Carbon Tolerant Ni/ScCeSZ SOFC Anode by Aqueous Tape Casting

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Motivation

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- Tape casting = mass manufacturing = low cost
- Reduced performance when switch to carbonaceous fuel using standard NiYSZ cell.
- Alternative anode that have high performance and tolerant to carbonaceous fuel
- Limited work on NiScCeSZ anode supported cell(ASC), and none using aqueous tape casting process.

Scandia cell expectation
Less/different carbon deposition behaviour
Higher ionic conductivity
Lower ohmic resistance
Good performance even at low temperature (~700C)

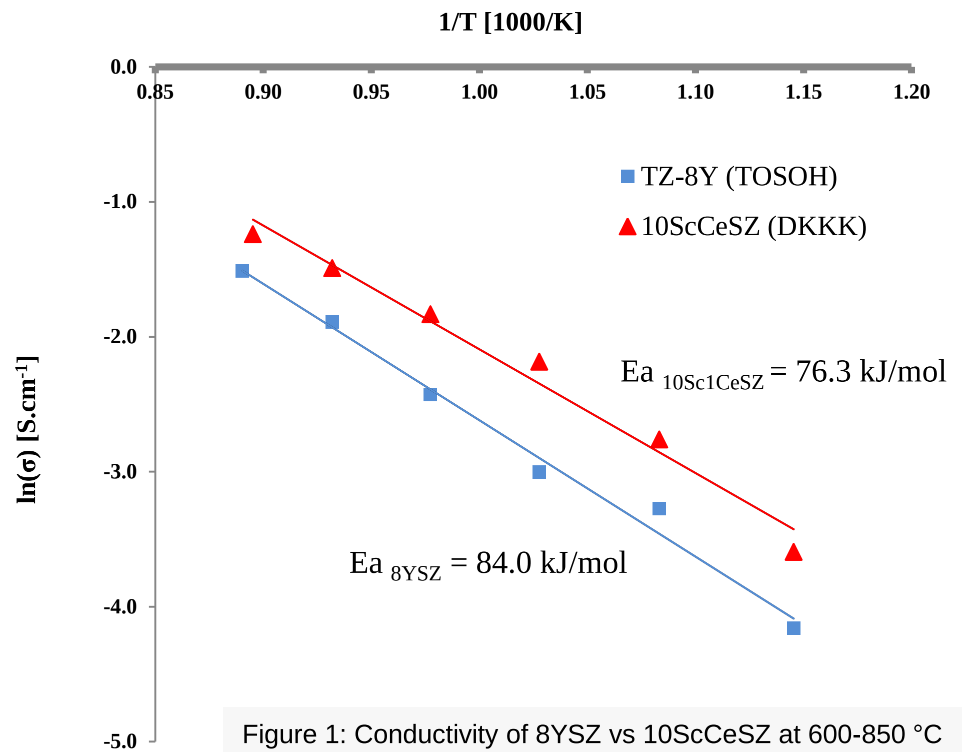
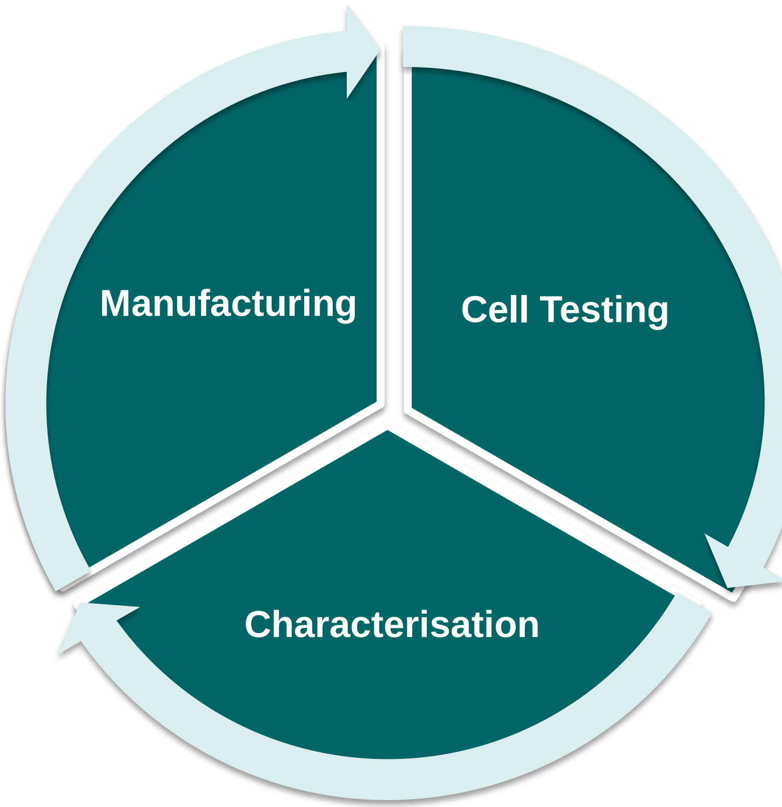


Figure 1: Conductivity of 8YSZ vs 10ScCeSZ at 600-850 °C

Research Overview

- Powder
  - Pre-calcination
- Cell
  - Tape Casting
  - Full Cell
  - Sintering
  - Cathode



- Current @ 0.7 V
- IV curve – maximum power density
- EIS
- TPO

- SEM
- XRD

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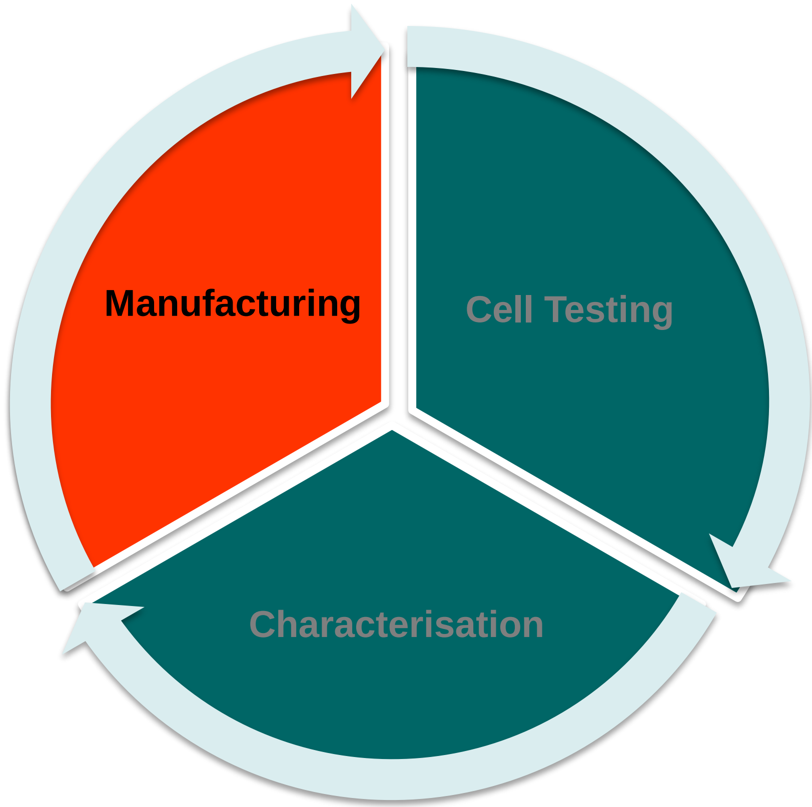

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Tape Casting: Aqueous VS Solvent

- Aqueous – using harmless distilled water as the solvent
- Solvent – use either toluene or MEK as the solvent
- Challenges in aqueous based system:
  - Poor tape quality
    - Pinholes - excessive bubbles from ball milling
    - Cracking (mud-cracking, crow feet defect)
    - Fish eye defect
  - Dewetting, difficult to spread on the film due to high surface tension of water
  - High slip viscosity

Figure 2: Lab tap casting machine (MTI Corp USA)

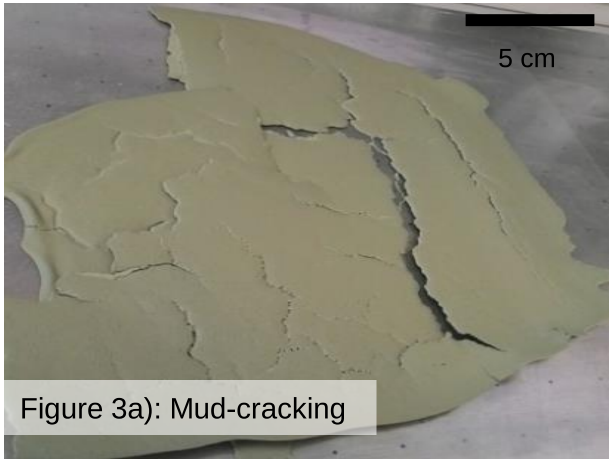

Figure 3a): Mud-cracking

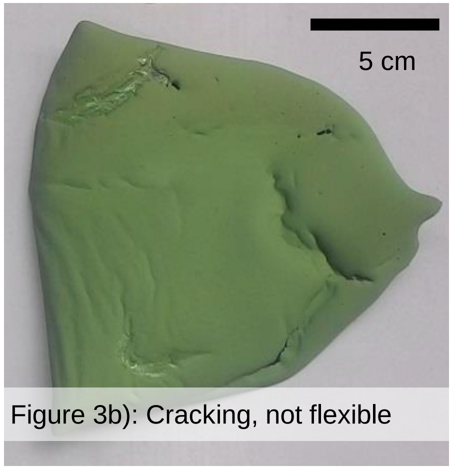

Figure 3b): Cracking, not flexible

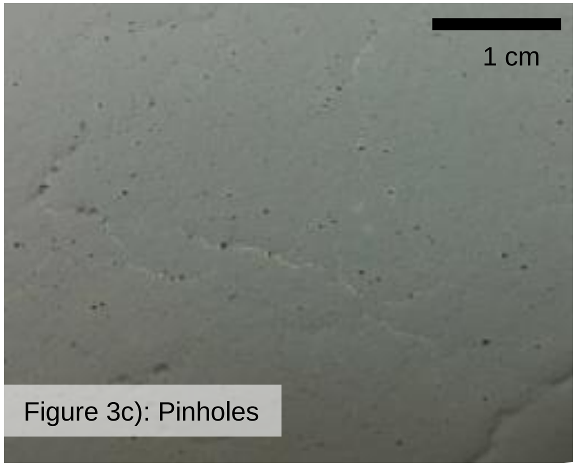

Figure 3c): Pinholes

Reverse tape-casting

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- ✓ Reverse Tape casting – Tape cast electrolyte layer first, followed by anode functional layer (AFL) and anode substrate (AS)

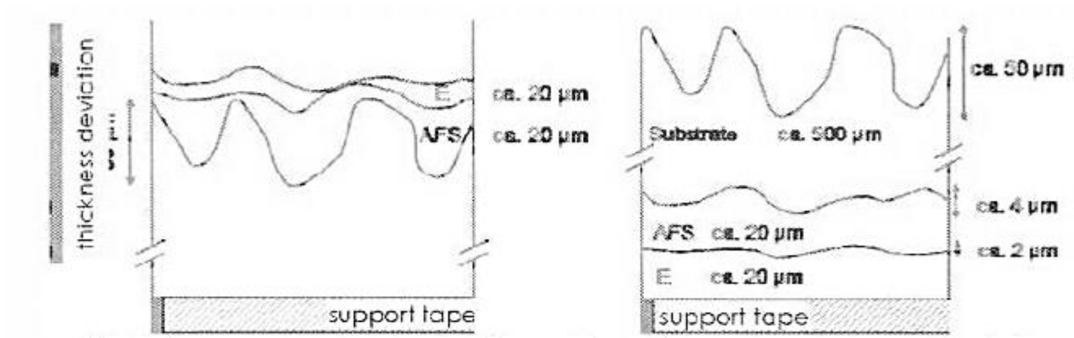

Figure 4: Menzler, N.H., Schafbauer, W *Advanced manufacturing technology for solid oxide fuel cells*. in *Ceramic Engineering and Science Proceedings*. 2011

Figure 5: Reverse tape casting consist of electrolyte, anode functional layer and anode substrate layer

Reverse tape-casting

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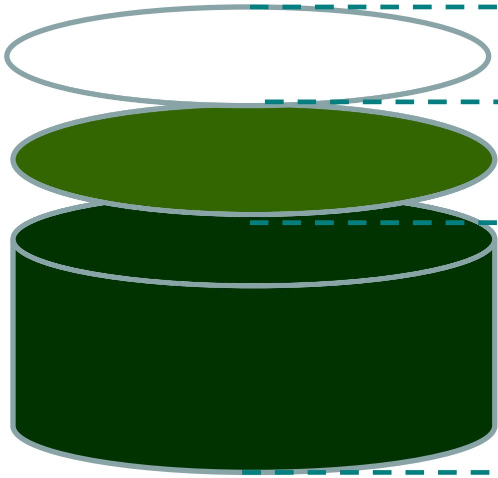

1st layer= Electrolyte 10-15 µm

2nd layer =Anode Functional Layer (AFL) 15-20 µm

3rd layer = Anode Substrate (AS) 500 µm

Figure 6: Cell layers and thickness

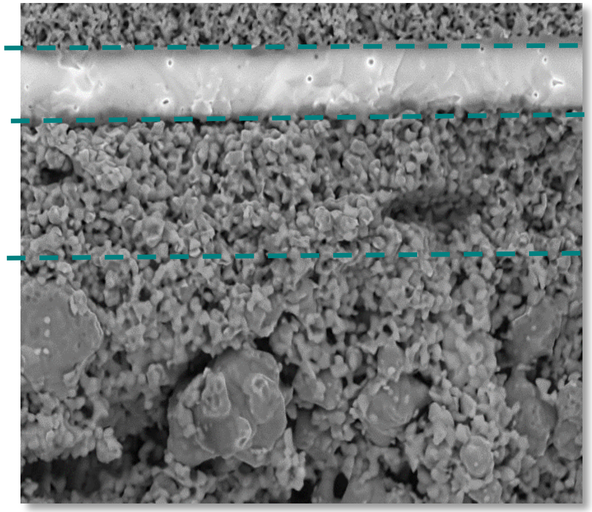

Figure 7: SEM images of the cell layers

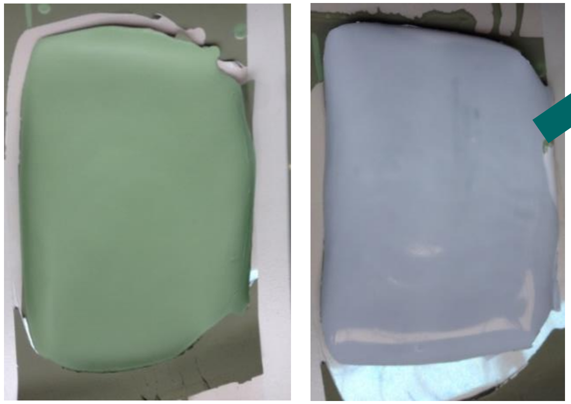

Figure 8a) Dried green tape on Anode substrate and electrolyte side

Fig 8b) Punched green tape

1350/1300°C

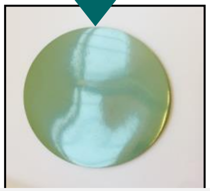

Fig 8c) Sintered half cell

Cell fabrication differences:

- Slurry stage: more plasticiser needed in Ni10ScCeSZ
- Tape casting: thicker electrolyte layer to get 1.0 V OCV
- Different TEC thus different powder pre-calcination temperature
- Different sintering temperature

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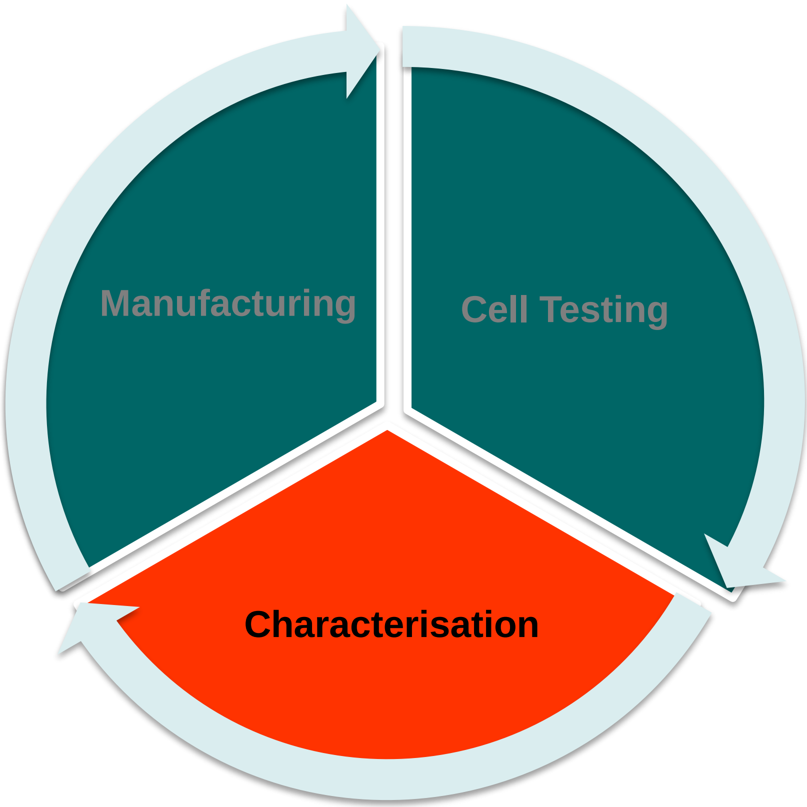

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Electrolyte microstructure comparison

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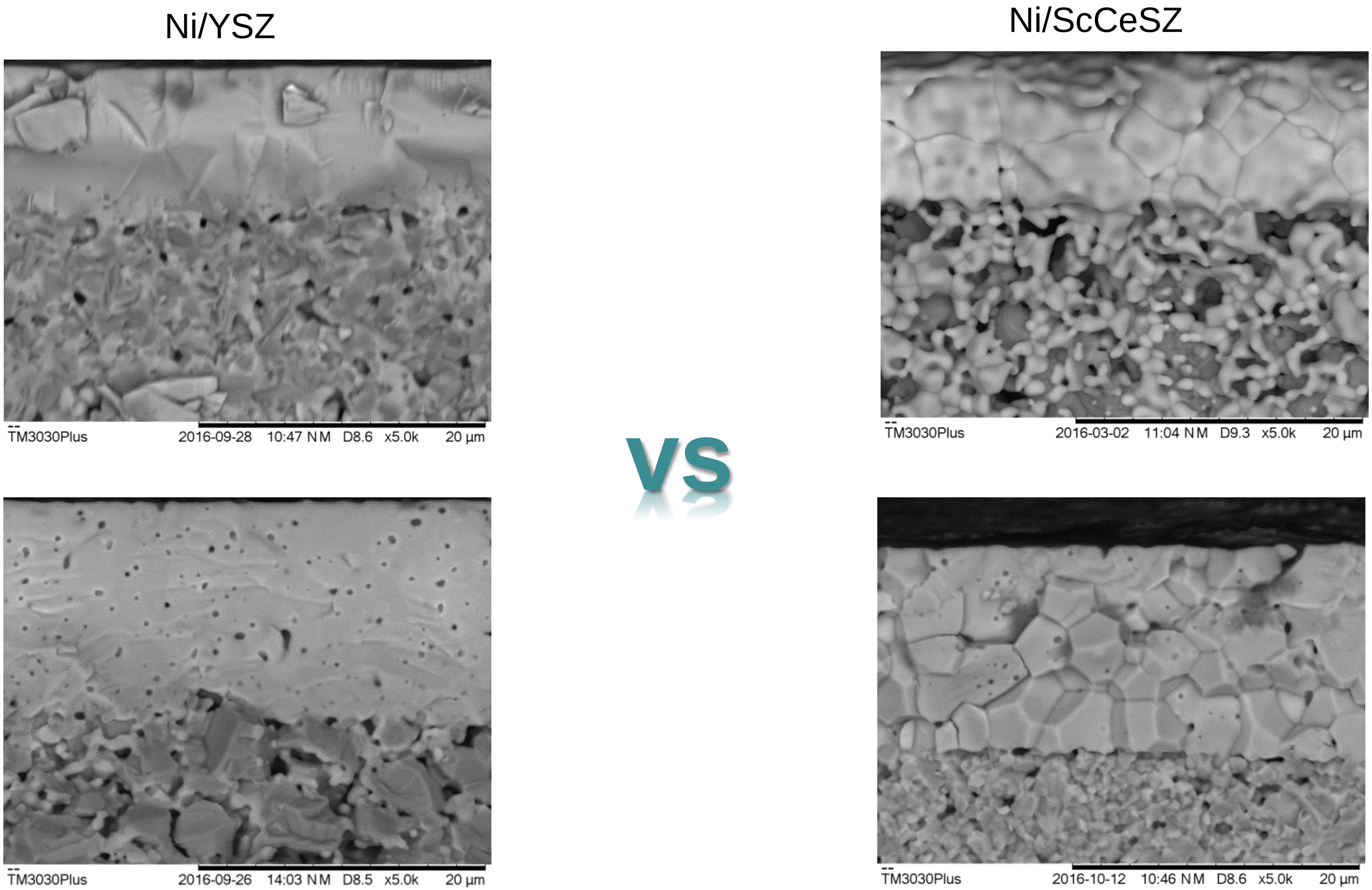

Figure 9: Different structure of electrolyte layers; a) Dense YSZ b) Porous YSZ c)Dense 10ScCeSZ d) Porous 10ScCeSZ

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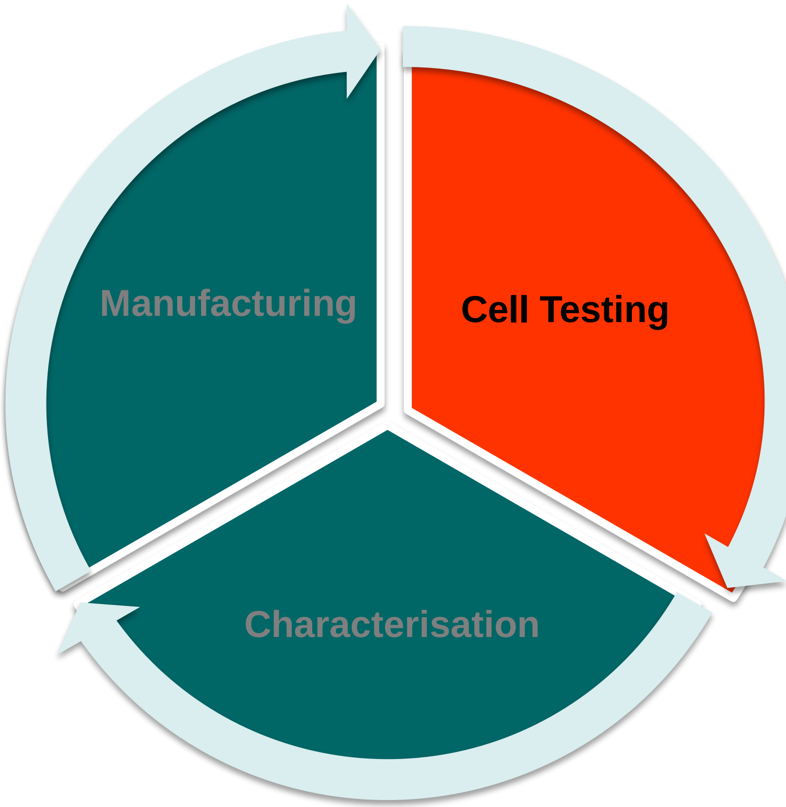

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Cell Test: Ni8YSZ vs Ni10ScCeSZ with High Flowrate of Hydrogen

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- Temp: 800 and 750°C
- 60 mL/min H_2
- Cathode: ambient air

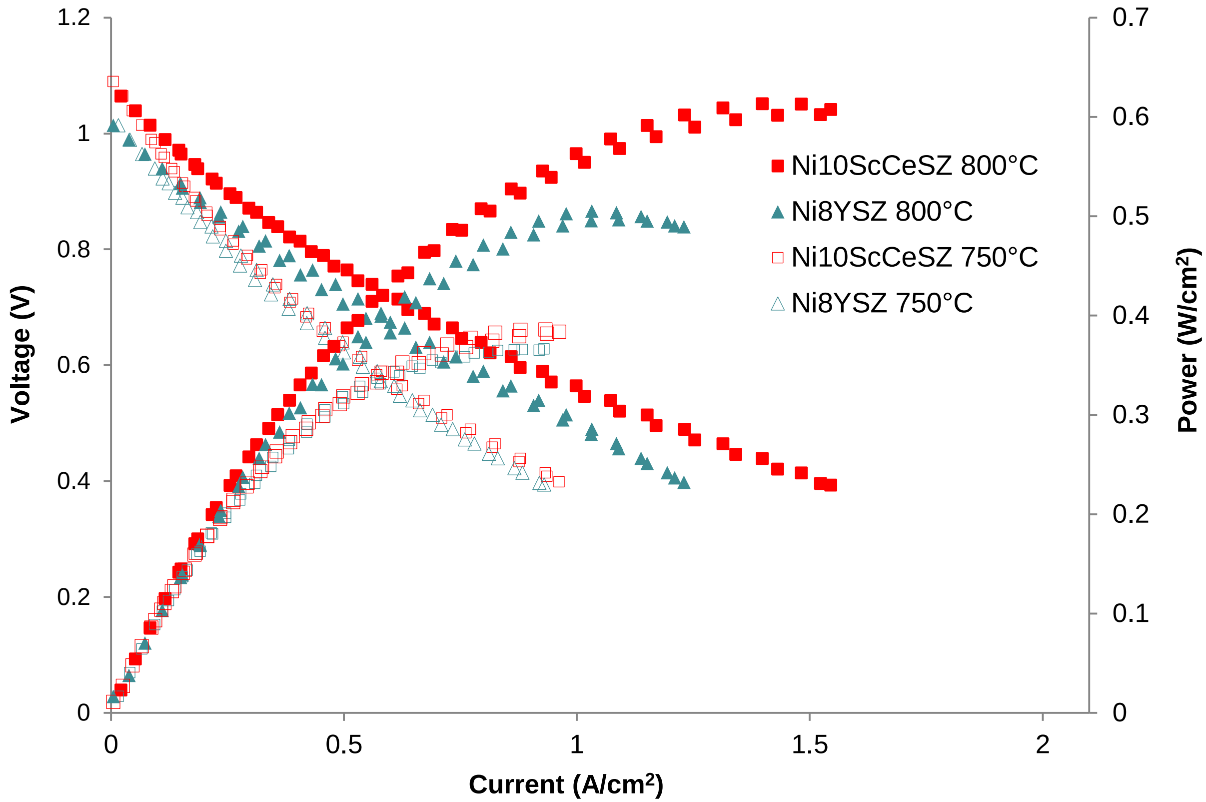

Figure 10: IV curve of the cells at different temperature with high flowrate

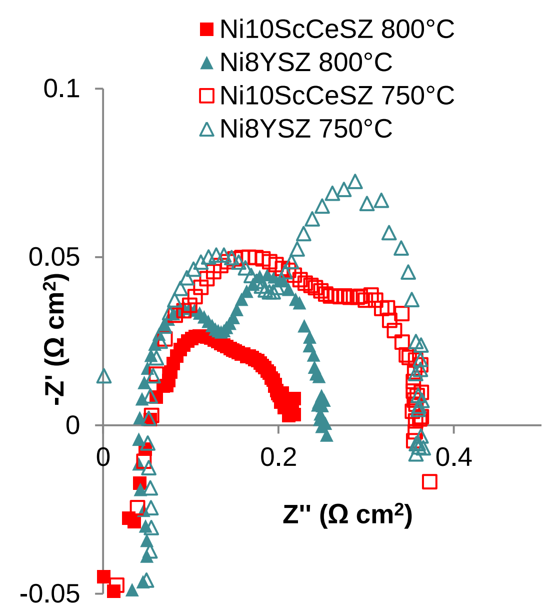

Figure 11: Corresponding impedance at high flowrate

- At 800°C- current produced at 0.7V in Scandia is **20% higher** (0.62 vs 0.50 A/cm²)
- Impedance Analysis
  - ✓ Ohmic resistance in Scandia is similar caused by thicker electrolyte layer
  - ✓ Total polarisation resistance in Scandia is slightly lower

Cell Test: Ni8YSZ vs Ni10ScCeSZ in Hydrogen and Dry Biogas

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- Temp: 750°C
- Total flowrate 28 mL/min
- In H_2: H_2: He 3:1
- In Biogas: CH_4:CO_2: He 2:1:1
- Cathode: ambient air

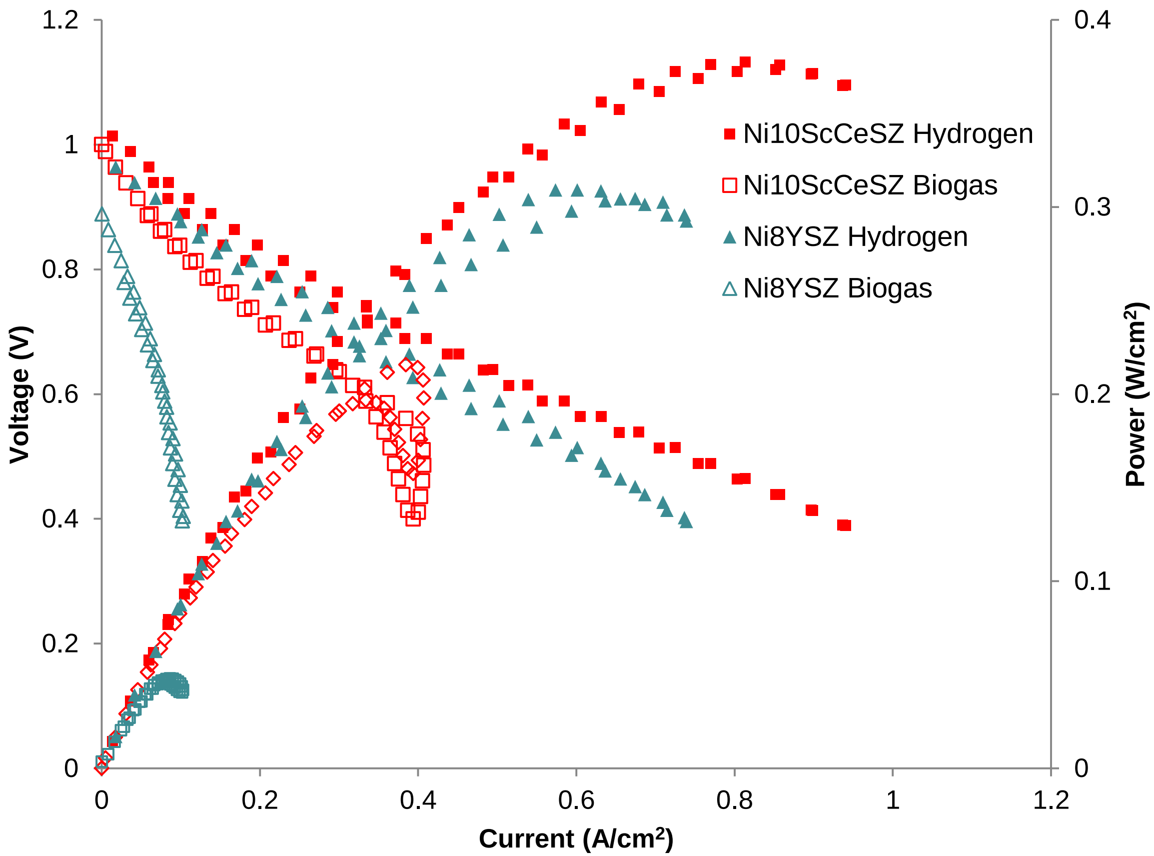

Figure 12: IV curve of the cells tested with Hydrogen and biogas

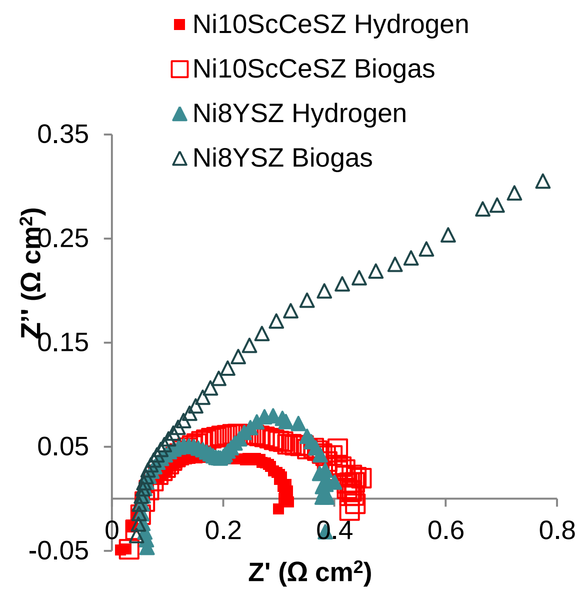

Figure 13: Corresponding impedance of the cells tested with Hydrogen and biogas

- Lower hydrogen flowrate = More significant difference on the performance of NiScCeSZ and Ni8YSZ
- Significant difference using NiYSZ and NiScCeSZ cells in biogas **(~80% vs ~40% reduction)**

Reactions of biogas fuel at anode

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Expected biogas dry reforming :

Dry Reforming: $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$ ----- (1)

Reverse water-gas shift reaction: $CO_2 + H_2 \leftrightharpoons H_2O + CO$ ----- (2)

Possible Carbon deposition:

Methane cracking: $CH_4 \leftrightharpoons C + 2H_2$ ----- (3)

Boudouard reaction: $2CO \leftrightharpoons C + CO_2$ ----- (4)

Reverse syn-gas reaction: $H_2 + CO \leftrightharpoons C + H_2O$ ----- (5)

In Ni/10Sc1CeSZ, additional reaction at the anode sides are:

$Ce_2O_3 + CO_2 \leftrightharpoons 2CeO_2 + CO$ ----- (6)

$2CeO_2 + C \leftrightharpoons Ce_2O_3 + CO$ ----- (7)

with reference Troskialina L, Improved Performance of Solid Oxide Fuel Cells Operating om Biogas using Tin-Anode-infiltration, PhD Thesis. University of Birmingham, 2016 and C. J. Laycock, et al, Biogas as a fuel for solid oxide fuel cells and synthesis gas production: effects of ceria-doping and hydrogen sulfide on the performance of nickel-based anode materials, *Dalton Transactions*, **40, 5494 (2011).

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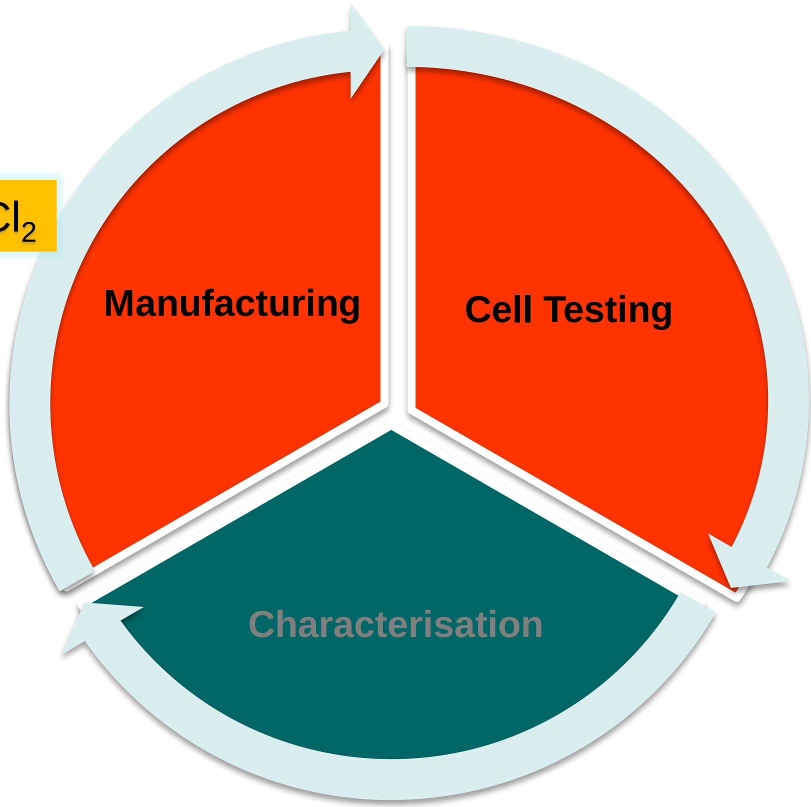
+$SnCl_2$



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Performance Test: Sn-doped NiScCeSZ in Hydrogen and Biogas

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- Temp: 750°C
- Total flowrate 28 mL/min
- In H_2: H_2: He 3:1
- In Biogas: CH_4:CO_2: He 2:1:1
- Cathode: ambient air

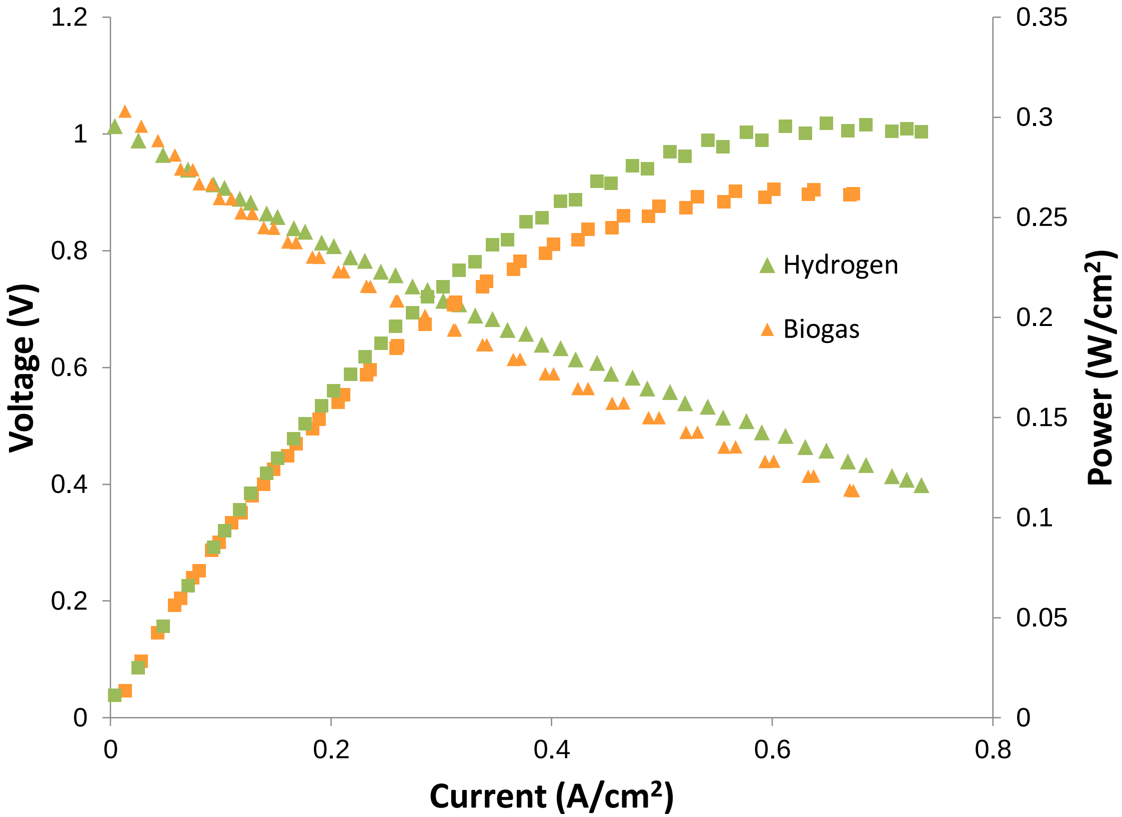

Figure 14: IV curve of the Tin-doped Ni10ScCeSZ celss at different temperature with high flowrate

- Significant improvement (from **40% to 10% reduction**) with Sn-doped
- Sn expected to form alloy with the Nickel

Conclusion

- Water based tape casting shown successfully produce good cells
- Better performance using NiScCeSZ cell in both hydrogen and biogas
- Lower polarisation resistance in Ni10ScCeSZ.
- Strengthen the argument that Sn as dopant can improve SOFC cell with biogas
- SOFC with biogas as fuel can be utilised and bring down the cost of using hydrogen

Further work

- Higher magnification SEM analysis to look at carbon formed
- Temperature Program Oxidation coupled with Mass Spec to quantify the amount of carbon deposited

Acknowledgement

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Supervisors:

Prof Tim Button
Prof Robert Steinberger-Wilckens

Colleagues (and ex-colleagues):

Dr Lina Troskialina, Dr Jong-Eun Hong and all my colleagues in Fuel Cell and Hydrogen Research Centre, University of Birmingham

Sponsors:

Malaysian Government - People's Trust Council (MARA)

Human Life Advancement Foundation (HLAF)

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Thank you!
Any Questions?

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