Infiltration of SOFC Anodes for Improved Performance at High Fuel Utilization

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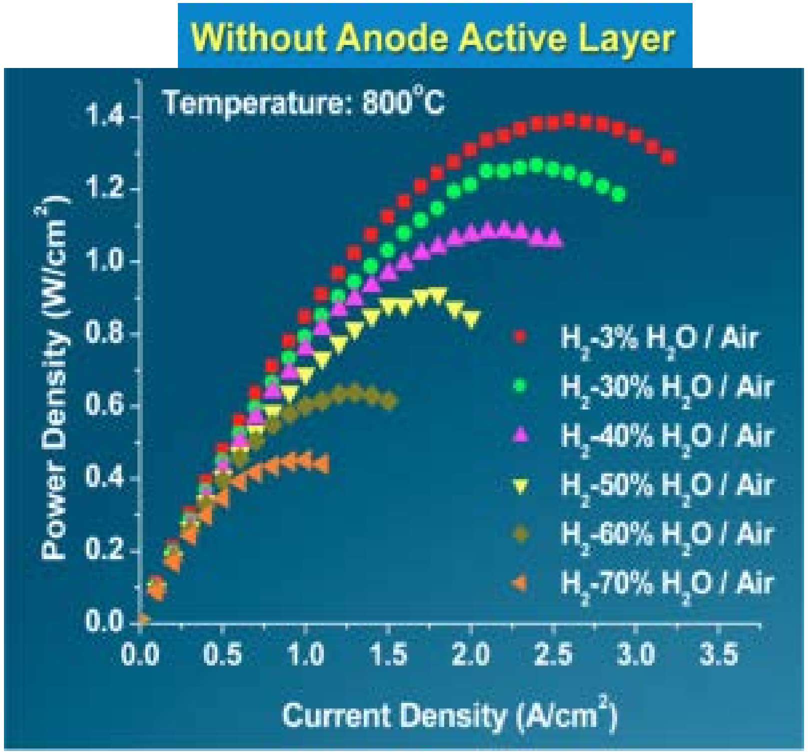
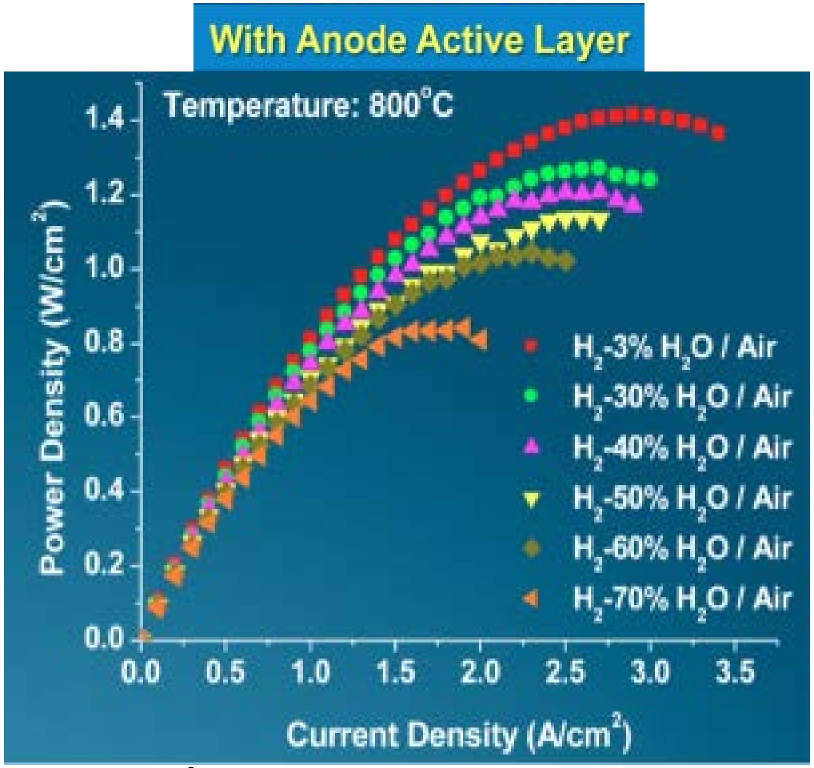
Presented at the 18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting, June 12-14, 2017, Pittsburgh, PA.

Motivations for Anode Infiltration

- Performance enhancement
- Ni reduction
- High fuel utilization tolerance
- Incorporation of alternate materials for
  - Sulfur tolerance
  - Coking tolerance



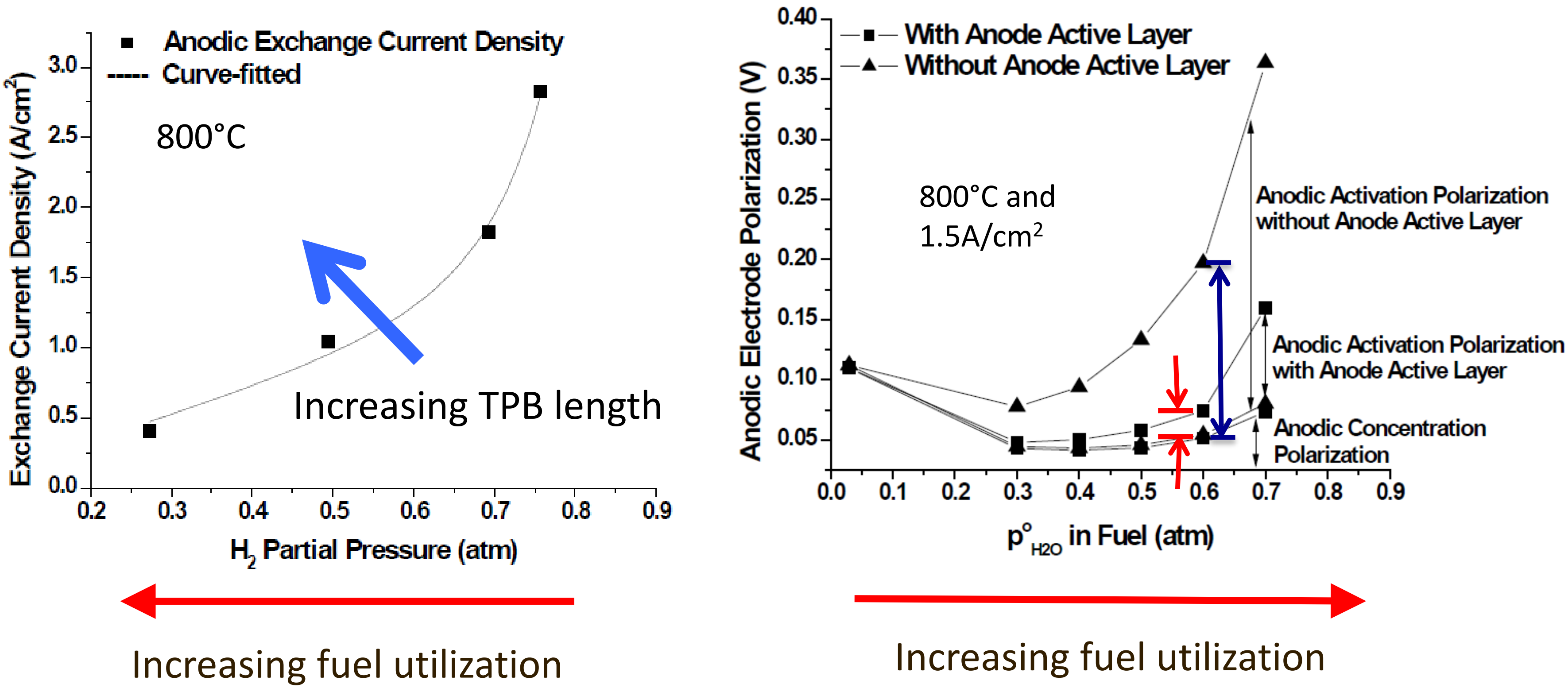


In a real stack, fuel utilization can exceed 85%

Problem is worse at lower temperature

Yoon et al., J. Electrochem. Soc., ***155****, 2008, pp B610*

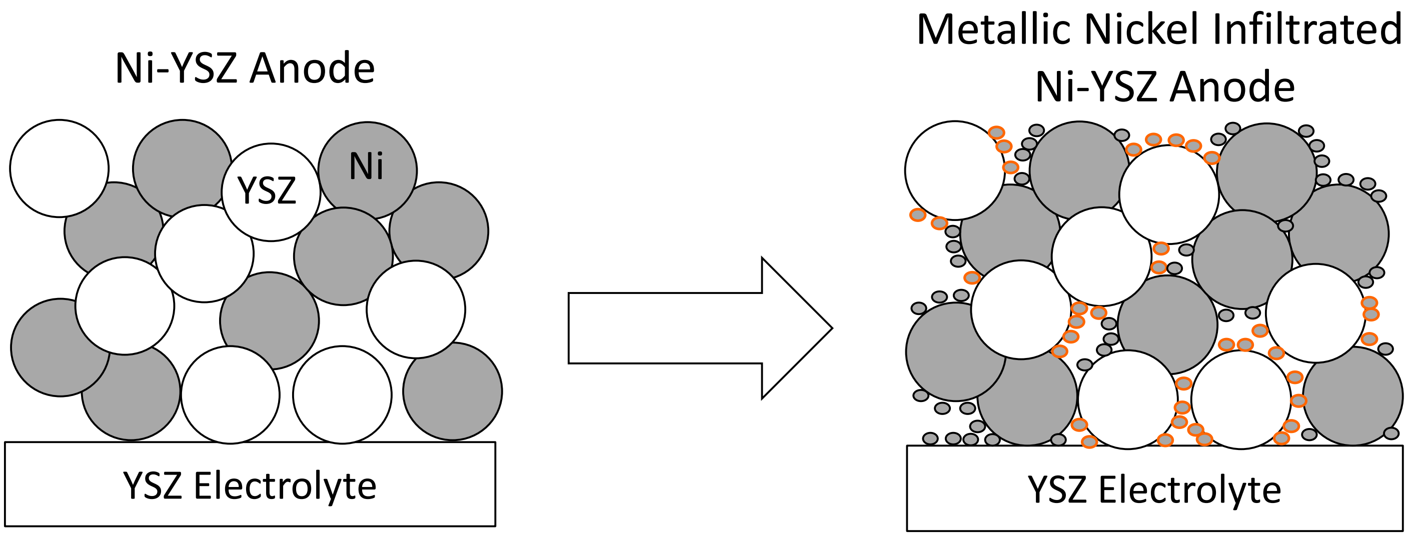
Anode performance at high fuel utilization



Increasing triple phase boundary (TPB) length improves performance at high fuel utilization by increasing the exchange current density and decreasing anode activation polarization

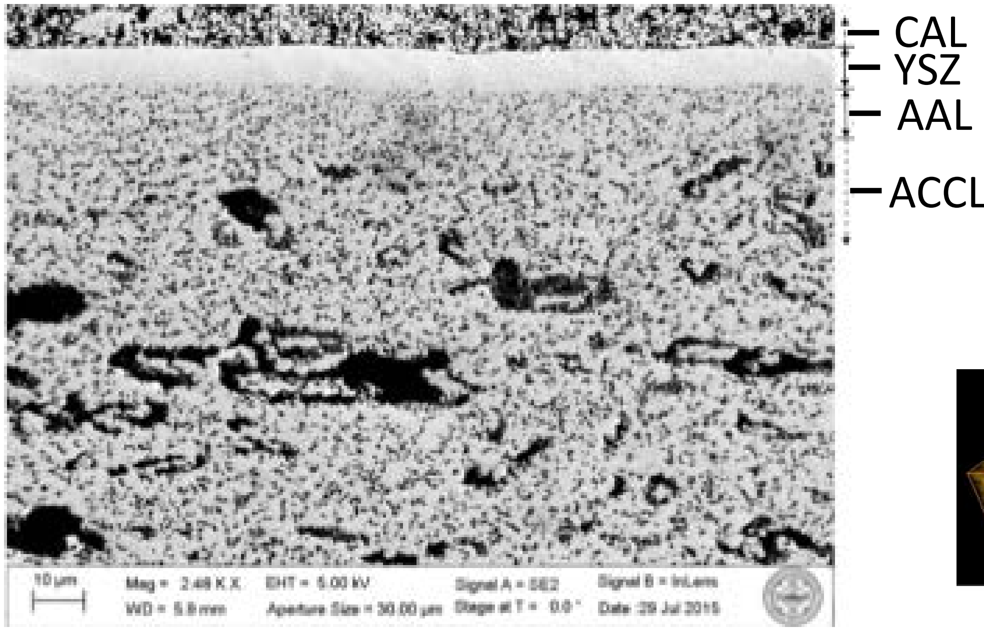
Solution to Performance Loss at High p(H_2O)

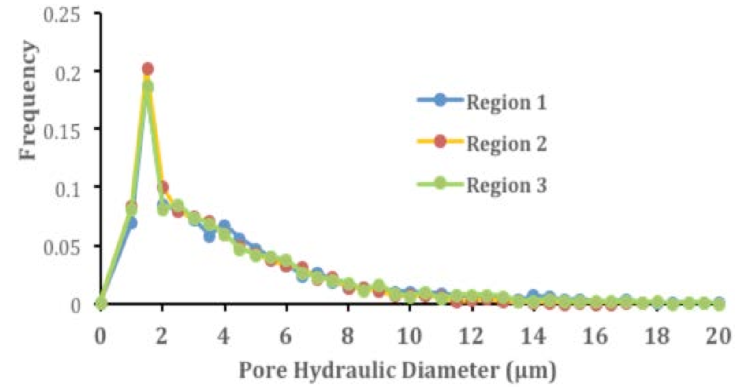
- Ni infiltration of commercial Ni/YSZ cermet anodes
- Ni/YSZ anodes are already percolating
- Only infiltrated Ni particles on YSZ will add to TPB length
- Additional TPB will help retain performance at high P(H_2O)

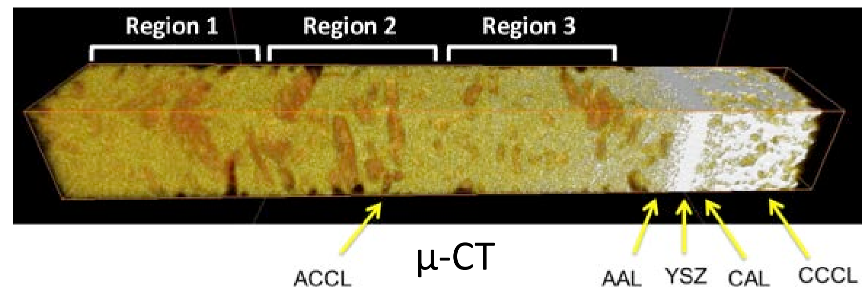


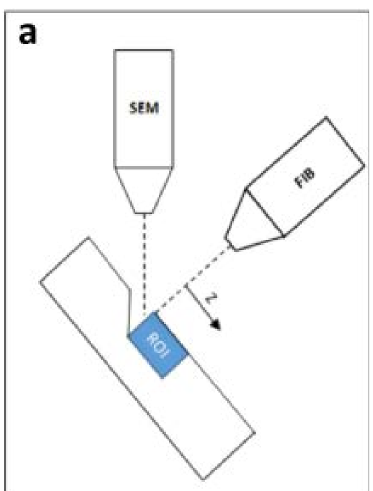
Characterization of MSRI Button Cells

SEM



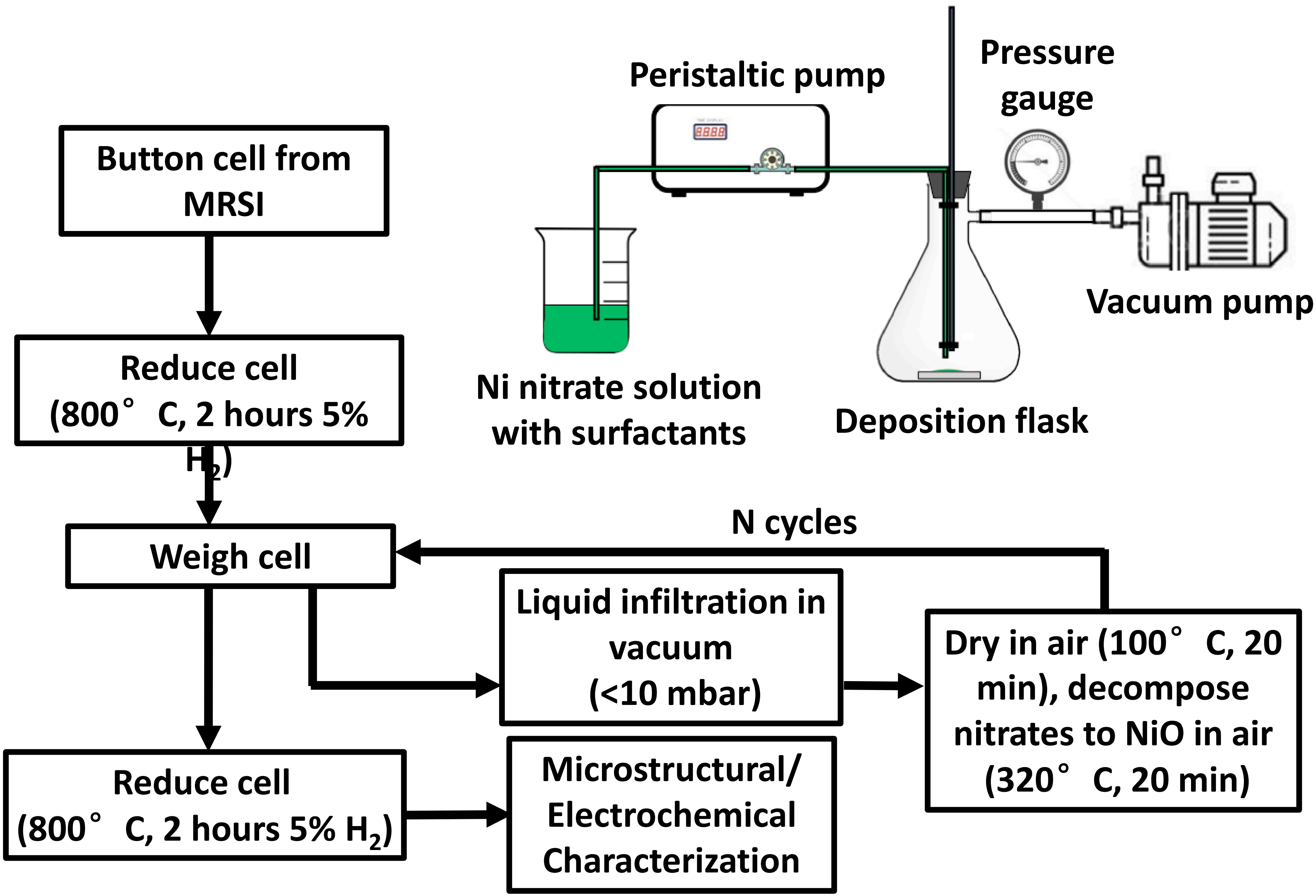




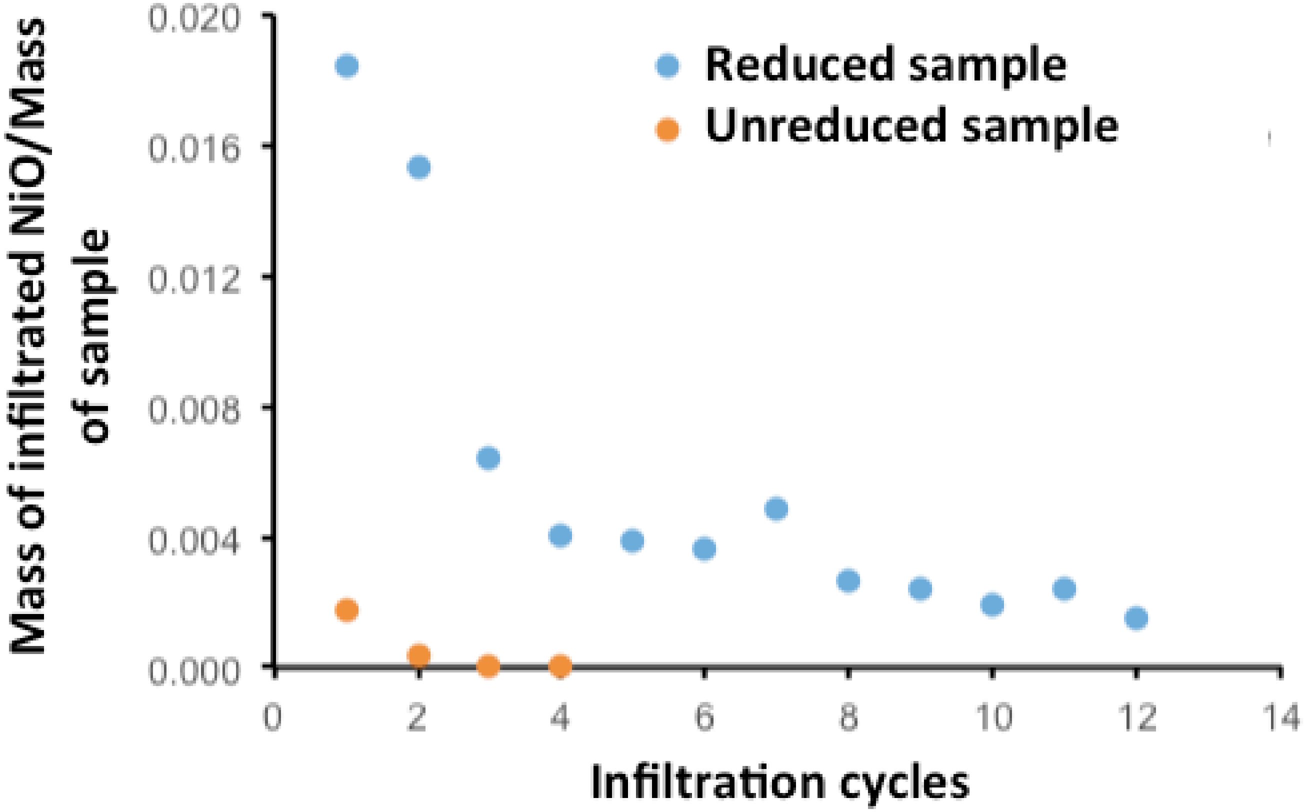


Reduced ACCL	
Porosity (%)	34.9
TPB length (µm/µm^3)	3.34

Liquid Infiltration of Ni-YSZ Anodes



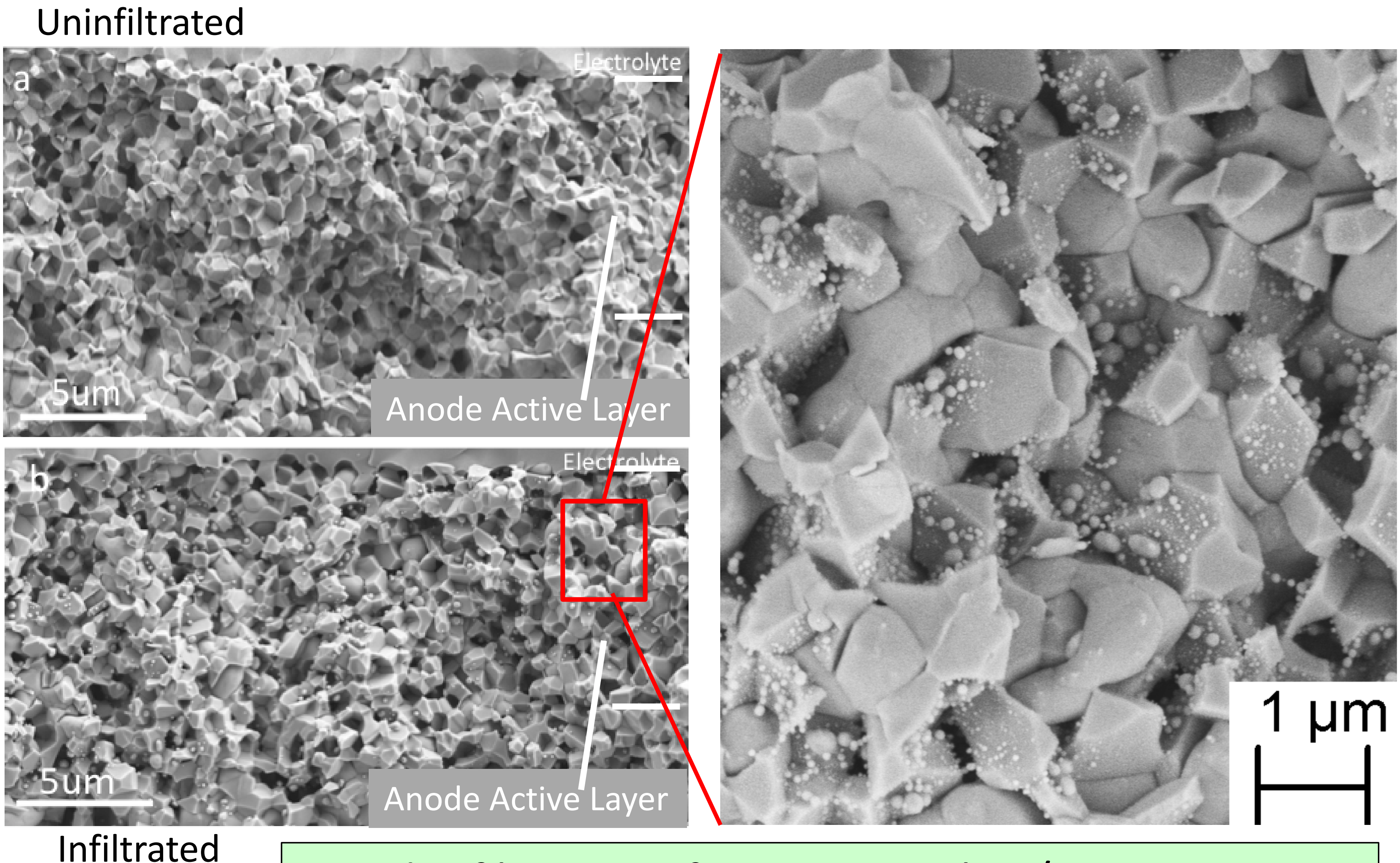
Results of Liquid Infiltration



For the reduced sample, after 12 cycles, the infiltrated Ni content corresponds to:

- 2.35 volume % of anode, or:
- 6.75 volume % of the pores

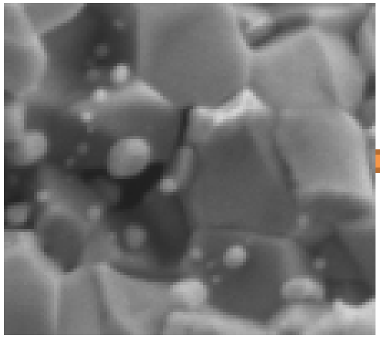
Characterization of Infiltrated Anodes

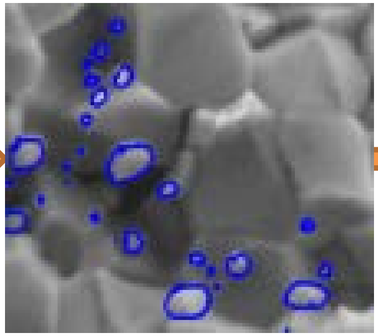


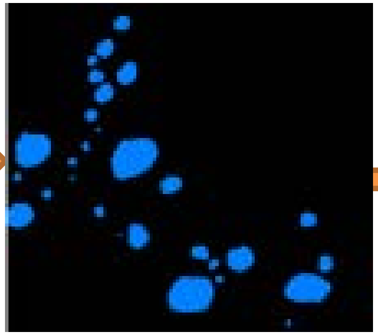
Liquid infiltration of conventional Ni/YSZ cermet can can lead to deposition in the anode active layer

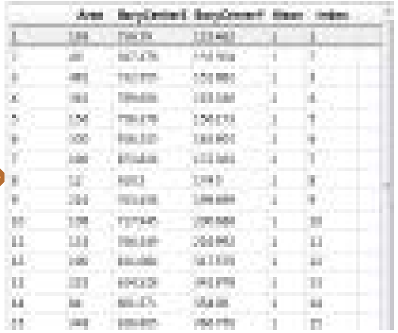
Quantification of Particle Size Distribution

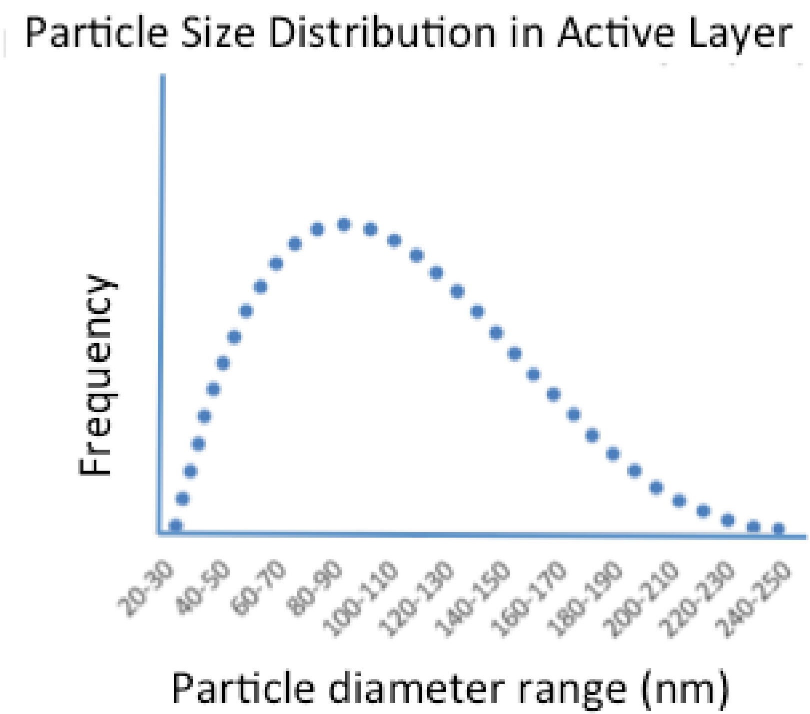
SEM Image → Ni Particle selection → Image separation → D_{eff} calculation



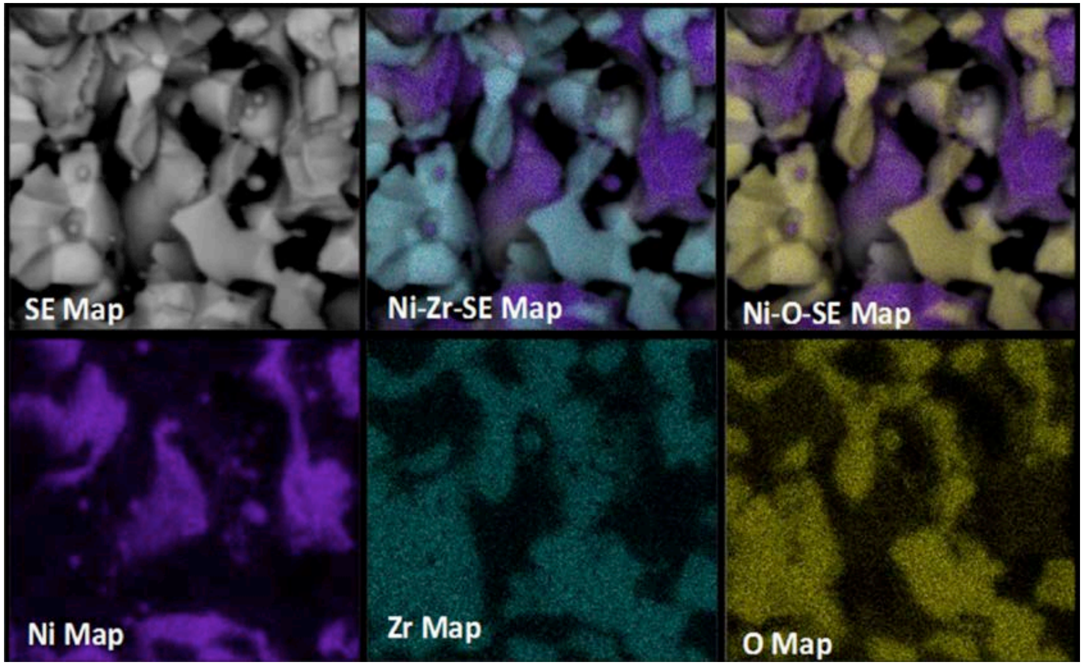


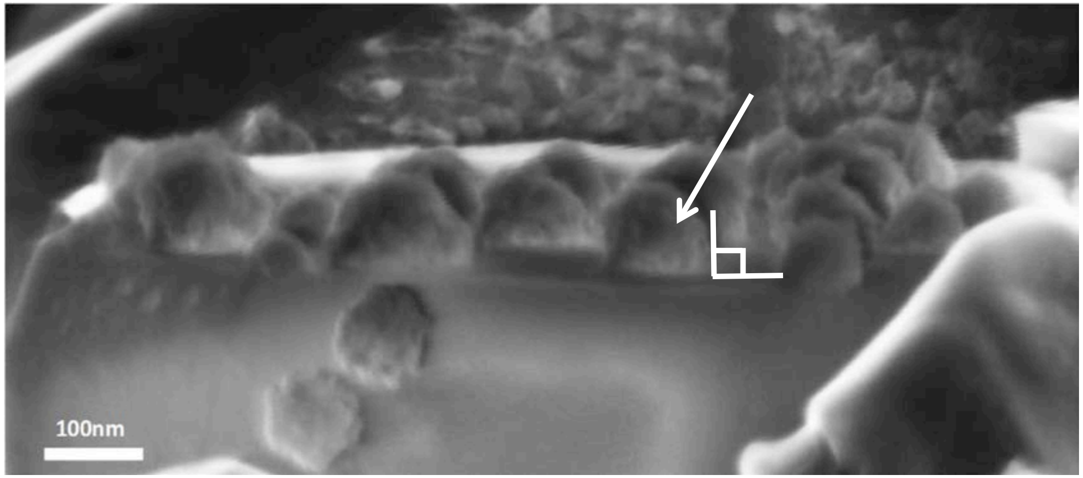






Location of Ni Nanoparticles



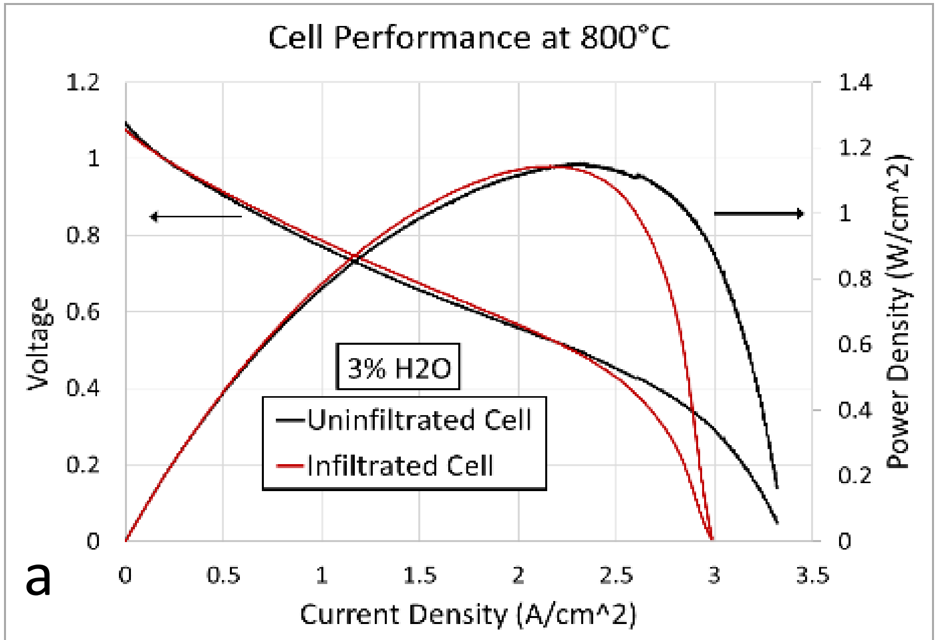


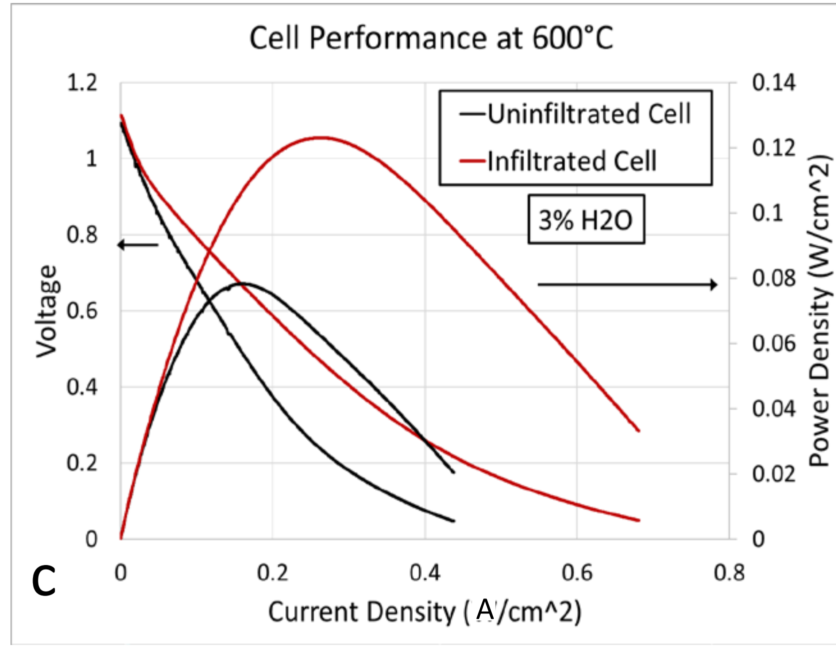
- Ni particles tend to strongly favor YSZ grains and are hemispherical
- Most Ni particles will contribute to TPB formation

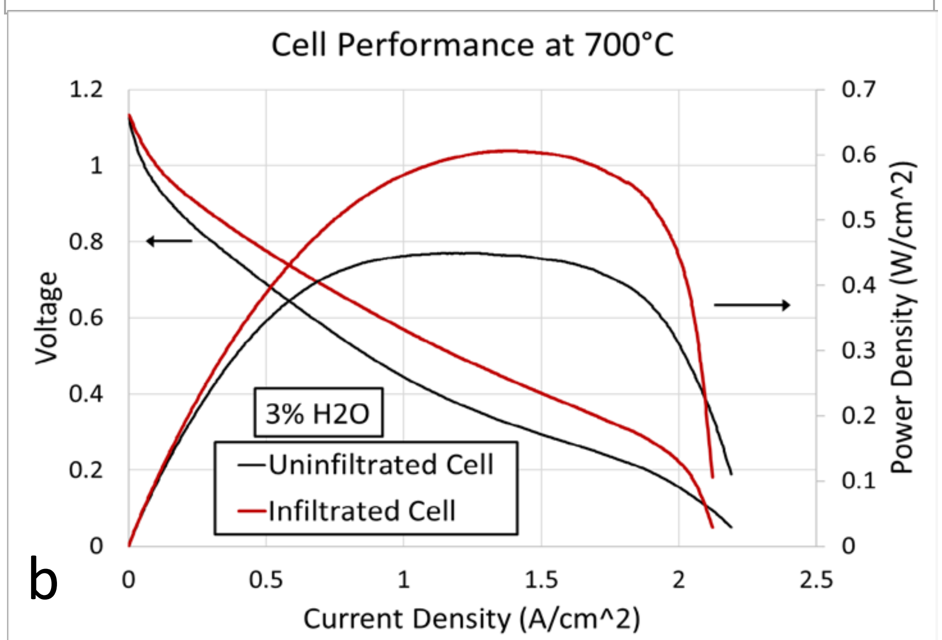
TPB in AAL ($\mu m/\mu m^3$)	
Original Ni/YSZ cermet	3.34
Ni Nanoparticles	6.82

Infiltration of Ni/YSZ anode triples AAL TPB length

I-V Curves: Infiltrated vs Uninfiltrated

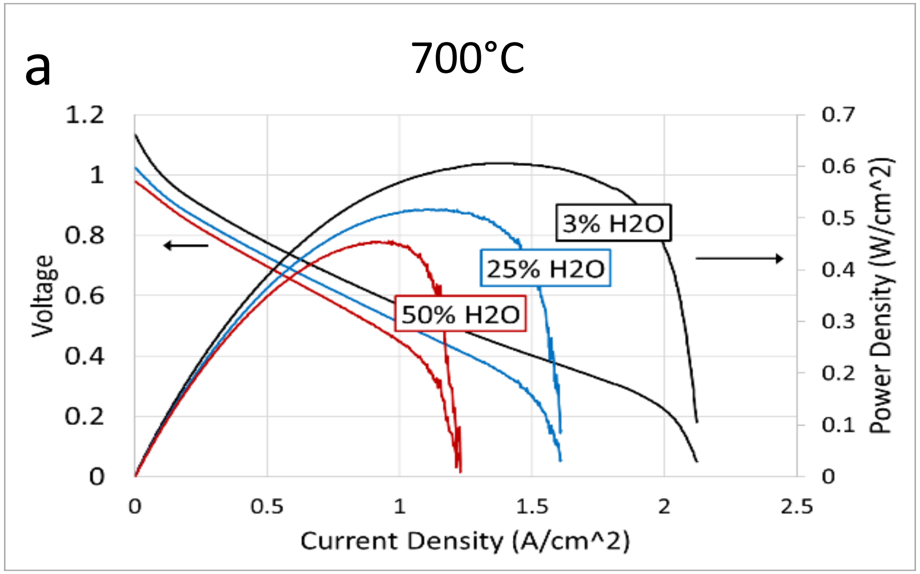


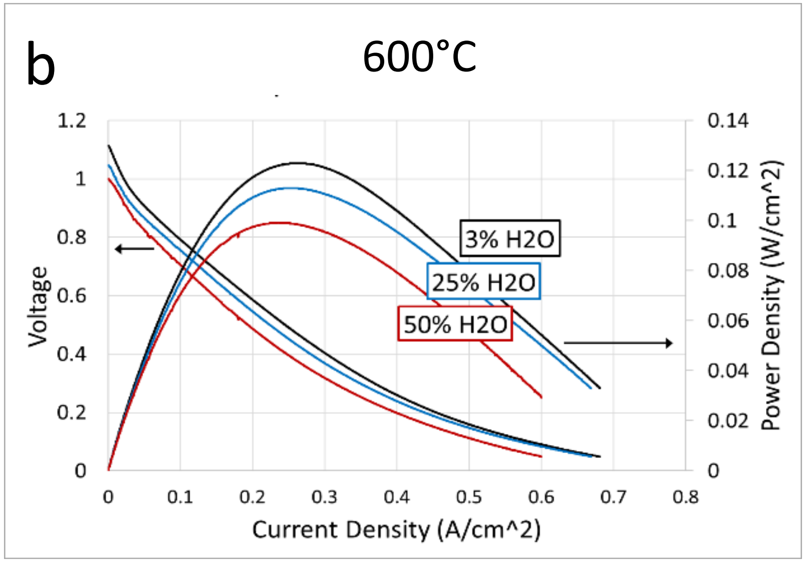




Temperature	MPD(I)/MPD(UI)
800°C	0.99

Effect of p(H_2O) and T on I-V Curves

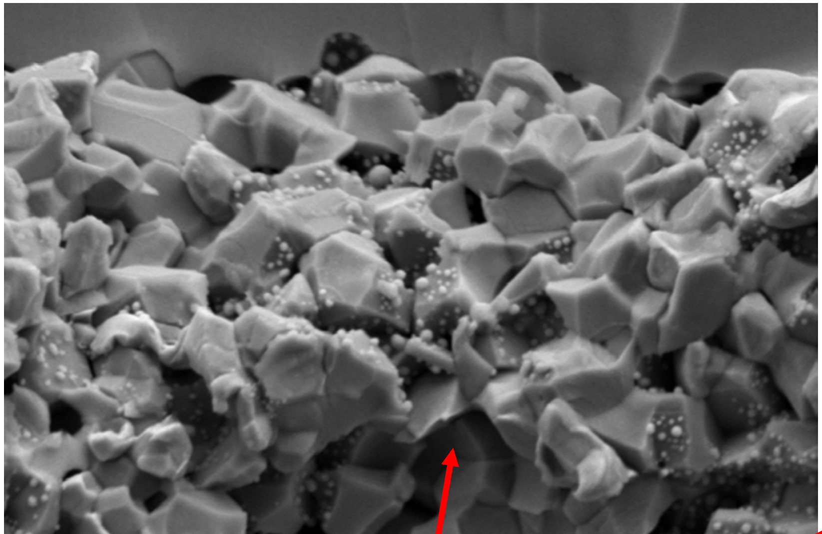


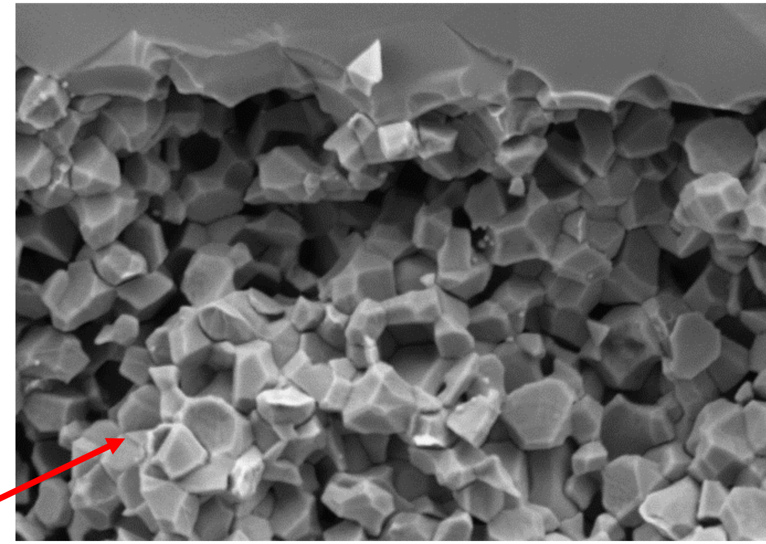


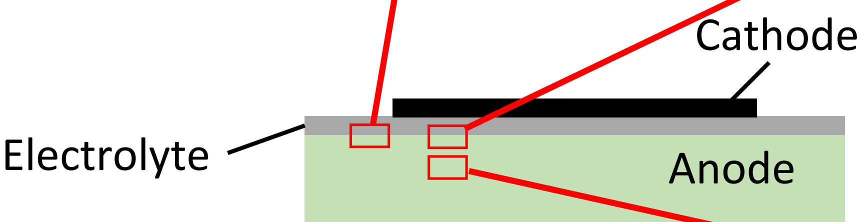
P(H_2O)	MPD(X%H_2O)/MPD(3%H_2O) 700°C	P(H_2O)	MPD(X%H_2O)/MPD(3%H_2O) 700°C
3%	**1**	3%	**1**
25%	**0.85**	25%	**0.96**
50%	**0.75**	50%	**0.86**

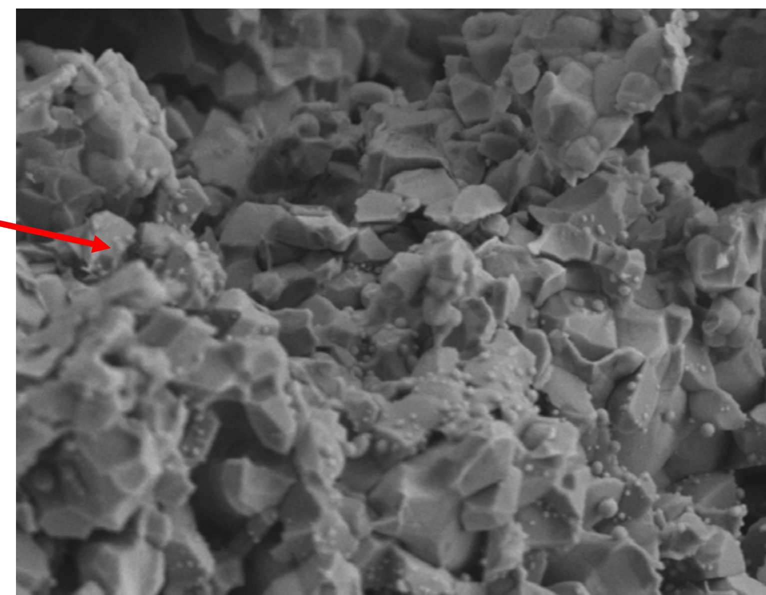
Mitigation of performance degradation at high fuel utilization by infiltration becomes more effective at lower temperatures

Ni Nanoparticle Instability at 800°C





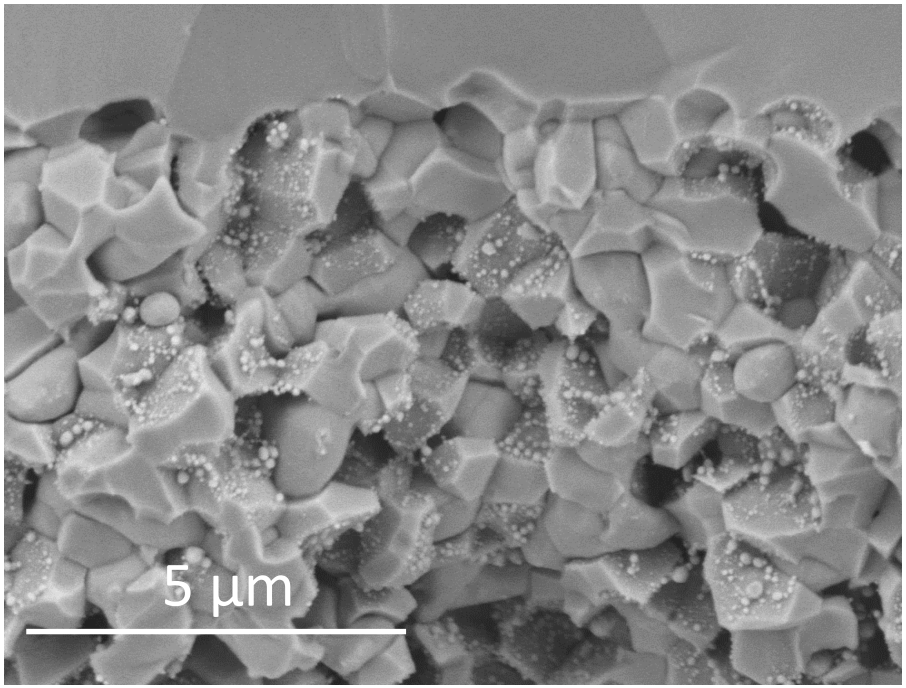




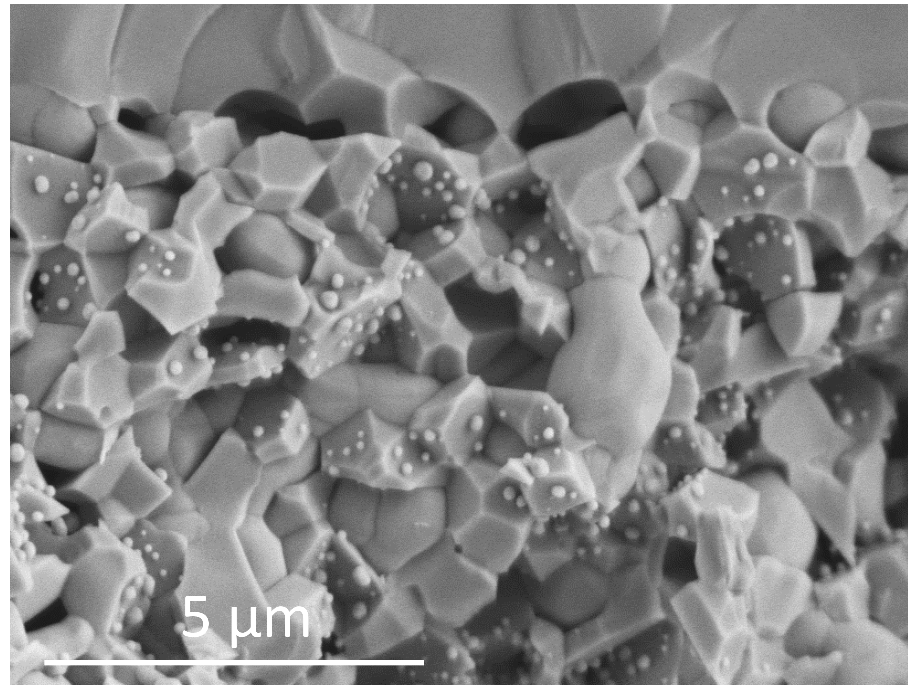
Ni nanoparticles disappear from sites of high local current density

Effect of High Temperature Exposure to $H_2O(v)$

As-infiltrated



After annealing
800°C, **90% H_2O**, 48 hours

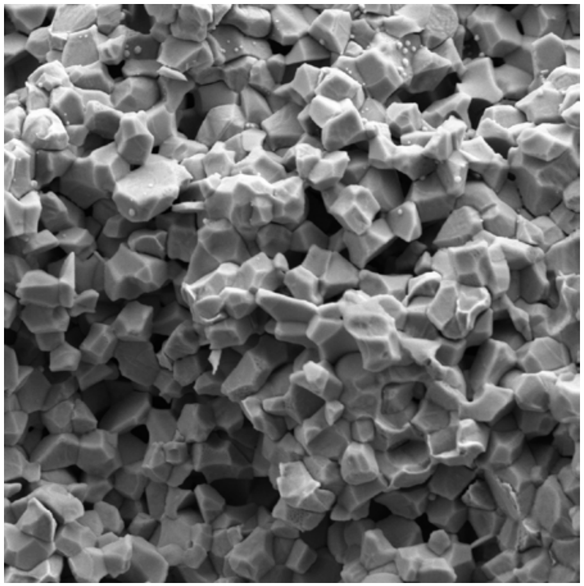


	As-infiltrated
Particle Density (#/um²)	26.11
Average Diameter (nm)	54.31
Particle Volume (nm³/nm²)	2.73

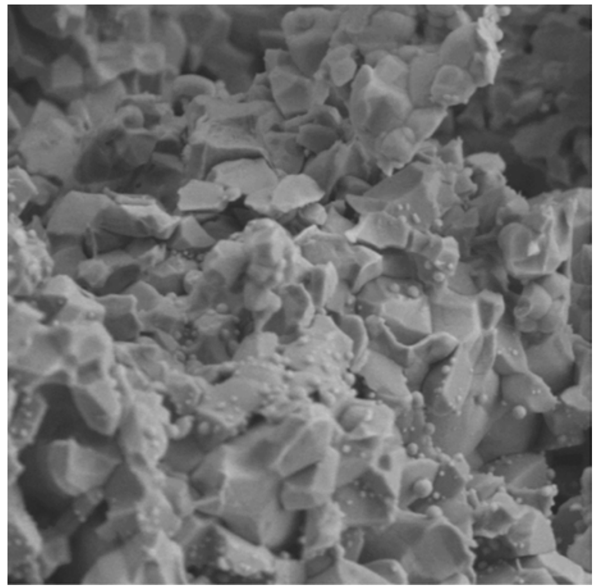
Annealing alone leads to coarsening, but not disappearance

Ni Nanoparticles in Ni-YSZ Anode at 800°C

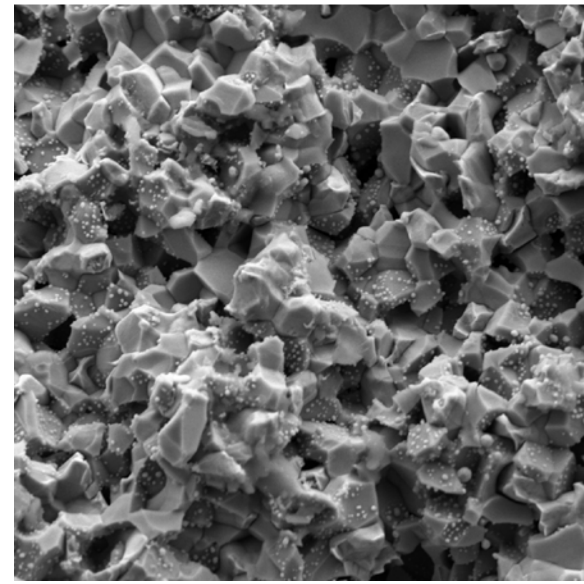
Anode Active layer under cathode
(Electrochemically active)



Anode bulk layer under cathode
(Electrochemically active)



Anode active layer not under cathode
(Electrochemically inactive)

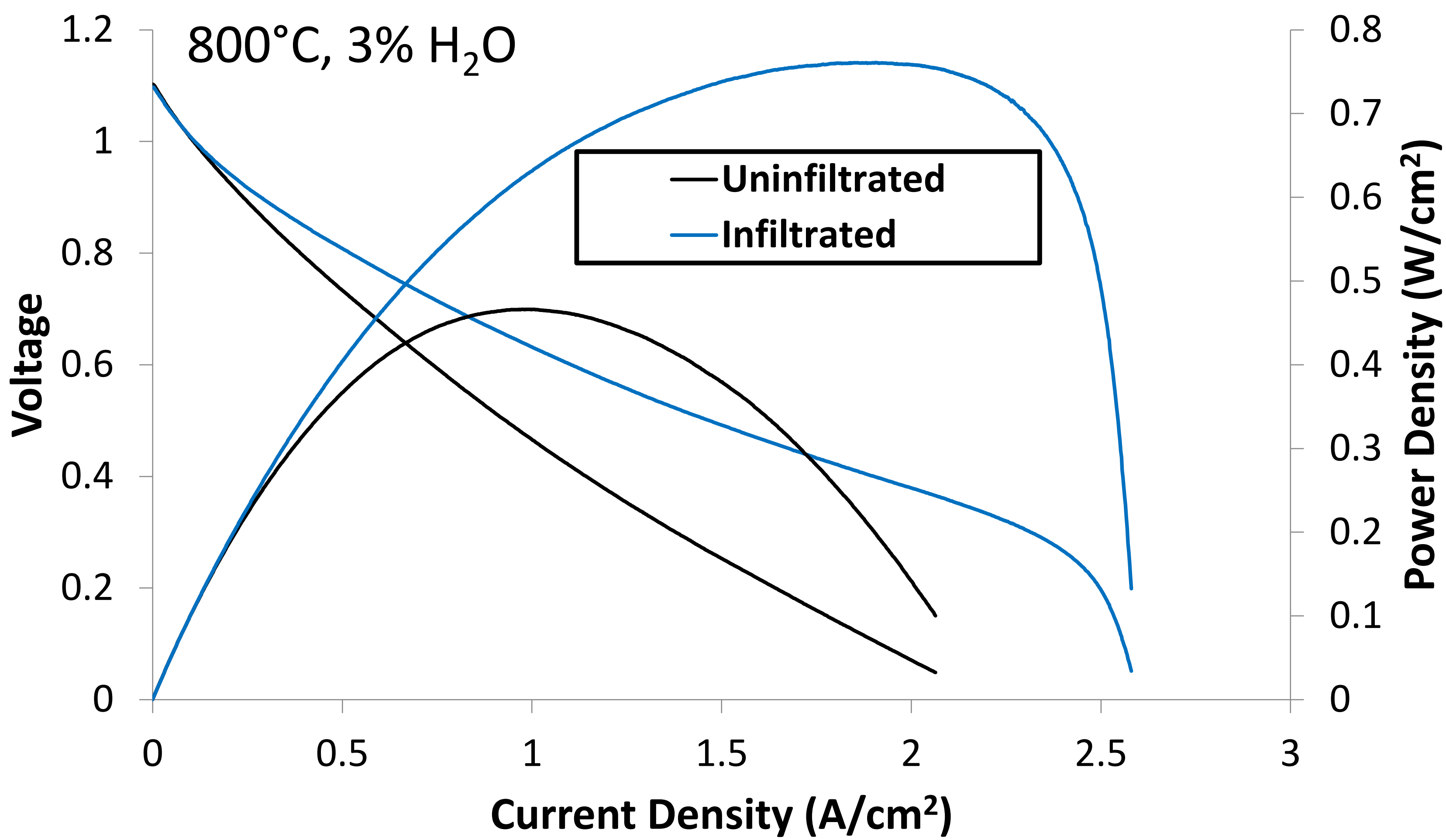


	Electrochemically active AAL
Particle Density (#/μm^2)	**1.37**
Particle Volume (nm^3/nm^2)	**0.367**

Decreasing local current density

Reducing Local Current Density by using MIEC

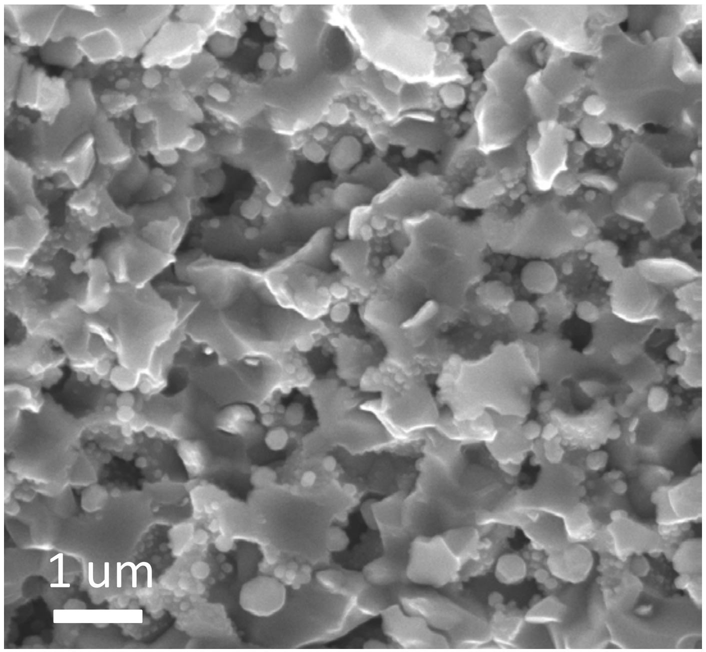
Replace Ni/YSZ with Ni/GDC Anode Active Layer



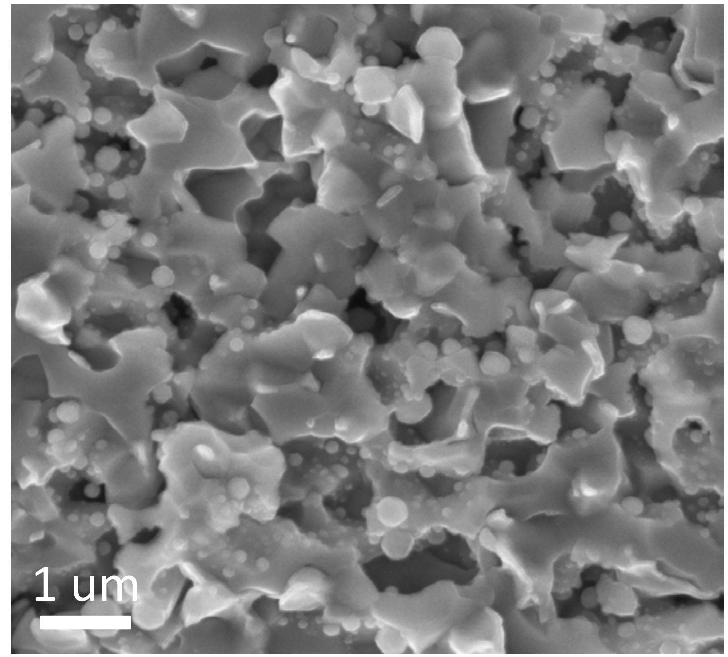
Overall performance not as good, but positive effects of Ni nanoparticles remain at 800°C

Ni Nanoparticles in Ni-GDC AAL at 800°C

AAL not under cathode
(Electrochemically



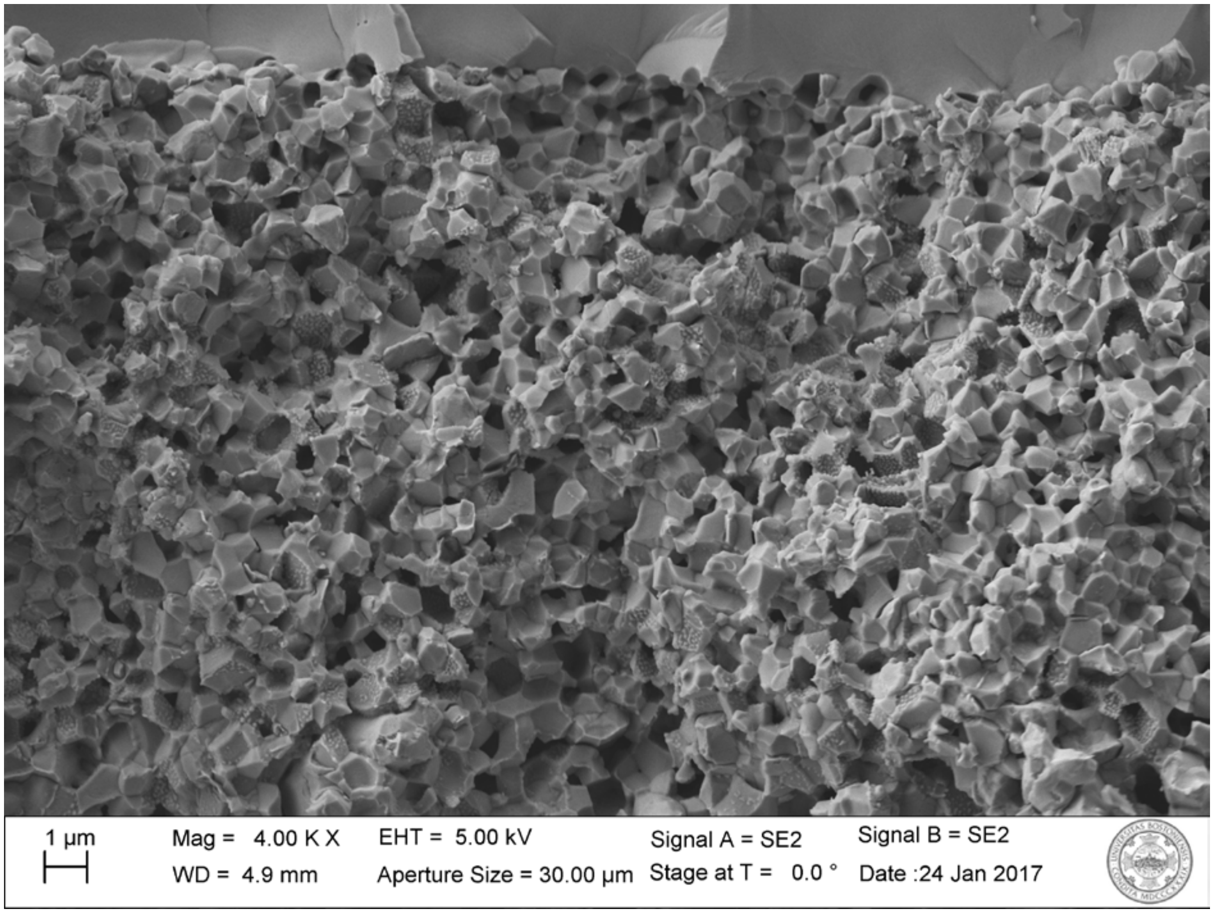
AAL under cathode
(Electrochemically active)

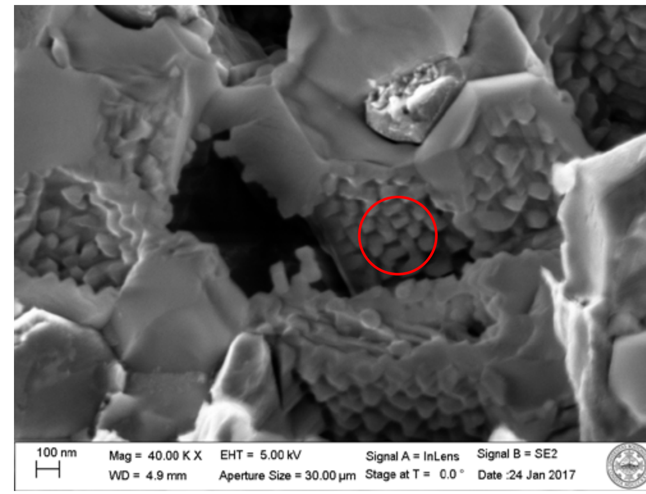


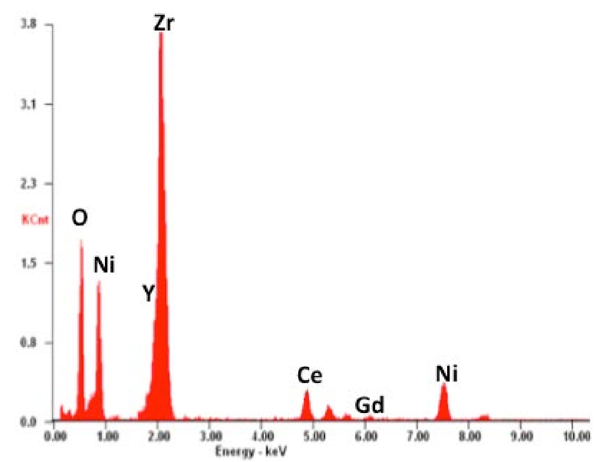
	Not Under Cathode
Particle Density (#/µm^2)	5.50
Average Diameter (nm)	113.72
Particle Volume (nm^3/nm^2)	4.45

Ni nanoparticles are more stable under reduced local current density (electric field) due to the presence of the MIEC (GDC) in the AAL

Co-infiltration of Ni and GDC in Ni/YSZ Anode

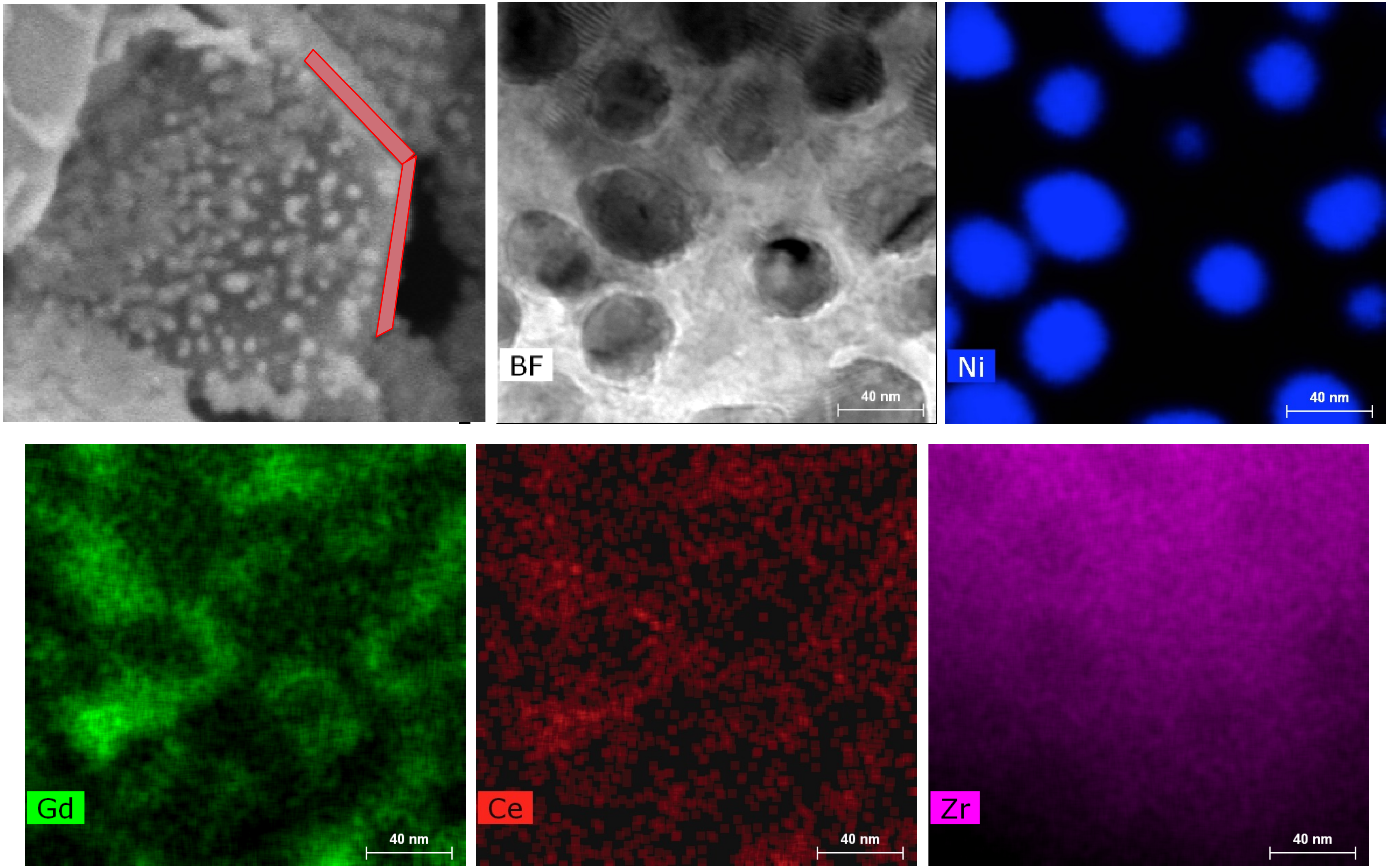




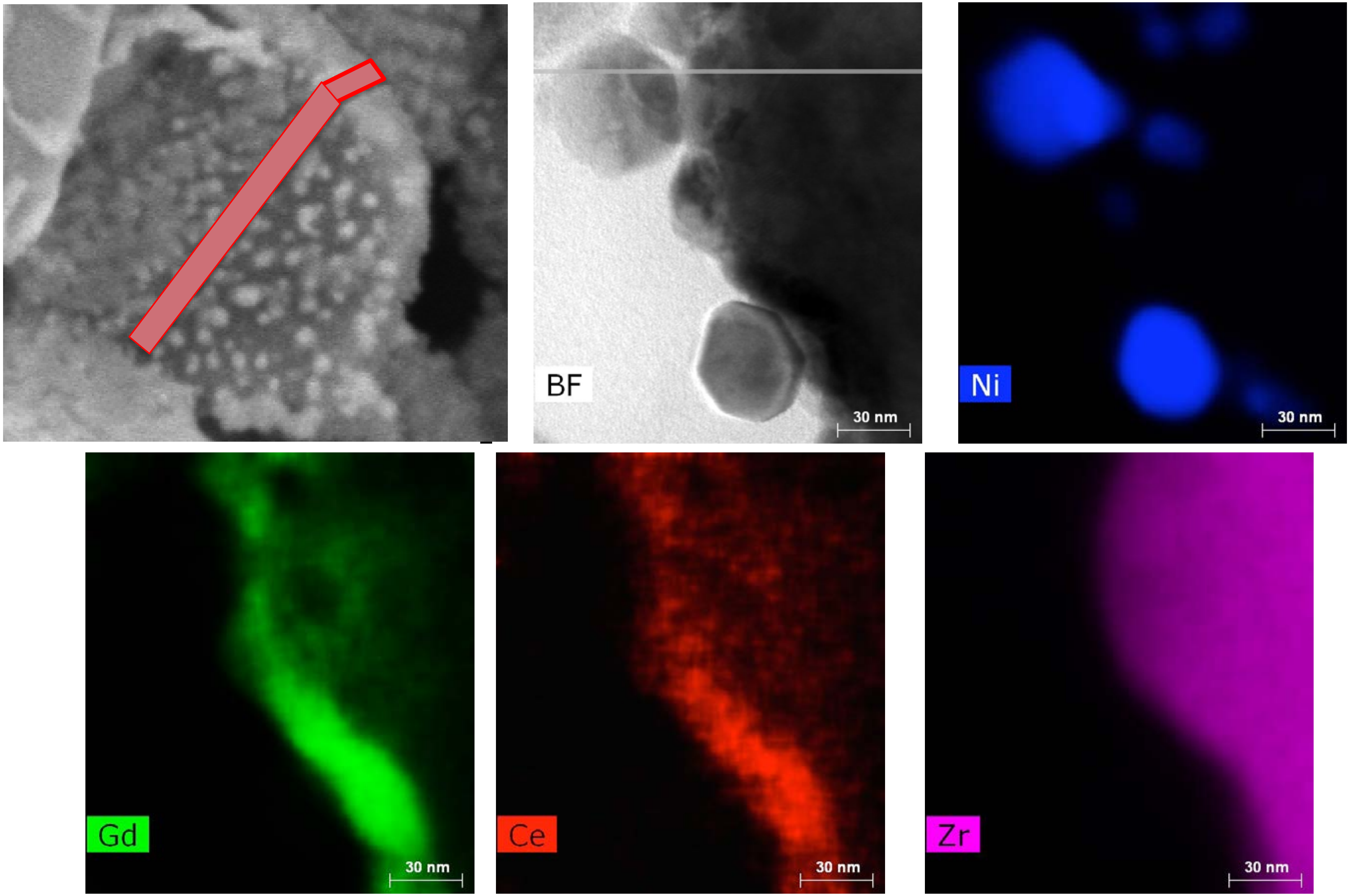


Ni:GDC molar ratio of 1:1

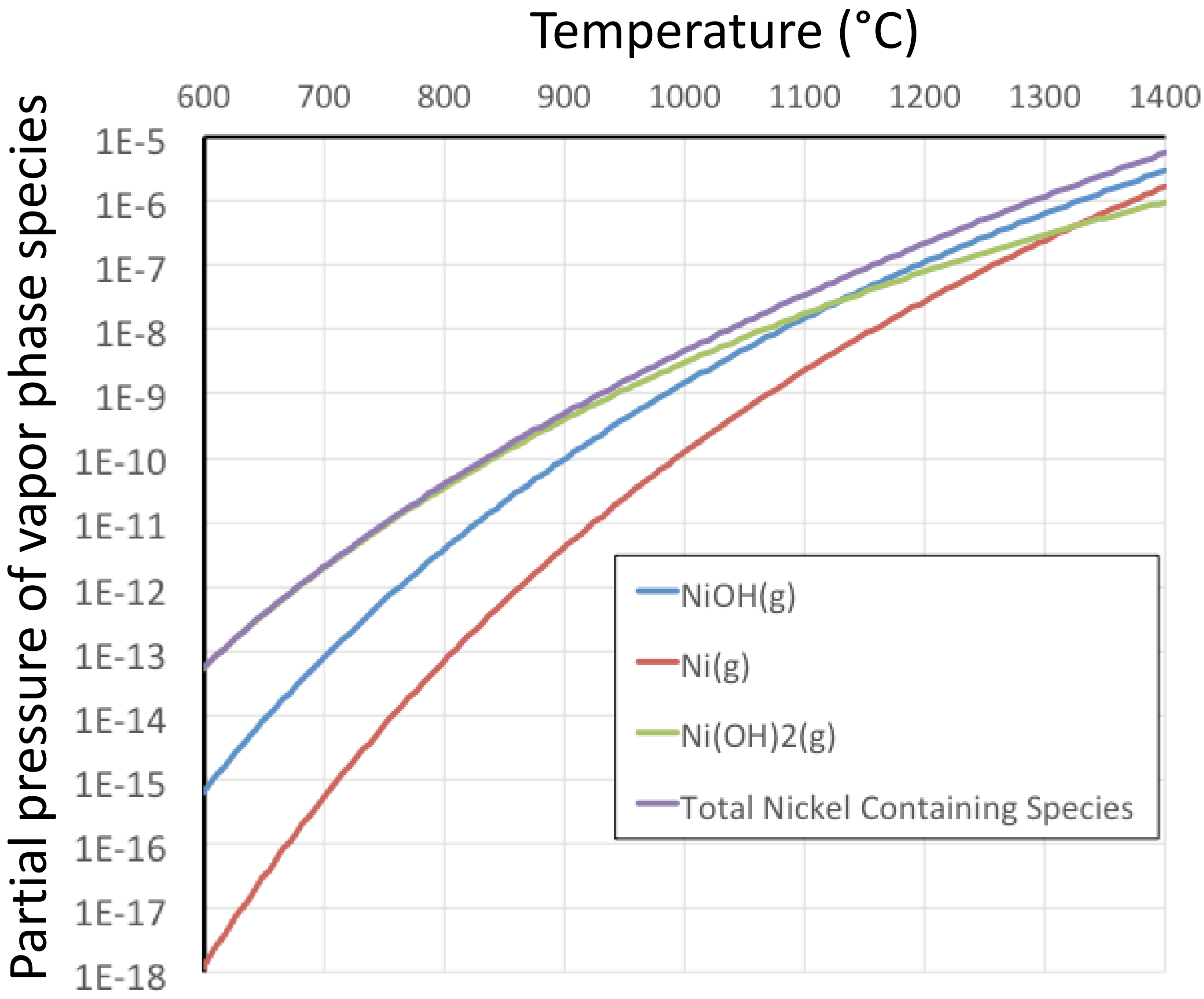
TEM of Ni/GDC Nanoparticles in Top View



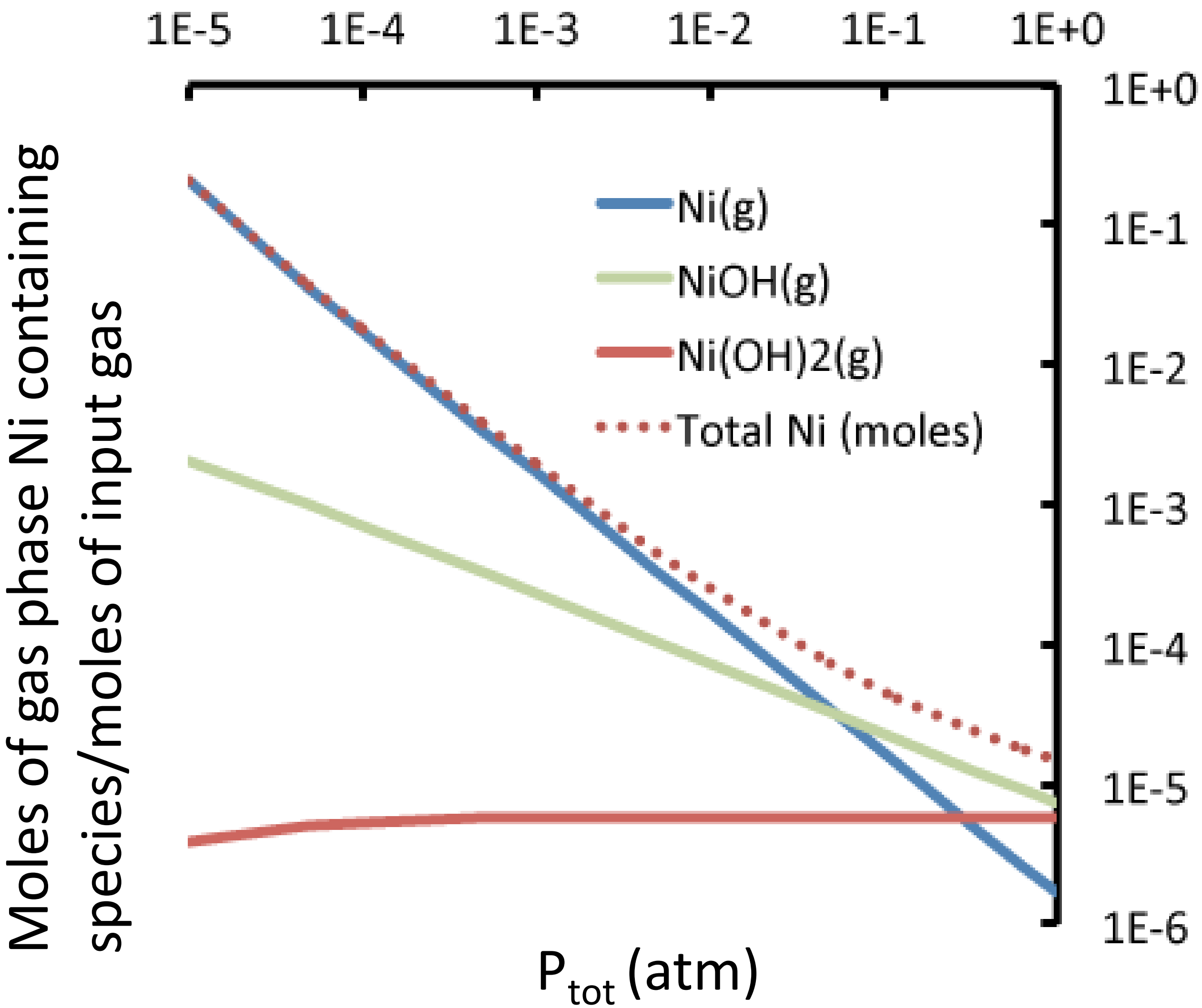
TEM of Ni/GDC Nanoparticles in Cross-Section



Nickel Vapor Thermodynamics



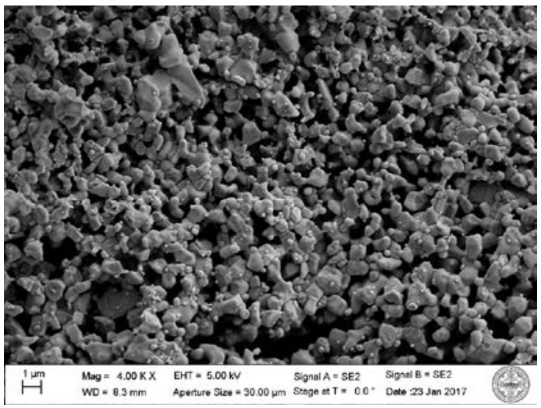
Nickel Vapor Thermodynamics



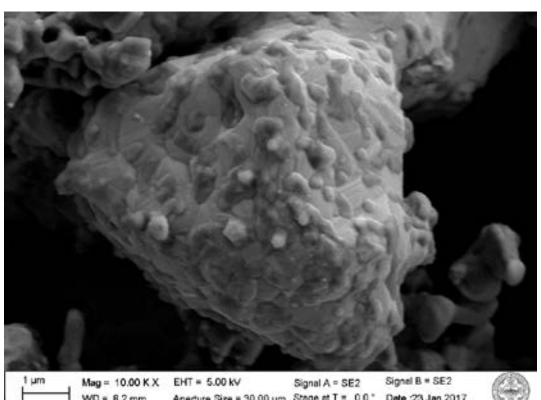
- 50% water vapor/ 50% forming gas ($5\%\ H_2$, 95% Ar)
- Unlimited Ni supply
- 1400°C

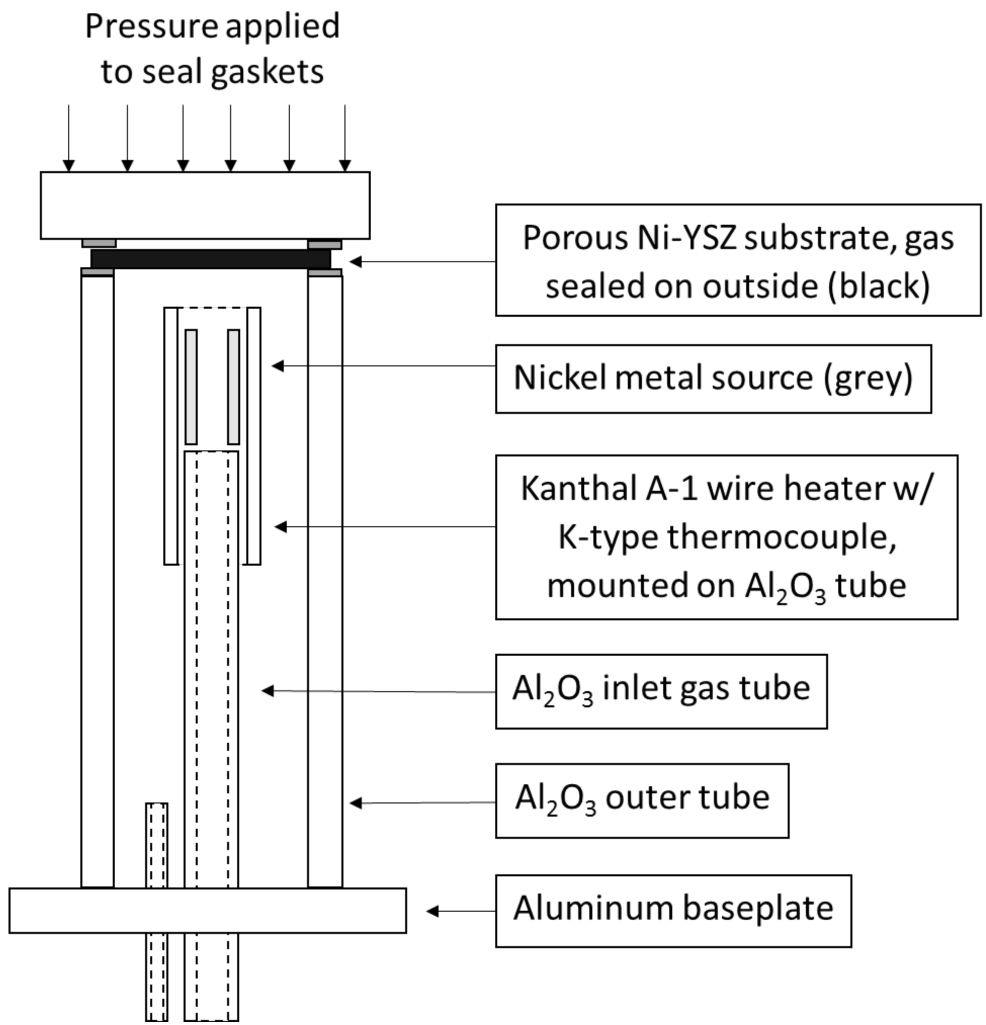
Vapor Phase Infiltration of Ni in Ni-YSZ Anodes

Nickel nanoparticles in Ni-YSZ anode active layer



Nickel nanoparticles in bulk Ni-YSZ anode





Vapor phase infiltration of Ni in commercial anodes is feasible

Conclusions

- At high fuel utilization, the cell performance degrades due to increased anodic activation polarization losses
- Liquid phase infiltration increases the TPB length in the anode active layer by a factor of 3.
- For 3% H_2O-97% H_2 fuel, the infiltrated cells show a 35% improvement at 700°C and a 58% improvement at 600°C compared to uninfiltrated cells.
- Anode infiltration becomes increasingly effective at lower temperatures, by mitigating the negative effects of performance degradation at high fuel utilization
- At 800°C, the Ni particles disappear only in the anode active layer in the region below the cathode, indicating that current density plays a role.
- Introduction of an MIEC like GDC can reduce the local current density and stabilize the nanoparticles
- An innovative *in-situ* vapor-phase infiltration of the anode directly by Ni has been demonstrated and process optimization is undergoing

Acknowledgements

Project funding: DOE/NETL Award #: DE-FE0026096

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