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# Tailoring the microstructure of impregnated SOFC electrodes for improved performance

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H2FC SUPERGEN
THE HYDROGEN AND FUEL CELL RESEARCH HUB
FCH2 2018
TECHNICAL CONFERENCE
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## *Technology Drivers*

- **Performance**
  - Materials, microstructure and processing, system management – nano is beneficial
- **Durability**
  - Materials, temperature, system – nano is problematic
- **Cost**
  - Manufacturing, materials – nano can be expensive
- **Fuel Flexibility**
  - Materials, system management - nano is beneficial
- **Retain focus on clean energy target**
  - Whole cycle analysis

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## Advancing SOFC technologies

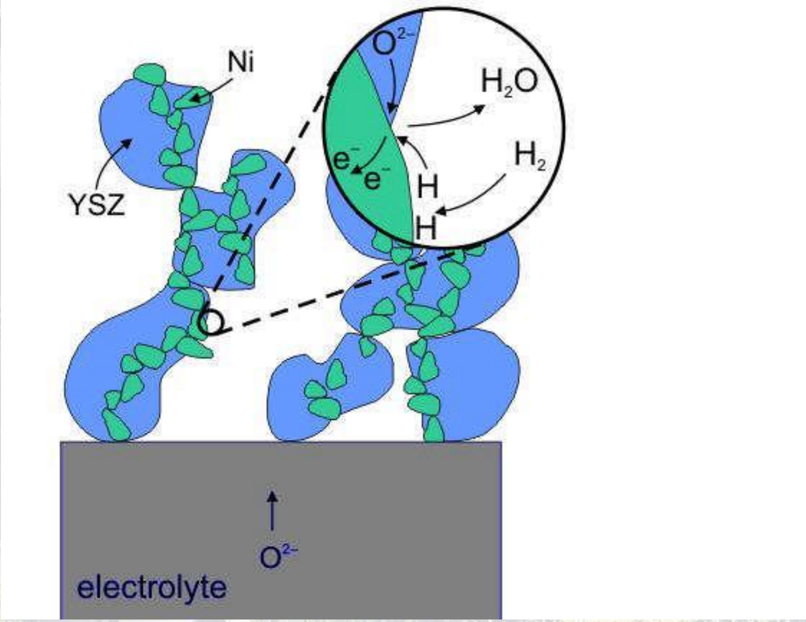
- The development of novel anode materials with excellent performance and stability at intermediate-temperatures and operating with various fuels- $H_2$, syngas and hydrocarbons is essential

- Two approaches in developing electrode materials:
  - optimising the state-of-the-art electrode materials or
  - exploring novel systems with high mixed ionic and electronic conductivity (MIEC).

**Ni/YSZ CERMET**

Good Current Collector

Steam reforming catalyst



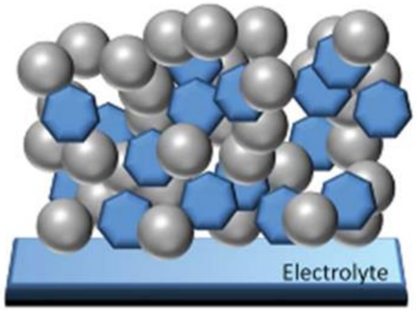

**Drawbacks:**

Promotion of carbon fibres, $C_nH_{2n+2} \rightarrow C$

Reaction with mercaptans $Ni + S \rightarrow NiS$

Ni coarsening, Degradation $2Ni + O_2 \rightarrow 2NiO$

# MIEC fabrication




Microstructure from bulk processing

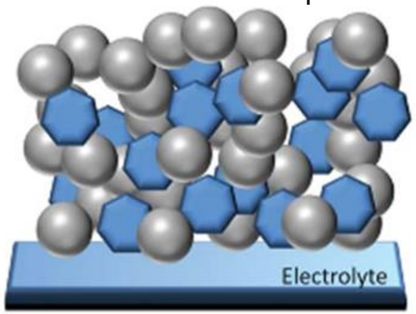
- Grain growth thus reduced active surface areas
- Detrimental interfacial reactions
- Mismatched thermal expansions
- Large amount of material to meet percolation

- Alternative mixed electronic and ionic conducting (MIEC) electrode materials require novel fabrication routes
- Impregnation method has been an effective approach for cell fabrication or performance optimisation
- Nano-sized species are impregnated into porous framework either to enhance the electronic or ionic conductivity of the electrode or its catalytic activity

# Impregnation technique

**High temperature sintering**

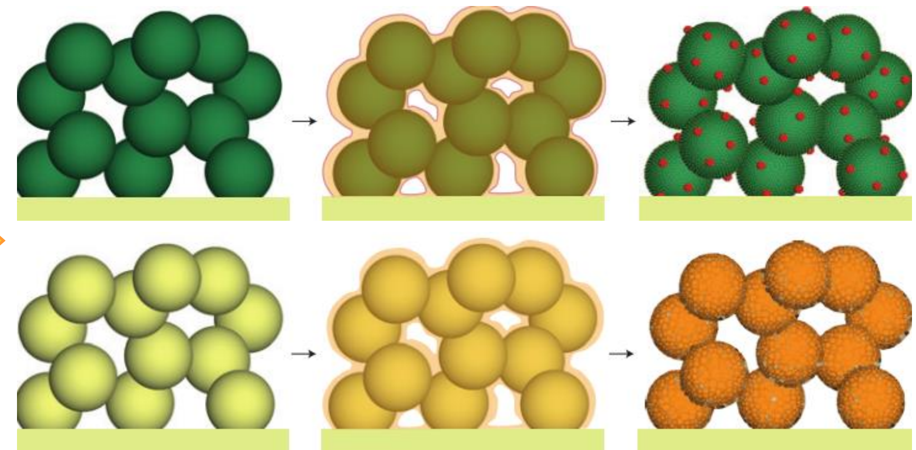
Conventional composite




Microstructure from bulk processing

Microstructure evolution

**High temperature sintering** | **low temperature processing**



Typical microstructures produced by solution impregnation: *above,* dispersed catalyst particle formation on top of an electron conducting backbone, *below*- a continuous layer of MIEC perovskite formed on top of an ion conducting backbone

***Nature Energy*, 1, Article number: 15014 (2016)**

# Impregnation technique

- ✓ Enhance the TPB
- ✓ Enhance electrocatalytic activity by adding low amounts of catalysts;
- ✓ Match in thermal stability;
- ✓ Potential for improved coking resistance and sulfur tolerance;
- ✓ Broaden the range of available materials;
- ✓ Flexibility in tailoring the electrode microstructure

- ✗ Clever process design
- ✗ Processing time and cost; could be wasteful especially when expensive materials are used
- ✗ Particles growth and agglomeration leading to degradation;
- ✗ Up-scaling;
- ✗ Fundamentals not well understood

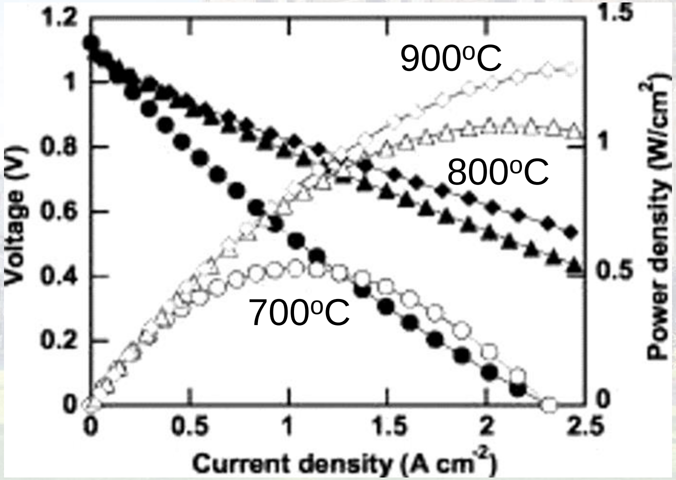
# Alternative ceramic anodes produced by impregnation:

Anode: Porous YSZ, 45 wt% $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM), 5 wt% ceria, 0.5 wt% Pd

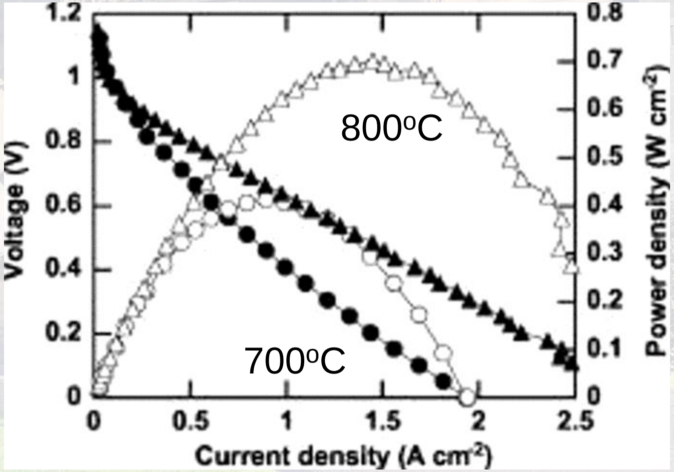
Cathode: Porous YSZ, 40 wt% LSF, Electrolyte: 60 microns YSZ

**Electrochemical performance is excellent, stable towards oxidation and tolerant to hydrocarbons:**

**97% $H_2$-3%$H_2O$**




**97% $CH_4$-3%$H_2O$**




*Electrochem. Solid-State Lett. 2008 volume 11, issue 2, B16-B19*

## Evolution of LSCM/YSZ nano/microstructure


(a) SEM images of the LSCM-YSZ composite with 45wt% LSCM calcined at 1200ºC in air. (b) The same composite after reduction in humidified $H_2$ at 800ºC for 4h and c) after re-oxidation at 800ºC for 5h

# Electrolyte supported cells with impregnated $La_{0.2}Sr_{0.25}Ca_{0.45}TiO_{3-\delta}$ (LSCT) anode backbone

E. Stefan, M. Cassidy, C. Savaniu, M. Verbraeken, J. Irvine
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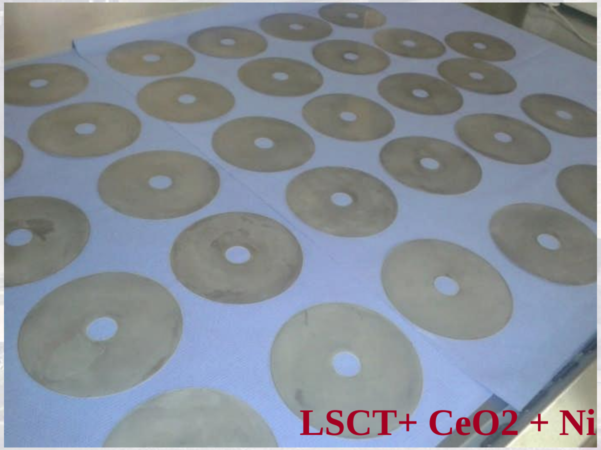
U. Weissen, B. Iwanschitz, A. Mai *Hexis AG*



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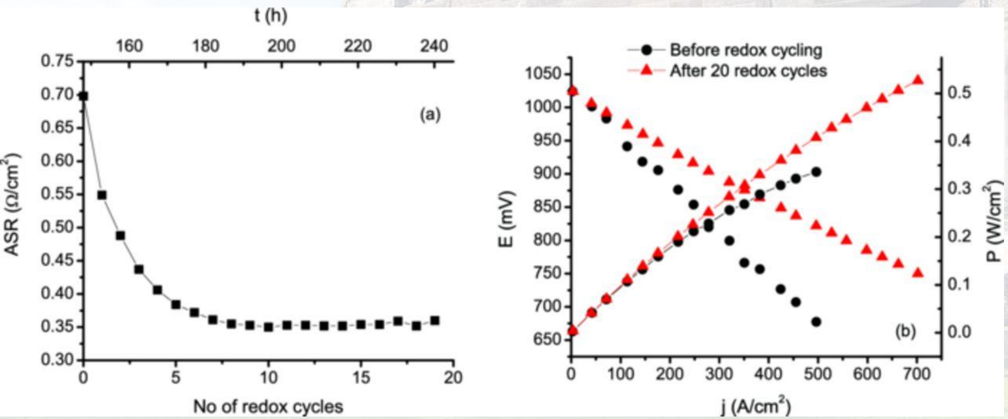
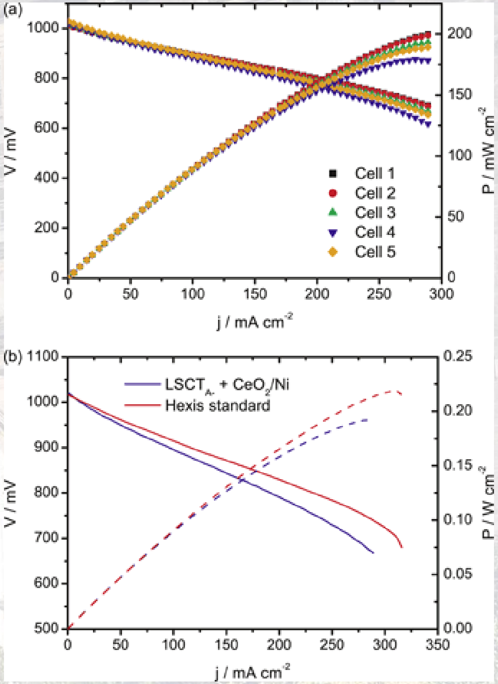
## Ni + $CeO_2$ impregnation into LSCT anode– Hexis

- 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

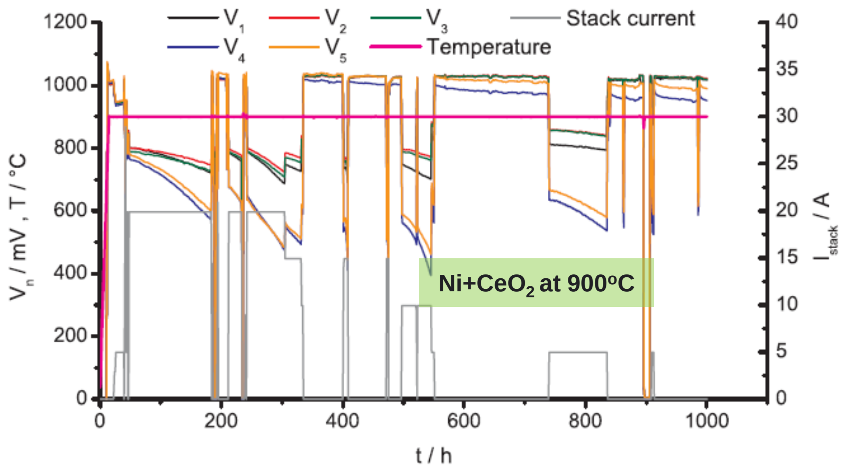


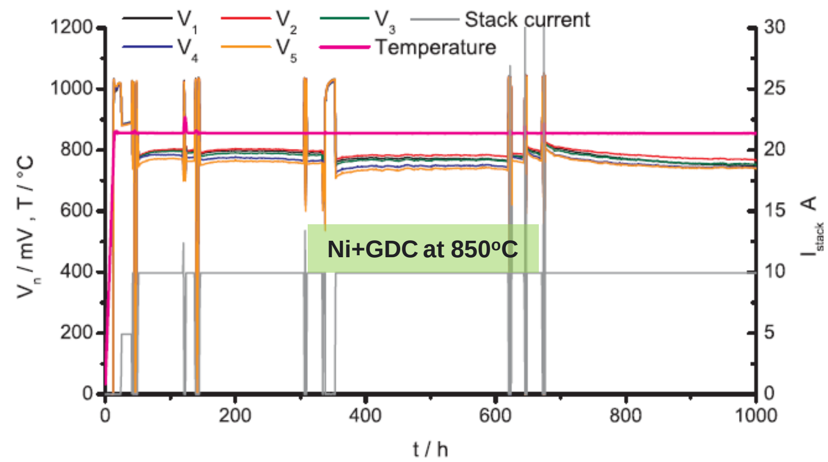

97% $H_2$ 3% $H_2O$ at 900°C




*I*–*V* for a 5 cell stack with Ni/$CeO_2$ impregnated LSCT$_{A-}$ anode at 900 °C in CPOx reformed natural gas (a). Comparison with standard HEXIS Ni cermet based anode (b)

# Perovskite $LSCT_{A-}$ anode scaffold impregnated with $CeO_2$/Ni



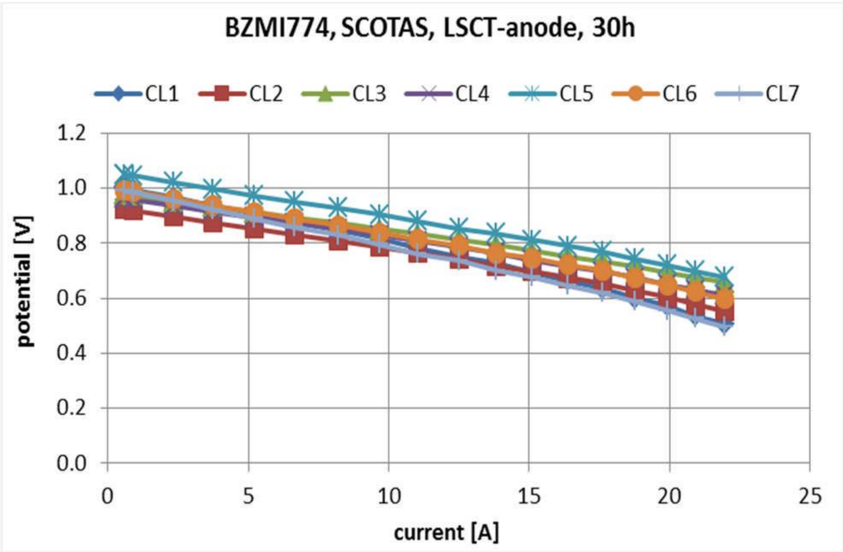



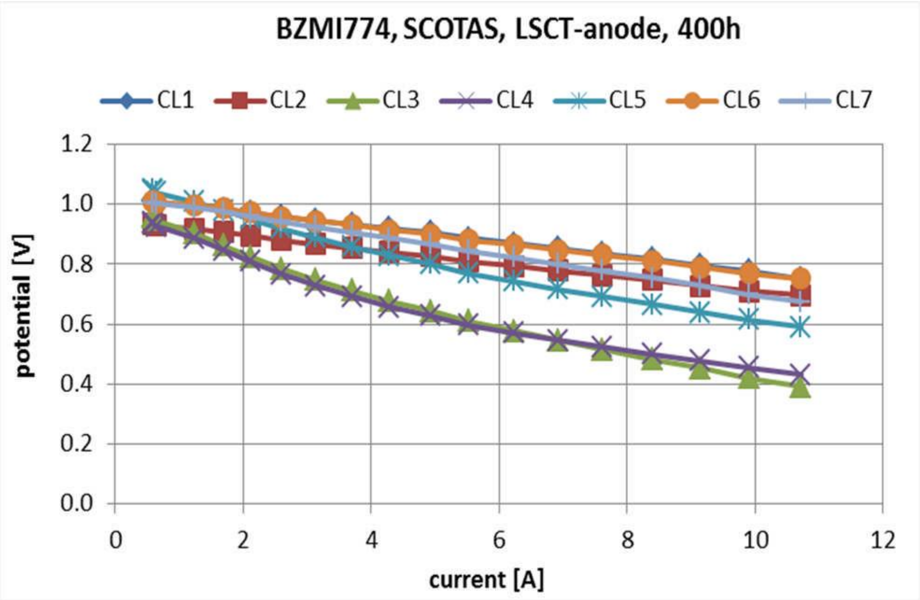

**Durability test of 5 cell stack (HEXIS) with $LSCT_{A-}$ anode with Ni +$CeO_2$ and Ni + GDC ($Gd_{0.2}Ce_{0.8}O_{1.90}$) as impregnated catalyst in 4g $h^{-1}$ of CPOx (catalytic partial oxidation) reformed natural gas.**

- ❑The Ni+$CeO_2$ infiltrated $LSCT_{A-}$ anode showed comparable performance with the standard HEXIS Ni-cermet anode;
- ❑ The Ni + GDC impregnated cell seemed more stable than the Ni + $CeO_2$ impregnated $LSCT_{A-}$ anode cell;

📖 ***Fuel Cells, 15, 682, 2015***

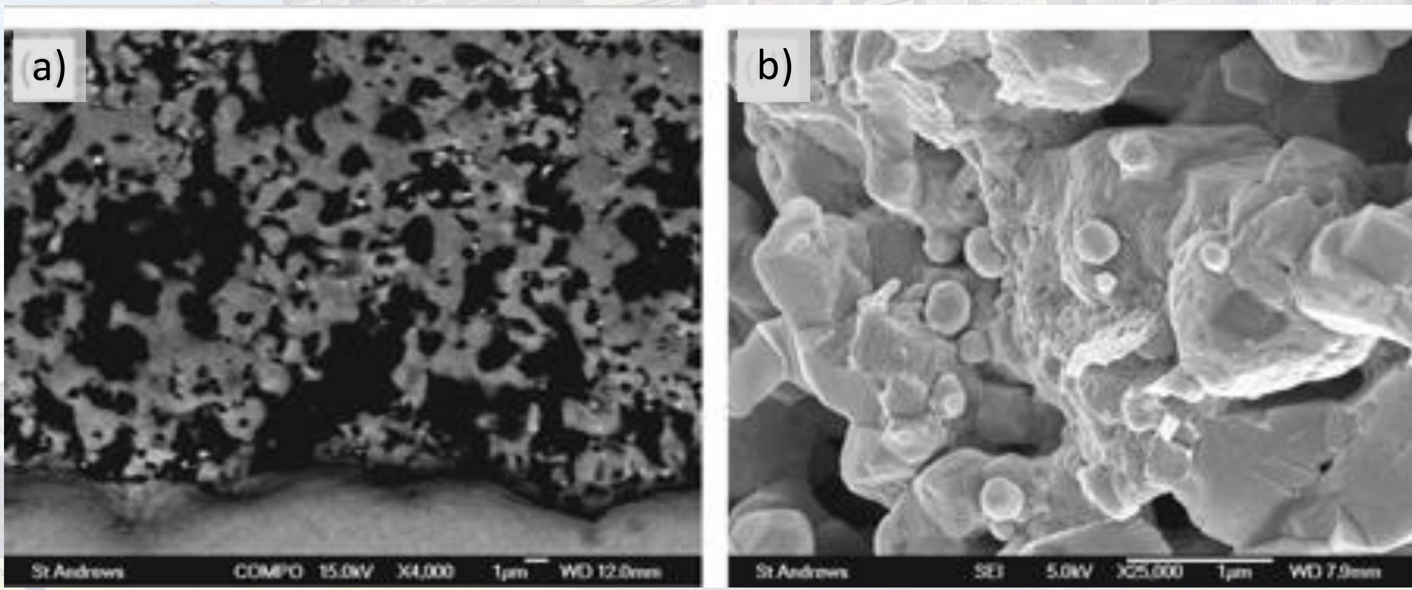
# Galileo Stack 1 kW with 3.3 kW reformed $CH_4$ input




60 cells, 1kWh stack, 850°C

# Ceramic backbone + catalyst




Ni particles 50 – 100 nm

Nanoparticles keep growing up to 300 nm after ~1000h

Ni/$CeO_2$ impregnated $LSCT_{A-}$ (c, d) after testing at 900 °C for 1,000 hours in CPOx reformed NG

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Imperial College London

UNIVERSITY OF CAMBRIDGE Department of Materials Science and Metallurgy

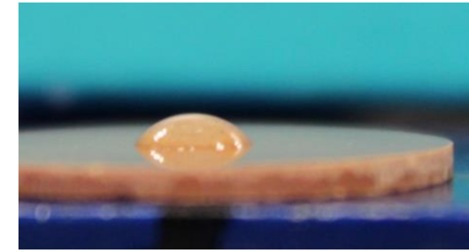
EPSRC
Engineering and Physical Sciences Research Council

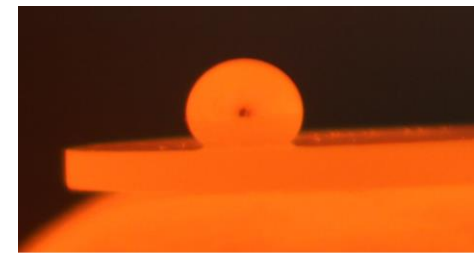
## “Tailoring the Microstructural Evolution in Impregnated SOFC Electrodes”

# Tailoring the microstructural evolution in impregnated electrodes

- Characterisation of Interfaces
  - Manufacture of porous substrates and Optimisation of Impregnation procedures
    - *In-situ* and *In-operando* Spectroscopy
      - Optimisation and Demonstration of cell performance and durability

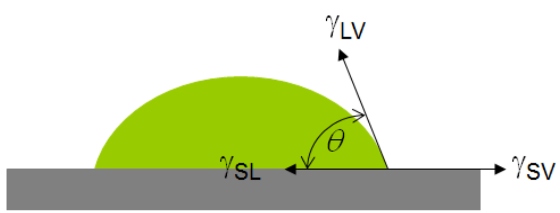
# Wetting and surface energy





Objectives:

- Evaluate the surface/interfacial properties of materials and the effect of material processing
- Contact angle measurements to determine the wetting properties
- Optimisation of the contact angle
- Correlate these properties with the electrochemical performance




$0^o < \theta < 90^o \rightarrow$ good wetting

$90^o < \theta < 180^o \rightarrow$ bad wetting

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 substrate
$\gamma_{LV}$ = surface energy of liquid
$\gamma_{SL}$ = interfacial energy
$\theta$ = contact angle

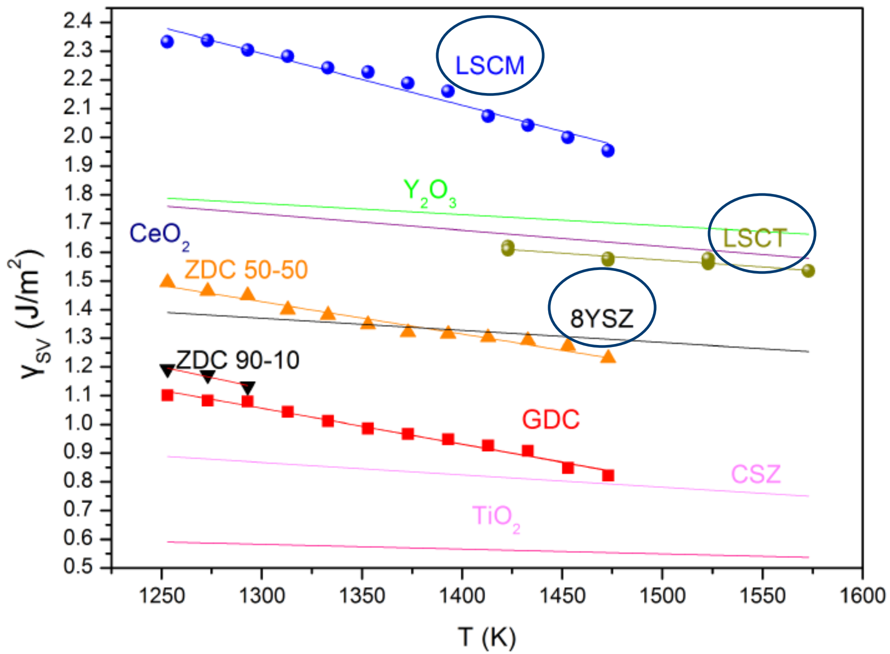
# Surface energy determination

General Energy Equation:

$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - W$

Young –Dupre equation

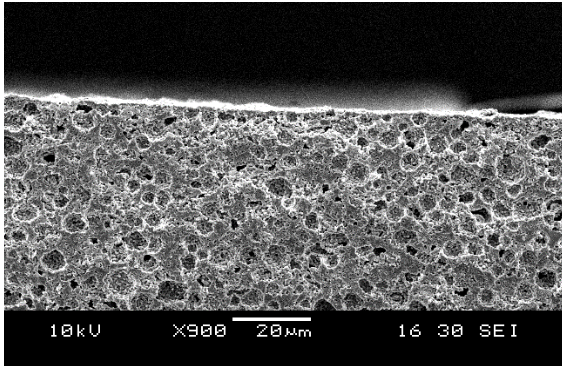
W = work of adhesion= $\gamma_{LV}$ (1+ cos $\theta$)



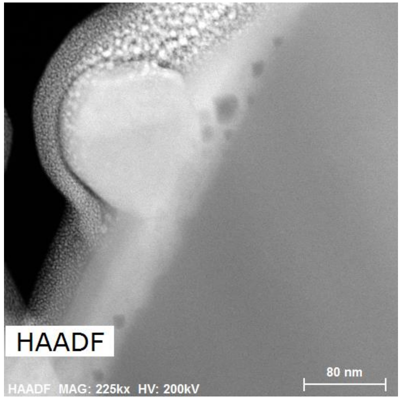

Surface energy of some typical materials with temperature

# Optimisation of porosity and Impregnation procedures

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

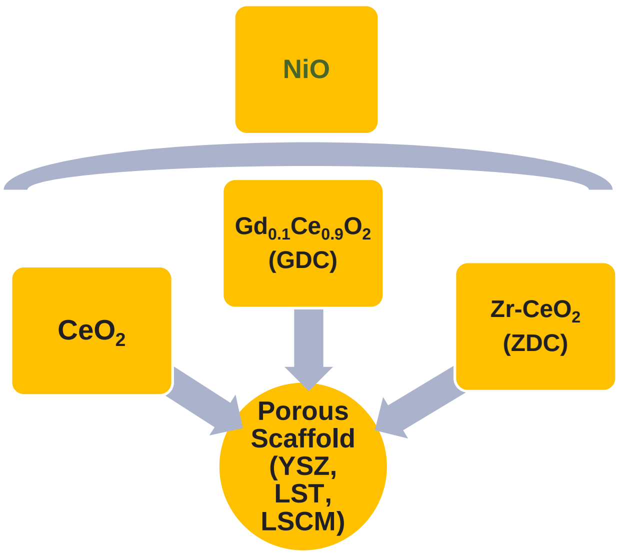


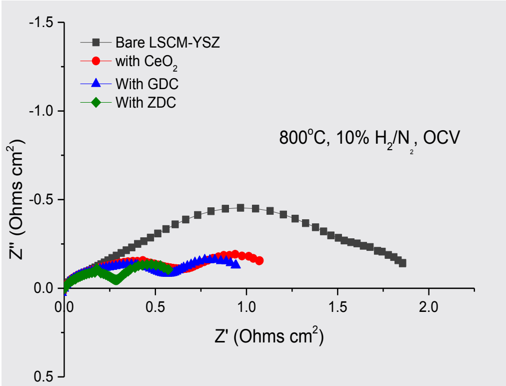

Microstructure of a YSZ backbone produced by aqueous tape casting using starch and PMMA as pore formers

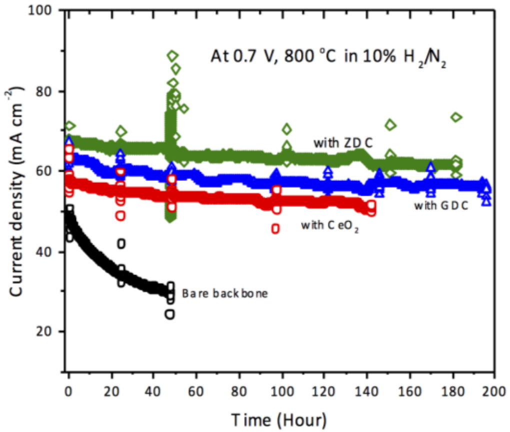



HAADF STEM image of an impregnated structure

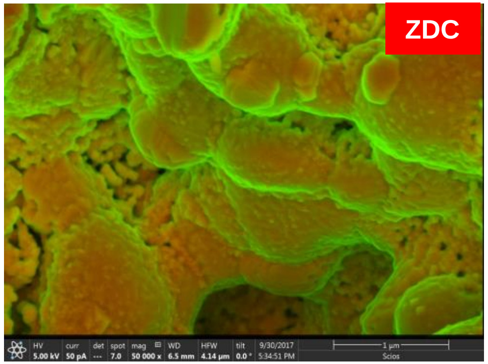
# Examples of impregnated SOFC anodes




Electrochemical performance of LSCM:YSZ backbone impregnated different cerias

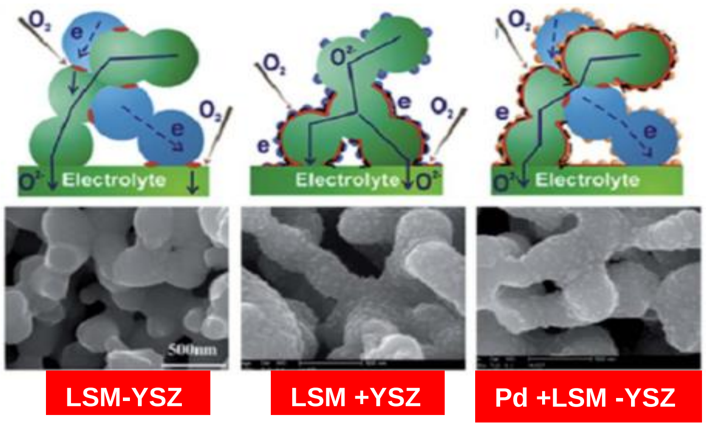


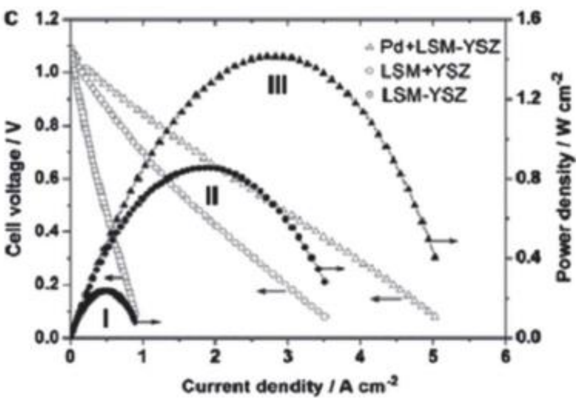
# Inkjet impregnation of functional coatings (Cambridge)

Inkjet technology features:

- High productivity, enabling rapid, accurate, non-contact deposition of small liquid drops
- Performance: enhanced thickness control and higher resolution compared to conventional processing
- Flexibility: restricted only be the rheology of the ink
- Cost: Lower cost and better scalability than vacuum, vapour deposition and lithographic routes.

**Promoting LSM-YSZ cathode activity by impregnation**



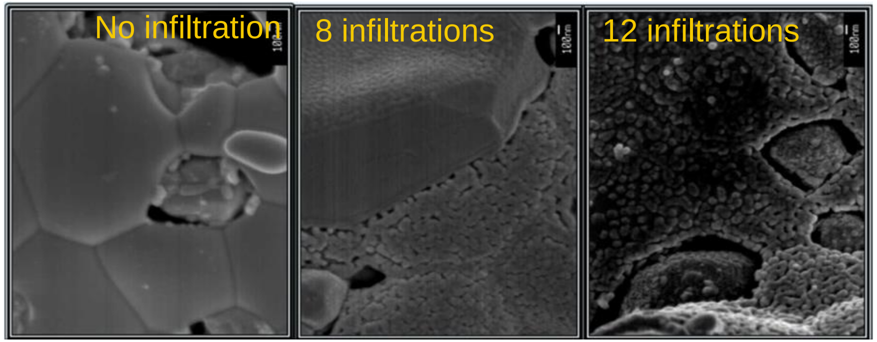



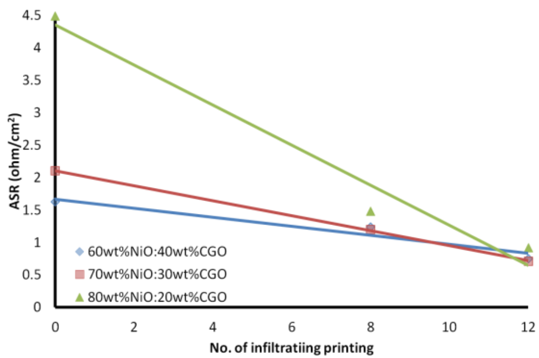

*Int. J. Hydrogen Energy, 37, 449, 2012*

Practical examples: Co-infiltrated LSM/YSZ, Co-Ceria LSCF cathodes

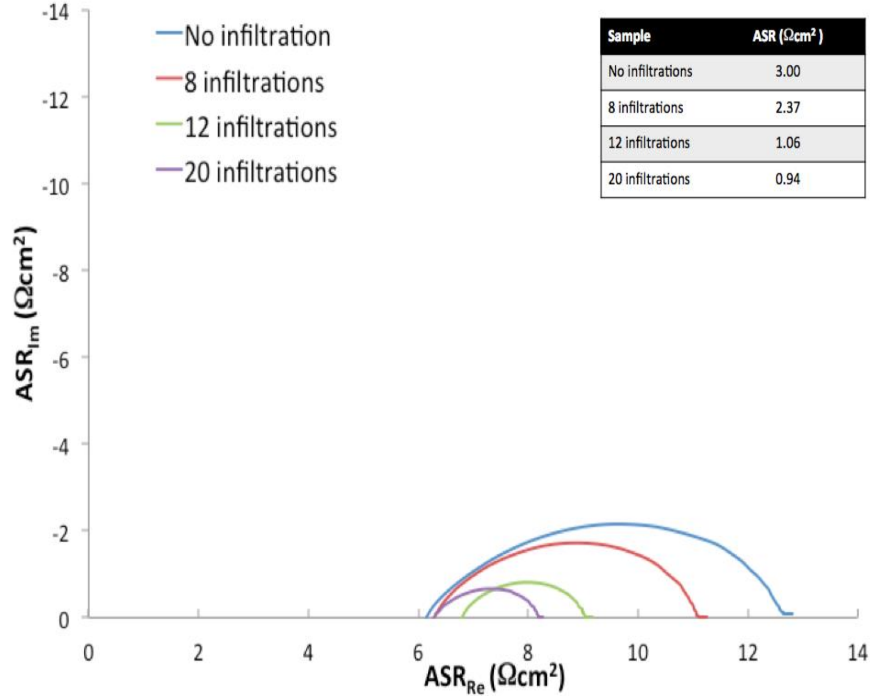
# Anode TPB engineering by inkjet printing infiltration

CGO impregnation into Ni/CGO composite anode




Ni/CGO anode

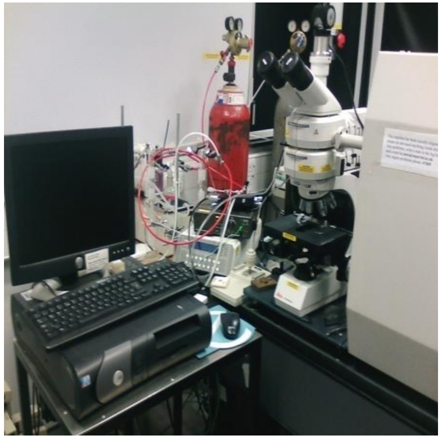


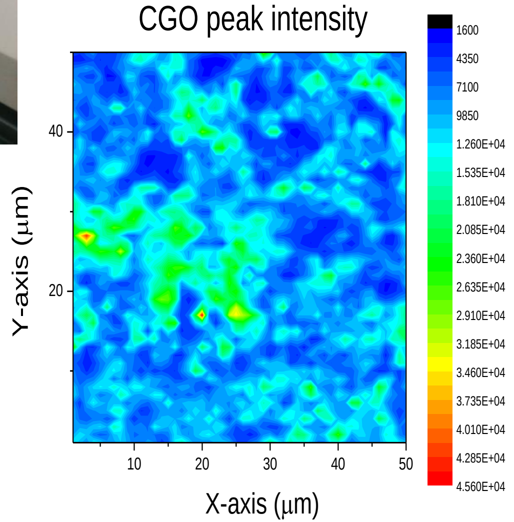

| Sample | ASR (Ωcm²) |
|---|---|
| No infiltrations | 3.00 |
| 8 infiltrations | 2.37 |
| 12 infiltrations | 1.06 |
| 20 infiltrations | 0.94 |

# Surface characterisation of impregnated electrodes

## *In-situ* Raman Spectroscopy (Imperial)

- A chemically specific, non-invasive, optical characterisation technique
- Near surface sensitivity, chemical specificity and high spatial resolution
- Technique developed to investigate reaction kinetics, temperature distribution, oxidation states and coking mechanism on SOFC operation with hydrocarbon fuels, under realistic conditions
- Well suited to examine the impact of impregnation on the reaction kinetics within a SOFC environment



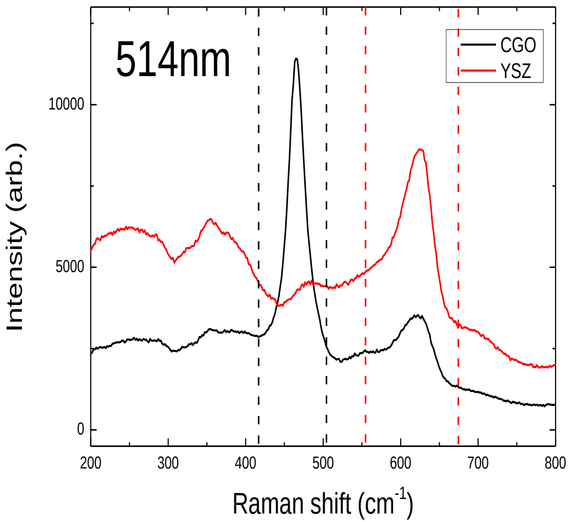


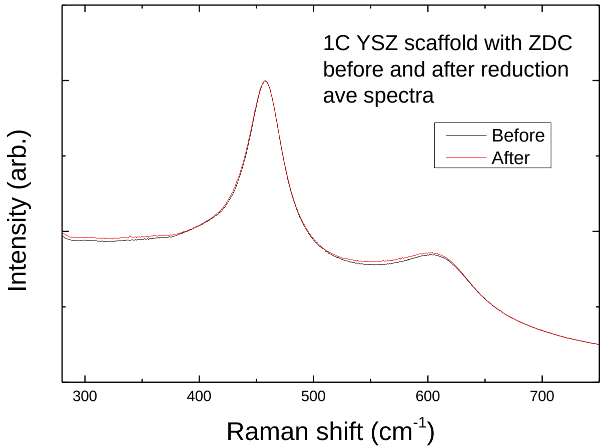

Surface distribution of species can be determined by Raman mapping through intensity integration

# Surface characterisation (Raman)

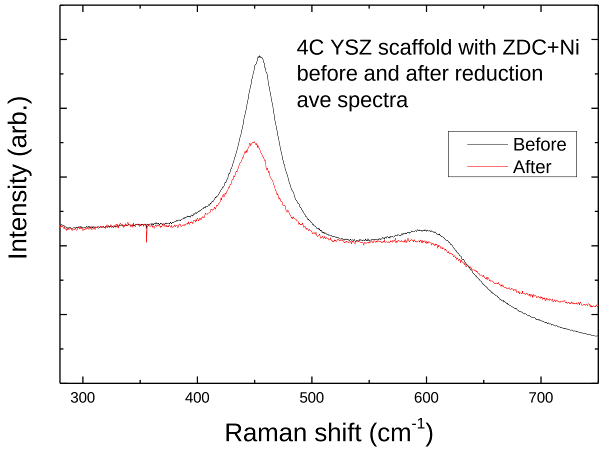
Surface composition

Peak positions and relative intensities give information on oxidation state of materials
Can monitor the changes in oxidation state of materials during in-situ redox cycling




8YSZ:ZDC

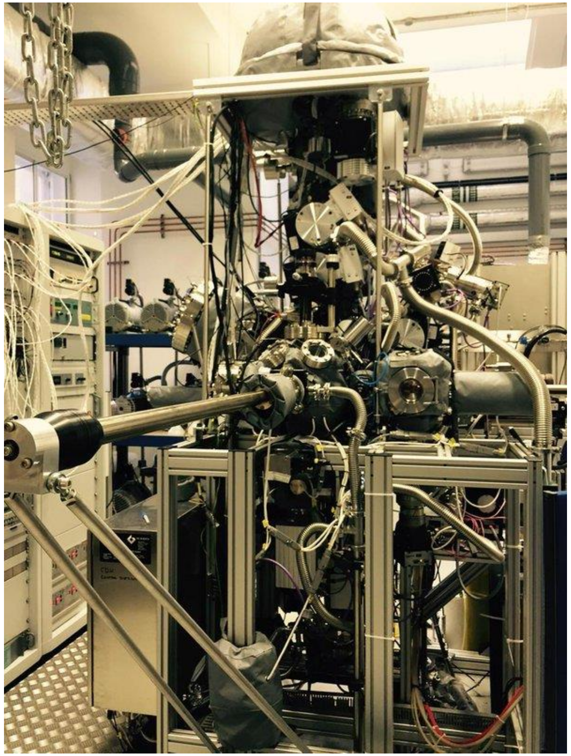



8YSZ:ZDC:NiO

# Surface characterisation of impregnated electrodes

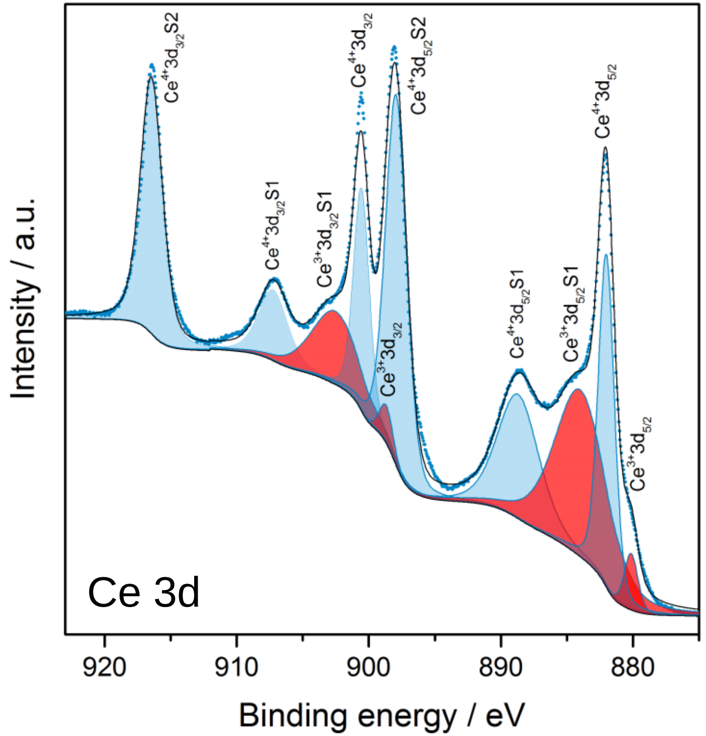
## In-situ X-ray Photoelectron Spectroscopy (XPS), Imperial

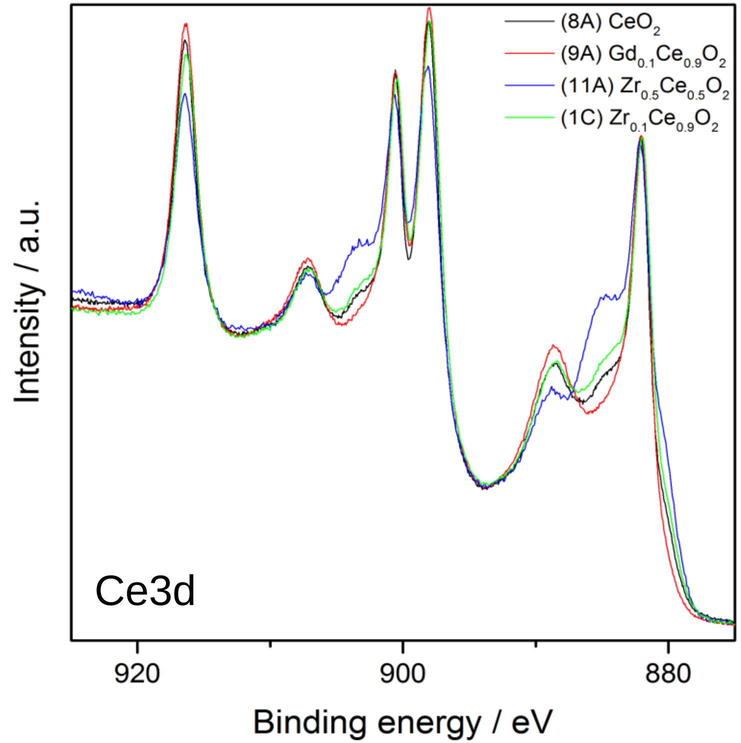
- XPS is a powerful surface characterisation technique.
  - Provides quantitative analysis of the elemental composition and oxidation states of the surface
  - Examines the active redox couples involved in electrode reactions, providing insights into reduction/oxidation kinetics
- In-situ XPS is very helpful for mechanistic understanding of interactions between impregnates and backbone.



HiPPES Scienta Omicron

# Surface characterisation (XPS)




| Sample | $Ce^{3+}$ (%) | $Ce^{4+}$ (%) |
|---|---|---|
| $CeO_2$ | 31.3 | 68.7 |
| GDC10 | 21.8 | 79.2 |
| ZDC10 | 34.6 | 65.4 |
| ZDC50 | 44.4 | 55.6 |

- Observations: Doping ceria with Gd decreases the amount of $Ce^{3+}$ while Zr dopant increases $Ce^{3+}$
  Nickel is present on the top layer of the sample and does not change the $Ce^{3+}/Ce^{4+}$ ratio

# Summary

- Wet impregnation has been demonstrated to be an effective approach to produce or optimise SOFC electrodes for enhanced performance and stability;

- Systematic, fundamental studies are required to study the interactions between impregnated particles and backbone and their influence on SOFC electrode performance and durability;

- Long-term tests are needed to fundamentally understand the promotion mechanism of the infiltrated nanoparticles and assess the structural stability of the nanoscale engineered electrodes under SOFCs operation conditions.

# Acknowledgements


- [1]X. Yue, R. Price, M. Cassidy, P.A. Connor, G. Triantafyllou, J.T.S. Irvine,
- [2]G. Kerherve, [2]D.J. Payne, [3]R. C. Maher, [3]L. F. Cohen,
- [4]R. Tomov, B.A. Glowacki, V.Kumar

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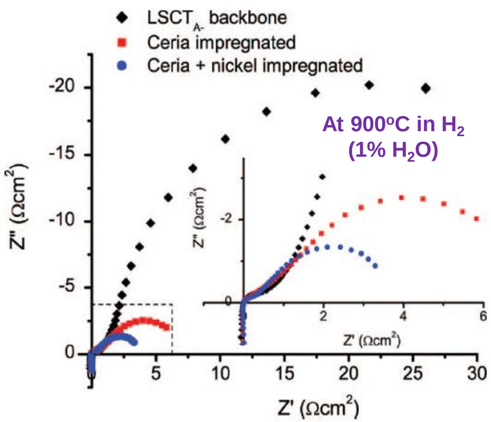
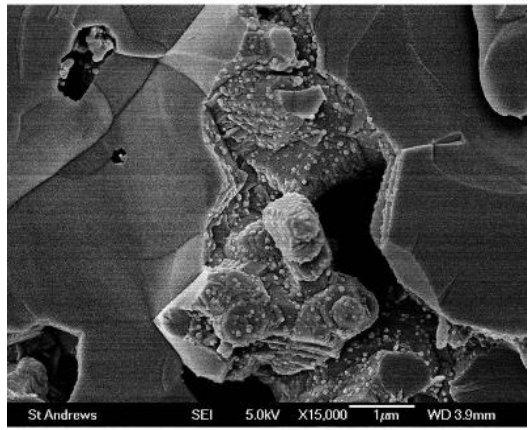
Thank you for attention!

# SOFC anode produced by impregnation

## Designing the microstructure with diverse combination of materials




Performance and microstructure of $La_{0.2}Sr_{0.25}Ca_{0.45}TiO_3$ (LSCT$_{A-}$) backbone with and without Ni (5wt%) and $CeO_2$ (10wt%) impregnates