Tailoring the microstructural evolution in impregnated SOFC electrodes

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Technology Drivers

- **Performance**
  - Materials, microstructure and processing, system management – nano is beneficial

- **Durability**
  - Materials, temperature, system – nano is problematic

- **Cost**
  - Manufacture, materials – nano can be expensive

- **Fuel Flexibility**
  - Materials, system management - nano is beneficial

- **Retain focus on clean energy target**
  - Whole cycle analysis
Solid Oxide Cells

Air electrode evolution

-2
Cathodic (fuel-cell mode)

-0.1
Activated by brief reduction

0
Open-circuit

0.1
Anodic (electrolysis mode)

0.3
Degradation

\[(\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_{3-\delta}\]

- 
Sr-enriched

- 
Zr\(_{0.84}\)Y\(_{0.16}\)O\(_{2-\delta}\)

- 
Y-enriched

- 
Mn\(^{2+}\)-enriched

\(\text{O}_2\)

\(\text{O}^{2-}\)
Fuel electrode evolution
(a) Electron conducting perovskite titanate backbone, \((\text{La, Sr, Ca})_{1-a}\text{TiO}_3\), is infiltrated with surface also modified by fine layer of CGO MIEC

(b) YSZ backbone coated with a MIEC perovskite, \((\text{La, Sr})(\text{Cr, Mn})\text{O}_3\)

Electrolyte supported
Impregnated La$_{0.2}$Sr$_{0.25}$Ca$_{0.45}$TiO$_{3-\delta}$

Elena Stefan, Mark Cassidy, Cristian Savaniu, Maarten Verbraeeken,
University of St Andrews

Ueli Weissen, Boris Iwansschitz, Andreas Mai
Hexis AG

Peter Holtappels DTU
Ni + CeO$_2$ impregnated

Ni particles 50 – 100 nm

Nanoparticles keep growing up to 300 nm after ~1000h
Galileo Stack 750 W with 3.3 kW reformed CH₄ input
(a) Electron conducting perovskite titanate backbone, \((\text{La}, \text{Sr}, \text{Ca})_{1-a}\text{TiO}_3\), is infiltrated with surface also modified by fine layer of CGO MIEC
(b) YSZ backbone coated with a MIEC perovskite, \((\text{La}, \text{Sr})(\text{Cr}, \text{Mn})\text{O}_3\)

Evolution of nano/microstructure

LSCM/YSZ, 800°C redox in air

H₂
TAILORING OF MICROSTRUCTURAL EVOLUTION IN IMPREGNATED SOFC ELECTRODES

WP2: Manufacture and Optimisation of Impregnation procedures into porous substrates

Xiangling Yue, Georgios Triantafyllou, Mark Cassidy, Cristian Savaniu, Paul Connor, and John Irvine
Wettability of solids

For a solid–liquid interface in thermodynamic equilibrium:

\[ \gamma_{SL} = \gamma_{SV} + \gamma_{LV} \cdot \cos \theta \] (Young equation)

\[ W_{SL} = \gamma_{LV} (1 + \cos \theta) \] (Dupre equation)

- \( \gamma_{SV} \) = surface energy of solid
- \( \gamma_{LV} \) = surface energy of liquid
- \( \gamma_{SL} \) = interfacial energy
- \( \theta \) = contact angle

\[ W_{SL} = \text{work of adhesion} \]
\[ \theta = 180 \rightarrow W_{SL} = 0 \text{ and} \]
\[ \theta = 0 \rightarrow W_{SL} = 2 \gamma_{LV} = \text{Work of cohesion} \]

For non-wetting and non-reactive ceramic/liquid metals systems:

\[ \gamma_{SV} = (A + \gamma_{LV}) \cos \theta + B \]

\[ A = 0.970 \times 10^{-3} T - 5.491 \]
\[ B = 1.825 \times 10^{-3} T - 3.106 \]
Surface energy of the materials

\[ \gamma_{LV(Ag)} = 0.912 - 0.15 \times 10^{-3} (T - T_m) \]
Surface energy of the materials

![Graph showing surface energy (YSV) as a function of temperature (T)](image)
Surface energy of the materials

Effect of reduction

\[ \gamma_{sv} = 4.88829 - 2.0 \times 10^{-3} T \text{ [J/m}^2\text{]} \]
\[ R^2 = 0.86519 \]
\[ T = 1200 - 1450 \text{ K} \]

\[ \gamma_{sv} = 2.40157 - 7.775 \times 10^{-4} T \text{ [J/m}^2\text{]} \]
\[ R^2 = 0.890 \]
\[ T = 773 - 1150 \text{ K} \]

\[ \gamma_{sv} = 2.37349 - 2.686 \times 10^{-4} T \text{ [J/m}^2\text{]} \]
\[ R^2 = 0.890 \]
\[ T = 1450 - 1773 \text{ K} \]

LSCM/(Sn,Ag,Cu) Ar–5%H\textsubscript{2}
Manufacture and Optimisation of Impregnation procedures into porous substrates

- Develop and define porous scaffold structures;
- Optimisation impregnation processing;
- Electrochemical performance;

Protocols for fundamental understanding

<table>
<thead>
<tr>
<th>CeO₂ into YSZ</th>
<th>Ni + CeO₂ into YSZ</th>
<th>Ni into YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd₀.₁Ce₀.₉O₂ (GDC) into YSZ</td>
<td>Ni + GDC into YSZ</td>
<td>Ni +ZDC into YSZ</td>
</tr>
</tbody>
</table>

YSZ pellets pressed and fired → Porous YSZ layer screen-printed and fired → catalyst precursor solution impregnation and heat treatment → Microstructure, Performance, In-situ spectroscopies

www.st-andrews.ac.uk
Microstructural evolution under FIB-SEM

- Different morphologies and impregnates populations observed, impregnation profiles, i.e. microstructure of samples with different cycles of impregnation, are under investigation

- Optimisation in loading and distribution
  - Varying solution properties
    - pH=1 → pH=3; pH=5 for aqueous nitrate precursor solution
    - Non-aqueous precursor solution
    - Adding chelating agent
  - Varying levels of catalyst loading
    - microstructure
    - Electrochemical performance and short-term stability
Manufacture with aqueous ceramic processing

- YSZ Scaffold from aqueous tape casting
  - Tailoring of tape formulation with various pore formers
  - Laminations with dense tape
- Impregnation processing based on feedback from pellet samples
- Demonstration of fuel cell performance and durability in methane

Microstructure of a green tape with rice starch and PMMA as pore formers
Raman
Renishaw RM-2000 CCD  JY High resolution LabRam

x5-x100 objectives – 1µm spot size

Excitation:488, 514, 633, 780 & 830nm

Temperature stages 77K-1000°C in a controlled atmosphere eg N₂, H₂

Coupled AFM

Mapping stages with 0.1µm resolution

- Lesley Cohen, Robert Maher
Materials characterisation

- Surface composition determined through Raman

- **Materials:**
  - 6A and 8A – CeO$_2$
  - 9A – (GdCe)O$_2$
  - 11A – (Zr, Ce)O$_2$
  - 14A – Bare 8YSZ backbone

- Peak positions and relative intensities give information on oxidation state of materials
Surface Characterisation

- Surface uniformity and species distribution can be determined by Raman mapping.

- Key spectral features from CGO and YSZ allow materials to be identified and distribution on surface mapped through intensity integration.
XPS results

K-alpha - Thermo

HiPPES Scienta Omicron

Gwilherm Kerherve, David Payne
## XPS in UHV: Quantification

<table>
<thead>
<tr>
<th>ID</th>
<th>Samples</th>
<th>XPS Data</th>
<th>Other Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>8A</td>
<td>CeO$_2$</td>
<td>Ce$<em>{0.93}$O$</em>{2.07}$</td>
<td>--</td>
</tr>
<tr>
<td>9A</td>
<td>Gd$<em>{0.1}$Ce$</em>{0.9}$O$_2$</td>
<td>Gd$<em>{0.09}$Ce$</em>{0.90}$O$_{2.00}$</td>
<td>--</td>
</tr>
<tr>
<td>1C</td>
<td>Zr$<em>{0.1}$Ce$</em>{0.9}$O$_2$</td>
<td>Zr$<em>{0.18}$Ce$</em>{0.82}$O$_{2.00}$</td>
<td>--</td>
</tr>
<tr>
<td>11A</td>
<td>Zr$<em>{0.5}$Ce$</em>{0.5}$O$_2$</td>
<td>Zr$<em>{0.54}$Ce$</em>{0.41}$O$_{2.04}$</td>
<td>--</td>
</tr>
</tbody>
</table>

### Samples with nickel

<table>
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<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>5B</td>
<td>Ni-CeO$_2$</td>
<td>Ni$<em>{0.59}$-Ce$</em>{1.00}$O$_{1.99}$</td>
<td>Na (0.14) &amp; P (0.42)</td>
</tr>
<tr>
<td>9B</td>
<td>Ni-Gd$<em>{0.1}$Ce$</em>{0.9}$O$_2$</td>
<td>Ni$<em>{0.51}$-Gd$</em>{0.14}$Ce$<em>{0.89}$O$</em>{1.96}$</td>
<td>Na (0.10) &amp; P (0.41)</td>
</tr>
<tr>
<td>3C</td>
<td>Ni-Zr$<em>{0.1}$Ce$</em>{0.9}$O$_2$</td>
<td>Ni$<em>{0.2}$-Zr$</em>{0.14}$Ce$<em>{0.85}$O$</em>{2.00}$</td>
<td>Na (0.03) &amp; P (0.07)</td>
</tr>
<tr>
<td>7B</td>
<td>Ni-Zr$<em>{0.5}$Ce$</em>{0.5}$O$_2$</td>
<td>Ni$<em>{0.45}$-Zr$</em>{0.67}$Ce$<em>{0.33}$O$</em>{2.00}$</td>
<td>Na (0.12) &amp; P (0.38)</td>
</tr>
</tbody>
</table>
Ce 3d core level is a complex structure in which each spin orbit consists of the main components and:
- 2 satellites for the Ce\(^{4+}\)
- 1 satellite for the Ce\(^{3+}\)
Doping the ceria with Gd decreases the amount of Ce$^{3+}$.
Doping the ceria with Zr increases the amount of Ce$^{3+}$.
Nickel does not change the Ce$^{3+}$/Ce$^{4+}$ ratio.
Both ToF-SIMS and XPS shows that nickel covers only the topmost layer of the sample.
Charging effect vanishes for temperature above 400°C
Ce 3d core level shows a slight reduction of Ce$^{4+}$ to Ce$^{3+}$ at 600°C
O 1s core level shows a reduction of the hydroxide at 400°C but an increase at 600°C – most likely due to the introduction of oxygen vacancies.
Inkjet printing and inkjet infiltration of functional coatings for SOFCs fabrication

R. I. Tomov, S. Hopkins, R. V. Kumar, B.A. Glowacki

Department of Materials Science and Metallurgy
Productivity: Enables rapid, non-contact deposition of small liquid drops with high placement accuracy.

Performance: Excellent solution for the deposition of functional materials, providing greater thickness control and higher resolution than conventional processing routes.

Flexibility: Restricted only by the rheology of the ink.

Cost: Lower cost and better scalability than vacuum and vapour deposition and lithographic routes.
Inkjet printing infiltration of CGO into NiO/CGO composite anode

The diameters of CGO particles, Ni particles and CGO nano hemisphere particle are around 1.1 μm, 1.1 μm and 120 nm respectively. These micro structural data are used as the parameters for modelling.
Polarization resistance of infiltrated anodes – number of infiltration cycles

![Graph showing the polarization resistance of infiltrated anodes](image)
Infiltrated button cells performances

The effect of anode microstructure modification (Gd-CeO$_2$ infiltration) on the i-V characteristics using 40 and 60 ml/min of wet hydrogen and air (at 600°C).
Inkjet printing infiltration of LSCF/CGO composite cathode with 0.5M CGO-EtOH ink

Aged for 30 h at 550°C (air)

Aged for 60 h at 550°C (air)

Uniform coverage of nano-decorations is observed with an average particle size of 30-50 nm. No detectable difference between CGO nano-particles size aged for 30 and 60 h at 550°C in ambient air was registered.
LSCF/CGO composite cathode infiltrated with 0.5M CGO-EtOH ink – variation of CGO:LSCF volume ratio

Ink jet printing infiltration without vacuum steps and intermediate high temperature sintering is introducing relatively small amount of ink (up to 5wt%).

Even such small amount of CGO nano-decoration can lead to a significant reduction of polarization resistance.
Acknowledgements