Tailoring the microstructural evolution in impregnated SOFC electrodes

Irvine, Cassidy, Connor, Savaniu (St Andrews)
Payne, Cohen, Offer (Imperial)
Kumar, Glowacki, (Cambridge)
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
Ni/YSZ CERMET

\[ \text{CH}_4 + 4\text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^- \]

Good Current Collector

Steam reforming catalyst

\[ C_n\text{H}_{2n+2} \rightarrow C \]

Promotion of carbon fibres

\[ \text{Ni} + \text{S} \rightarrow \text{NiS} \]

Reaction with mercaptans

\[ 2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO} \]

(Ni coarsening, Degradation)
Electrochemical performance is excellent, stable towards oxidation, and tolerant to hydrocarbons:

Anode: 45-wt% LSCM, 5-wt% ceria, 0.5-wt% Pd
Cathode: 40-wt% LSF
Electrolyte: 60 micron YSZ

97% H₂-3% H₂O

900°C

800°C

700°C

97% CH₄-3% H₂O

800°C

700°C
Evolution of nano/microstructure

LSCM/YSZ, 800°C redox in air
Electrolyte supported
Impregnated \( \text{La}_{0.2}\text{Sr}_{0.25}\text{Ca}_{0.45}\text{TiO}_{3-\delta} \)

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

Ueli Weissen, Boris Iwanschitz, Andreas Mai
*Hexis AG*

*OA 14 Peter Holtappels DTU*
Ceramic backbone + catalyst loading

Impregnate using metal nitrate solutions
Nanosized catalyst particles
Catalyst loading small
  No percolation
  No structural function
Ni + CeO$_2$ impregnation – Hexis

- Initial activation of ASR with time
- Improvement upon redox cycling
  - Improved contacting with Ni mesh
- ASR = 0.35 Ωcm$^2$ – 0.5 Ωcm$^2$
- Stable for 250 hours

97% H$_2$ 3% H$_2$O at 900°C
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 CH$_4$ input
Limitations of Impregnation

- Time consuming
  - Clever process design
- May be difficult to scale up
  - Can be achieved
- Infiltration of Whole Electrode Structure
  - Wasteful especially where expensive catalysts utilised
- Durability of impregnate
WP1
Characterization Of Interfaces

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

Tailoring of microstructural evolution in impregnated SOFC electrodes
Role of interfacial phenomena

**Interface:** The point or area between two faces or orientations

Sintering of (single or multi-phase) materials, Nucleation, Grain growth, Mass transport, Mechanical – electrical – thermal properties

**Aim of this work:**
- Evaluate the surface/interfacial properties of materials/systems
- Connect these properties with the materials electrochemical performance
Wettability of solids

General Energy Equation:
\[ \gamma_{\alpha\beta} = \gamma_\alpha + \gamma_\beta - W_{\alpha\beta} \]

\( \gamma_{\alpha\beta} \) = interfacial energy
\( \gamma_\alpha \) = surface energies of phase \( \alpha \)
\( \gamma_\beta \) = surface energies of phase \( \beta \)
\( W_{\alpha\beta} \) = work of adhesion

For a solid–liquid interface in thermodynamic equilibrium:
\[ \gamma_{SL} = \gamma_{SV} + \gamma_{LV} \cdot \cos \theta \] (Young equation)

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

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

For \( \theta = 180 \): \( W_{SL} = 0 \) and for \( \theta = 0 \): \( W_{SL} = 2 \gamma_{LV} \) = Work of cohesion
**Surface energy GDC – LSCM**

**GDC/Ag Ar–5%H₂**

**LSCM/Ag Ar–5%H₂**

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>θ GDC/Ag</th>
<th>θ LSCM/Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>980</td>
<td>124.8</td>
<td>132.1</td>
</tr>
<tr>
<td>1000</td>
<td>123.9</td>
<td>131.3</td>
</tr>
<tr>
<td>1020</td>
<td>123.2</td>
<td>130.2</td>
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<tr>
<td>1040</td>
<td>121.9</td>
<td>128.8</td>
</tr>
<tr>
<td>1060</td>
<td>120.7</td>
<td>127.9</td>
</tr>
<tr>
<td>1080</td>
<td>119.6</td>
<td>126.7</td>
</tr>
<tr>
<td>1100</td>
<td>118.7</td>
<td>125.8</td>
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<tr>
<td>1120</td>
<td>117.7</td>
<td>124.9</td>
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<tr>
<td>1140</td>
<td>116.7</td>
<td>123.7</td>
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<tr>
<td>1160</td>
<td>115.8</td>
<td>122.9</td>
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<tr>
<td>1180</td>
<td>114.0</td>
<td>121.8</td>
</tr>
<tr>
<td>1200</td>
<td>112.9</td>
<td>120.4</td>
</tr>
</tbody>
</table>

\[ \gamma_{LV(Ag)} = 0.912 - 0.15 \times 10^{-3} (T - T_m) \]
Surface energy GDC – LSCM

\[ \gamma_{sv} \text{ (GDC)} = 2.290 - 1.2 \times 10^{-3} T \text{ (J/m}^2\text{)} \]

\[ \gamma_{sv} \text{ (LSCM)} = 2.792 - 1.08 \times 10^{-3} T \text{ (J/m}^2\text{)} \]
Surface energy GDC – LSCM

![Graph showing the surface energy of GDC and LSCM compared to other oxides such as CeO₂, YSZ, and TiO₂ as a function of temperature (T) in Kelvin (K).]
Wetting of GDC and LSCM by polar liquids in room temperature

GDC/Formamide, 20°C

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\gamma_{LV}$ [mJ/m²]</th>
<th>$\gamma_{LV}^d$ [mJ/m²]</th>
<th>$\gamma_{LV}^o$ [mJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>72.4</td>
<td>21.7</td>
<td>50.7</td>
</tr>
<tr>
<td>N.S.</td>
<td>71.3</td>
<td>23.8</td>
<td>47.5</td>
</tr>
<tr>
<td>E.G.</td>
<td>47.7</td>
<td>30.1</td>
<td>17.6</td>
</tr>
<tr>
<td>Glycerol</td>
<td>63.4</td>
<td>37</td>
<td>26.4</td>
</tr>
<tr>
<td>Formamide</td>
<td>58.2</td>
<td>39.5</td>
<td>18.7</td>
</tr>
</tbody>
</table>
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, St Andrews
Rumen Tomov, Vasant Kumar, Bartek Glowacki, Cambridge
Pellet samples for initial in-situ spectroscopy

Characterisation

SEM
- Microstructure
- Impregnates distribution and particle size

XRD
- Phase identification of impregnates

Wetting behaviour
- Contact angle measurement
Microstructure of ceria infiltrated YSZ

- Nano-particles can be observed with particle size in the range of 10-50nm;
- No differences were seen between different types of ceria particles
Pellet samples for initial in-situ spectroscopy

Microstructure of NiO-ceria infiltrated YSZ

- Nano-particles from both NiO and ceria observed;
- Reduction will be done and the microstructure from backscattering electron imaging will be inspected to see the distribution of Ni and ceria
Aqueous tape casting

- YSZ tapes with 30 vol% pore formers (PFs)
- Acrylic PFs composition
  Polyethyl methacrylate (PEMA, 35-45 μm)-Polymethyl methyacrylate-co-ethylene glycol dimethacrylate (PMMA-EGMA, 8μm)
  70-30, 60-40, 50-50, 40-60
- Different ways of organics compensation as a result of adding pore formers were tried
- Effects including tape thickness, drying conditions were considered
YSZ tape without PFs

Recipe for starting

<table>
<thead>
<tr>
<th>content</th>
<th>Mass (g)</th>
<th>Vol. (ml)</th>
<th>wt% in suspension</th>
<th>Vol.% in suspension</th>
<th>Vol.% in dried tape</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stage 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8YSZ</td>
<td>15</td>
<td>2.521</td>
<td>45.29</td>
<td>12.64</td>
<td>39.27</td>
</tr>
<tr>
<td>Water</td>
<td>5</td>
<td>13.527</td>
<td>40.76</td>
<td>67.82</td>
<td>N/A</td>
</tr>
<tr>
<td>KD6</td>
<td>0.27</td>
<td>0.27</td>
<td>0.82</td>
<td>1.35</td>
<td>4.21</td>
</tr>
<tr>
<td>Defoamer</td>
<td>0.15</td>
<td>0.15</td>
<td>0.45</td>
<td>0.75</td>
<td>2.34</td>
</tr>
<tr>
<td>Stage 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>poly ethylene glycol 300</td>
<td>0.9</td>
<td>0.8</td>
<td>2.72</td>
<td>4.01</td>
<td>12.46</td>
</tr>
<tr>
<td>glycerol</td>
<td>1.8</td>
<td>1.4286</td>
<td>5.43</td>
<td>7.16</td>
<td>22.25</td>
</tr>
<tr>
<td>PVA</td>
<td>10</td>
<td>1.25</td>
<td>4.53</td>
<td>6.27</td>
<td>19.47</td>
</tr>
<tr>
<td>Total</td>
<td>33.12</td>
<td>19.9466</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
YZS tape with 30 vol.% PFs

- Tape thickness seemed uniform and compact after sintering at 1400°C.
- Dry tape was not as smooth as without PFs, particles seen on surface.

Weight compensation

Cross-section view

Surface view
YSZ tape with 30 vol.% PFs

Volume compensation

Microstructure of thick tapes after sintering at 1400°C
Inkjet printing and infiltration of SOFC electrodes

R.I. Tomov, Chenlong Gao, Chingfu (Eric) Wang, R.V. Kumar, B. A. Głowacki

Department of Materials Science and Metallurgy, University of Cambridge, UK
Anode TPB engineering by inkjet printing infiltration

Optimum printing parameter

- Suspension inks - (NiO:CGO, 60wt%:40wt%, 70wt%:30wt% and 80wt%:20wt%) – pressure 0.4 bar and opening time of 300 μs.
- Sol gel CGO inks - pressure 0.6 bar and opening time of 350 μs.

EIS Measurement condition

- Solartron 1260,
- Symmetrical cell configuration
- Gas (96% argon, 4% hydrogen) flow rate 200ml/min
- In-situ reduction at 800°C 1h
- Measurement performed at 600 °C
- Applied AC voltage of amplitude of 10mV
- Frequency scan range from 1MHz to 0.1Hz
Anode scaffolds (without infiltration) of different compositions (a) 50wt%NiO: 50wt%CGO (b) 60wt%NiO: 40wt%CGO (c) 70wt%NiO: 30wt%CGO.

Calculated total TPB density vs. nickel fraction. Parameters for the model were obtained from the SEM image.
The CGO precursor solution (1.5M total metal concentration) was prepared by dissolving cerium (III) acetate hydrate (99.9%, Sigma-Aldrich) and gadolinium (III) acetate hydrate (99%, Sigma-Aldrich) in two steps in propionic acid. The precursor was further diluted in order to reduce the viscosity to a level suitable for printing. 1-propanol was selected for viscosity adjustment (0.75M).

Each drop (9 nL, determine by drop visualisation) contains 0.44 µg of CGO nanoparticles, and each layer of infiltration (resulting from the infiltration of 368 drops) contain 161 µg of CGO nanoparticles. Hence each infiltration cycle deposits on average 62 CGO nanoparticles on a Ni$_{\text{scaffold}}$ particle.
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.
Tailoring of Microstructural evolution in impregnated SOFC electrodes

WP3: *In-situ and In-operando* Spectroscopy

Robert Maher, David Payne, Lesley Cohen, Greg Offer

*Imperial*
Sample set 1: Overview

- 5 samples received
  - 6A and 8A – CeO$_2$ infiltrated 8YSZ
  - 9A – (GdCe)O$_2$ infiltrated 8YSZ
  - 11A – (Zr, Ce)O$_2$ infiltrated 8YSZ
  - 14A – Bare 8YSZ backbone
- All samples characterised using 514, 633, 830nm lasers
- 8A, 9A, 11A, 14A quartered
- Reduction monitored in 10% H$_2$ using 514nm laser, at 600 and 700°C
Sample set 1: Initial Raman characterisation

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

![Graph showing Raman shift vs. intensity for different samples](image)
Sample set 1: Initial Raman characterisation

- **6A and 8A** – CeO$_2$
- **9A** – (GdCe)O$_2$
- **11A** – (Zr, Ce)O$_2$
- **14A** – Bare 8YSZ backbone
Sample set 1: Reduction monitoring

- Reduction monitored using Raman *in-situ*
- Reduction carried out in 10% H\textsubscript{2} : 90% N\textsubscript{2}
- Raman spectra collected every 10 seconds for 1 hour for each sample at each temperature
- Reductions carried out at 600 and 700°C
Sample set 2: Initial Raman characterisation

- CeO$_2$ + Ni infiltrated 8YSZ – 2B,5B
- (GdCe)O$_2$ + Ni infilled 8YSZ – 3B,8B
- (Zr, Ce)O$_2$ infiltrated 8YSZ – 4B,7B
Sample set 2: Initial Raman characterisation

- CeO$_2$ + Ni infiltrated 8YSZ – 2B,5B

- (GdCe)O$_2$ + Ni infilled 8YSZ – 3B,8B

- (Zr, Ce)O$_2$ infiltrated 8YSZ – 4B,7B

![Raman shift graph with various samples]
Sample set 2: Comparison to sample set 1

- Ni infiltration doesn’t appear to affect the Raman response

- More spectra would need to be taken to confirm

- Reduction effect?
Initial UHV XPS results

David Payne, Department of Materials
Bare YSZ (no 14A)

Survey

Zr 3d

Y 3d

O 1s

C 1s

Valence
Sample (Gd,Ce)O$_2$ on YSZ (no 9A)

- **Survey**
- **Zr 3d**
- **Ce 3d**
- **O 1s**
- **C 1s**
- **Gd 4d**
- **Valence**
Tailoring of Microstructural evolution in impregnated SOFC electrodes

WP4: Optimisation and Demonstration of cell performance and durability

Xiangling Yue, Georgios Triantafyllou, Mark Cassidy, Cristian Savaniu, Paul Connor, and John Irvine, St Andrews
Four Work Tasks

- WT4.1
  - Testing of impregnated electrodes with realistic fuels
- WT4.2
  - Investigation of S tolerance of impregnated catalysts
- WT4.3
  - Scale up of promising materials & techniques
- WT4.4
  - Testing of larger impregnated cells under realistic conditions
Testing jigs

- a variety
- two or three electrode

- Gas supply
  - all 5%H$_2$, H$_2$, Air and O$_2$
  - also CO, CO$_2$ on some
  - full biogas simulation rig
    - N$_2$, H$_2$, CO$_2$, CO, CH$_4$, H$_2$O