - Compatibility with perovskite cathode
    - La(Sr)CoO₃₋ₓ, excellent cathode for 650°C operation
  - Metal interconnect challenges are reduced
  - Lower system cost
  - 650 - 700°C operation well-suited for partial internal reformation; offering a significant reduction in heat exchanger requirement
Challenges

**Materials**
- **Synthesis**
  - Phase Purity
- **Ceramic processing**
  - Densification
  - Thin layer fabrication
- **Strength**
- **Cost**

**Fuel Cell**
- **Anode material compatibility**
  - Reactivity with nickel
- **Cathode material**
- **Long-term stability**
- **Stack performance**
Synthesis

- **Multi-cation perovskite**
  - Preferred phase: La(Sr)Ga(Mg)O$_{3-\delta}$
  - Potential second phases: SrLaGaO$_4$ and SrLaGa$_3$O$_7$, La$_4$Ga$_2$O$_9$

- **Approach**
  - Precursor control
  - Milling / Calcination temperature
Process control: Phase pure LSGM

![Graph showing the phase pure LSGM](image-url)
Ceramic processing

- **Densification**
  - Sintering temperature (literature: 1450 - 1550°C for several hrs)
    - Reactivity with setters
    - Ga evaporation?
  - Control of powder characteristics (e.g. surface area) allows reduction in sintering temperature 1400 - 1450°C
  - Sintering aid
Sintering Study

Density of LSGM

- LSGM (attritor milled)
- LSGM (doped with 5 wt% LSGMC)
- LSGM (doped with 10 wt% LSGMC)
- LSGMC
- LSGM (phase 2 average)

Co doping on Mg-site

High surface area (~ 6 m²/gm)

Low surface area (~ 1 m²/gm)

Co doped LSGM as sintering aid
Thin LSGM electrolyte

- Multiple approaches to making thin LSGM electrolyte

- Tape cast support
- Screen printed electrolyte
- Tape cast laminated structure
Strength

- **Limited information in the literature**
  - 147 MPa (isopressed bar) Du et al.
  - 113 MPa Sammes et al.

- **Preliminary Result: 129 MPa**

- **Additional work done at Sandia National Lab.**
  (Raj Tandon and Ron Loehman)
LSGM Strength

![Graph showing the strength of LSGM under different conditions]

**Strength, MPa**

- RT test
- RT test after 800°C in air for 100 hrs.
- RT test after 800°C in reducing atm for 100 hrs.
- RT test after RT to 800°C in air, 10 cycles
- RT test after RT to 800°C in reducing, 10 cycles
- Test at 800°C

*Sample Pretreatment*
Test Conditions: 800 C exposure for 100 hr. in air, strength=168 MPa

Sample # T2 22

Failure origin appears to be a near surface defect
Strength test at 800 C in air; 132 MPa

Sample #T1-41

Failure origin appears to be a near surface defect
Summary of strength test

- Pores are still the major failure causing defects
- Exposure to high temperature in air - slight reduction in strength
- Exposure to high temperature in hydrogen - no change
- Thermal cycling in air - slight reduction
- Thermal cycling in hydrogen - increase in strength
- Test at high temperature - reduction in strength
- Process improvement in reducing flaws should improve strength
Anode material compatibility

- Reduce Ni reaction with modified anode composition

- Powder mixture (LSGM + modified anode) calcination at 1350°C for four hours
Cost

- Parametric cost estimate of raw material oxides
  (using USGS published cost of high purity oxides)
Single Cell Performance

- ASR at 700°C, thin LSGM supported on anode structure: ~ 0.5 ohm.cm²
Single cell long-term test

- Stable button cell performance (anode as support)

Temperature: 700°C
Current Density: 1 Amp/cm²

Cell: ASG_0080

Power Density, W/cm²

Time, Hours
Cathode as support

• Benefits
  - Materials compatibility - Perovskite electrolyte and cathode
  - Allows use of thin anode => high fuel utilization
  - No phase change from fabrication to operation compared to anode that undergoes reduction (associated volume shrinkage)
Cell Performance (Cathode Support)

- Electrolyte thickness 75 µm
Cathode supported cell

![Image](image_url)

**Graph:**
- **Closed symbols:** Air
- **Open symbols:** Oxygen

**Current Density, A/cm²**
- 750 = 0.54 ½.cm²
- 700 = 0.80 ½.cm²
- 650 = 1.39 ½.cm²
Performance Improvement

- 75 micron electrolyte
- Additional porosity in thick cathode structure
Single cell stability

- ASR at 700°C with thin LSGM supported on cathode structure: ~ 0.5 ohm.cm²
Cell Scale-up

- Tape cast development to fabricate 10 x 10 cm cells
Stack Test (10x10cm 8-Cells)
Stack test

Stack Voltage = 5 V
(0.625 V/cell)
Temperature = 800°C

- LSGM 8-cell Stack
- Electrolyte Size = 10 cm x 10 cm
- Electrolyte Thickness = 300 microns
- Active Area = 62 cm²

Fuel Interruption

Time, Hrs

Stack Power, W
Fuel Utilization, %
Stack post-test analysis

- Interaction of Cr from interconnect with Sr in cathode

![Cr map](image1)
![Sr map](image2)
Anode-Electrolyte Interface

- Post-test analysis (1200-hr test) did not show evidence of Ni diffusion
Summary

- LSGM is a promising electrolyte candidate for intermediate temperature SOFC
- Technical hurdles can be solved by a combination of basic and applied R&D
  - Cathode as support provides certain benefits not available to anode supported cells
- Progress in zirconia stack R&D can be applied directly (e.g., metal interconnects)