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Infiltration of Nickel Nanoparticles in Ni/YSZ Solid Oxide Fuel Cell Anodes for Improved Performance

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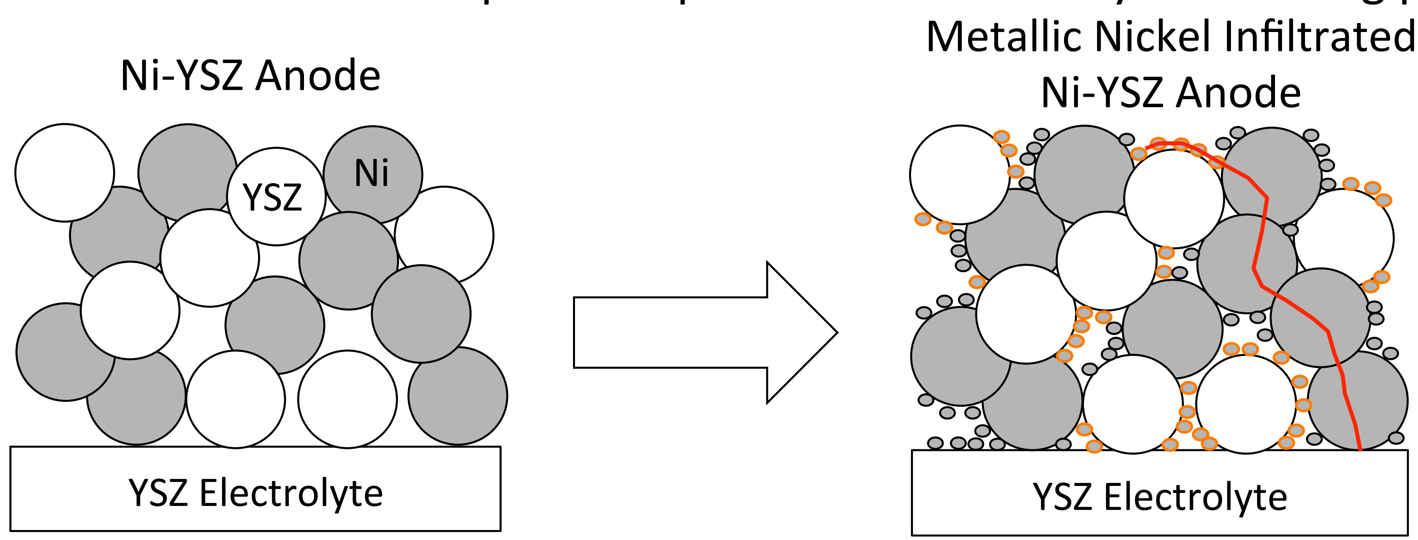
Presented at the 2019 DOE Hydrogen and Fuel Cells Program Annual Merit Review and Peer Evaluation Meeting, April 29 – May 1, 2019, Washington, D.C.

Research Approach

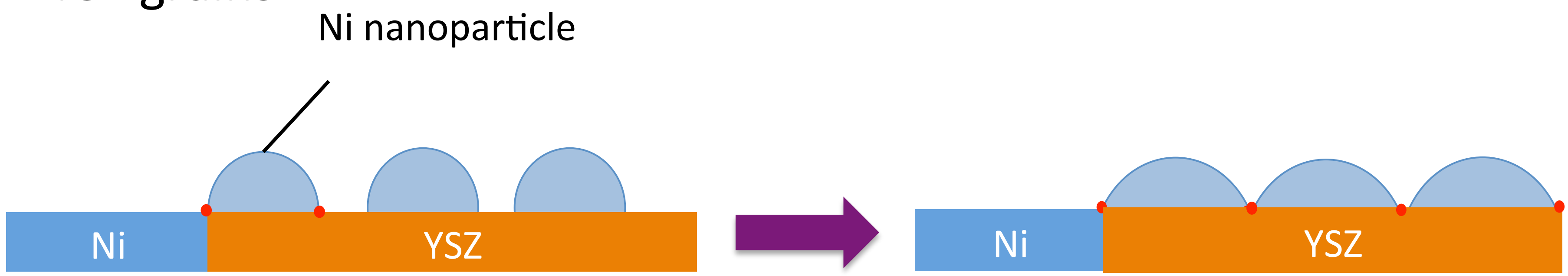
- Ni infiltration of commercial Ni/YSZ cermet anodes
  - Ni/YSZ anodes are already percolating
- Increase in TPB density
  - Decrease in activation polarization
  - Increase in anodic exchange current density
- Only infiltrated Ni particles on YSZ will add to TPB length
  - Quantify added TPB length by SEM study of fracture cross sections
- Additional TPBs will be active only if they have an electrically conducting pathway
  - When are the infiltrated particles part of an electrically conducting pathway?



Activating Additional TPBs

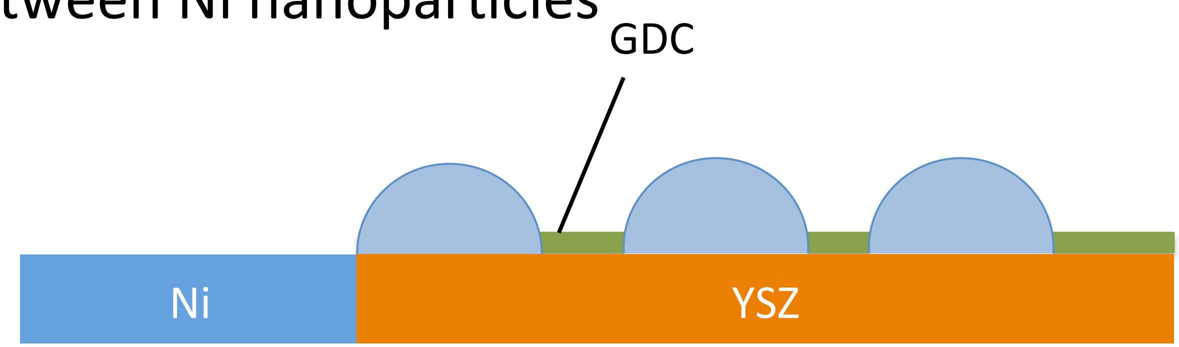
Approach 1

Spread the Ni nanoparticles to form a percolating Ni network on YSZ grains



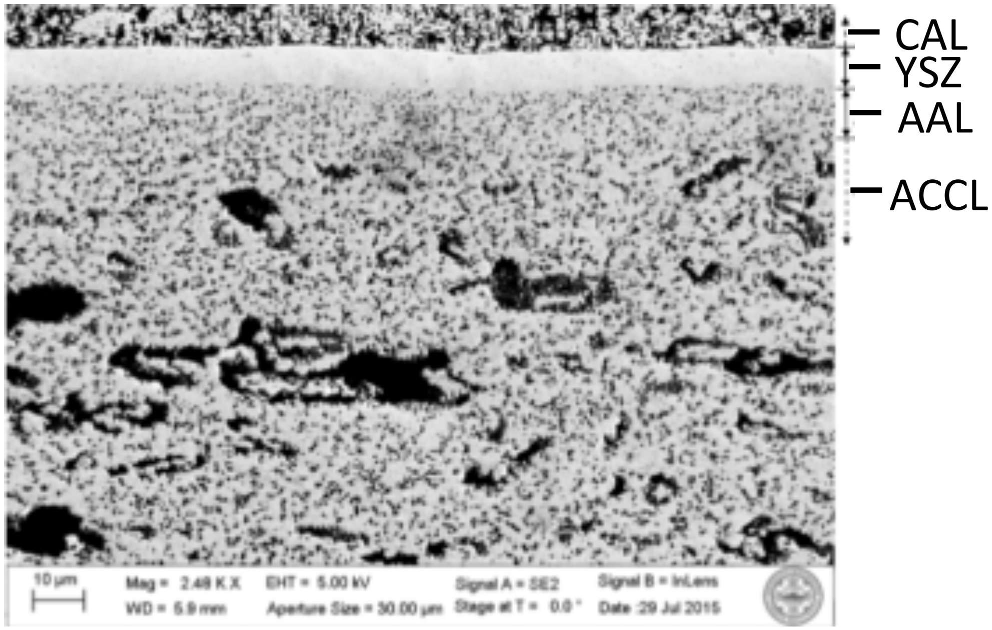
Approach 2

Co-infiltrate Ni nanoparticles with an MIEC like GDC for electronic pathway between Ni nanoparticles

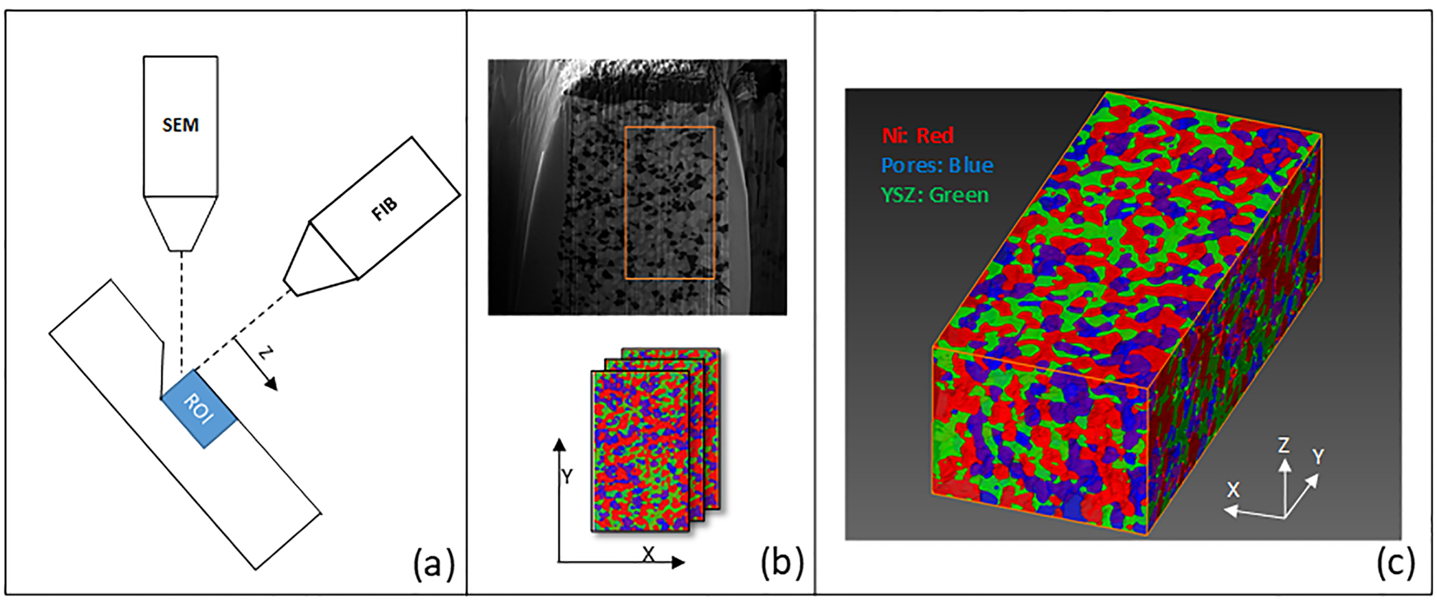


Characterization of Button Cell Microstucture

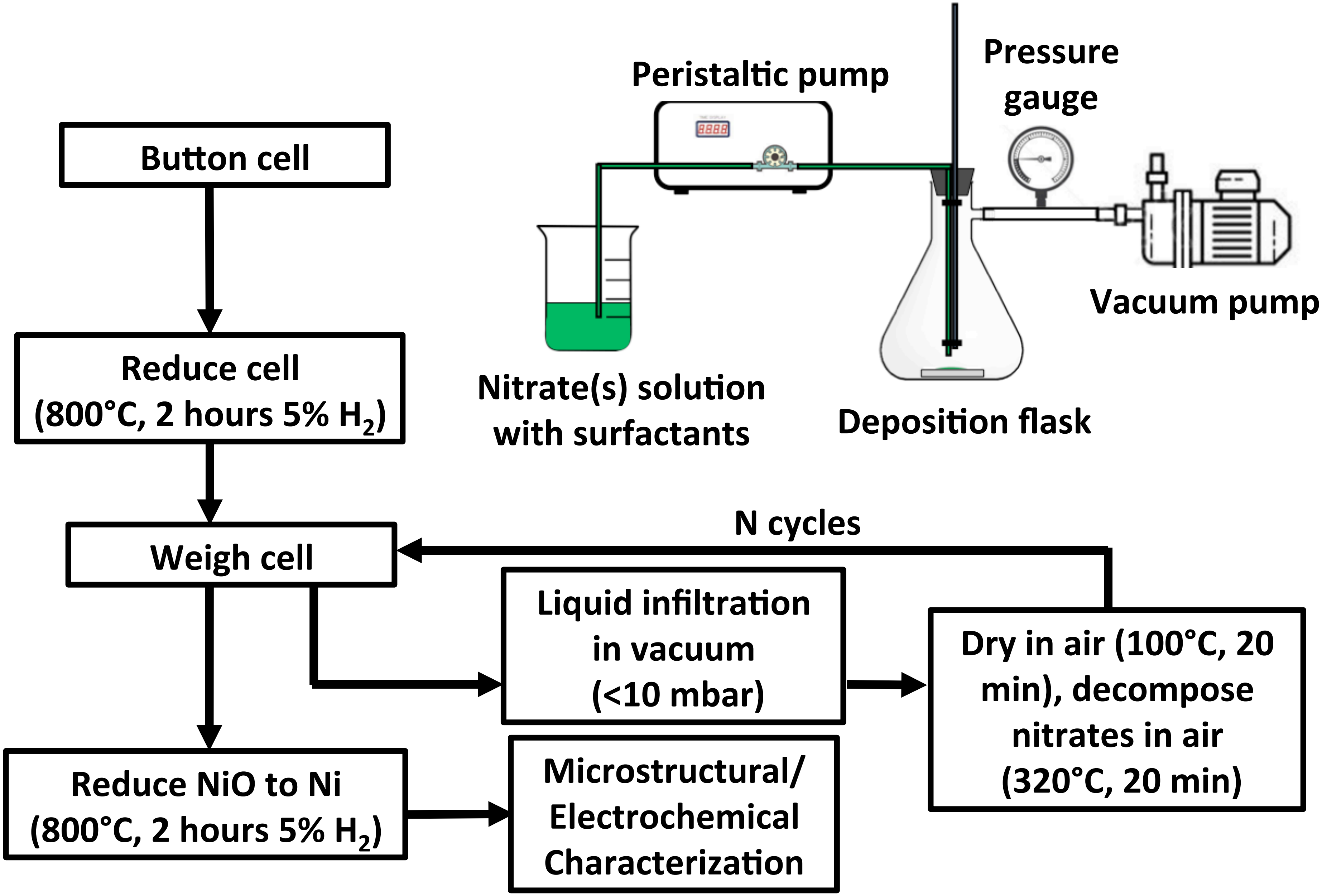
SEM



Phase	Volume Fraction	TPB density (µm µm^{-3})
Nickel	38.8%	2.39
YSZ	32.5%	
Pores	28.7%	



Liquid Infiltration of Ni-YSZ Anodes



Details of Liquid Infiltration

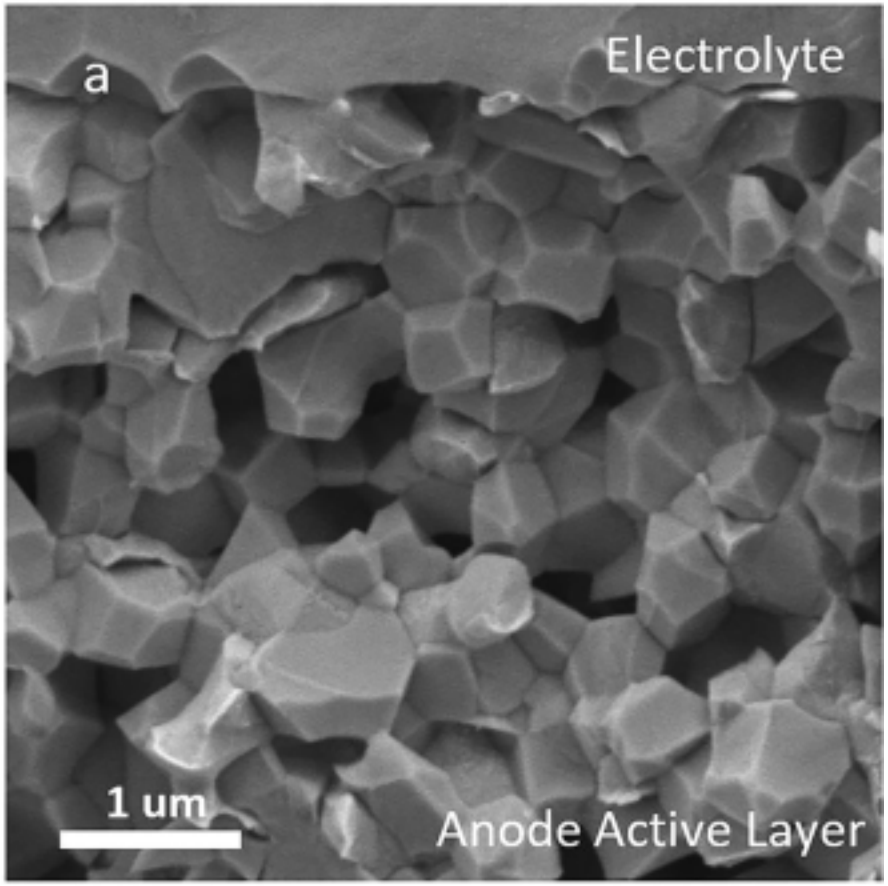
Nanoparticles	Ni	Ni/GDC	GDC
Nitrate solution molarity	1 M $Ni(NO_3)_2$	2M $Ni(NO_3)_2$ 0.2M $Gd(NO_3)_3$ 1.8M $Ce(NO_3)_3$	0.2M $Gd(NO_3)_3$ 1.8M $Ce(NO_3)_3$
Rounds of infiltration	5	1	1
Infiltrate	NiO	NiO+GDC	GDC
Weight gain	1.62 wt % NiO (1.27% Ni)	1.24 wt% Ni+GDC	1.3 wt% GDC

For the reduced Ni infiltrated sample, after 5 cycles, the infiltrated Ni content is:

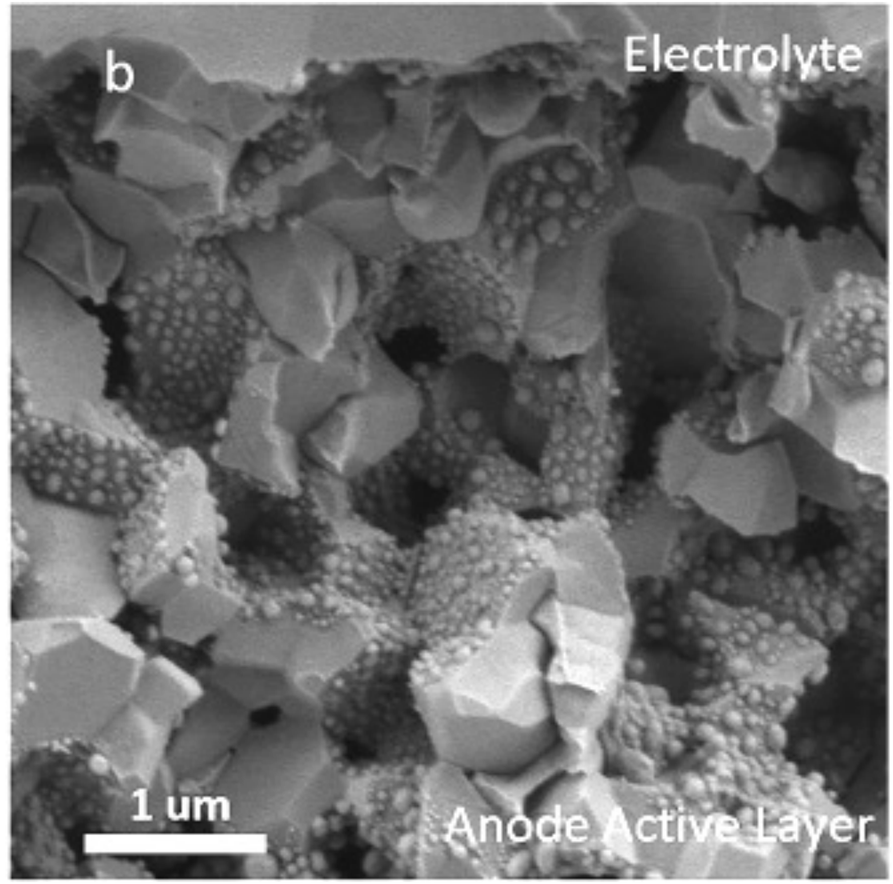
- 2.33 volume % of anode, or:
- 8.1 volume % of the pores

Ni Nanoparticles in Liquid Infiltrated Anodes

Uninfiltrated

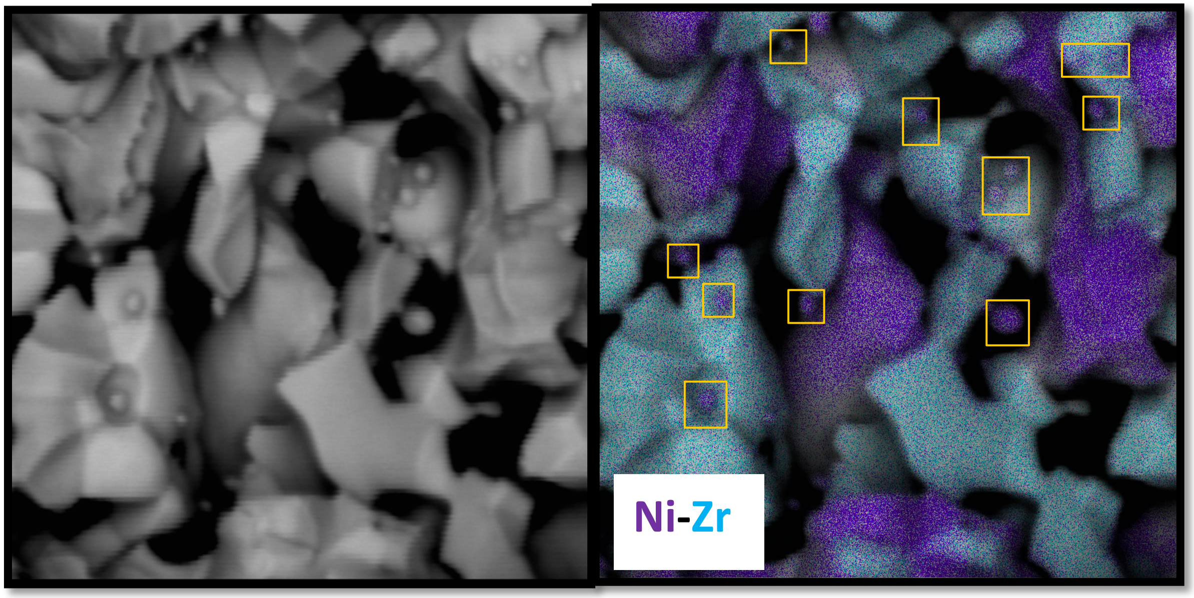


Infiltrated

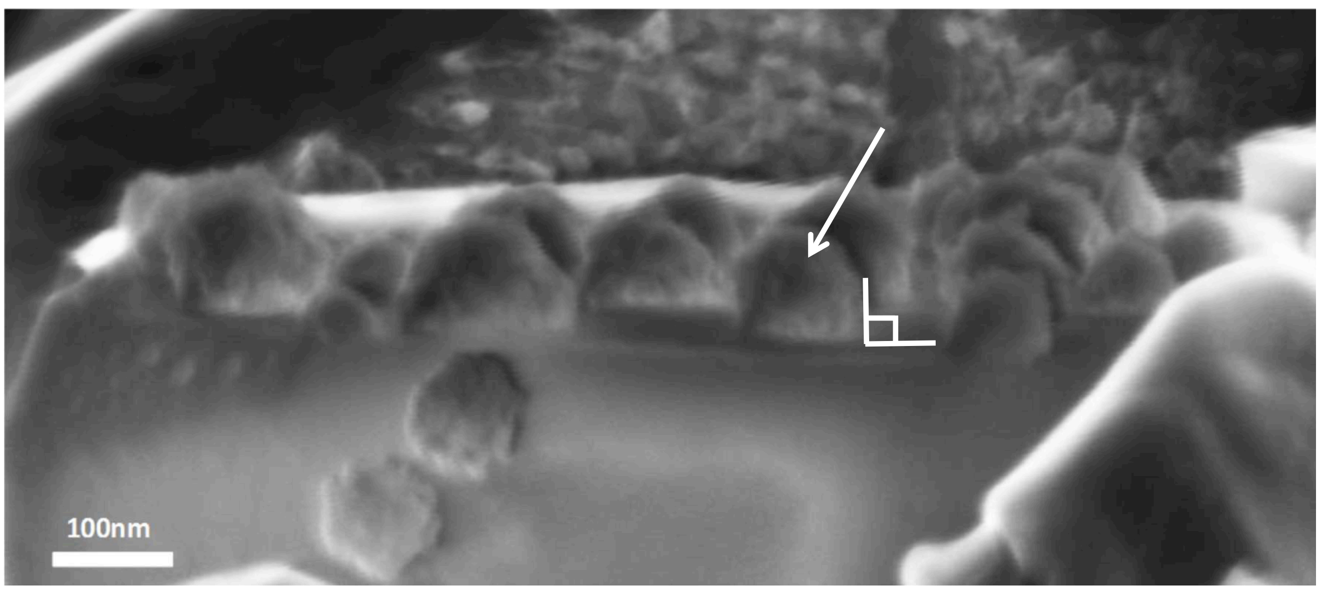


Liquid infiltration of conventional Ni/YSZ cermet can lead to deposition in the anode active layer

Location of Ni Nanoparticles



- Ni nanoparticles on YSZ grains have rounded shapes
- The shape of the nanoparticles are approximately hemispherical



Ni nanoparticles on YSZ grains will create TPBs

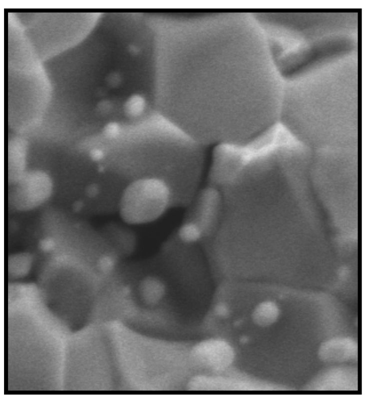
Calculation of Added TPB Density

$$TPB_{inf} = n\pi\bar{d}\left(\frac{S}{V}\right)v$$

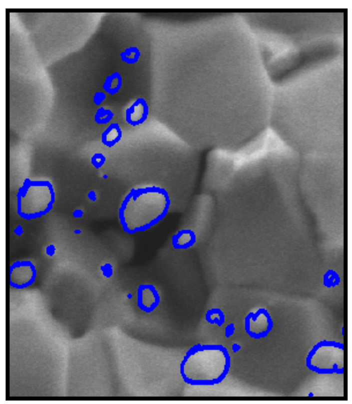
- TPB_{inf}: Additional TPB density in AAL (µm/µm³)
- n: Areal particle density in AAL (#/µm²)
- $\bar{d}$: Average particle diameter in AAL (µm)
- $\frac{S}{V}$: Surface area of pores per unit volume of AAL (µm²/µm³)
- v: Volume fraction of pores in AAL

SEM of Fracture Cross-Sections (areal particle density, average particle diameter)

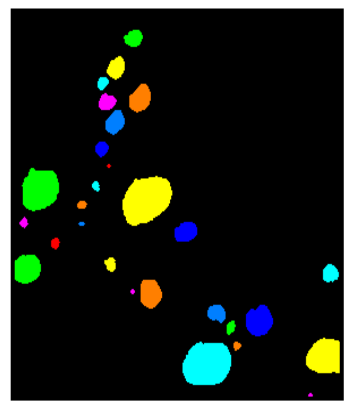
FIB-SEM (surface area of pores per unit volume, volume fraction of pores)



SEM of fracture cross-section



Ni Particle Selection



Particle Separation

Index	Area	Diameter	Volume
1	488.162	24.93085	4056.764
2	1240.75	39.74635	16438.43
3	589.863	27.40505	5388.409
4	325.442	20.35597	2208.229
5	447.482	23.86947	3560.387
6	813.604	32.1856	8728.777
7	772.924	31.37065	8082.375
8	1017	35.98451	12198.75
9	1037.34	36.34257	12566.53
10	874.624	33.37073	9728.948
11	650.883	28.78767	6245.802
12	366.122	21.59076	2634.951
13	589.863	27.40505	5388.409
14	1098.37	37.39637	13691.68
15	976.325	35.25756	11474.28
16	447.482	23.86947	3560.387

Particle Statistics

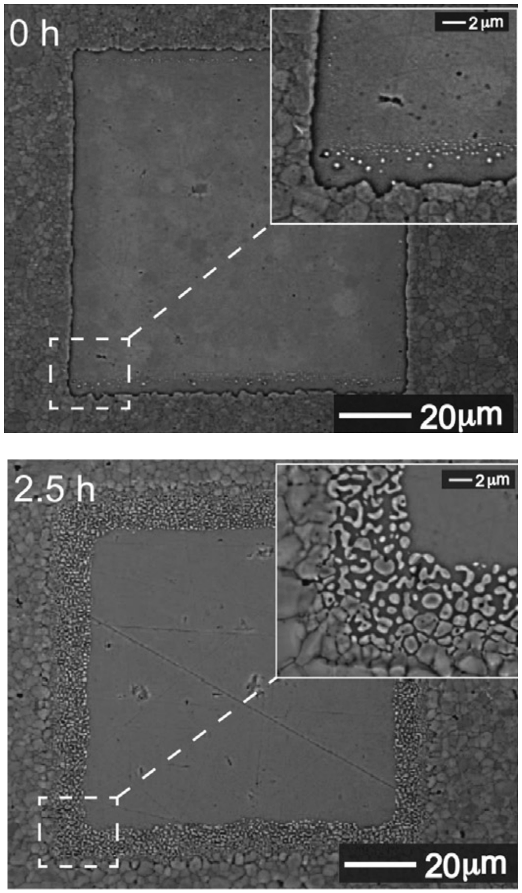
Additional TPB Density

TPB in AAL (μm/μm^3)	
Original Ni/YSZ cermet	2.39
Ni nanoparticles	5.99
Total in infiltrated sample	8.38

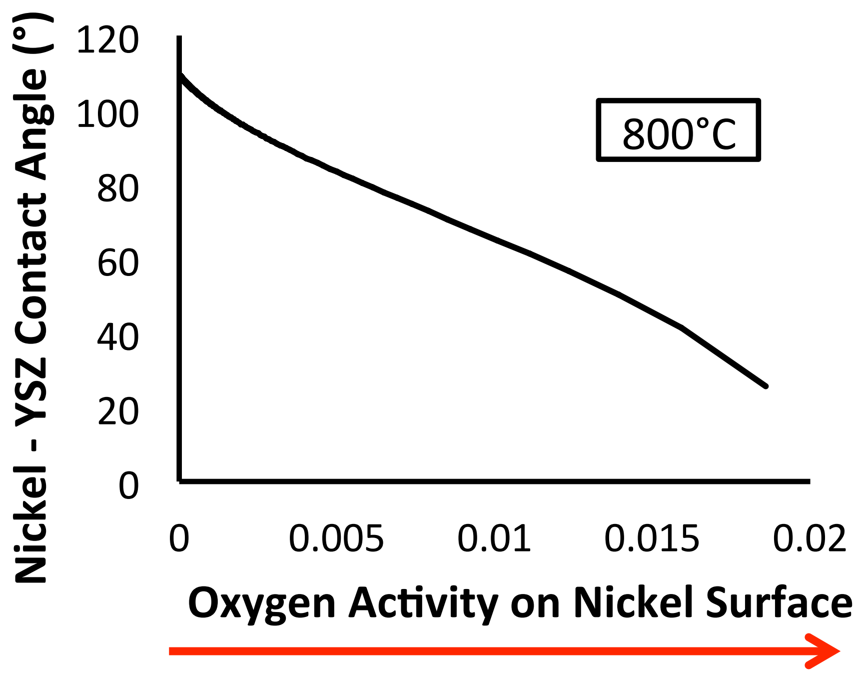
Question?

Are these TPBs active, i.e., are they a part of an electrically conductive pathway?

Creating Percolating Ni Nanoparticles



Ni-YSZ Contact Angle: Thermodynamic Model



Higher current density

Higher cathodic pO_2

Z. Jiao and N. Shikazono, *Acta Mater.*, vol. 135, p. 124-131, 2017

Electrochemical Ni Spreading Procedure

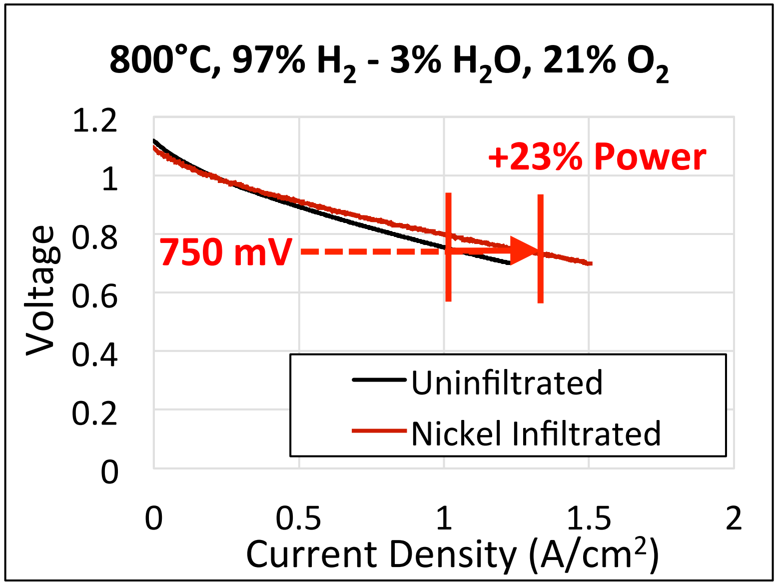
Group 1: With Ni spreading

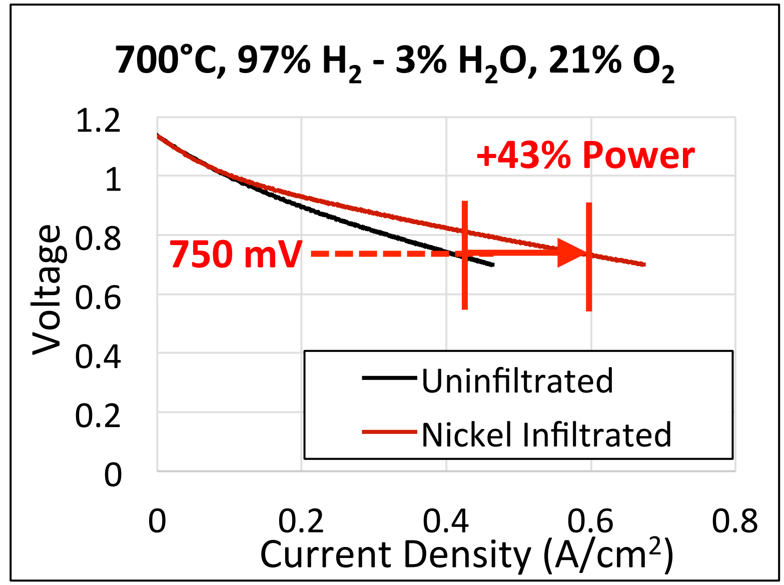
- Ni spreading was carried out at high current densities with:
  - Pure O_2 on cathode side, 97%H_2-3%H_2O on anode side
  - 800°C
  - I-V down to **400 mV** (into the anode mass transfer limit)
- Cathode atmosphere was switched to dry air without cooling
- I-V curves at different temperatures (data presented).

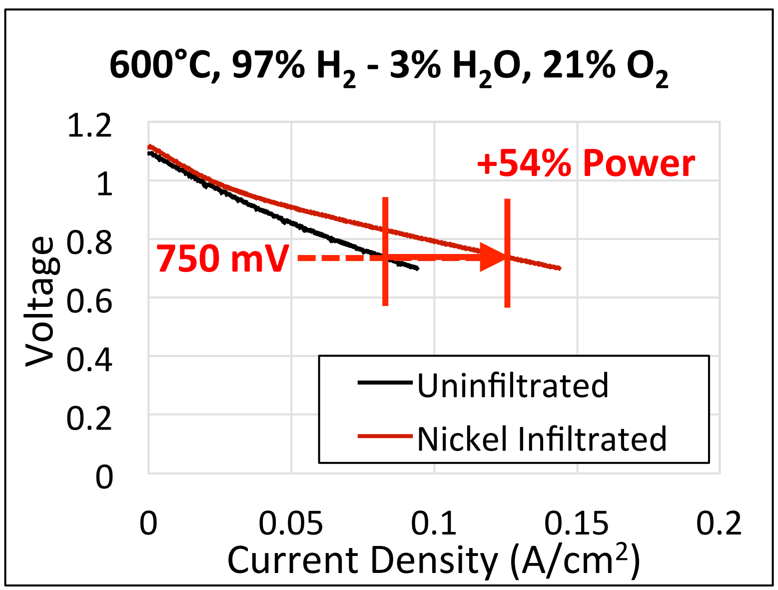
Group 2: No Ni spreading

- I-V measurement carried out at low current densities with:
  - Pure O_2 on cathode side, 97%H_2-3%H_2O on anode side
  - 800°C
  - I-V only to **725 mV** (not into the anode mass transfer limit)
- Cathode atmosphere was switched to dry air without cooling
- I-V curves at different temperatures (data presented).

Group 1: Ni Infiltration with Spreading



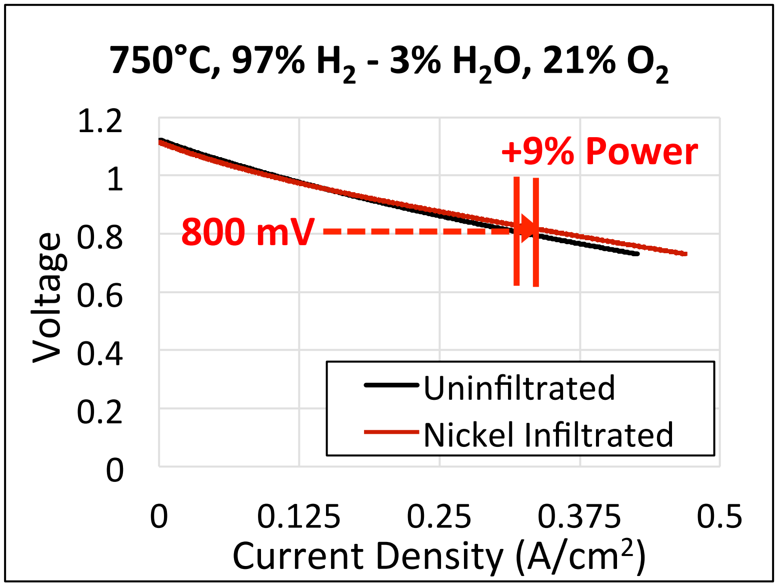


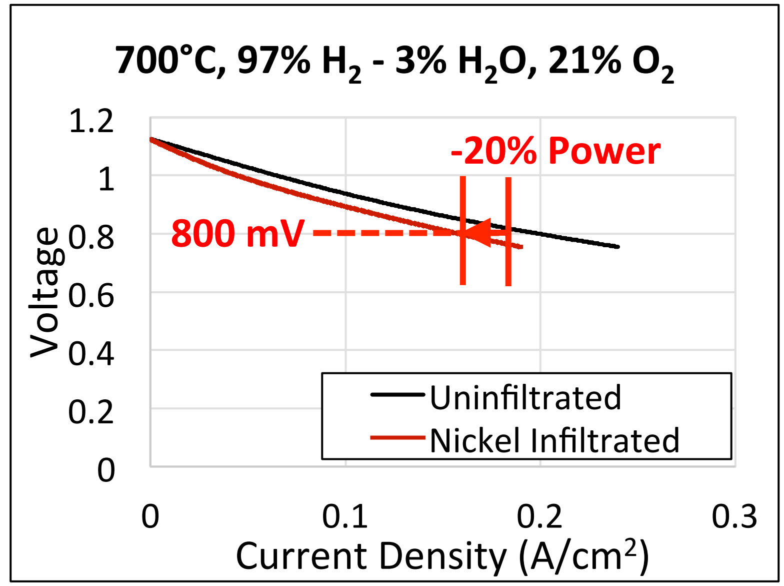


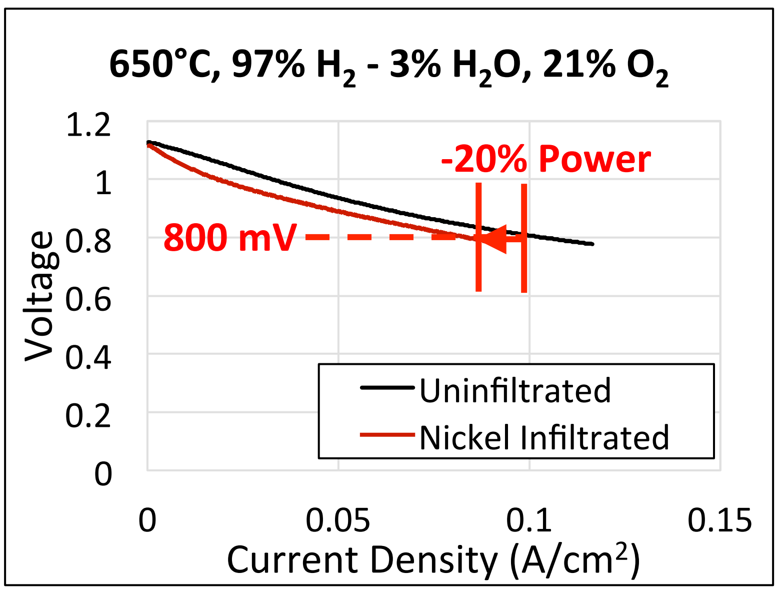
Power Density at 750 mV (W/cm^2)			
Temperature	**Uninfiltrated**	**Ni-infiltrated**	**Change**
800°C	0.762	0.930	+23%
700°C	0.292	0.418	+43%
600°C	0.058	0.090	+54%

- Ni spreading activates infiltrated Ni nanoparticles
- Performance improvement increases with decreasing temperature

Group 2: Ni Infiltration Without Spreading







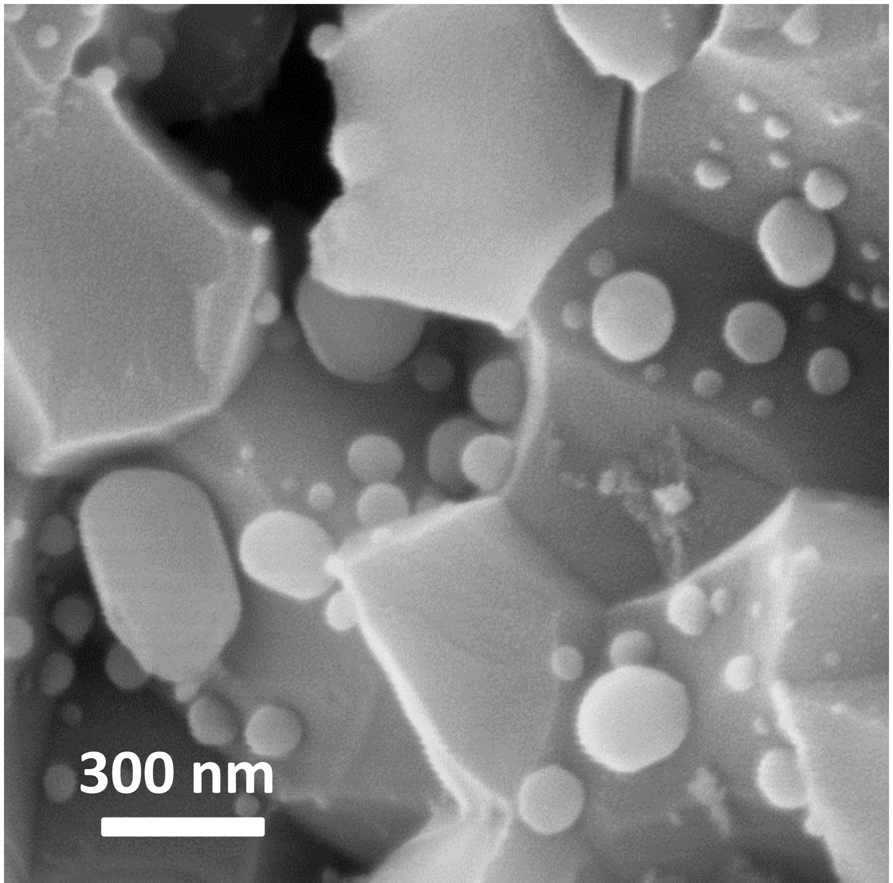
Power Density at 800 mV (W/cm^2)			
Temperature	**Uninfiltrated**	**Ni-infiltrated**	**Change**
750°C	0.264	0.288	+9%
700°C	0.16	0.128	-20%
650°C	0.08	0.064	-20%

- Ni infiltration without Ni spreading is deleterious to cell performance

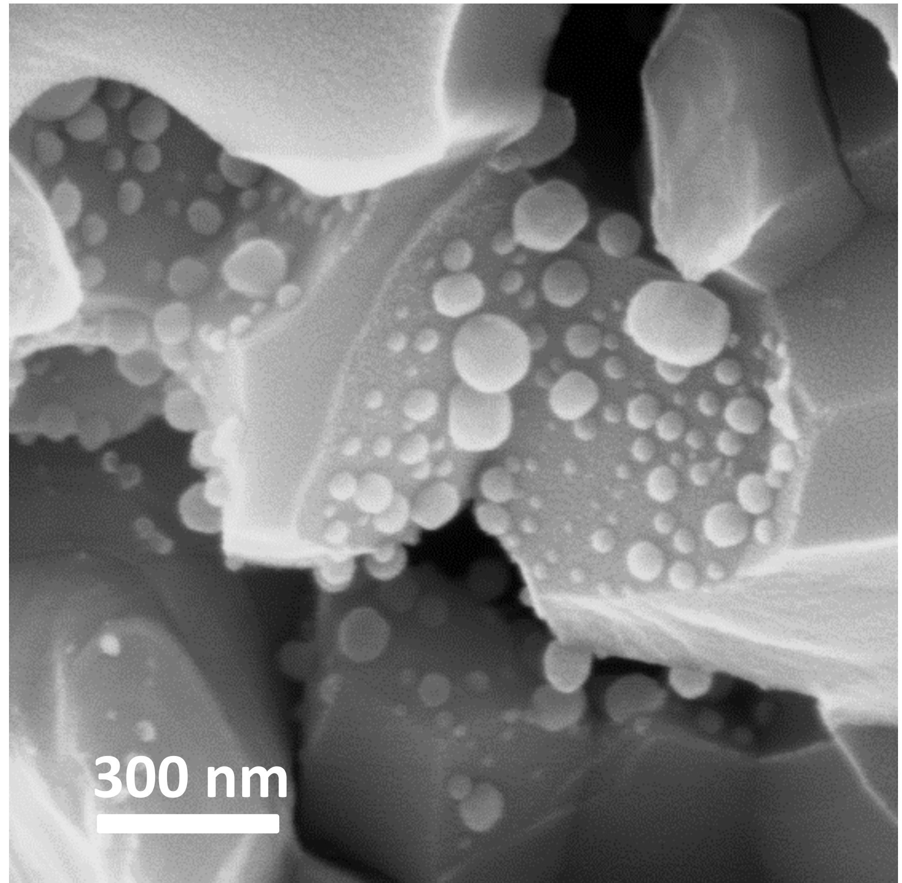
Nanoparticles After High Current Densities

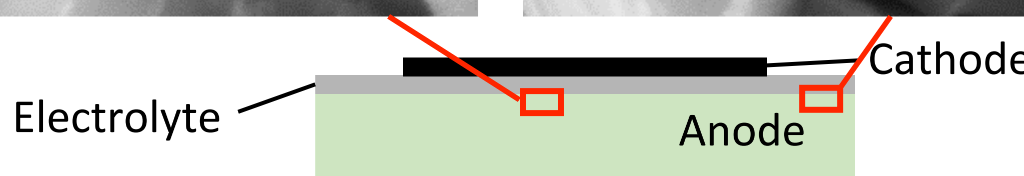
After Ni spreading and electrochemical testing at 800°C

Anode Active layer under cathode
(Electrochemically active)

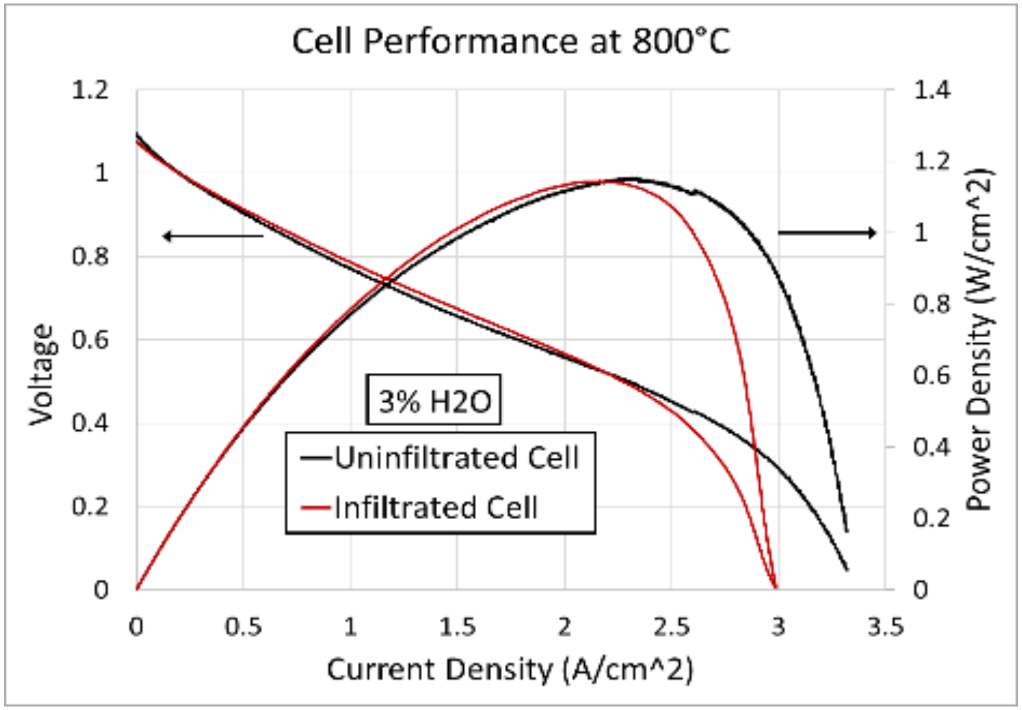


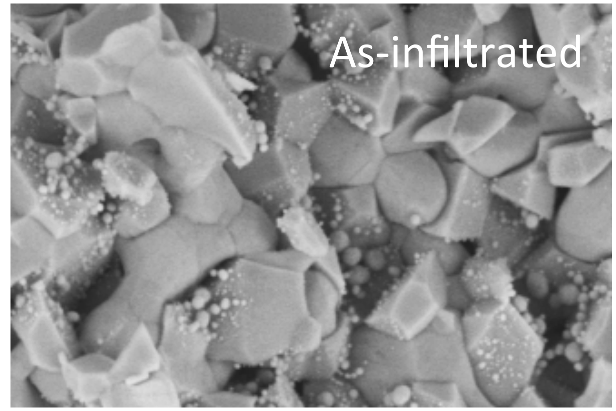
Anode active layer not under cathode
(Electrochemically inactive)

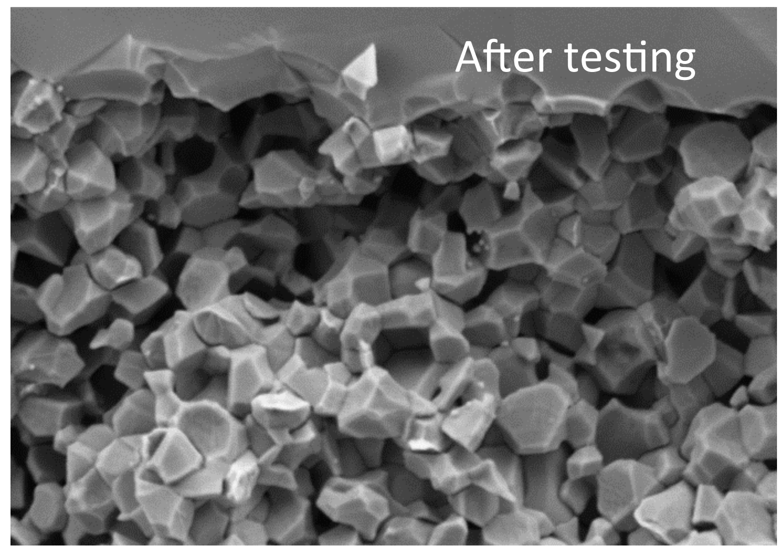




Nanoparticles After Extreme Current Densities



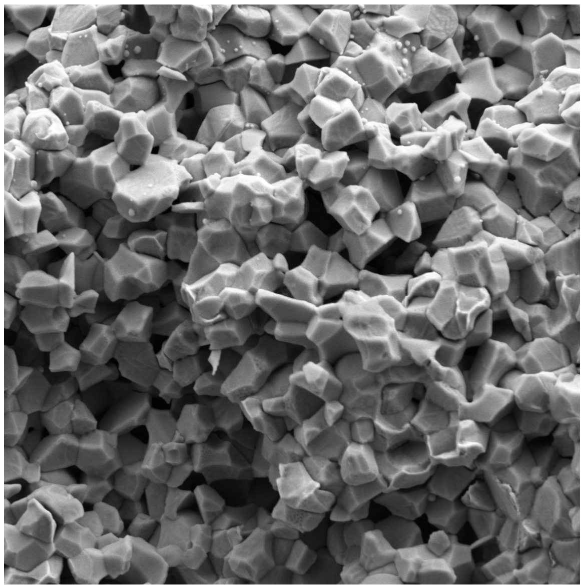




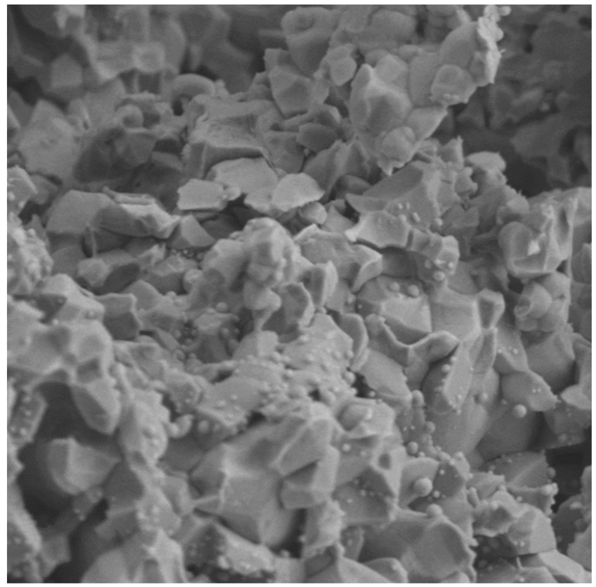
Ni mostly nanoparticles disappeared from the AAL at extremely high current densities

Nanoparticles After Extreme Current Densities

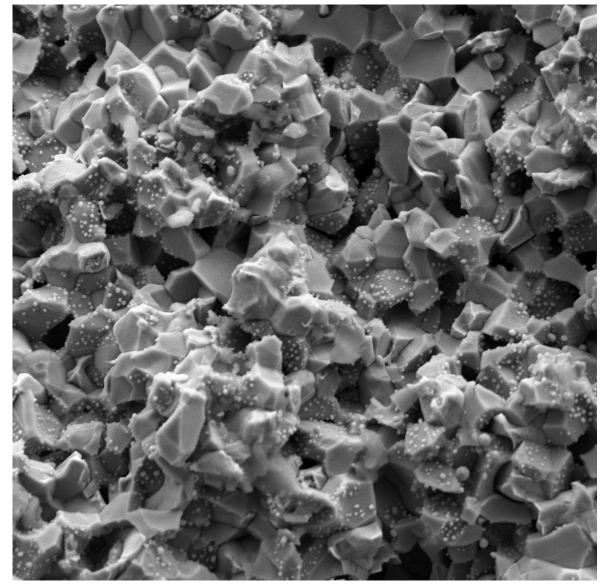
Anode Active layer under cathode
(Electrochemically active)



Anode bulk layer under cathode
(Electrochemically active)



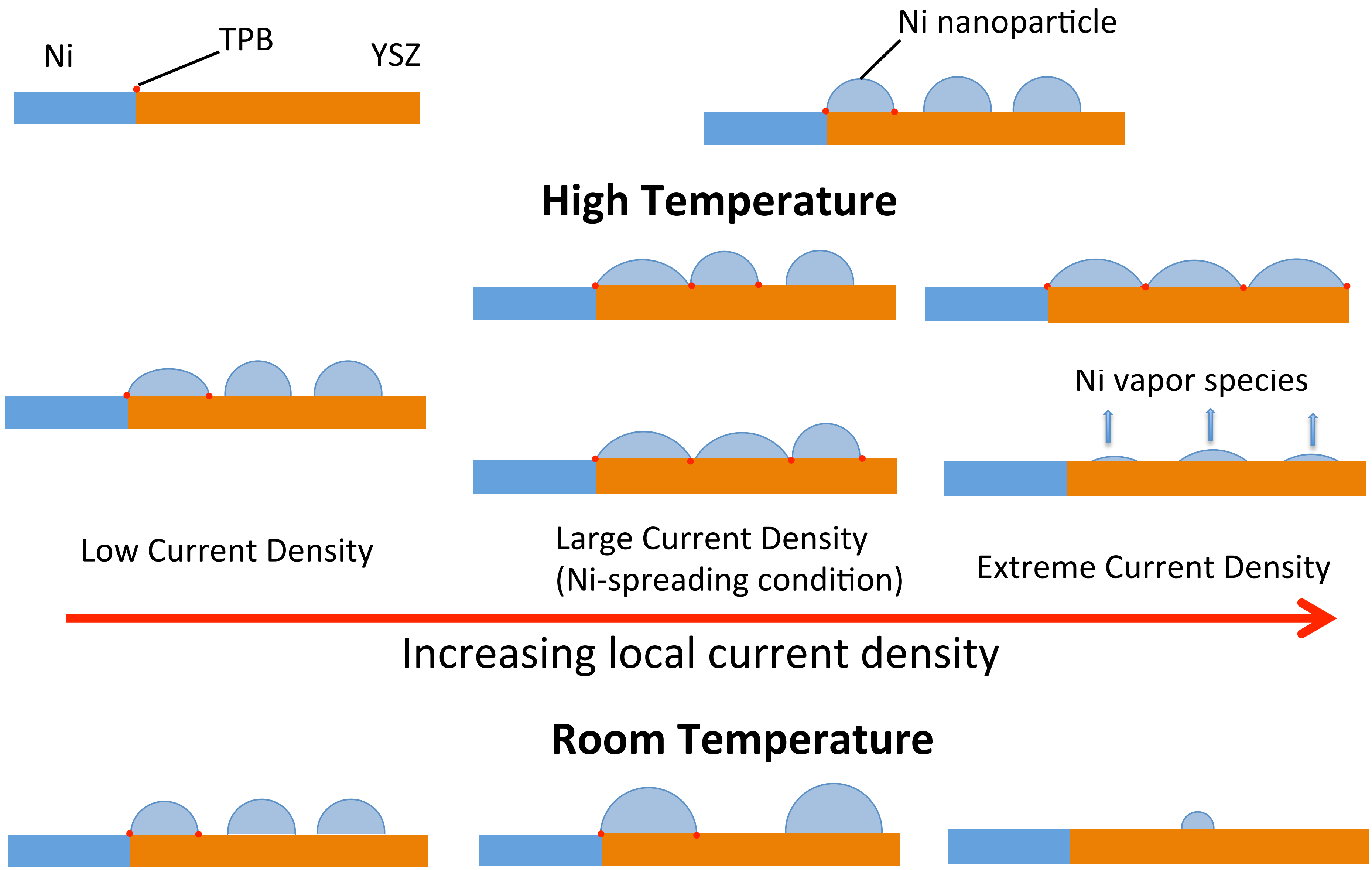
Anode active layer not under cathode
(Electrochemically inactive)



	Electrochemically active AAL	**Electrochemically active bulk anode**	**Electrochemically inactive AAL**
Particle Density (#/μm^2)	**1.37**	**8.42**	**15.42**
Particle Volume (nm^3/nm^2)	**0.367**	**0.878**	**1.98**

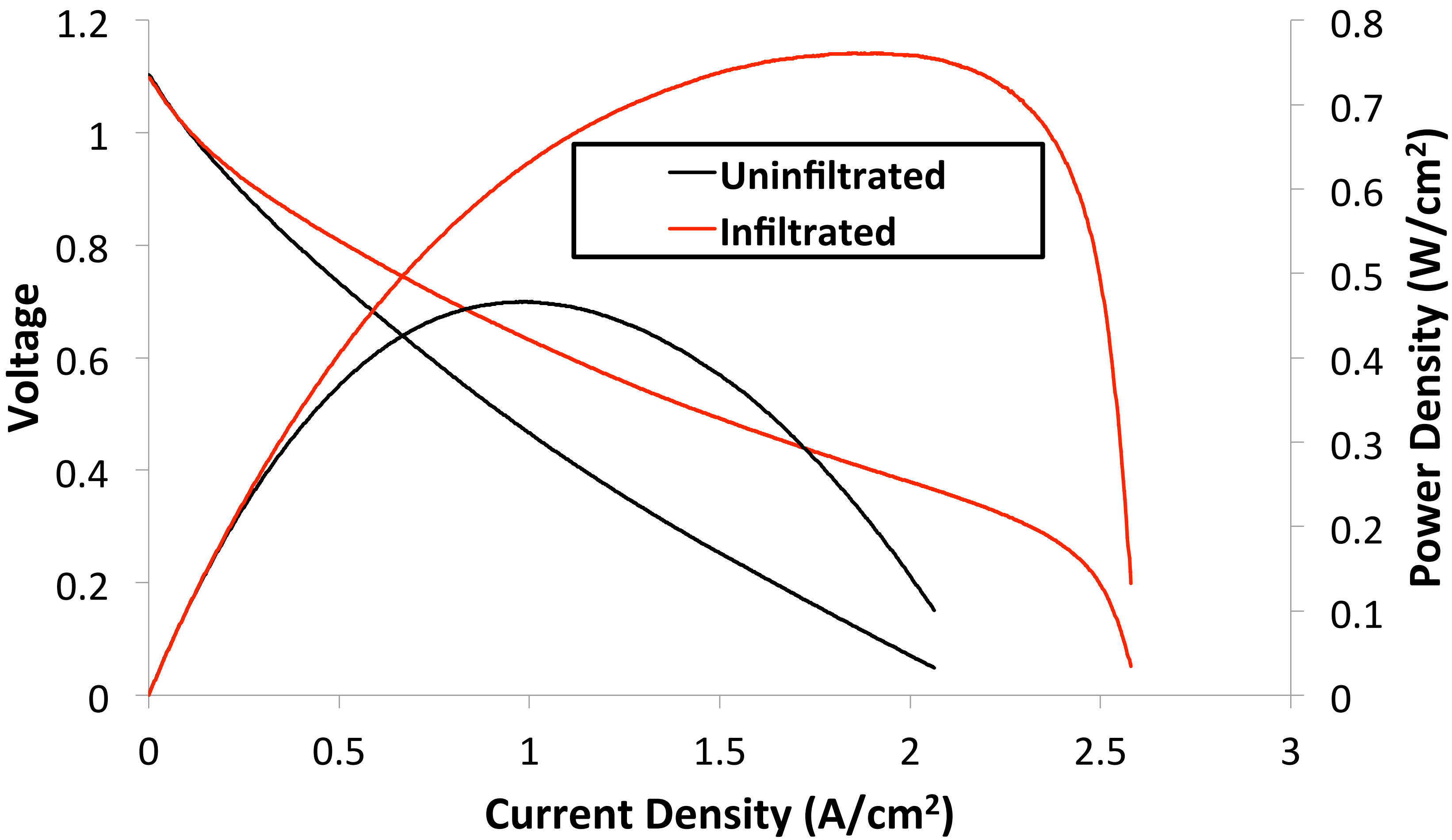
→ Decreasing local current density

Mechanism of Morphology Changes



Reducing Local Current Density by using MIEC

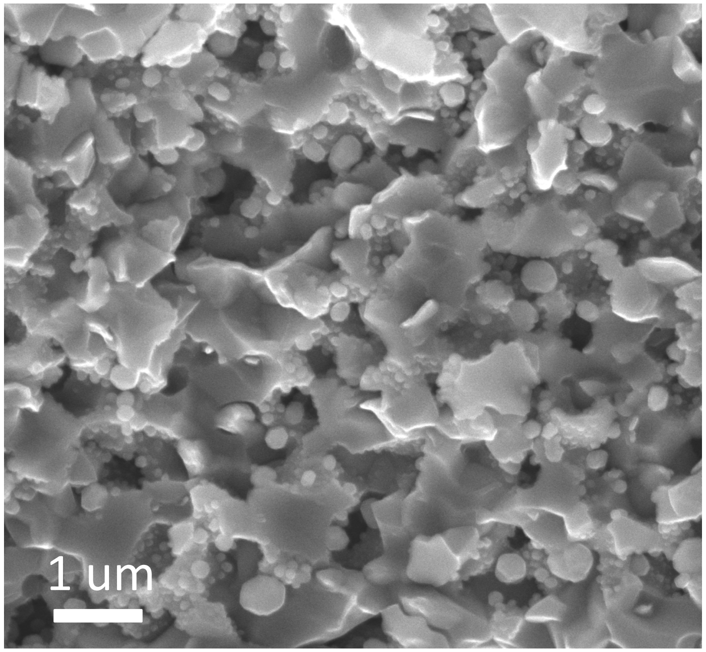
Replace Ni/YSZ with Ni/GDC Anode Active Layer
Infiltrate Ni, expose to extreme current condition at 800°C



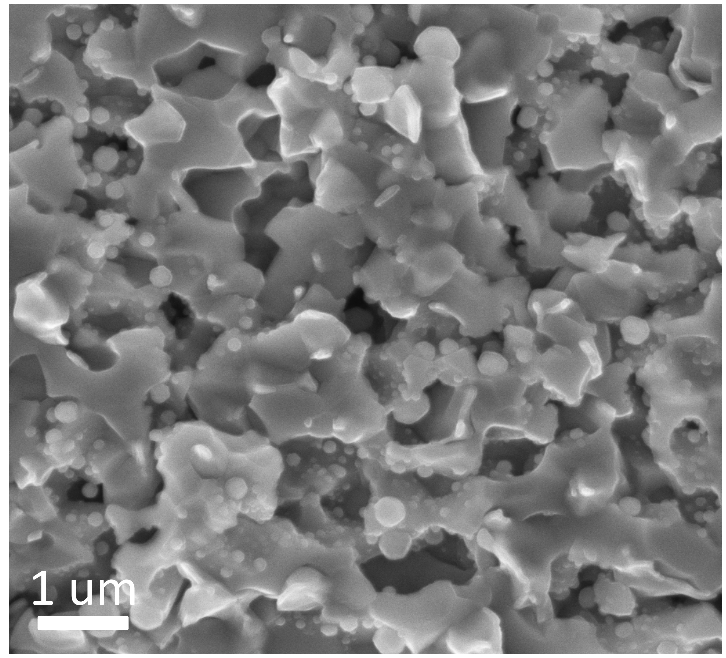
Overall performance poorer, but positive infiltration effects remain

Ni Nanoparticles in Ni-GDC AAL at 800°C

AAL not under cathode
(Electrochemically inactive)



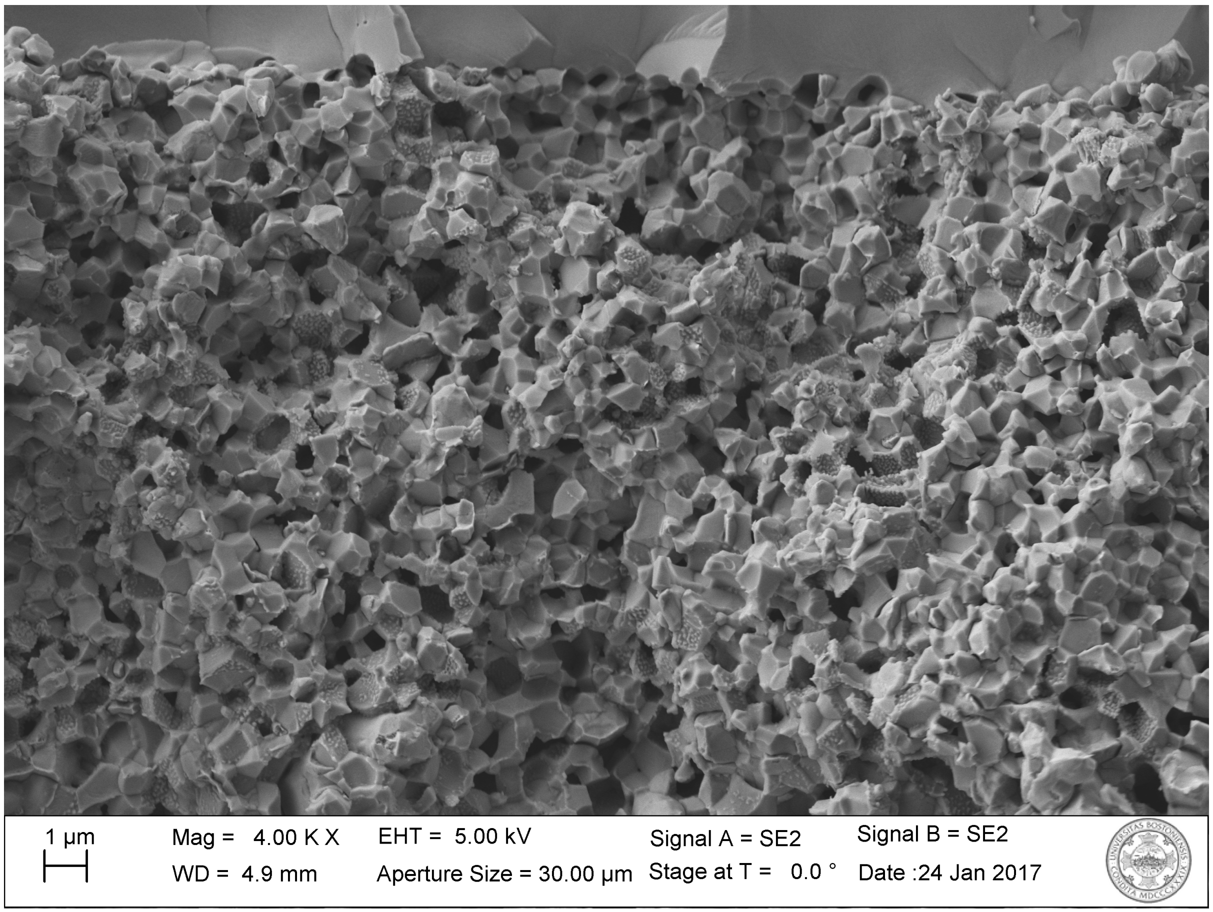
AAL under cathode
(Electrochemically active)

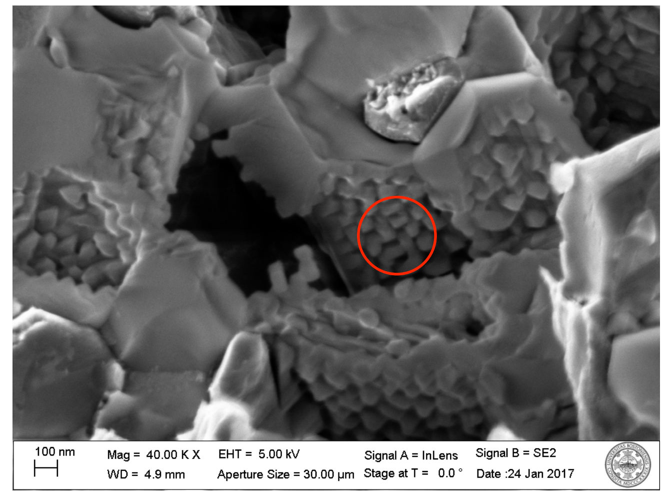


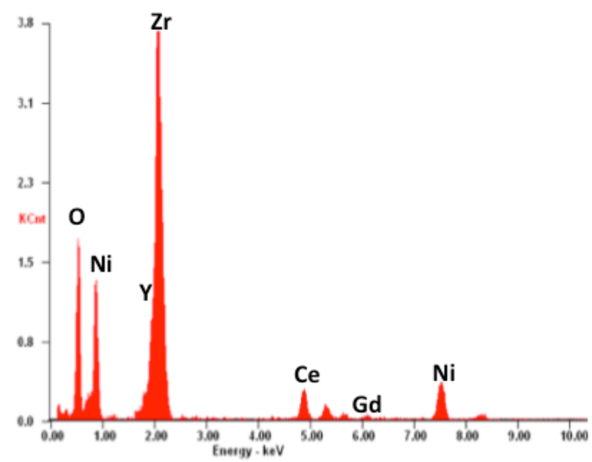
	Not Under Cathode	Under Cathode
Particle Density (#/μm²)	5.50	4.13
Average Diameter (nm)	113.72	130.94
Particle Volume (nm³/nm²)	4.45	4.24

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

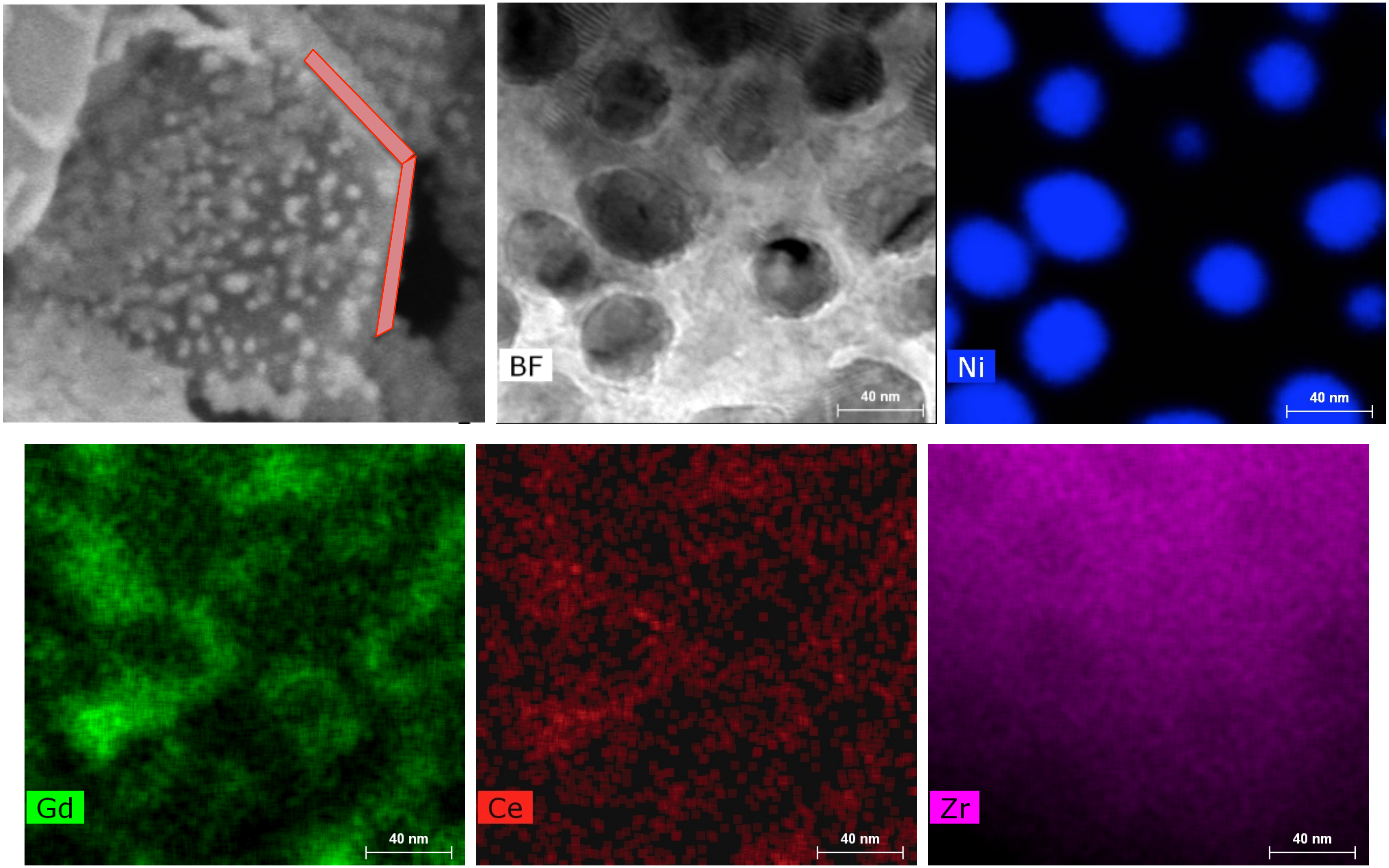




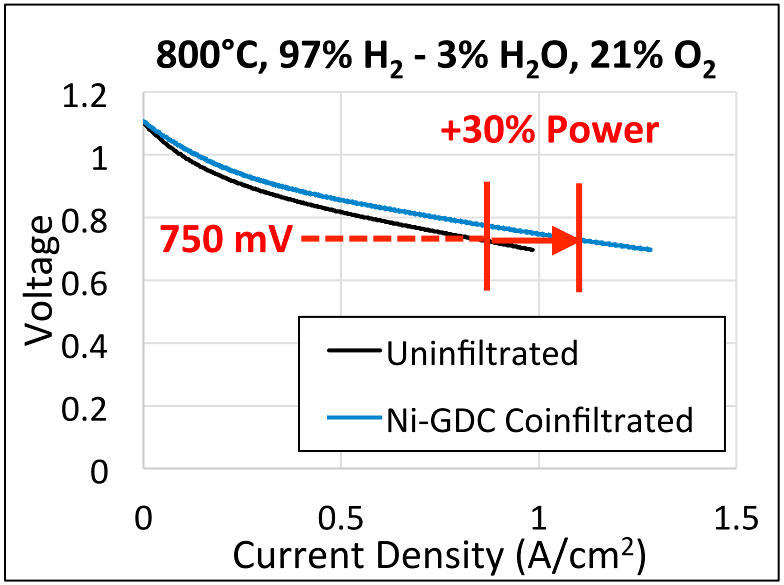


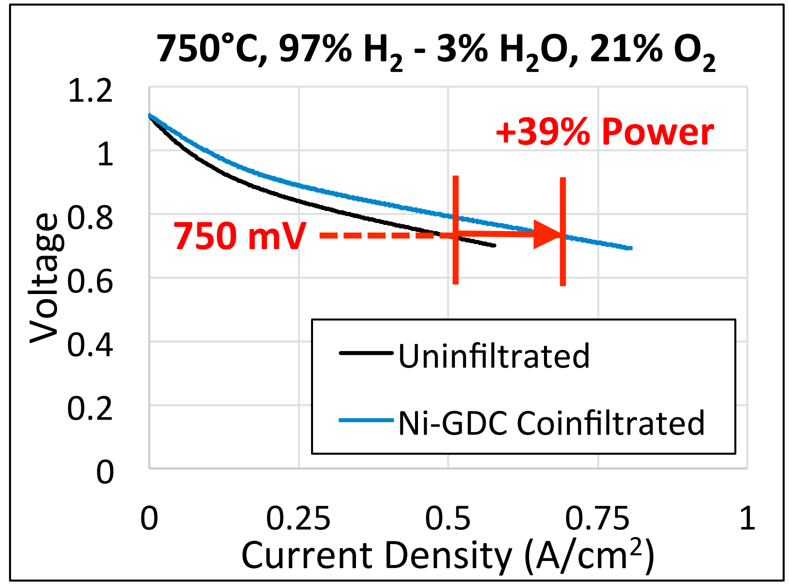
Ni:GDC molar ratio of 1:1

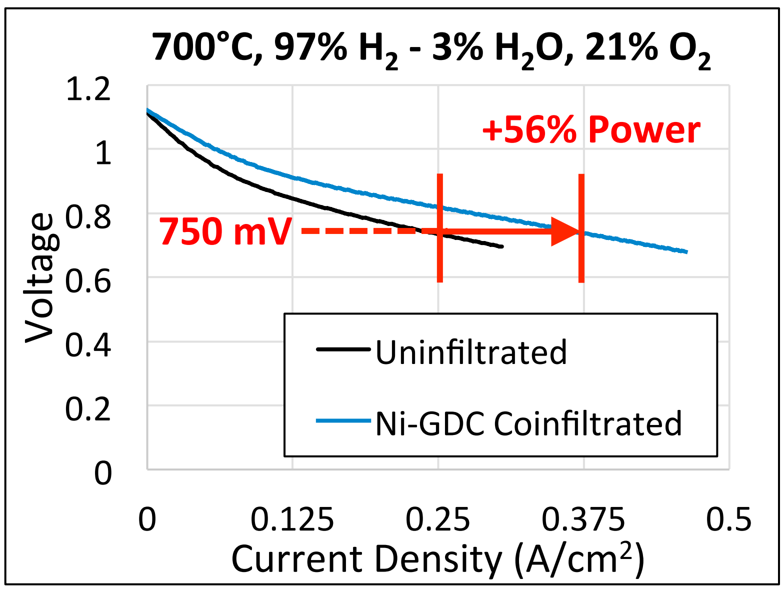
TEM of Ni/GDC Nanoparticles in Top View



Ni-GDC Co-infiltration With No Spreading



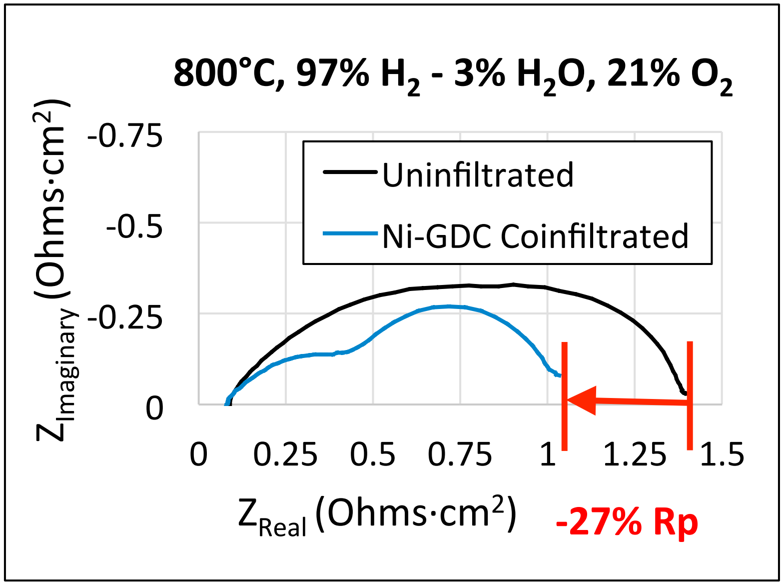


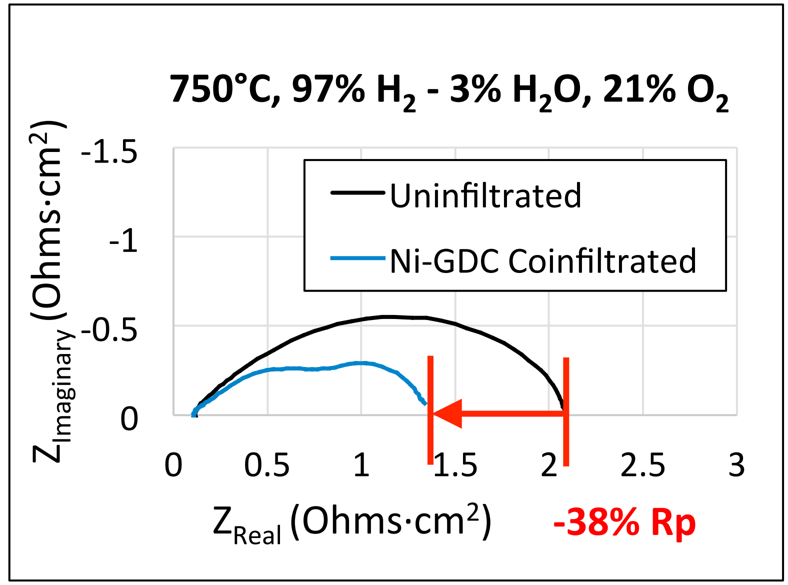


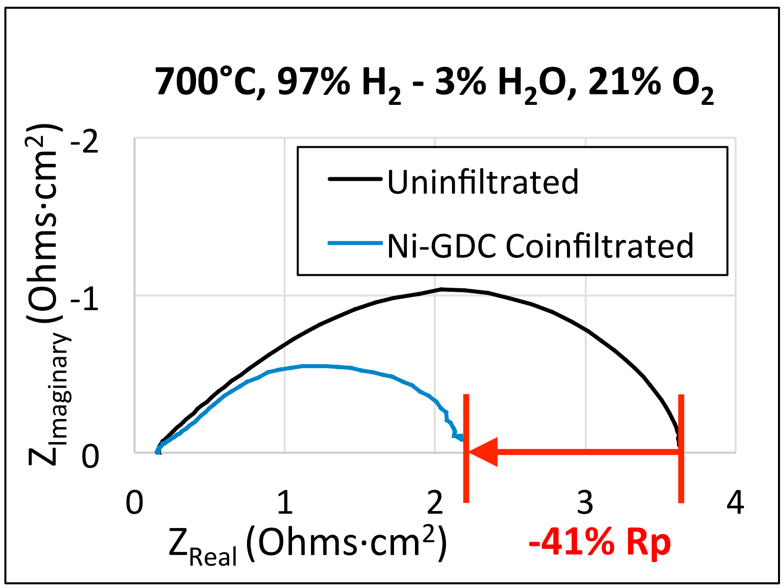
Power Density at 750 mV (W/cm^2)			
Temperature	Uninfiltrated	Ni-GDC Coinfiltrated	Change
800°C	0.57	0.74	+30%
750°C	0.34	0.47	+39%
700°C	0.17	0.27	+56%

- Ni-GDC infiltration is effective even without Ni spreading

Ni-GDC Co-infiltration With No Spreading







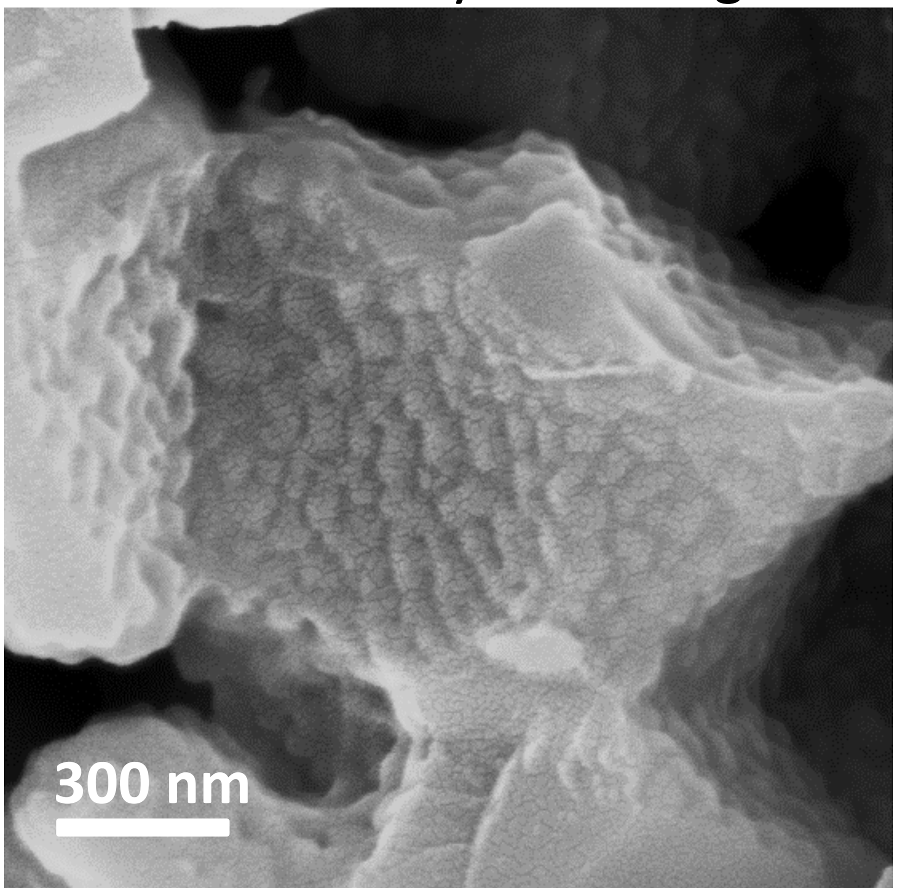
$R_p (\Omega \cdot cm^2)$			
Temperature	**Uninfiltrated**	**Ni-GDC Coinfiltrated**	**Change**
800°C	1.31	0.95	-27%
750°C	1.97	1.23	-38%
700°C	3.47	2.05	-41%

- Ni-GDC co-infiltration reduces activation polarization

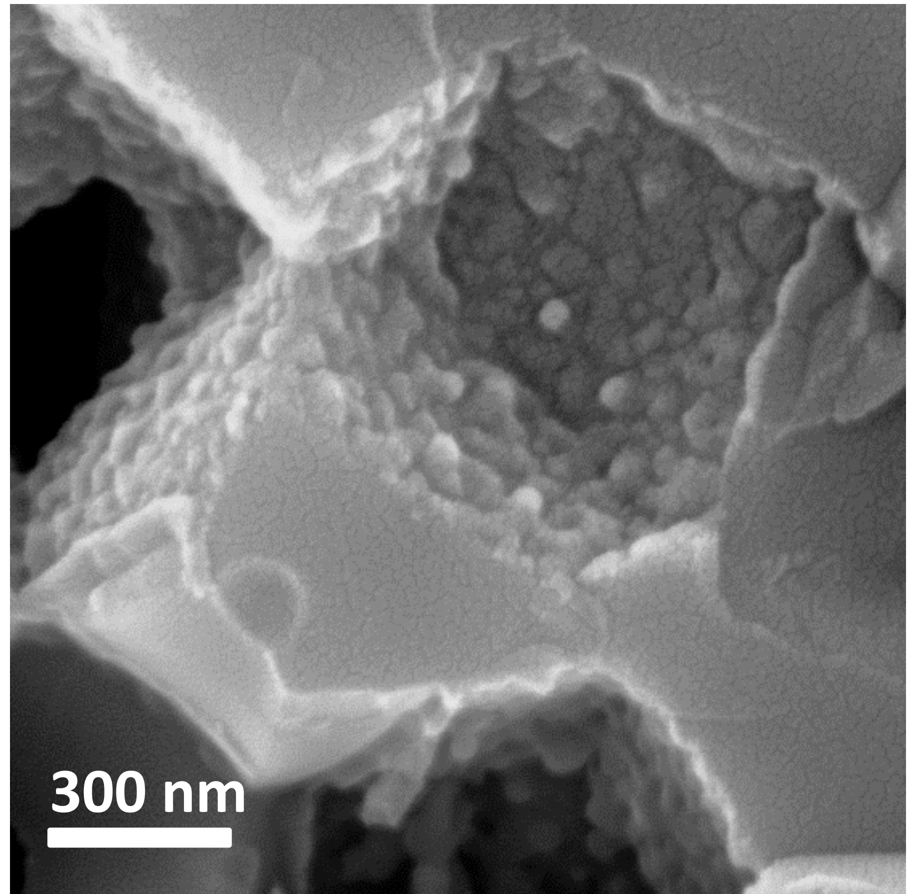
Morphological Stability of Ni-GDC

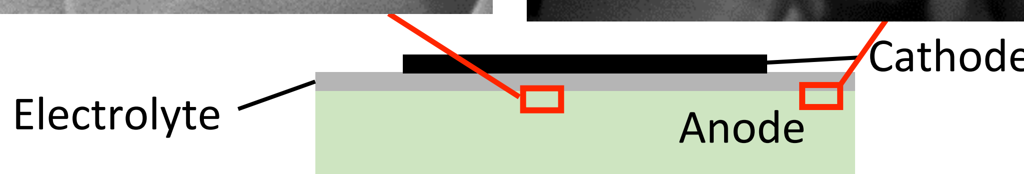
Co-infiltrated Ni-GDC sample was subject to extreme current density

Electrochemically active region



Electrochemically inactive region

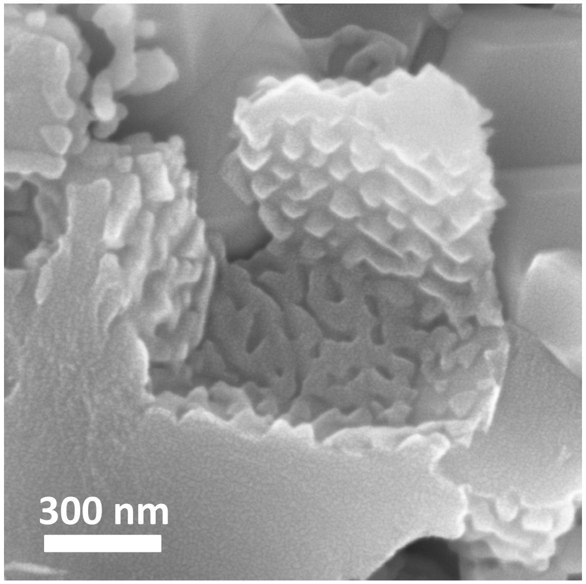


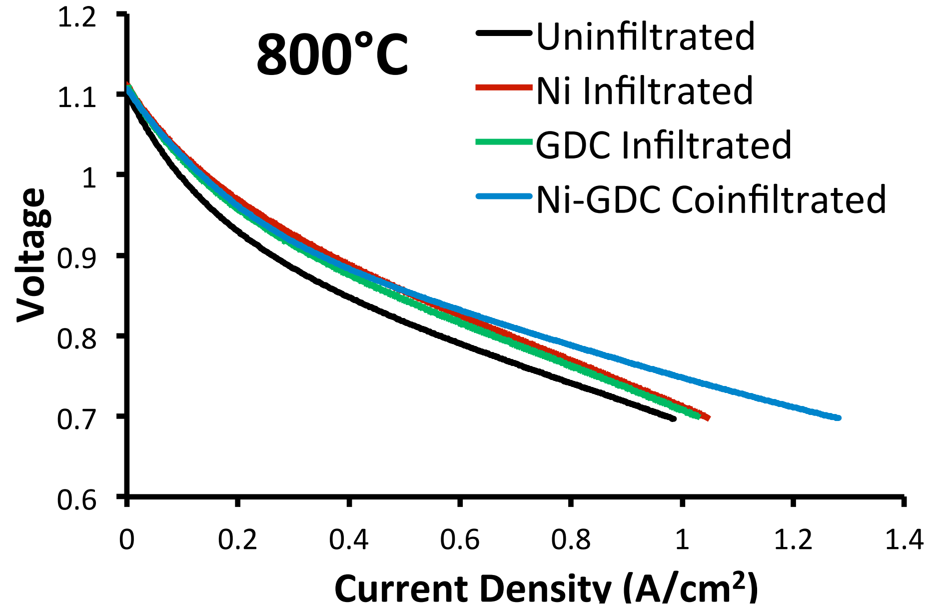


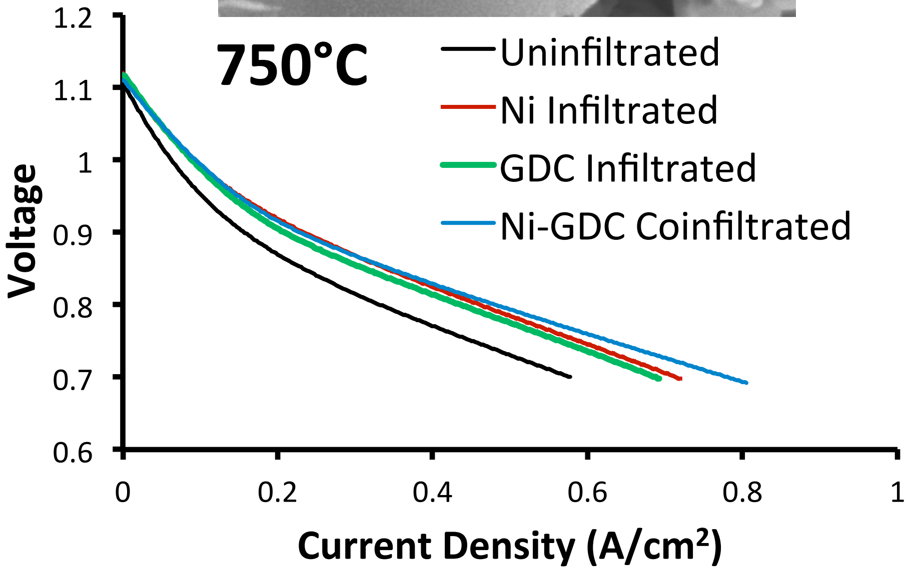
- Ni-GDC morphology is extremely stable

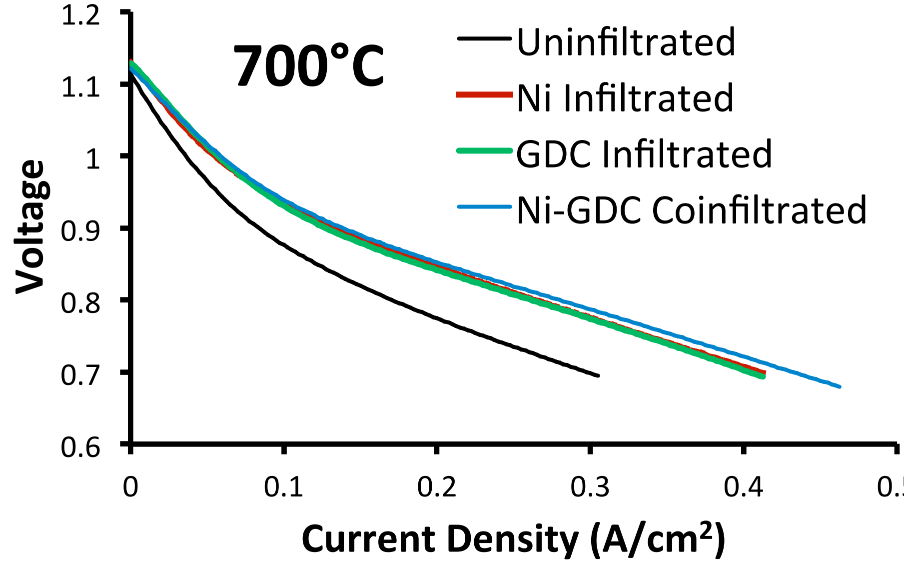
GDC Infiltration

97% H_2 - 3% H_2O, 21% O_2





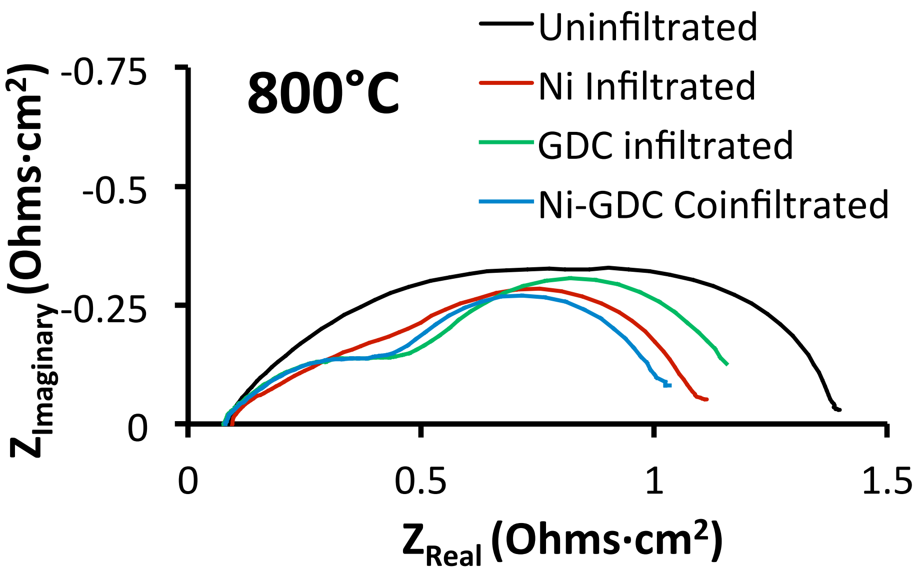


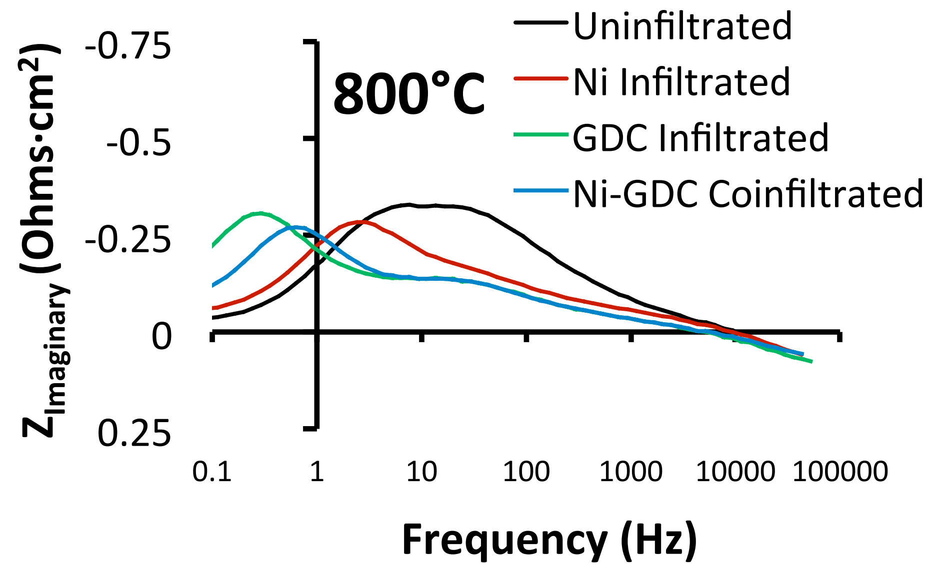


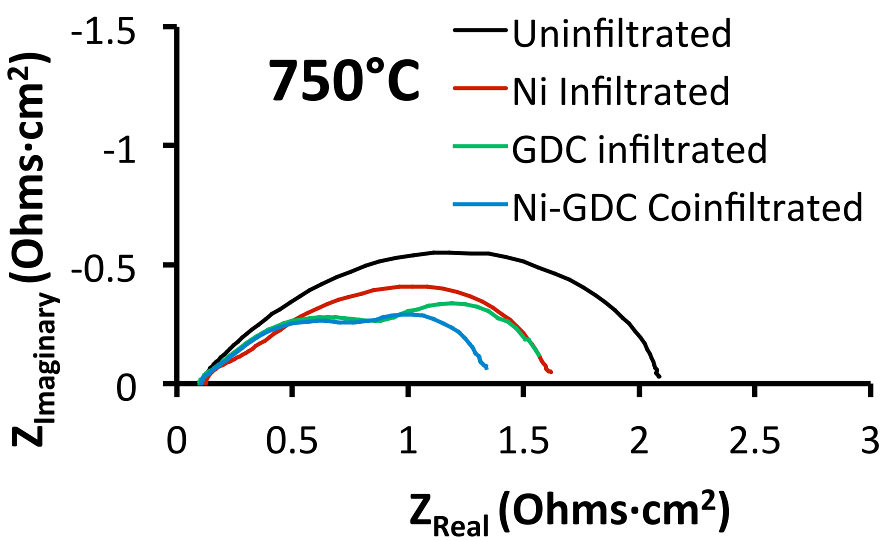
GDC nanoparticles have catalytic activity

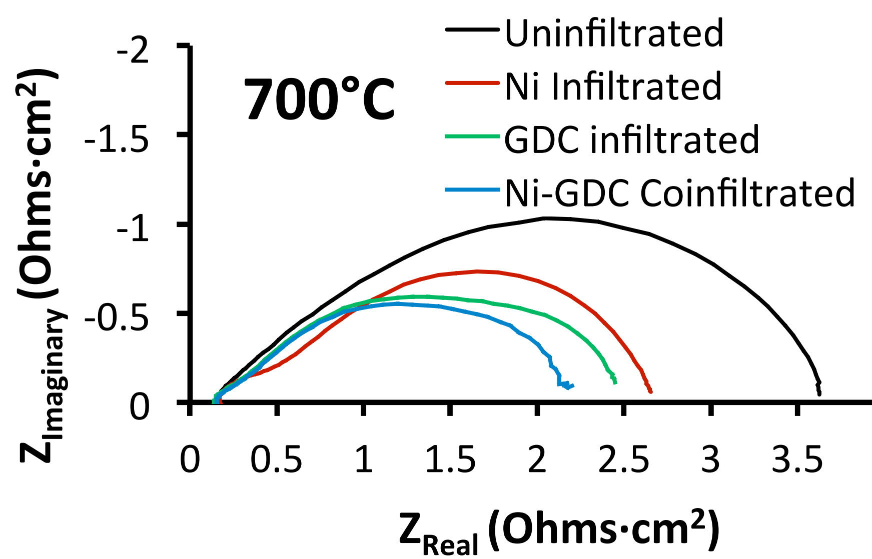
Activation Polarization of Infiltrated Cells

97% H_2 - 3% H_2O, 21% O_2



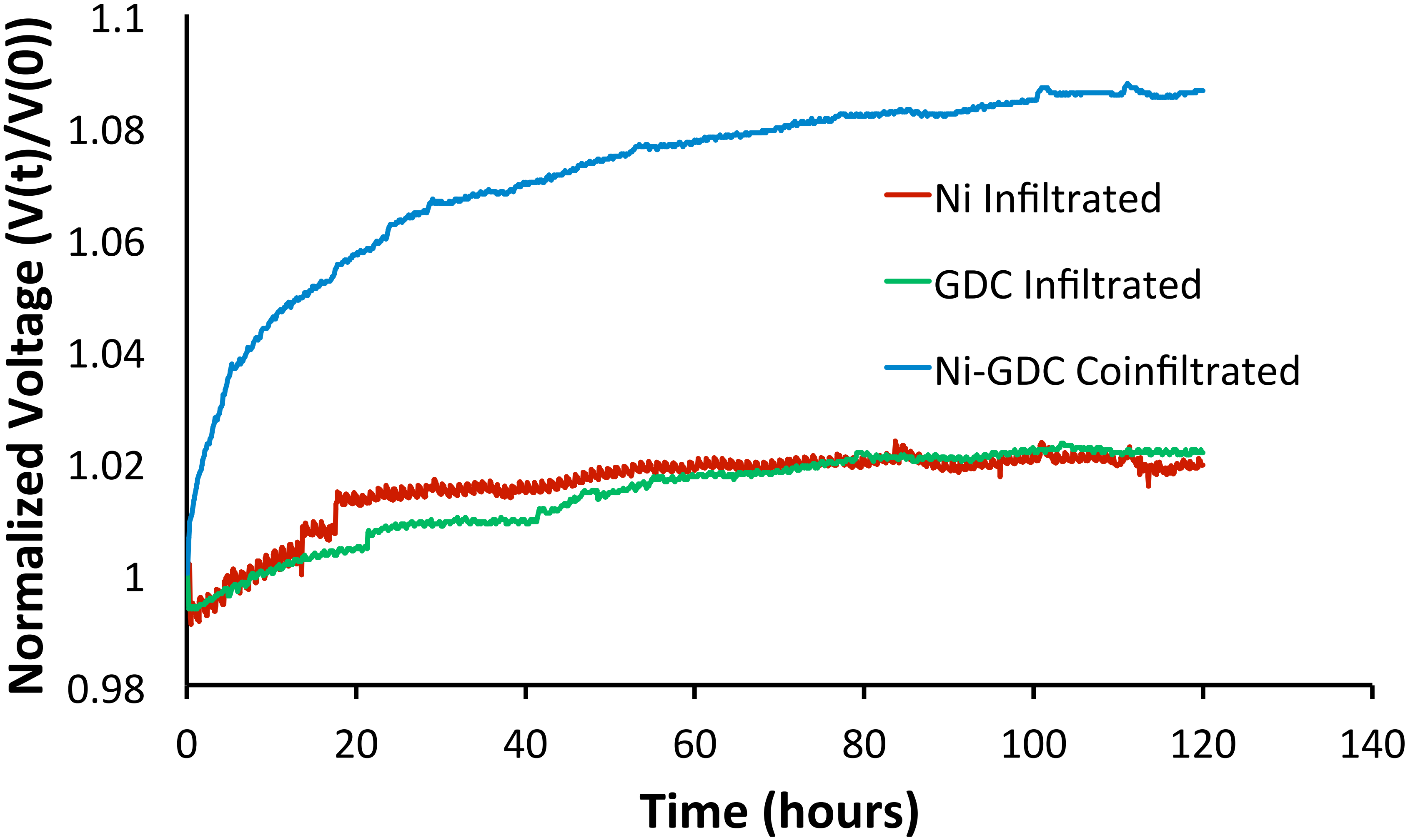






Nanoparticles Stability Test

1 A·cm^{-2} current, 120h, 800°C, 97% H_2-3% H_2O, 21% O_2



Conclusions

- Ni infiltration is ineffective if Ni nanoparticles are not percolating
- An initial exposure to anodic concentration polarization conditions is required to spread and percolate the Ni nanoparticles and improve cell performance
- On cooling, percolated nanoparticles exhibit some coarsening without significant material loss
- Exposure to very high current densities should be avoided since it leads to material loss
- Co-infiltration of Ni-GDC is an effective way to provide stable, electrically percolating Ni nanoparticles with morphological stability that leads to improved performance and lower polarization resistance
- Infiltrated GDC appears to have catalytic activity

Acknowledgements

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

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