Surface-Modified Electrodes: Enhancing Performance Guided by In-situ Spectroscopy and Microscopy

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What’s the nature of the active site?  
What controls ORR activity and stability?
Unintentional surface rearrangement

**Intrinsic**

natural segregation of cations and precipitation of secondary phase

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Unintentional surface rearrangement

**Intrinsic**

natural segregation of cations and precipitation of secondary phase

Electrocatalyst → \( \Delta t \) → HEAT

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Ambient Pressure XPS: presence of surface strontium species

Ambient Pressure XPS: increased Sr presence in LSCF series

Ambient Pressure XPS: increased Sr presence in LSCF series

\[ \text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta} \]

 Bulk Co:(Co+Fe), \( x \)

- \( \text{Sr}_{\text{surface}} / \text{Sr}_{\text{bulk}} \)
- \( \text{Sr}_{\text{secondary}} / \text{Sr}_{\text{bulk}} \)

unpublished data

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Morphological and composition instability

unpublished data

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Ambient Pressure XPS: increased Sr presence in LSCF series

$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$

$\frac{\text{Sr}_{\text{surf}}}{\text{Sr}_{\text{bulk}}}$

$\frac{\text{Sr}_{\text{secondary}}}{\text{Sr}_{\text{bulk}}}$

$\text{Bulk Co: (Co+Fe), } x$

unpublished data

unpublished data
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ attractive / commercially relevant

unpublished data
Unintentional surface rearrangement

**Intrinsic**

natural segregation of cations and precipitation of secondary phase


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Intentional surface modification

**Extrinsic**

intentional introduction of secondary material

Electrocatalyst

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**Intrinsic**

natural segregation of cations and precipitation of secondary phase

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Surface modification can give improvements but why?

<table>
<thead>
<tr>
<th>Infiltrate</th>
<th>Cathode backbone</th>
<th>Electrolyte</th>
<th>Cell configuration</th>
<th>Infiltrated</th>
<th>Baseline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd$<em>{0.2}$Ce$</em>{0.8}$O$_{2-\delta}$</td>
<td>LSM</td>
<td>YSZ</td>
<td>Asymmetrical cell</td>
<td>$R_p$: 0.21 $\Omega$ cm$^{-2}$ at 700 °C</td>
<td>11.8 $\Omega$ cm$^{-2}$</td>
</tr>
<tr>
<td>Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{2-\delta}$</td>
<td>LSM</td>
<td>SDC</td>
<td>Symmetrical cells</td>
<td>$R_p$: 0.23 $\Omega$ cm$^{-2}$ at 700 °C</td>
<td>5.3 $\Omega$ cm$^{-2}$</td>
</tr>
<tr>
<td>Gd$<em>{0.2}$Ce$</em>{0.8}$O$_{2-\delta}$</td>
<td>LSM</td>
<td>YSZ</td>
<td>Asymmetrical cell</td>
<td>$R_p$: 0.60 $\Omega$ cm$^{-2}$ at 750 °C</td>
<td>8.19 $\Omega$ cm$^{-2}$</td>
</tr>
<tr>
<td>Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{2-\delta}$</td>
<td>LSM</td>
<td>SDC</td>
<td>Symmetrical cells</td>
<td>$R_p$: 1.13 $\Omega$ cm$^{-2}$ at 600 °C</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Full cells</td>
<td>$P_{\text{max}}$: 0.14 W cm$^{-2}$ at 600 °C</td>
<td>n/a</td>
</tr>
<tr>
<td>Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{2-\delta}$</td>
<td>LSM</td>
<td>SDC</td>
<td>Full cells</td>
<td>$P_{\text{max}}$: 0.20 W cm$^{-2}$ at 600 °C</td>
<td>0.17 $^b$ W cm$^{-2}$</td>
</tr>
<tr>
<td>Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{2-\delta}$</td>
<td>LSM</td>
<td>YSZ</td>
<td>Symmetrical cells</td>
<td>$R_p$: 0.19 $\Omega$ cm$^{-2}$ at 700 °C</td>
<td>10 $^b$ $\Omega$ cm$^{-2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Full cells</td>
<td>$P_{\text{max}}$: 0.53 W cm$^{-2}$ at 700 °C</td>
<td>n/a</td>
</tr>
<tr>
<td>Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{2-\delta}$</td>
<td>LSM</td>
<td>YSZ</td>
<td>Symmetrical cells</td>
<td>$R_p$: 0.048 $\Omega$ cm$^{-2}$ at 800 °C</td>
<td>n/a</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Full cells</td>
<td>$P_{\text{max}}$: 1.10 W cm$^{-2}$ at 800 °C</td>
<td>n/a</td>
</tr>
<tr>
<td>Sm$<em>{0.2}$Ce$</em>{0.8}$O$_{2-\delta}$</td>
<td>LSM</td>
<td>YSZ</td>
<td>Full cells</td>
<td>$P_{\text{max}}$: 1.25 W cm$^{-2}$ at 800 °C</td>
<td>1.10 $^b$ W cm$^{-2}$</td>
</tr>
</tbody>
</table>

Table 1 — Performance and promotion factors of various nano-structured electrode systems.

Surface modification can give improvements but why?

### Table 1 – Performance and promotion factors of various nanoparticles

<table>
<thead>
<tr>
<th>Impregnated nanoparticles</th>
<th>Scaffold/skeleton</th>
<th>Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode of SOFC</td>
<td>LSM</td>
<td>$R_p$: 0.21 $\Omega$ cm$^{-2}$ at 700 °C</td>
</tr>
<tr>
<td>GDC (5.8 mg cm$^{-2}$)</td>
<td>LSM/YSZ</td>
<td>$R_p$: 0.23 $\Omega$ cm$^{-2}$ at 700 °C</td>
</tr>
<tr>
<td>Pd (1.8 mg cm$^{-2}$)</td>
<td>LSCF</td>
<td>$R_p$: 0.60 $\Omega$ cm$^{-2}$ at 750 °C</td>
</tr>
<tr>
<td>Pd (1.2 mg cm$^{-2}$)</td>
<td>YSZ</td>
<td>$R_p$: 1.13 $\Omega$ cm$^{-2}$ at 600 °C</td>
</tr>
<tr>
<td>GDC (1.5 mg cm$^{-2}$)</td>
<td>YSZ</td>
<td>$P_{\text{max}}$: 0.14 W cm$^{-2}$ at 600 °C</td>
</tr>
<tr>
<td>LSM (~2 mg cm$^{-2}$)</td>
<td>YSZ</td>
<td>$P_{\text{max}}$: 0.20 W cm$^{-2}$ at 600 °C</td>
</tr>
<tr>
<td>LSCF (1.1 mg cm$^{-2}$)</td>
<td>YSZ</td>
<td>$P_{\text{max}}$: 0.19 $\Omega$ cm$^{-2}$ at 700 °C</td>
</tr>
<tr>
<td>LSCF (12.5 vol%)</td>
<td>YSZ</td>
<td>$P_{\text{max}}$: 0.53 W cm$^{-2}$ at 750 °C</td>
</tr>
<tr>
<td>$La_{0.8}Sr_{0.2}CoO_3$ (30 vol%)</td>
<td>YSZ</td>
<td>n/a</td>
</tr>
<tr>
<td>$La_{0.8}Sr_{0.2}CoO_3$ (55 wt%)</td>
<td>SDC</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Controlled coverage by Pulsed Laser Deposition (PLD)

**Surface modification**

- **SDC (~20nm)**
- **YSZ electrolyte substrate**
- **LSCF (~200 nm for testing)**

Diagram showing a layered structure with SDC (~20nm) as the base, followed by LSCF (~200 nm) and finally the YSZ electrolyte substrate.
Controlled coverage by Pulsed Laser Deposition (PLD)

Surface modification

![Diagram showing the layers of LSCF, SDC, and YSZ electrolyte substrate with a controlled coverage by PLD.](image-url)

- **LSCF**: ~200 nm for testing
- **SDC (~20nm)**
- **YSZ electrolyte substrate**
Controlled coverage by Pulsed Laser Deposition (PLD)

Surface modification

LSCF
~200 nm for testing

SDC (~20nm)

YSZ electrolyte substrate

SDC well-oriented

LSCF nanocrystalline
Surface modification layers on La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$

<table>
<thead>
<tr>
<th>Surface Modification</th>
<th>SDC</th>
<th>YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma_{\text{ion}}$ / S cm$^{-1}$ *</td>
<td>0.03 [1]</td>
<td>0.03 [2]</td>
</tr>
<tr>
<td>$\sigma_{\text{eon}}$ / S cm$^{-1}$ *</td>
<td>$\sim 6 \times 10^{-8}$ [1]</td>
<td>?</td>
</tr>
<tr>
<td>Lattice Constant (Å)</td>
<td>$\sim 5.42$</td>
<td>$\sim 5.14$</td>
</tr>
<tr>
<td>Strain % wrt. LSCF @ RT [3]</td>
<td>-3%</td>
<td>-8%</td>
</tr>
</tbody>
</table>

*at 650 °C, 21% O$_2$

Dense LSCF deposition-dependent

Tested in 21% O₂, OCV

Temperature / °C

625 650 675 700 720 750

1000 T⁻¹ / K⁻¹

ASR / Ω cm²

Eₐ = 2.5 eV

Eₐ = 1.8 eV

This study

Baumann et al, PhD Thesis

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SDC lowers degradation rate

Degradation rate / Ω cm² h⁻¹

Thickness / nm

SDC
- 0-3 hrs
- 3-8 hrs
- 8-15 hrs

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YSZ lowers degradation rate

![Graph showing the effect of YSZ on degradation rate over thickness](chuehlab.stanford.edu)
Low-frequency arc change with surface modification

Conditions: 650 °C at 21% O₂, OCV after 3 hrs

![Graph showing impedance data with a peak at 5.1 Hz](image-url)
Low-frequency arc change with surface modification

Conditions: 650 °C at 21% O₂, OCV after 3 hrs
Low-frequency arc change with surface modification

Conditions: 650 °C at 21% O₂, OCV after 3 hrs
SDC overlay: 4x reduction in oxygen exchange kinetics

4x reduction

Thickness / nm

Contribution to ASR / Ω cm²

SDC
SDC overlayer: MF is constant

SDC

Contribution to ASR / Ω cm²

High
Mid
Low

Thickness / nm
SDC overlay: HF contribution increase

Contributions to ASR / Ω cm²

Thickness / nm

High
Mid
Low

SDC
Area Specific Resistance contributions: YSZ overlayer

*Contribution to ASR / $\Omega \cdot \text{cm}^2$*

![Graph showing contribution to ASR over thickness](image-url)
Area Specific Resistance contributions: YSZ overlayer

Contribution to ASR / Ω cm² vs Thickness / nm

High, Mid, Low
Area Specific Resistance contributions: YSZ overlayer

![Graph showing contribution to ASR vs. thickness for YSZ overlayer with High, Mid, and Low regions highlighted.](https://chuehlab.stanford.edu)
Electronic transport limited

![Graph showing HF contribution to ASR vs Thickness in nm for SDC and YSZ]

- **SDC**
- **YSZ**

**Y-axis**: HF contribution to ASR / Ω cm²

**X-axis**: Thickness / nm

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Electronic transport limited

\[ \sigma = 7 \times 10^{-7} \text{ S cm}^{-1} \]

\[ \sigma_{\text{eon}}^{[1]} \approx 6 \times 10^{-8} \text{ S cm}^{-1} \]

SDC less resistive than YSZ and more active
Diffusion of Co and Fe into the overlayer

**SDC : 10 nm**

<table>
<thead>
<tr>
<th>Element</th>
<th>As Deposited</th>
<th>Annealed</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Sr</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Co</td>
<td>12%</td>
<td>9%</td>
<td>0%</td>
</tr>
<tr>
<td>Fe</td>
<td>1%</td>
<td>7%</td>
<td>0%</td>
</tr>
<tr>
<td>Ce</td>
<td>66%</td>
<td>62%</td>
<td>80%</td>
</tr>
<tr>
<td>Sm</td>
<td>21%</td>
<td>21%</td>
<td>20%</td>
</tr>
</tbody>
</table>

**YSZ : 10 nm**

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<td>0%</td>
</tr>
<tr>
<td>Sr</td>
<td>1%</td>
<td>1%</td>
<td>0%</td>
</tr>
<tr>
<td>Co</td>
<td>1%</td>
<td>2%</td>
<td>0%</td>
</tr>
<tr>
<td>Fe</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>Zr</td>
<td>85%</td>
<td>85%</td>
<td>84%</td>
</tr>
<tr>
<td>Y</td>
<td>13%</td>
<td>12%</td>
<td>16%</td>
</tr>
</tbody>
</table>
TM diffusion not only along grain boundaries in SDC

Sample as-deposited
Conclusions

<table>
<thead>
<tr>
<th></th>
<th>Oxygen exchange rate</th>
<th>Overall Resistance</th>
<th>Degradation rate</th>
<th>Optimal Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDC</td>
<td>increases</td>
<td>decreases*</td>
<td>decreases</td>
<td>2-10 nm</td>
</tr>
<tr>
<td>YSZ</td>
<td>decreases</td>
<td>increases</td>
<td>decreases</td>
<td>2-10 nm</td>
</tr>
</tbody>
</table>

*at small thicknesses

- Nominally pure ionic conductors (YSZ & SDC) are effective surface coatings for LSCF cathodes.

- SDC exhibits superior oxygen exchange kinetics, ~ 4x lower ASR than LSCF. 10-nm layer gives negligible increase in the electronic transport resistance.

- YSZ lowered oxygen exchange kinetics on LSCF.

- Both SDC and YSZ improve the stability of LSCF significantly, possibly related to the absence of Sr diffusion to the surface.

- Significant diffusion of Co and Fe from LSCF to SDC/YSZ likely explains the higher than expected electronic conductivity, which is needed for the electrode to function.
Acknowledgements

Briggs White, Steve Markovich, Joe Stoffa

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Graduate Research Fellowship Program

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Surface roughening with annealing

As-deposited

LSCF - bare
RMS 1.6 nm
500 nm

SDC - 10nm
1.4 nm

YSZ - 10nm
1.2 nm

24-hr anneal
650 °C, 21% O₂

LSCF - bare
2.2 nm

SDC - 10nm
2.0 nm

YSZ - 10nm
1.7 nm