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Nano-composite Nickel Yttria-Stabilised Zirconia Anode

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Outline

- Benefits and Challenges of integration of nanoparticles into SOFC electrode
- Properties of the Composite Nanopowder
- Electrode Fabrication
- Microstructure
- Electrochemical Performance
- Degradation Test

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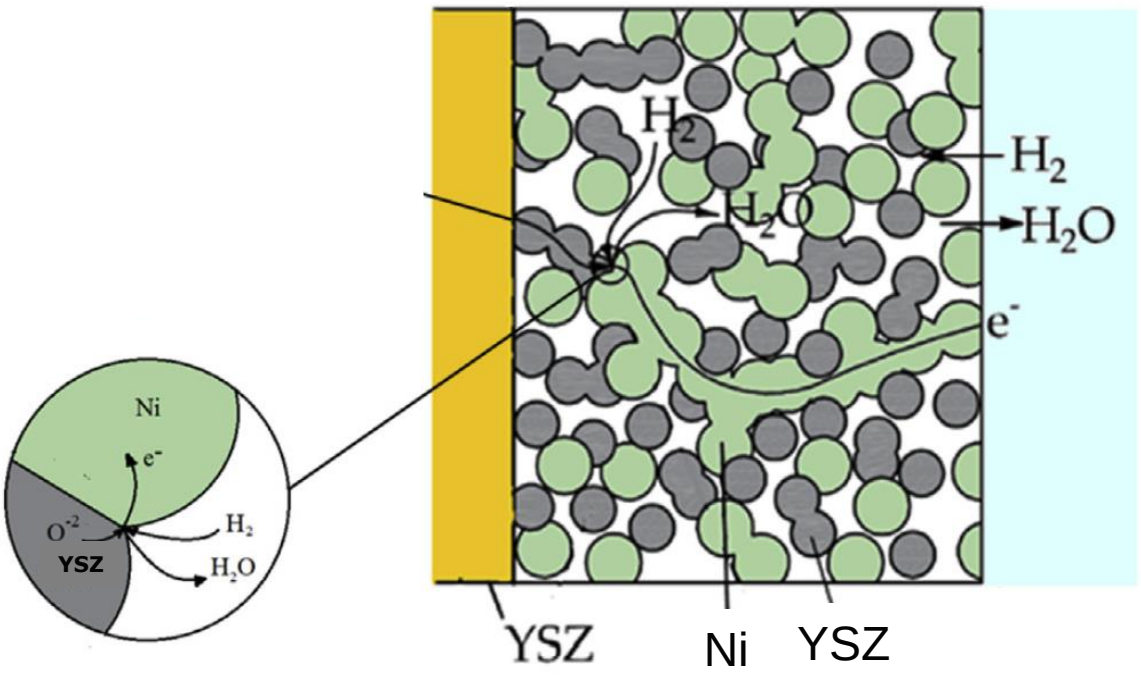
Reactions at the SOFC Anode



Nickel:
Electron Conductor
YSZ:
Oxygen Ion Conductor
Pore:
Gaseous Transfer

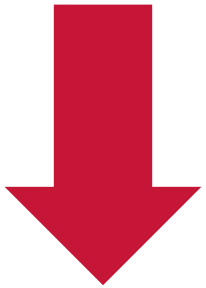
- **TPB Density**
- **Gas Diffusion**

Schematics modified from *Bertei, A. et al. Validation of a physically-based solid oxide fuel cell anode model combining 3D tomography and impedance spectroscopy. Int. J. Hydrogen Energy* ***41,*** *22381–22393 (2016).*

Integrating nano-size features in the electrode

Benefits of nano-structured electrode

- High Catalytic Activity
- Enhance TPBs for anodic reactions



Enhance Electrochemical Performance

Integrating nano-size features in the electrode

Challenges:

- **Processability**
(high surface energy)

- **Lifetime**
(nickel coarsening)

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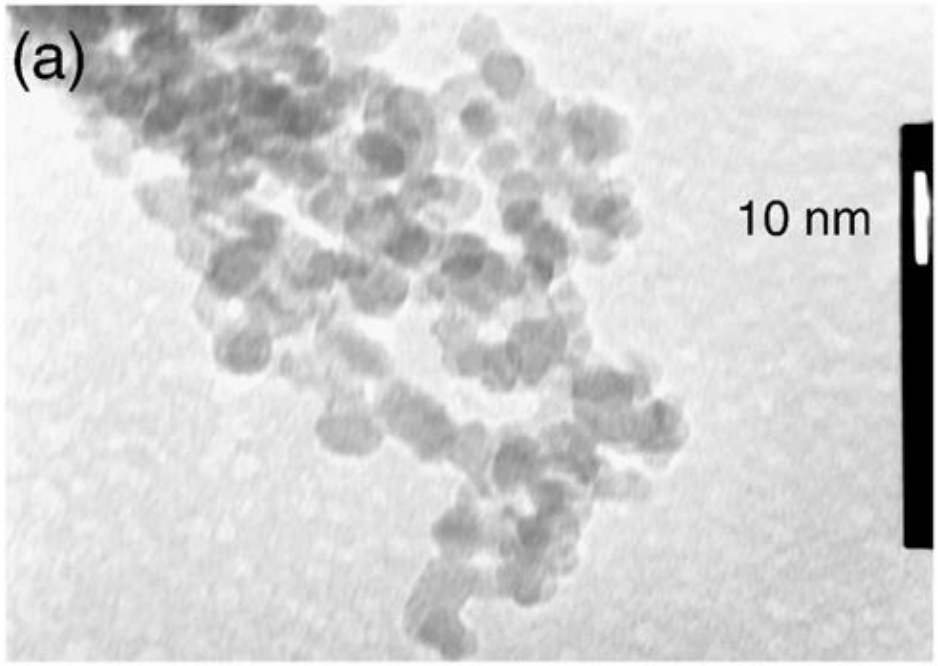
Nanopowder made in hydrothermal flow system

*Weng, X. et al. Highly conductive low nickel content nano-composite dense cermets from nano-powders made via a continuous hydrothermal synthesis route. Solid State Ionics **181,** 827–834 (2010)*



TEM image of the YSZ powder in the system (average particle size 5.0 ± 0.8 nm)

NiO-YSZ co-precipitates:

Nickel nitrate hexahydrate, yttria nitrate hexahydrate and zirconyl nitrate hexahydrate were dissolved in de-ionised water and mixed with KOH in the pumped flow, and then brought to a superheated water feed.

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Fabrication Route of the Electrode

50 wt% NiO and 50 wt% YSZ nanopowder slurry

Freeze-dried

- Laser Scattering
- BET

Calcined at 700 ^{o}C for 30 min

Milled for 30 hr at 300 rpm

- Laser Scattering
- BET

Symmetrical Cell on YSZ electrolyte

- X-ray Diffraction
- Electrochemical impedance
- FIB-SEM

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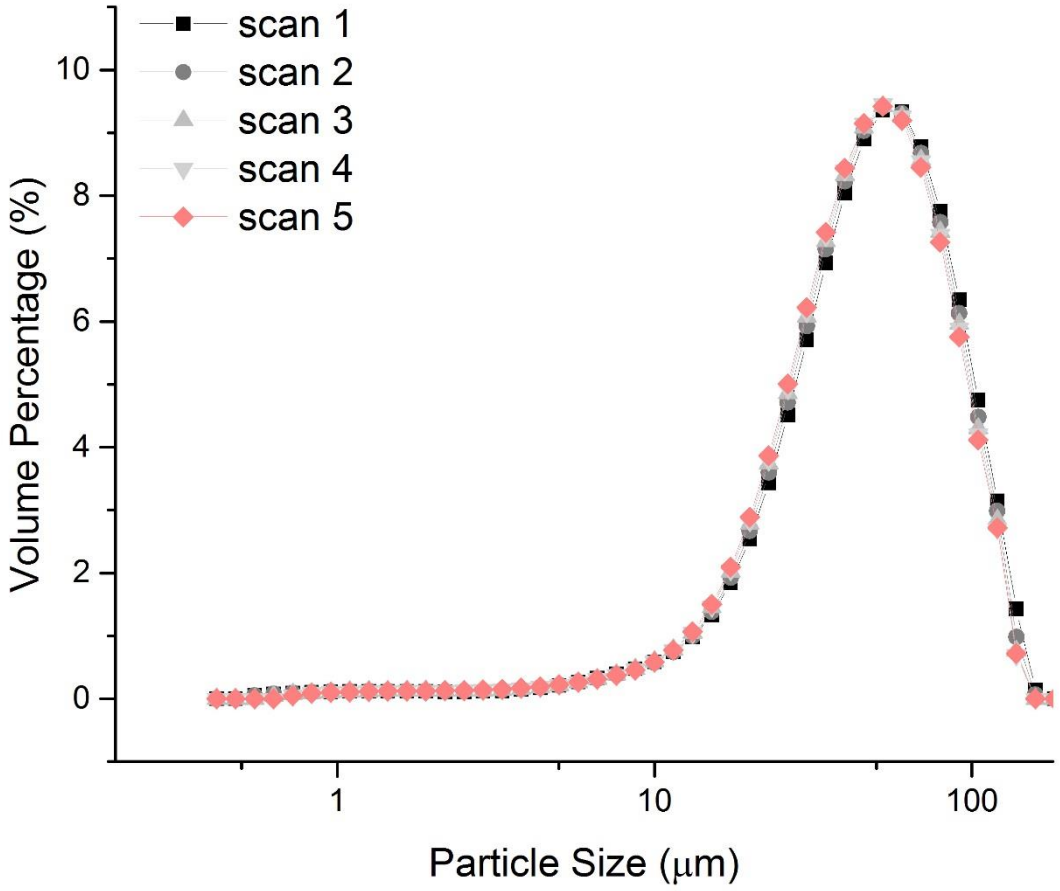
Particle size of the loose agglomerates

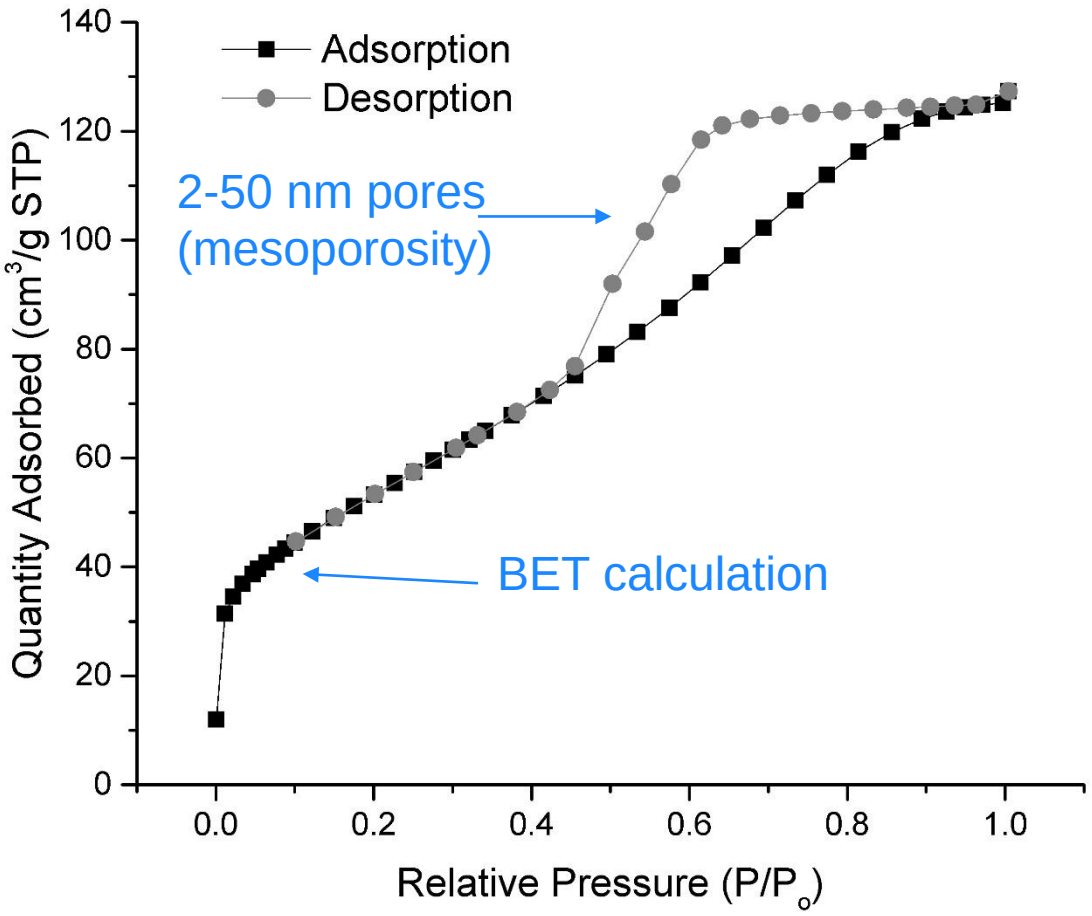


After the slurry was freeze-dried, the nanopowder formed soft agglomerate

D[4,3] Volume averaged mean:

50 μm

BET Surface Area



BET surface area:
189 ± 1 m²/g

50 wt% NiO and 50 wt% YSZ nanopowder slurry

Freeze-dried

- Laser Scattering
- BET

Calcined at 700 ^{o}C for 30 min

Milled for 30 hr at 300 rpm

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Symmetrical Cell on YSZ electrolyte

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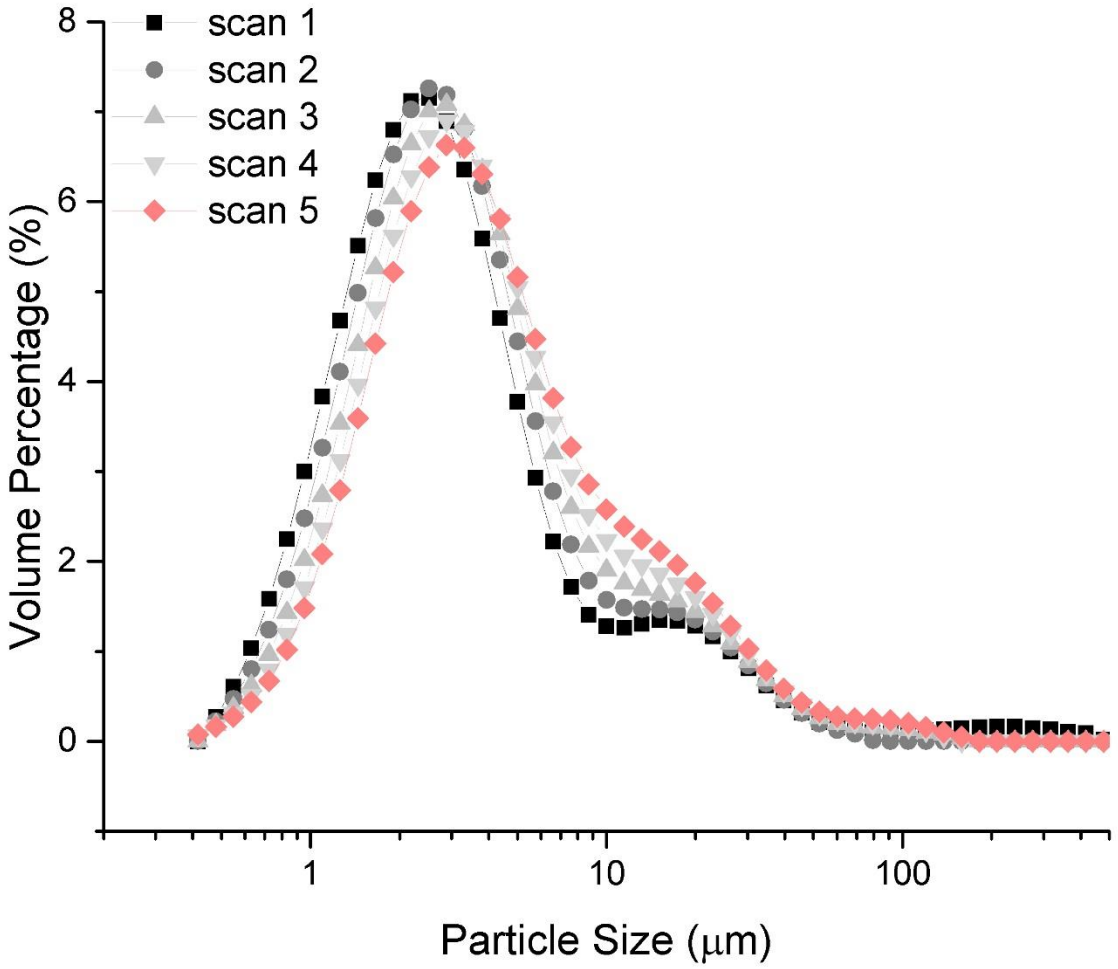
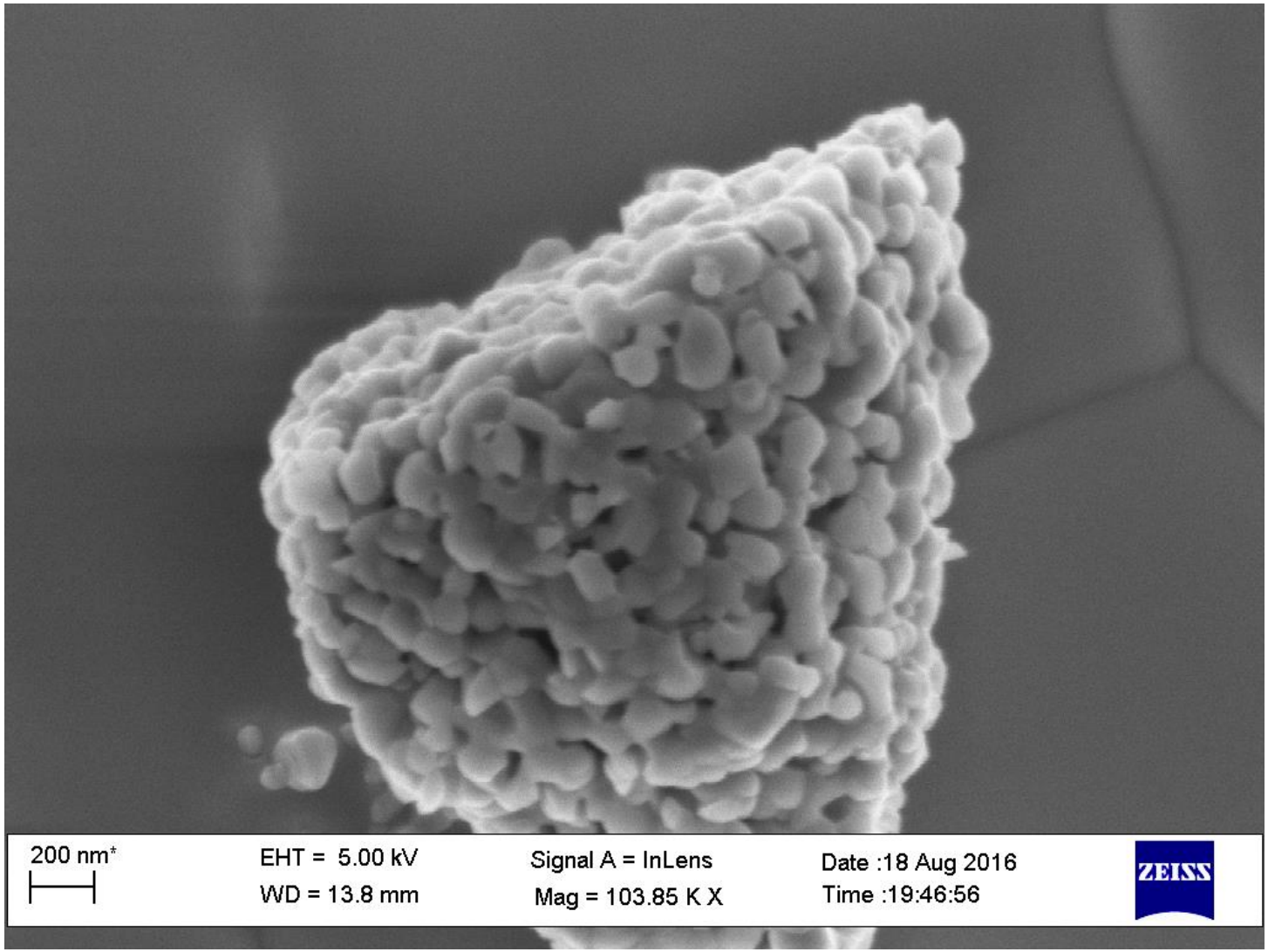


After calcination and ball-milling

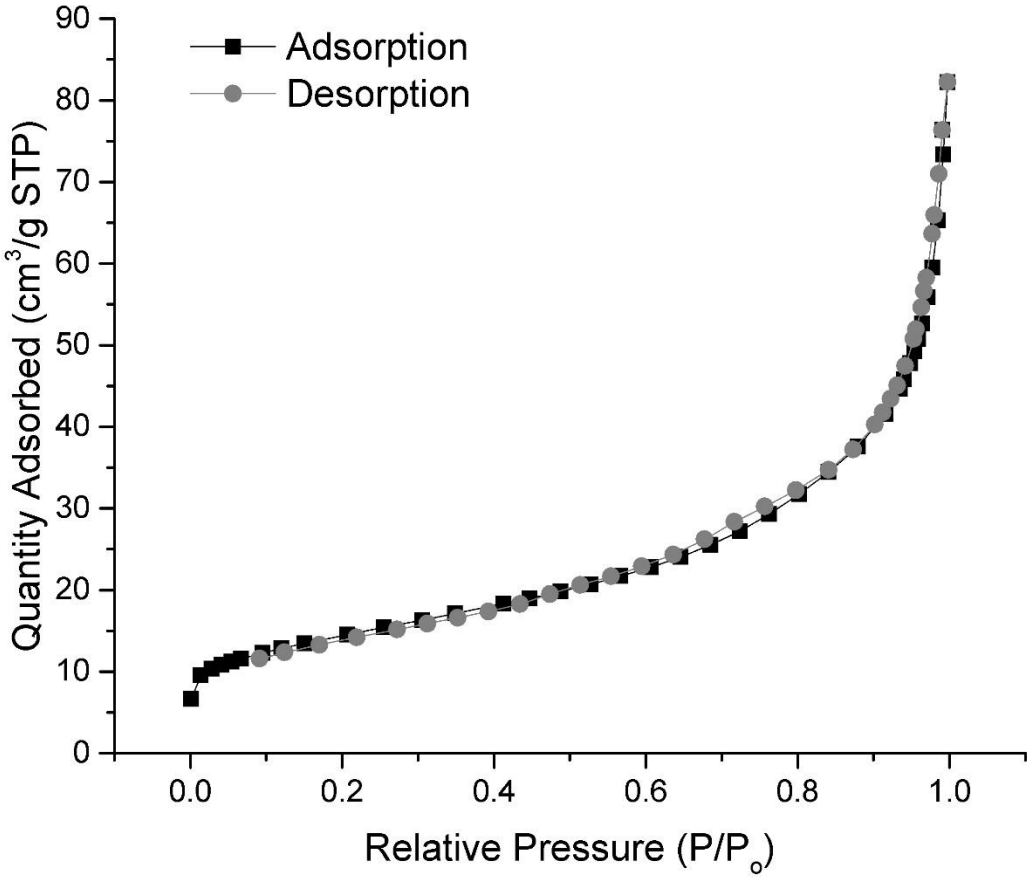
D[4,3] Volume averaged mean:

7 μm

Soft Agglomerate of NiO-YSZ nanoparticles



BET Surface Area



BET surface area:
51.3 ± 0.2 m²/g

Surface Area of Micropores (≤ 2 nm)
22.7 m²/g

External Surface Area:
28.6 m²/g

50 wt% NiO and 50 wt% YSZ nanopowder slurry

Freeze-dried

- Laser Scattering
- BET

Calcined at 700 ^{o}C for 30 min

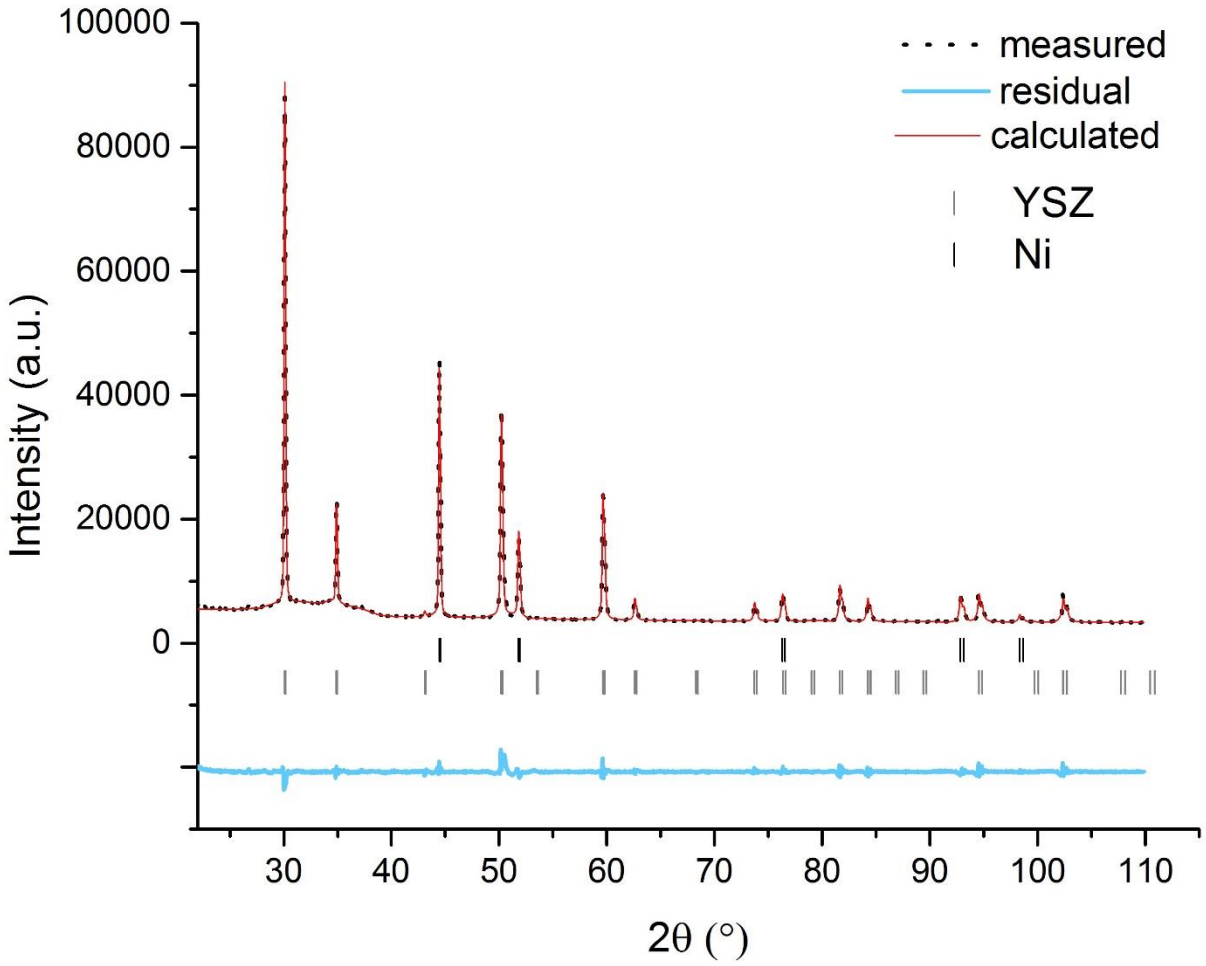
Milled for 30 hr at 300 rpm

- Laser Scattering
- BET

Symmetrical Cell on YSZ electrolyte

- X-ray Diffraction
- Electrochemical impedance
- FIB-SEM

XRD on the Ni-YSZ electrode

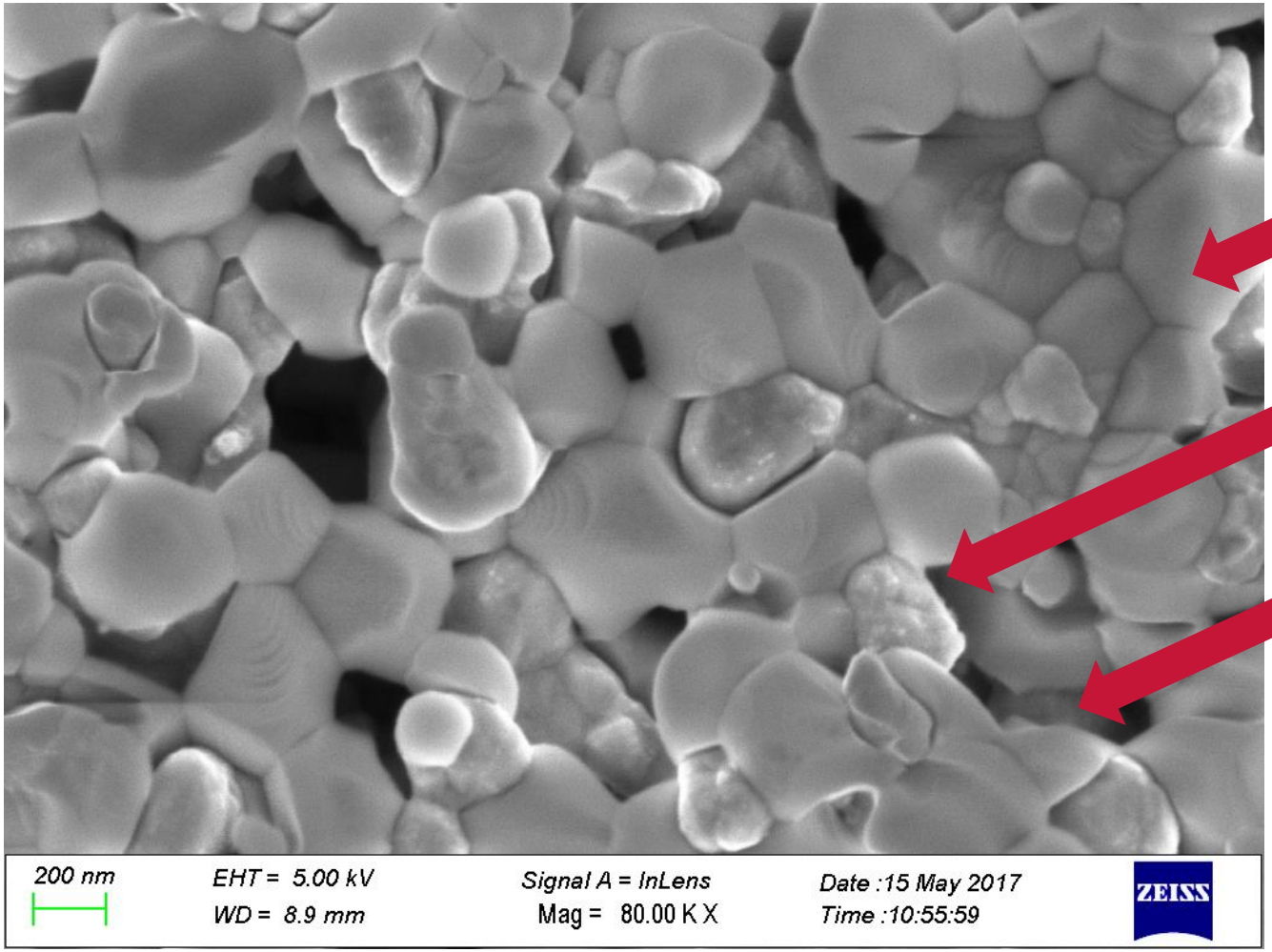


Quantitative Analysis via Rietveld Refinement

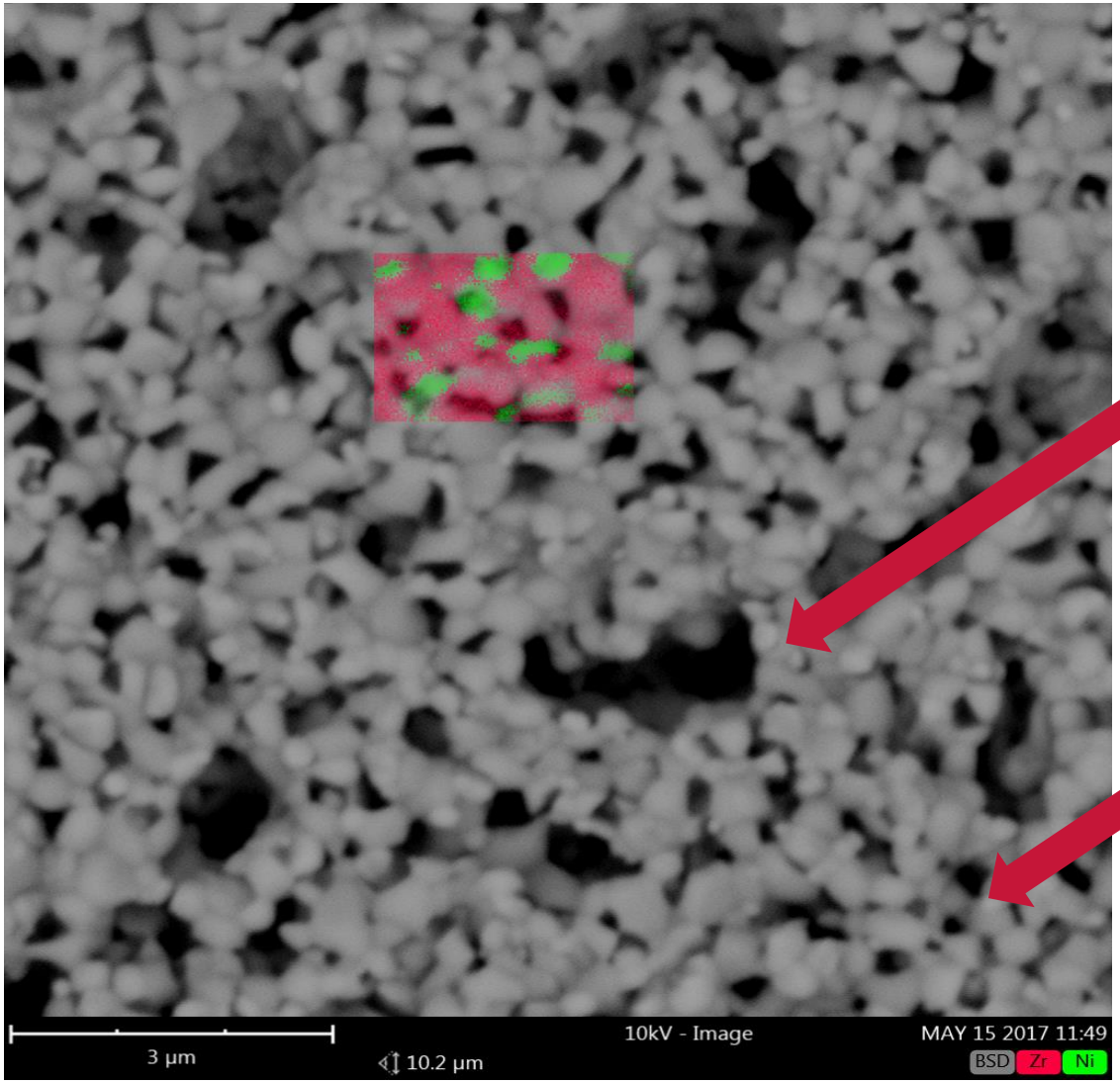
Nickel
41 wt%

YSZ
59 wt%

Microstructure – SEM image



Microstructure – EDX mapping



Ni

Zr

Large Pores
(1-3 µm)

Small Pores
(100-500 nm)

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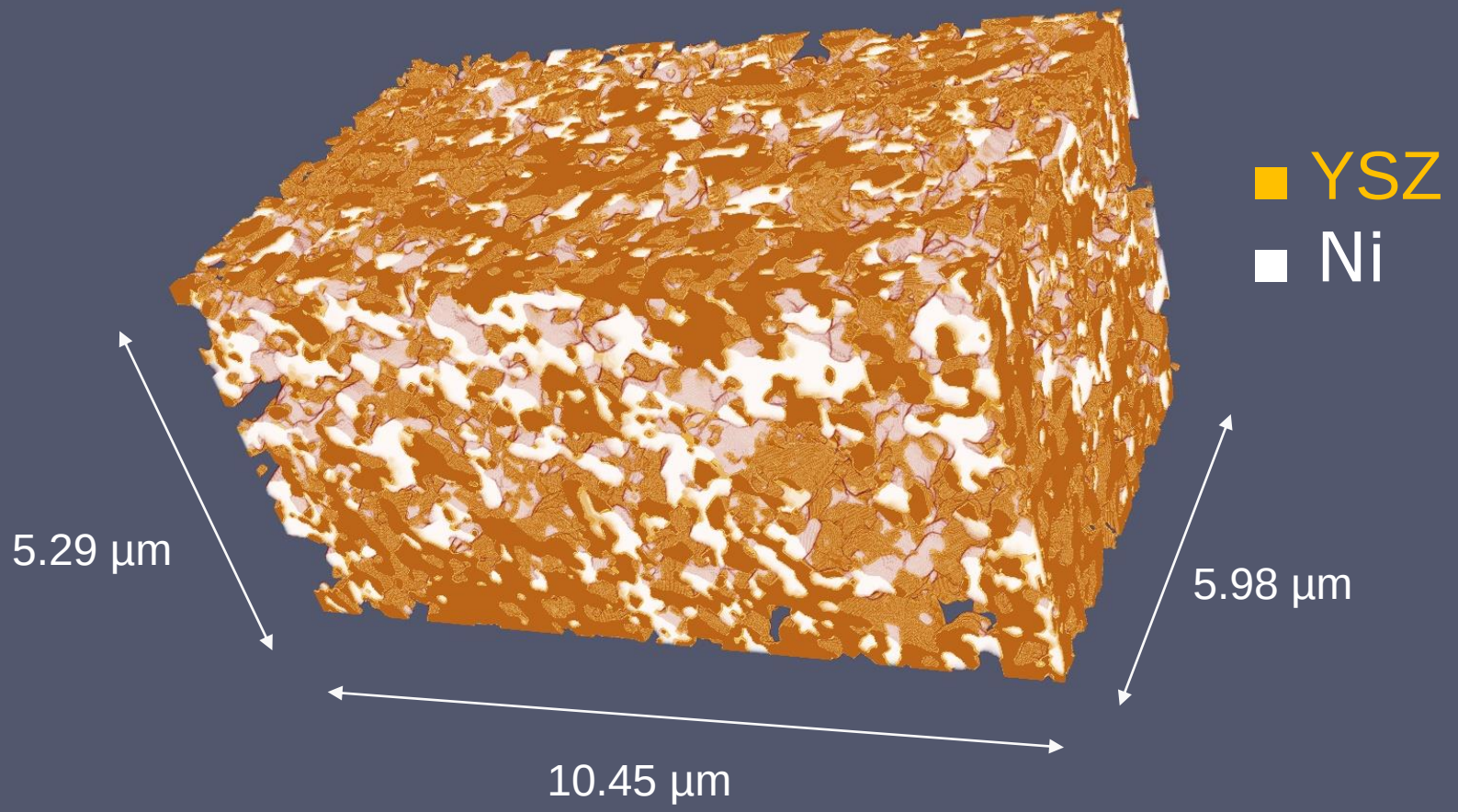
Microstructure – FIB-SEM 3D Reconstruction



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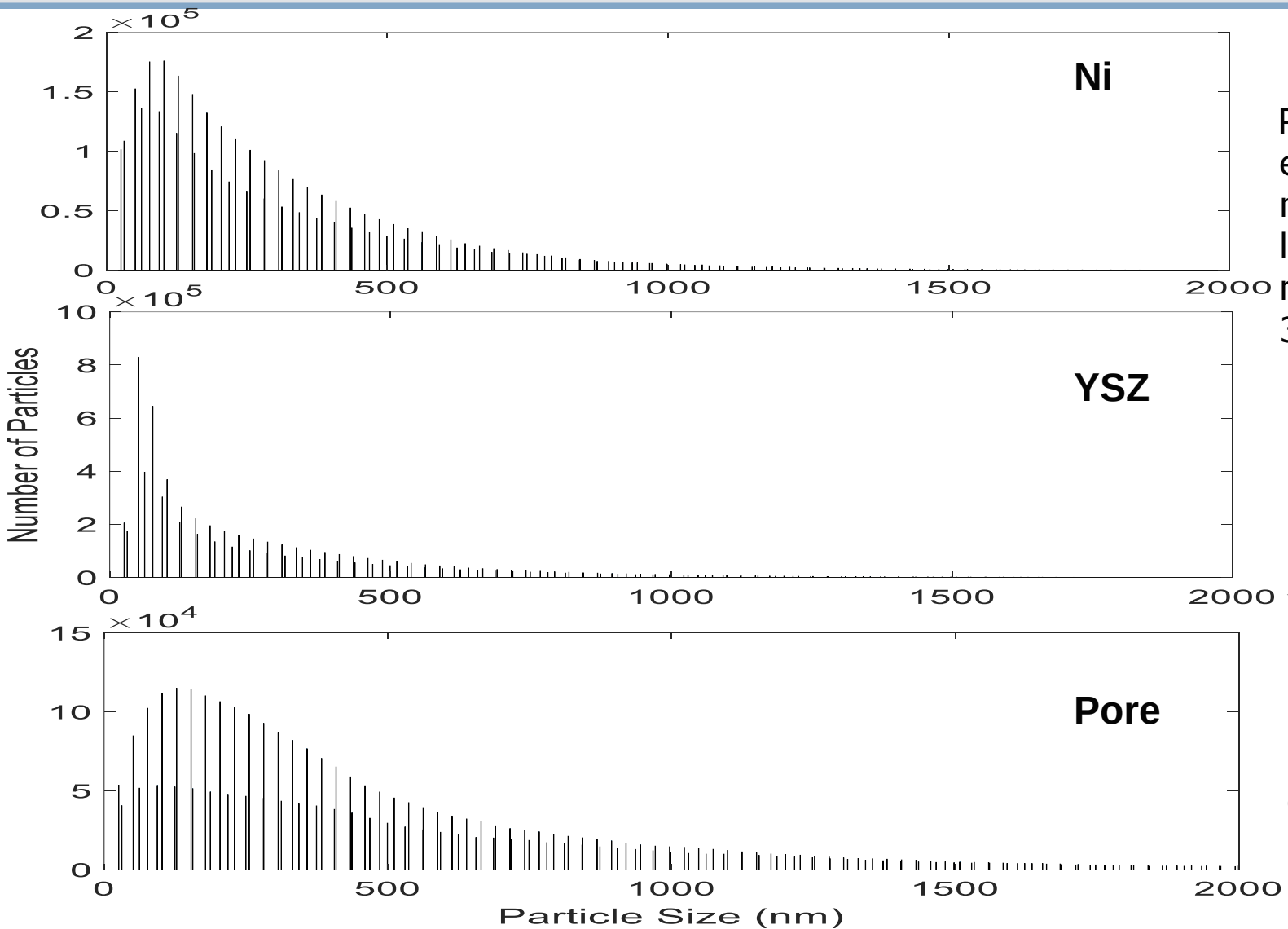
Microstructure



Particle size of each phase measured by line intercept method in the 3D image stack

Ni:
Peak at 30 nm
YSZ:
Peak at 30 nm
Pore:
Peak at 100 nm and 800 nm

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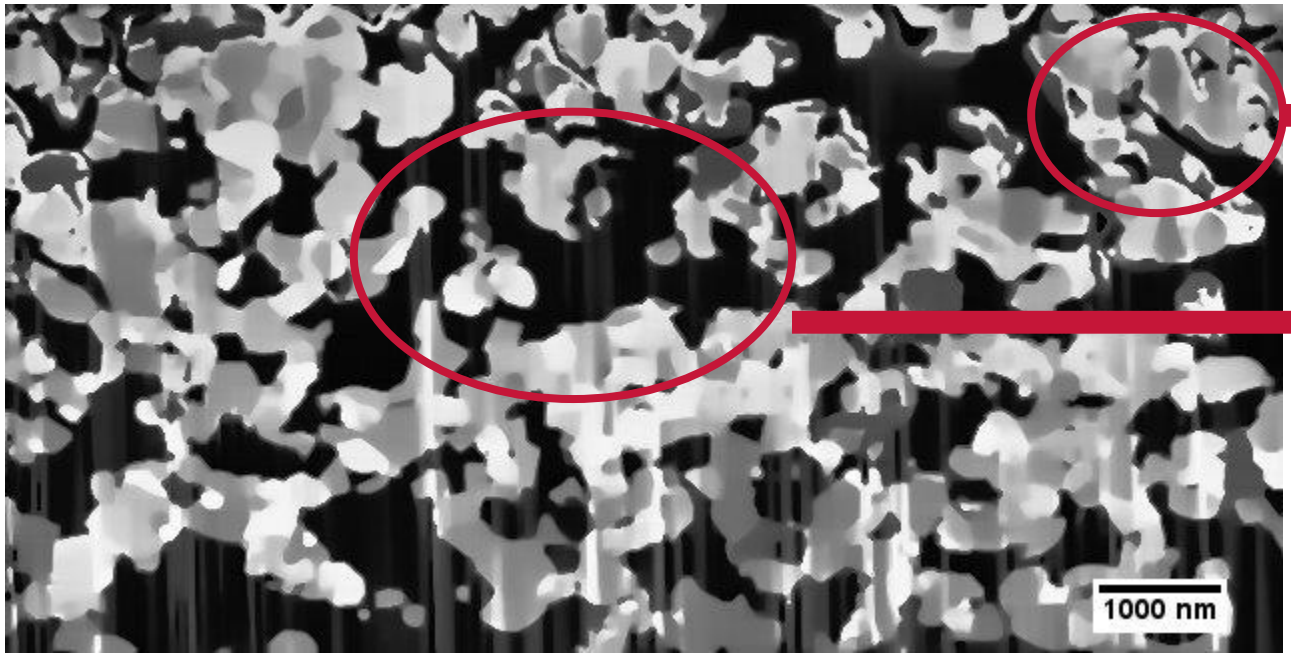
Microstructure – Dual Porosity Structure



Small particles and pores to enhance TPB density

Large pores to facilitate diffusion of gas

■ Pore ■ YSZ ■ Ni

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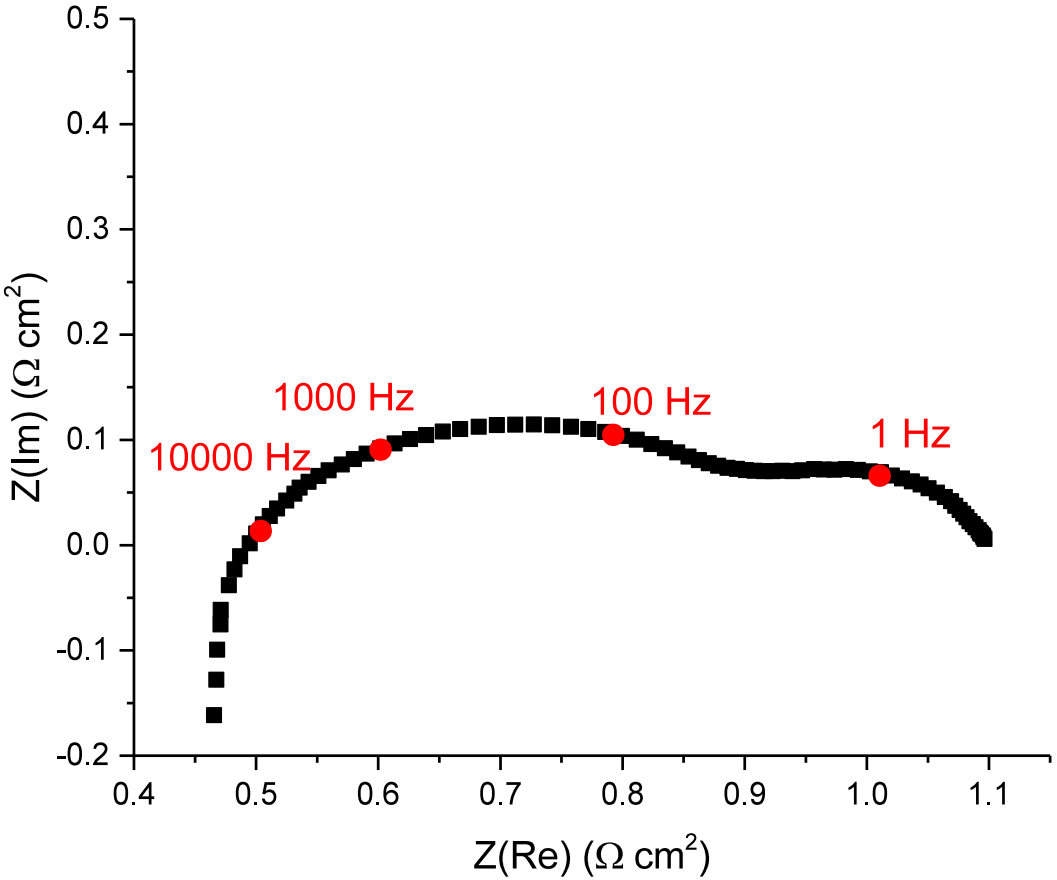
Electrochemical Performance

Electrochemical impedance spectra measured at 800 °C in 5% wet hydrogen



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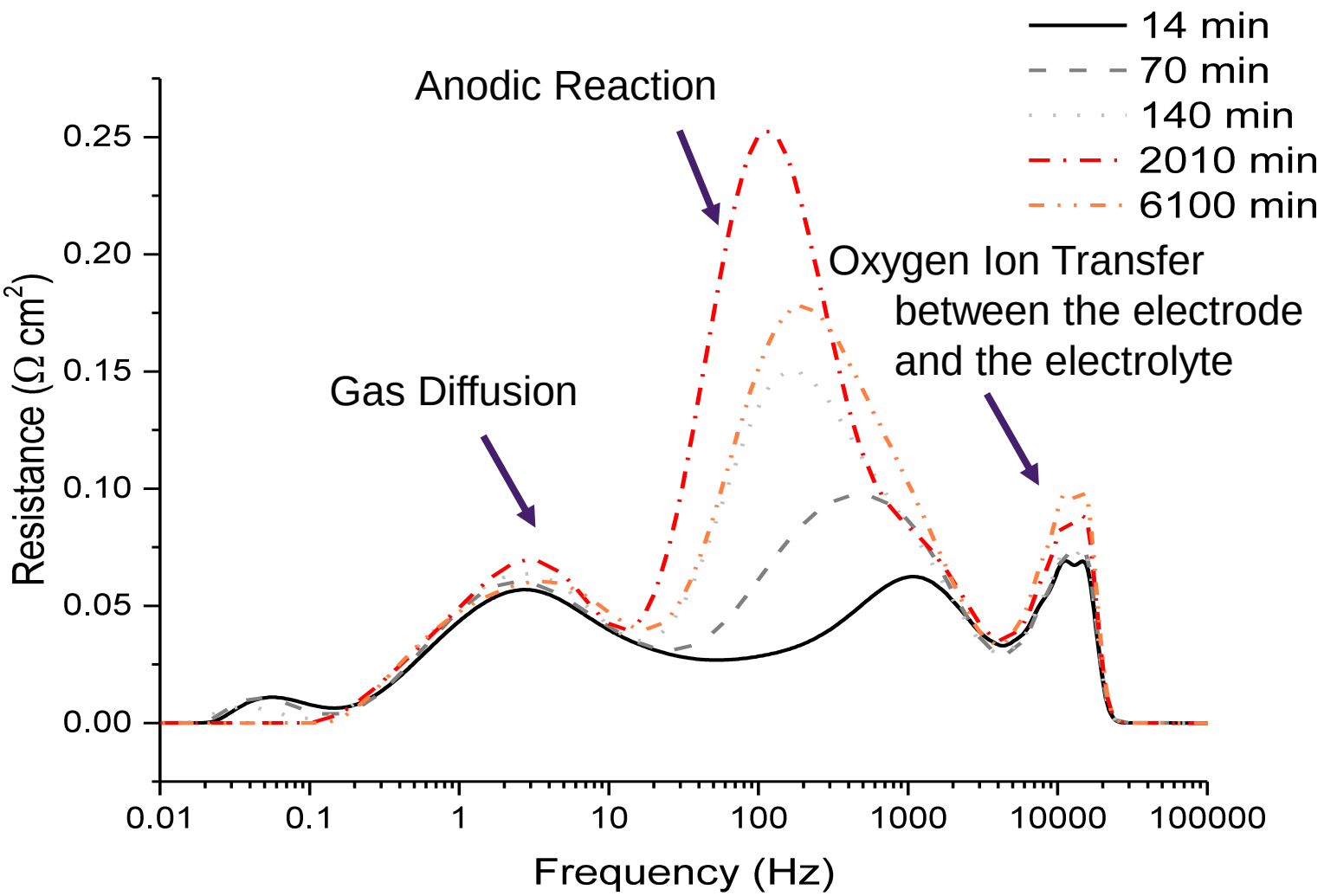
Electrochemical Performance

Distributions of Relaxation Time at 800 °C in 5% wet hydrogen



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Electrochemical Performance

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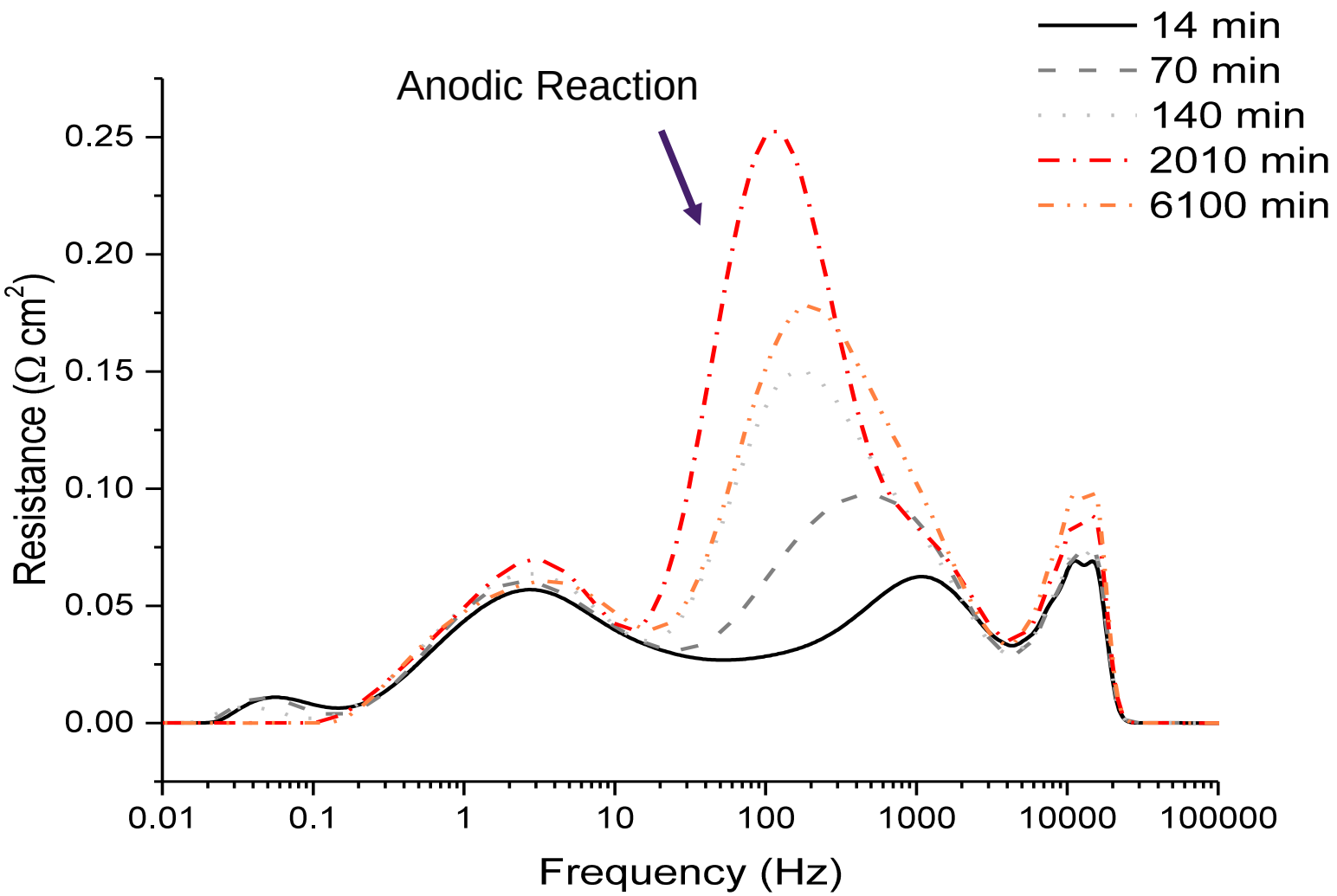

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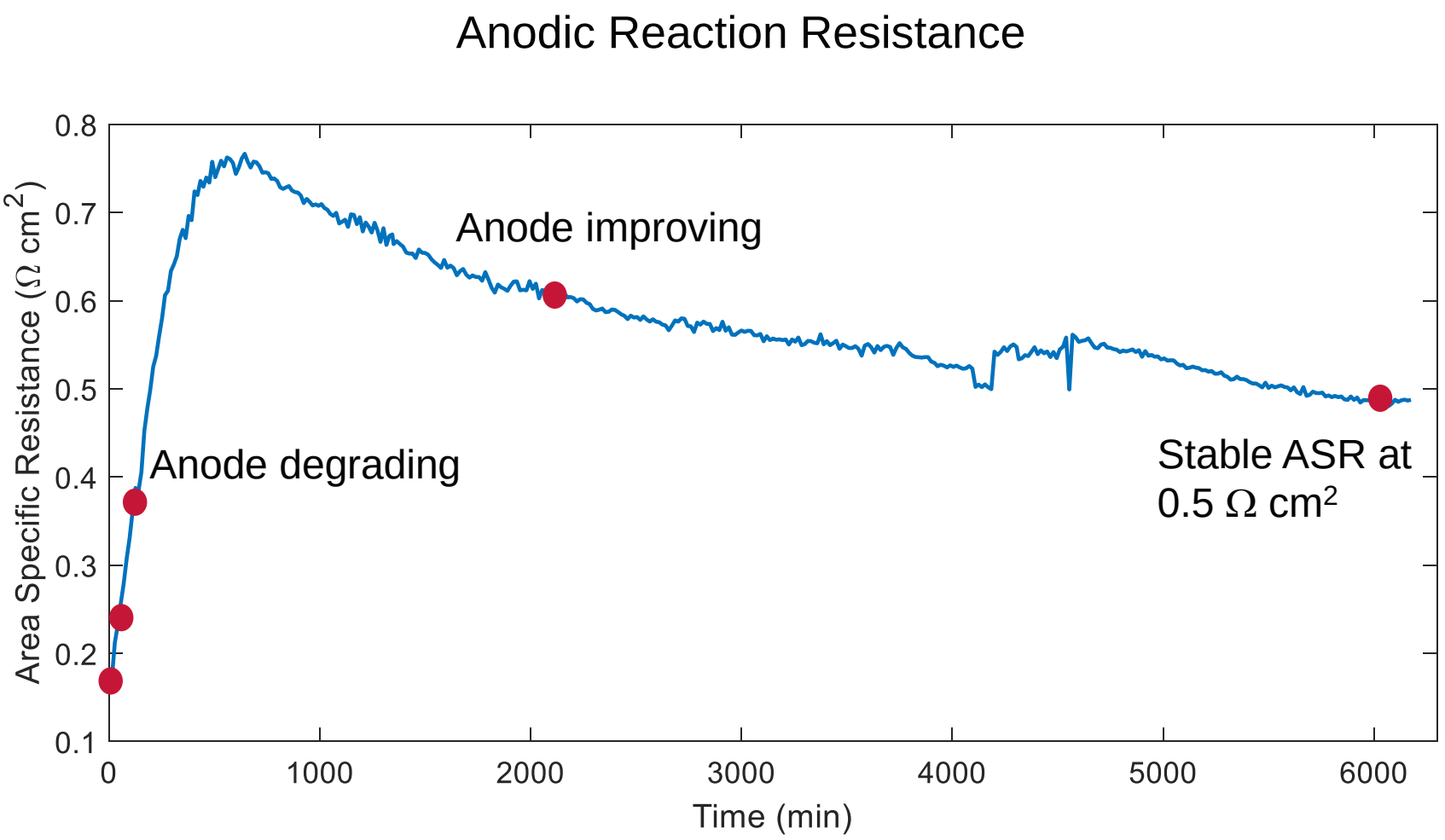
Degradation Test



Conclusion

- Fabrication of SOFC fuel electrode using nanopowder made by continuous hydrothermal flow synthesis is achievable.
- Electrode shows fine nanocomposite microstructures for both the nickel and the YSZ phases.
- Electrode shows porosity on two length-scales,100 nm and 1 µm.
- Nano-composite electrode shows promising electrochemical performance
- Electrode stability is encouraging but needs further investigation

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Acknowledgement

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国家留学基金管理委员会 CHINA SCHOLARSHIP COUNCIL

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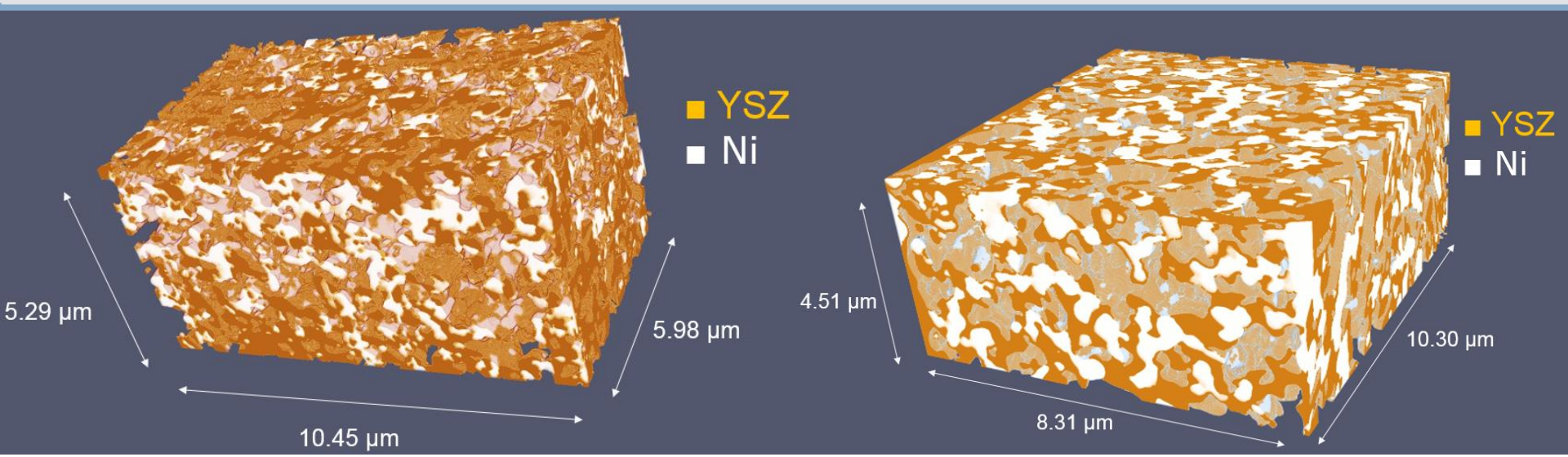
Post-Mortem Analysis



Aging Time	60 min	6000 min
Percolated TPB density (μm^{-2})	11.1	10.0
tortuosity of Pore	3.03	3.81
tortuosity of Ni	5.54	8.98
tortuosity of YSZ	4.34	2.44

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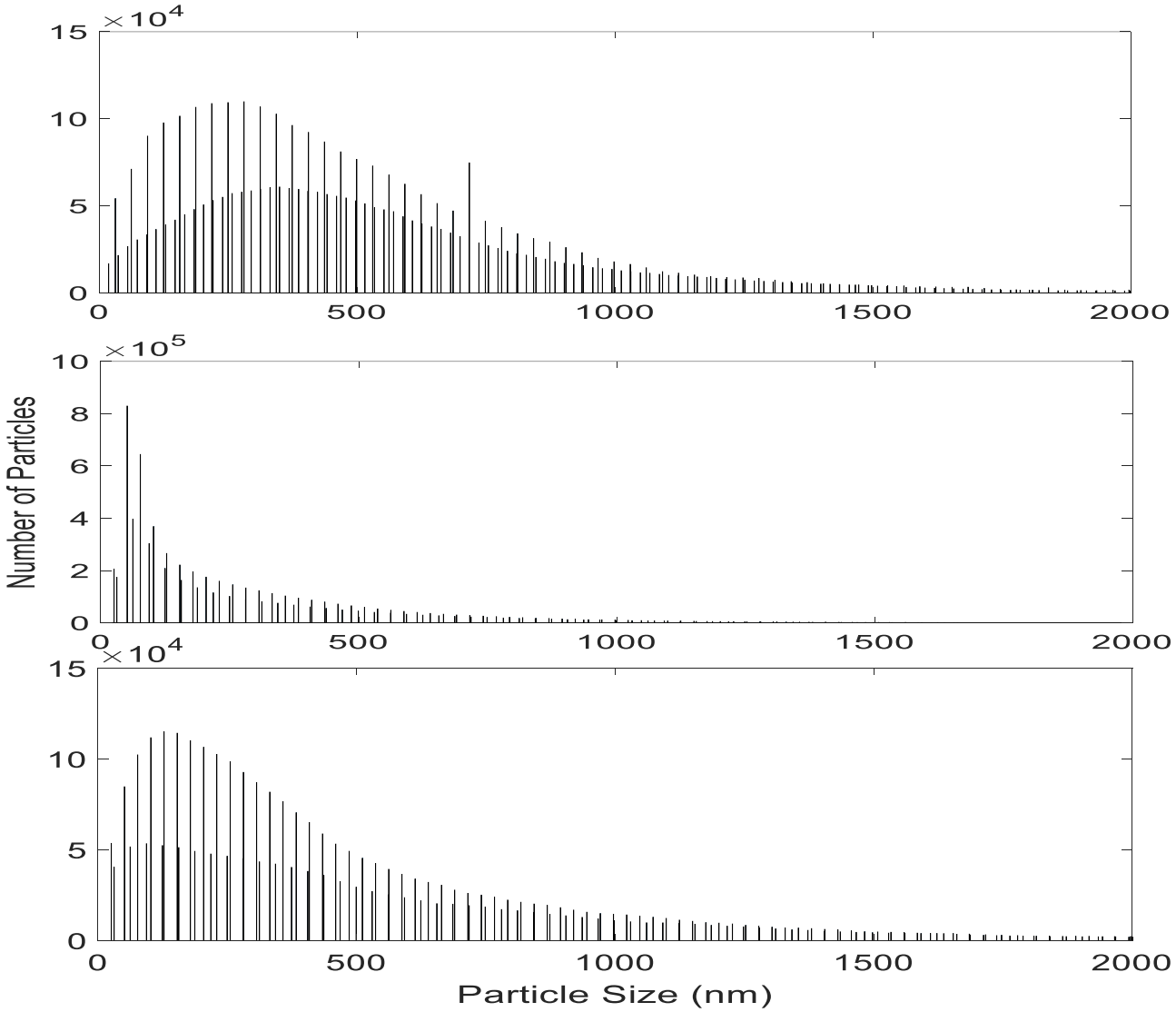
Post-Mortem Analysis –Particle Size Distribution



Ni :
250 nm

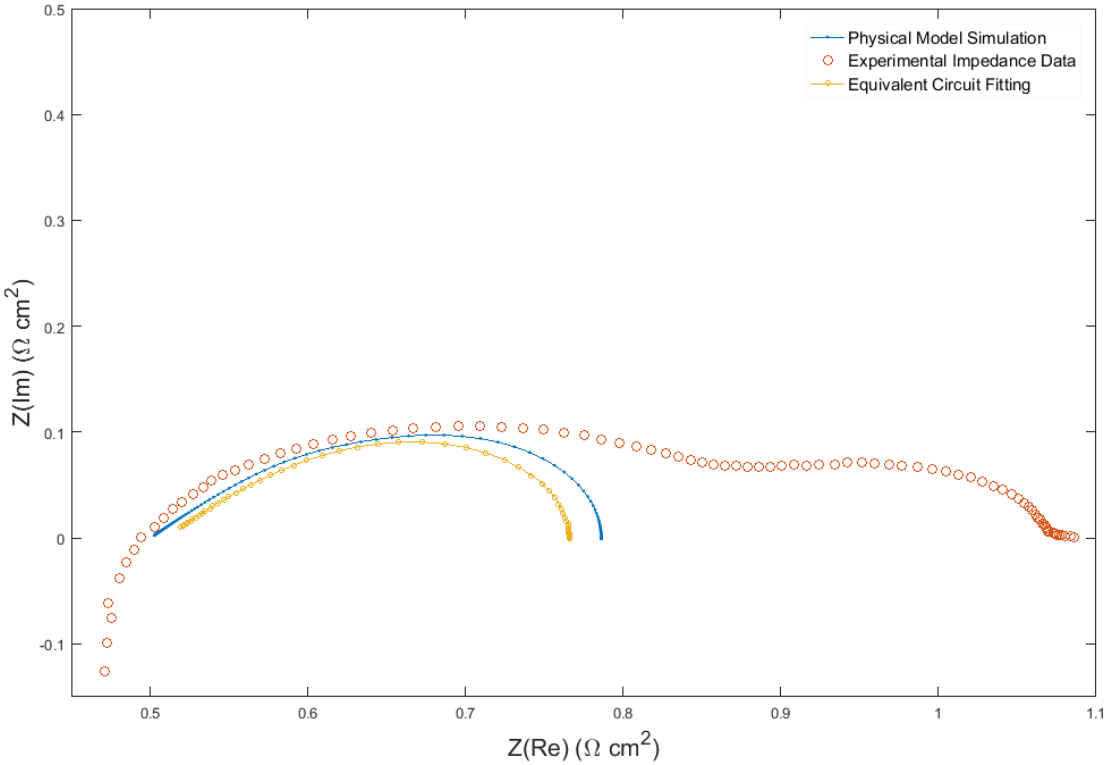
YSZ :
100 nm

Pore:
200 nm and 1000 nm

Transmission Line Model

$$Z = L(\rho_1 + \rho_2)\frac{\cosh(\Gamma)+\Omega[2+\Gamma\sinh(\Gamma)-2\cosh(\Gamma)]}{\Gamma\sinh(\Gamma)}$$

$$\Omega = \frac{\rho_1\rho_2}{(\rho_1+\rho_2)^2} \qquad \Gamma = \sqrt{i_0^{\nu} f L^2(\rho_1+\rho_2) + j\omega c^{\nu} L^2(\rho_1+\rho_2)}$$



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Post-mortem Analysis – FIB-SEM 3D Reconstruction