BOSTON UNIVERSITY

Deposition of Nickel Nanoparticles in SOFC Anodes to Improve Performance

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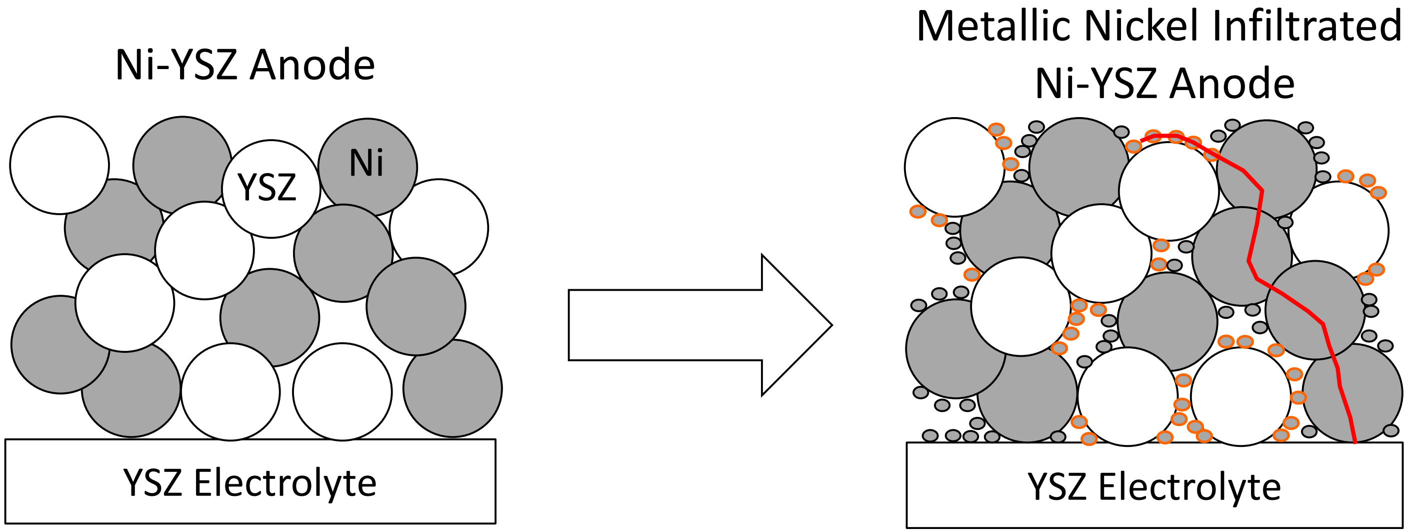
Motivations for Anode Infiltration

- Incorporation of alternate materials for
  - Sulfur tolerance
  - Coking tolerance
- Ni reduction
- Increase in TPB density
  - decrease in activation polarization
  - Increase in anodic exchange current density

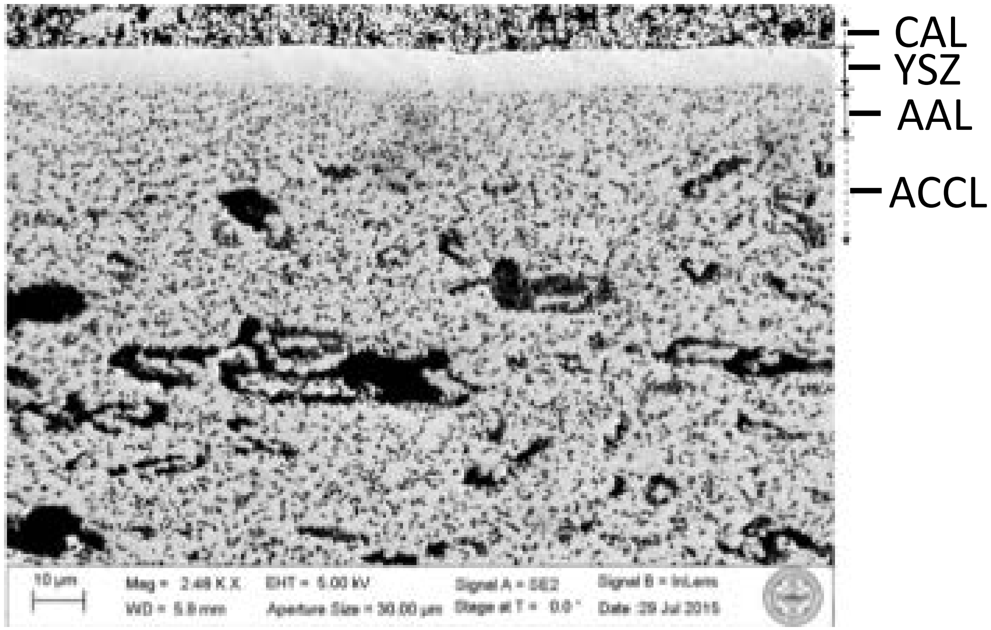
Research Approach

- Ni infiltration of commercial Ni/YSZ cermet anodes
  - Ni/YSZ anodes are already percolating
- Explore liquid phase and vapor phase infiltration
- 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?

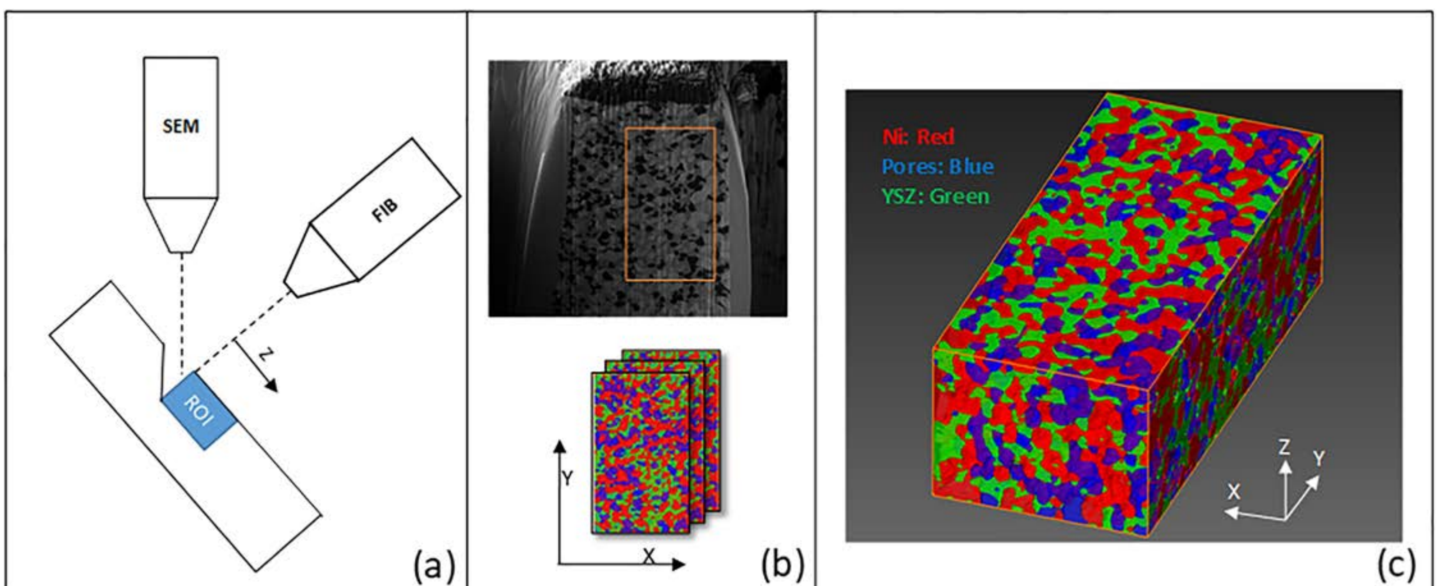


Characterization of Button Cell Microstucture

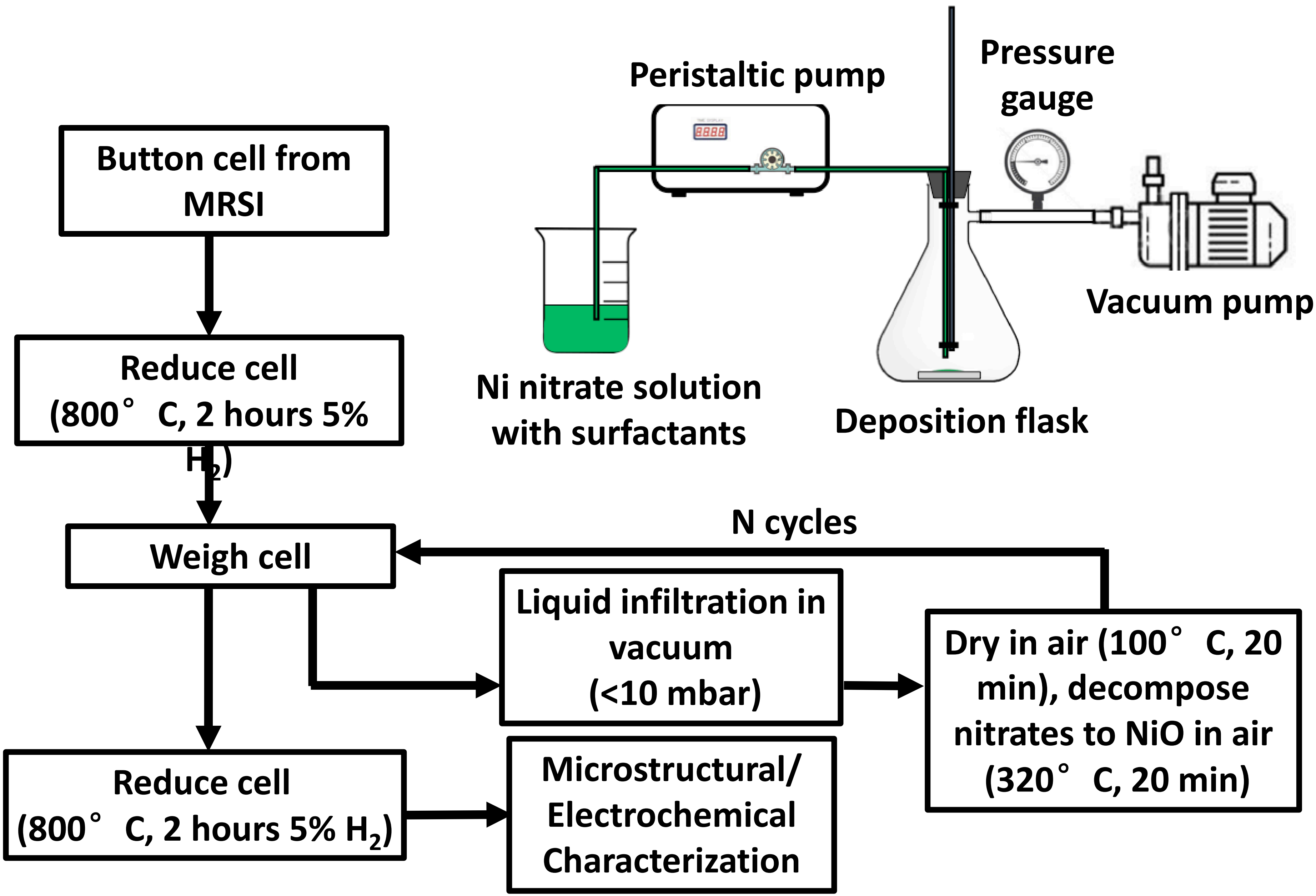
SEM



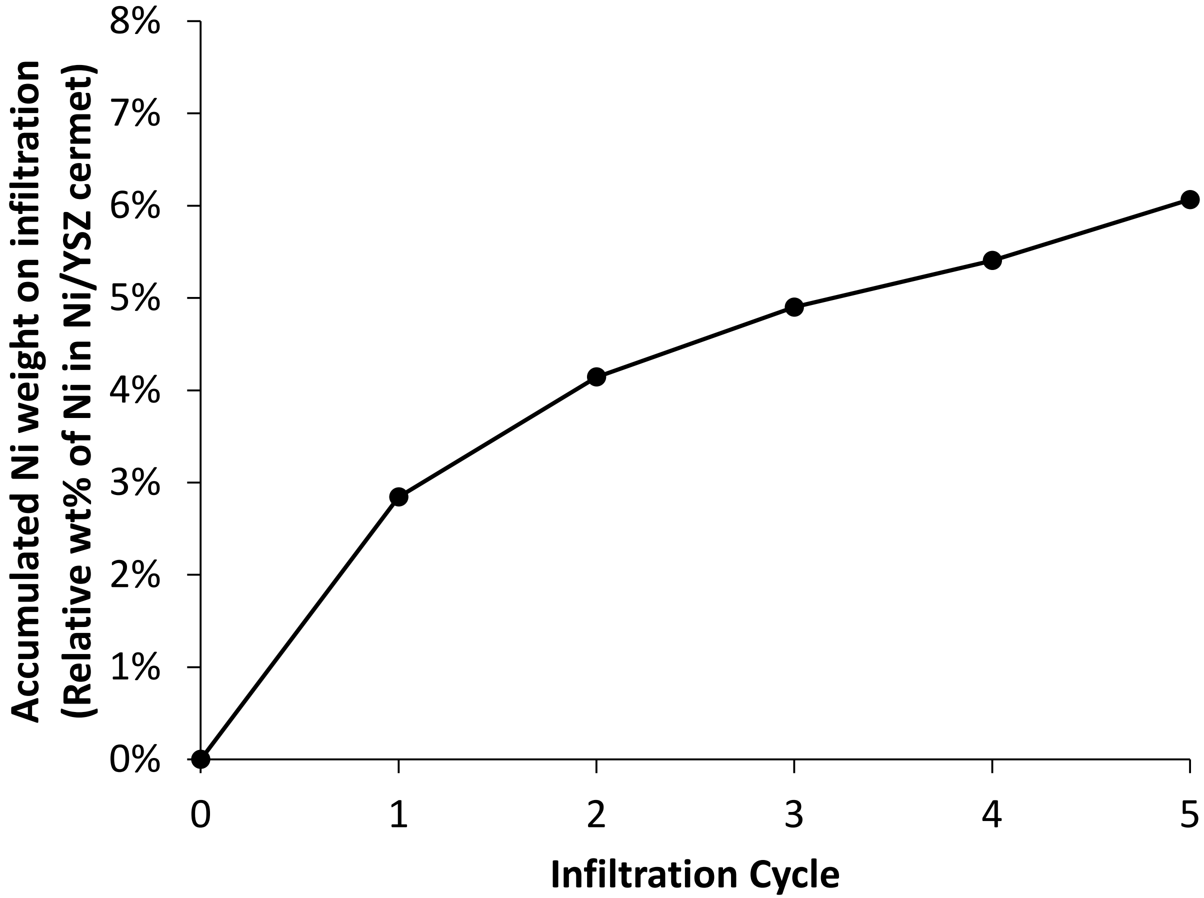
Phase	Volume Fraction	TPB density (μm μm^{-3})
Nickel	38.8%	2.39
YSZ	32.5%	
Pores	28.7%	



Liquid Infiltration of Ni-YSZ Anodes



Results of Liquid Infiltration

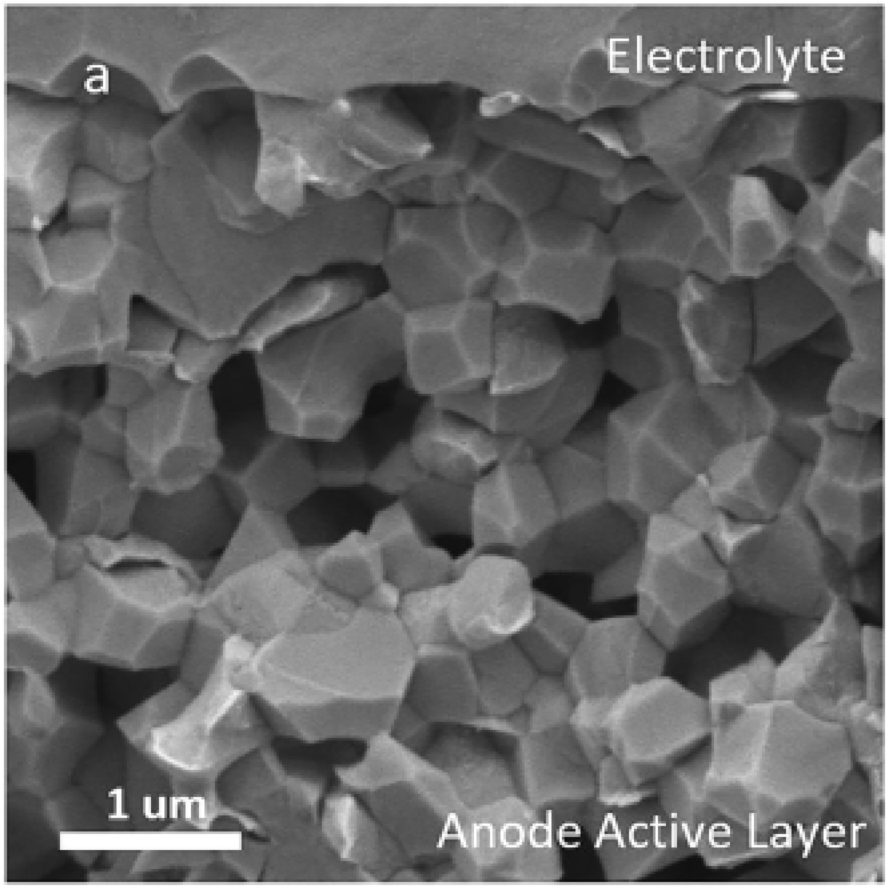


For the reduced sample, after 5 cycles, the infiltrated Ni content is:

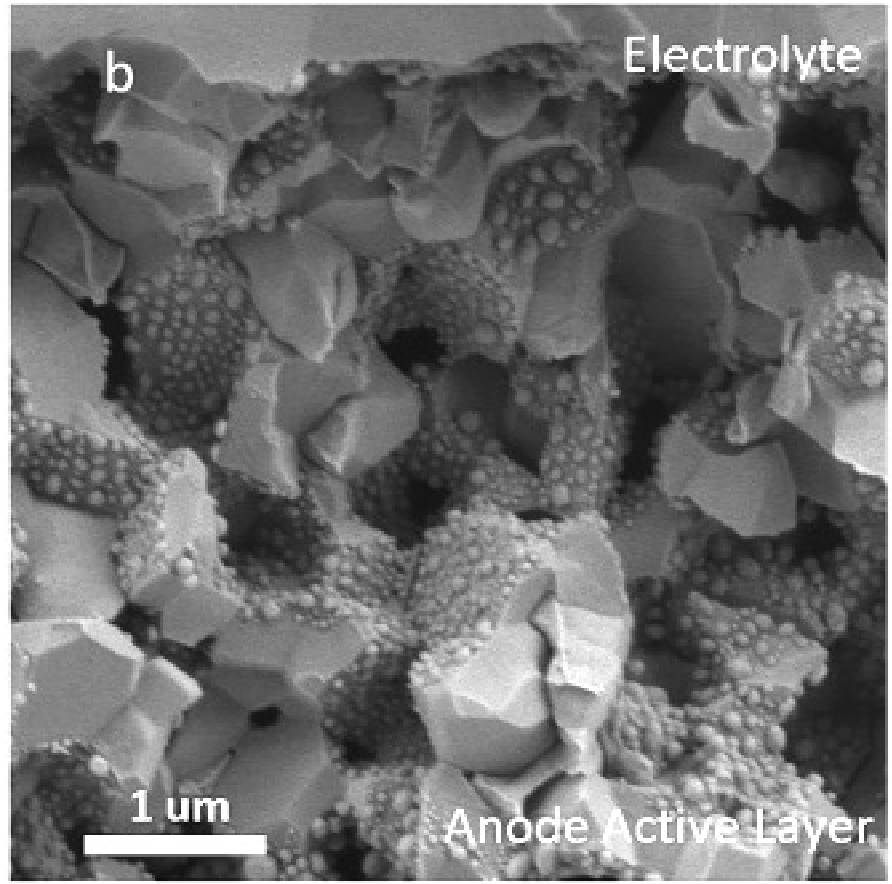
- 2.33 volume % of anode, or:
- 8.1 volume % of the pores

Ni Nanoparticles in Liquid Infiltrated Anodes

Uninfiltrated



Infiltrated



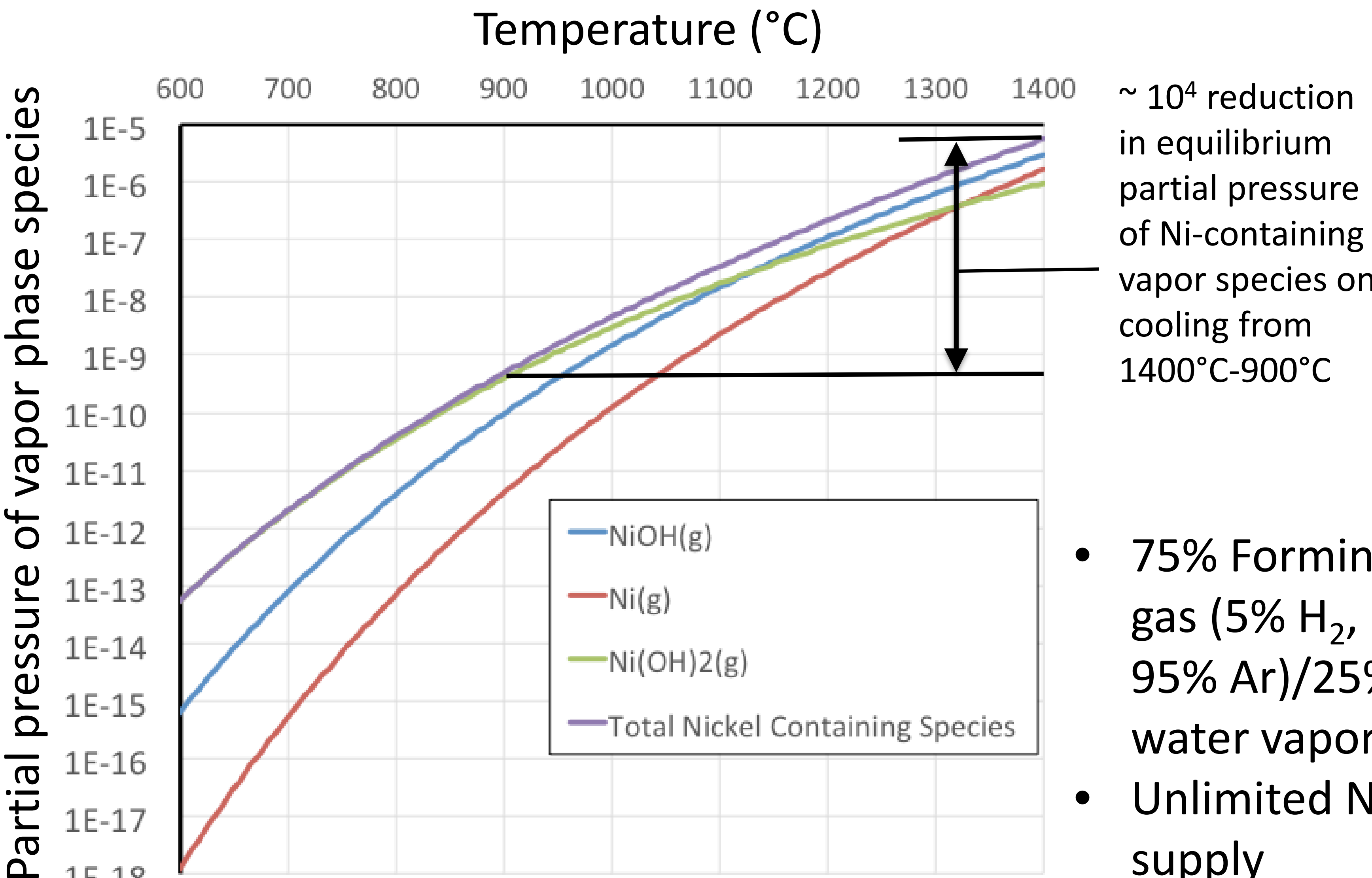
Liquid infiltration of conventional Ni/YSZ cermet can can lead to deposition in the anode active layer

Challenges of Liquid Infiltration

- Time consuming procedure
- Thermal cycling introduces possibility of electrolyte failure
- Maintaining cell integrity in reduced state during processing steps and electrochemical testing is challenging

Alternate approach:
Vapor phase infiltration of metallic Ni into anode using water vapor and forming gas

Thermodynamics of Ni Vaporization: Effect of T

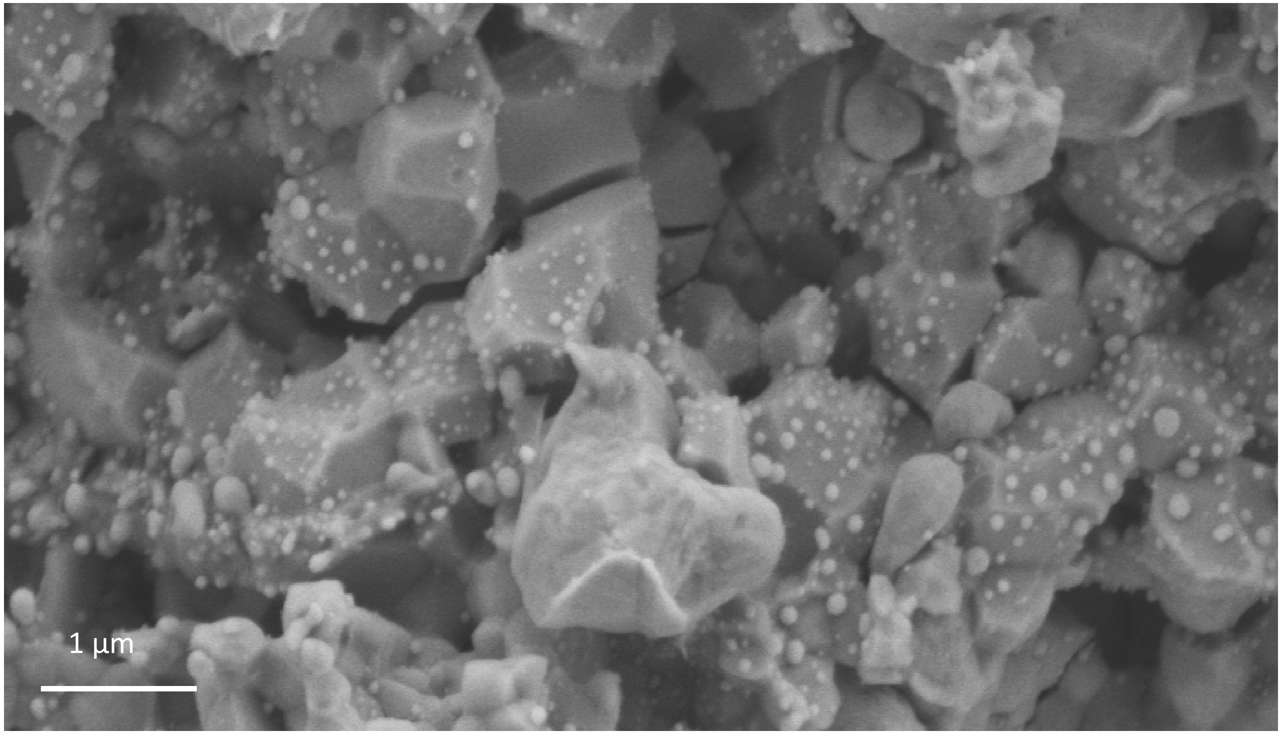


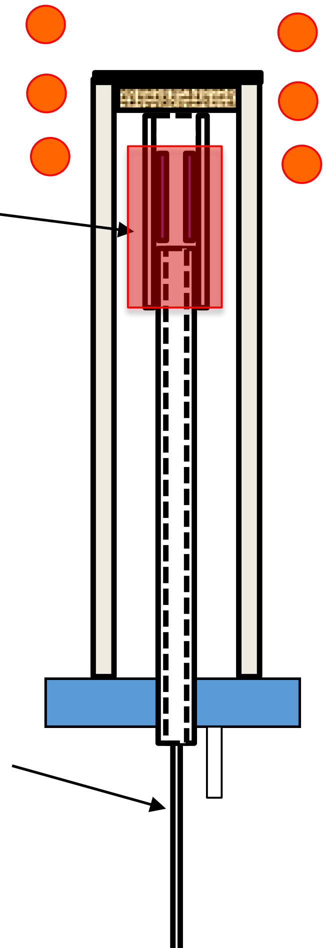
Calculations conducted in HSC Chemistry 6.0.

- 75% Forming gas (5% H_2, 95% Ar)/25% water vapor
- Unlimited Ni supply

Vapor Phase Infiltration of Ni in Ni-YSZ Anodes

Vapor phase deposited Ni nanoparticles

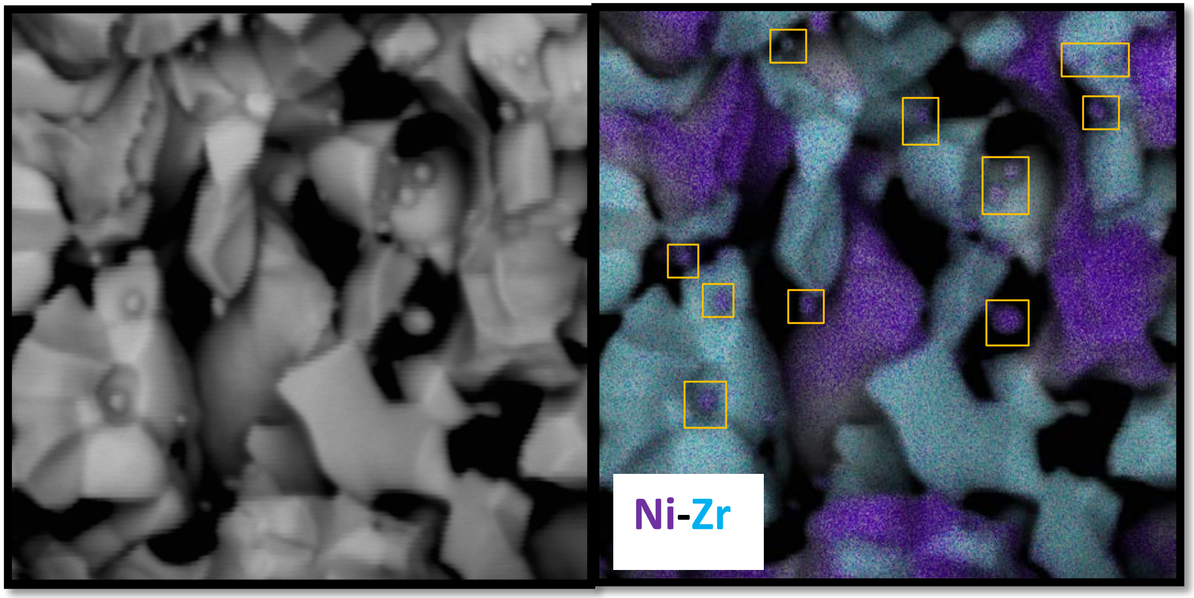




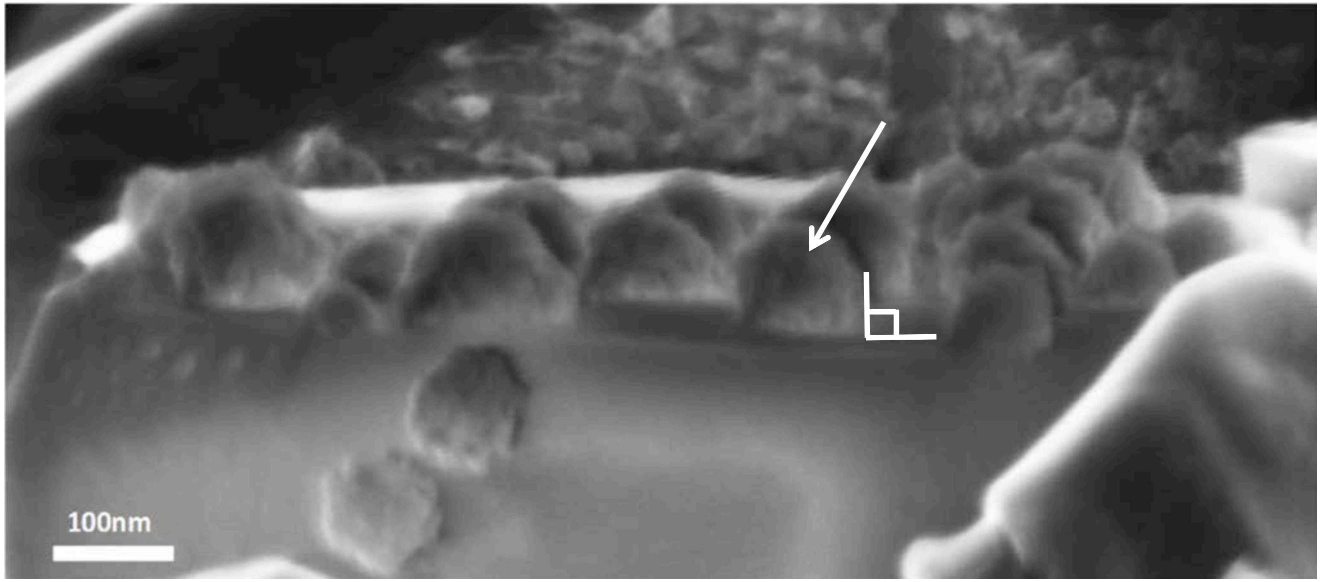
Vapor phase infiltration of Ni in commercial anodes is feasible

‘*Nano-particle deposition in porous and on planar substrates*’, U.S. Patent Application No. 62/364757 filed

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

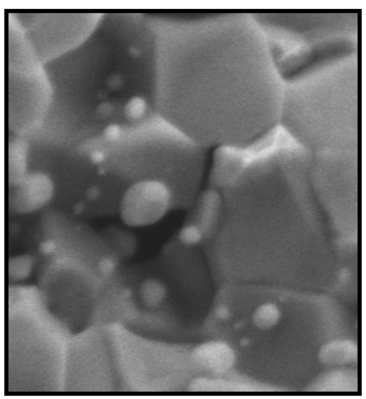
Calculation of Added TPB Density

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

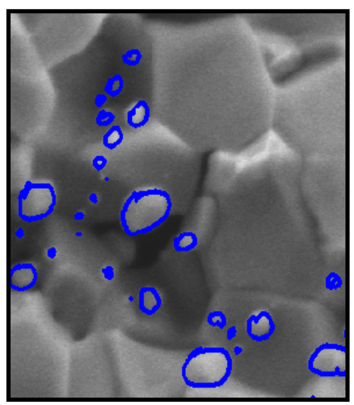
- TPB_{inf} — Additional TPB density in AAL (μm/μm³)
- n — Areal particle density in AAL (#/μm²)
- $\bar{d}$ — Average particle diameter in AAL (μm)
- $\frac{S}{V}$ — Surface area of pores per unit volume of AAL (μm²/μm³)
- v — Volume fraction of pores in AAL

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

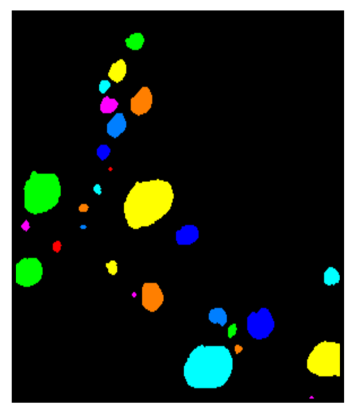
FIB-SEM (surface area of pores per unit volume, volume fraction of pores)



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

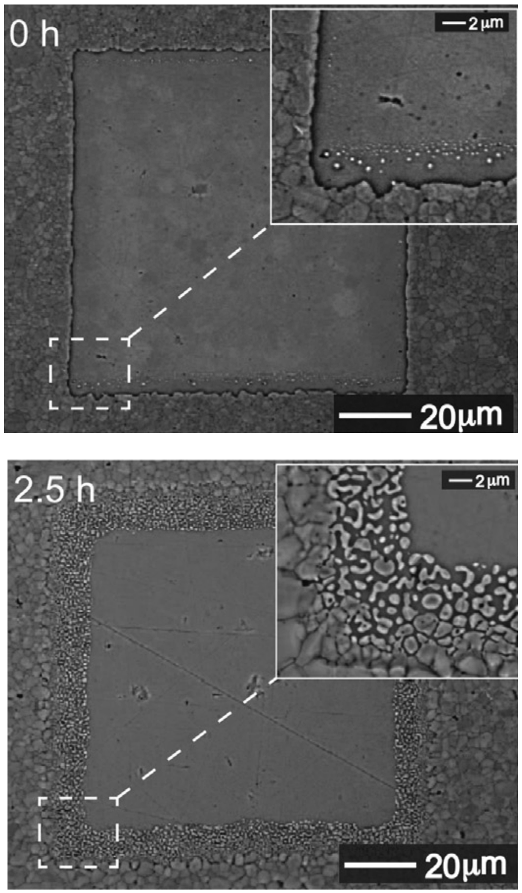
Additional TPB Density

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

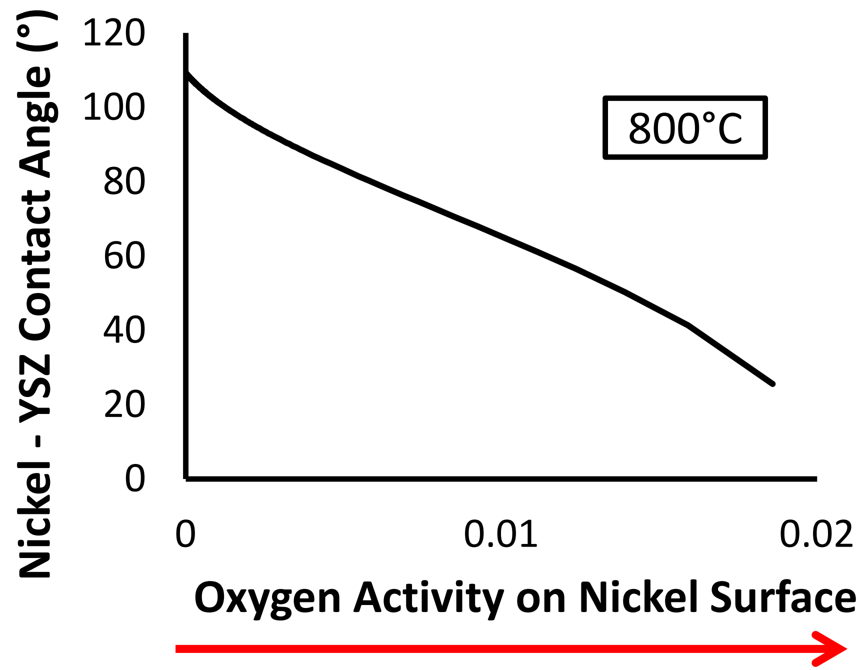
Question?

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

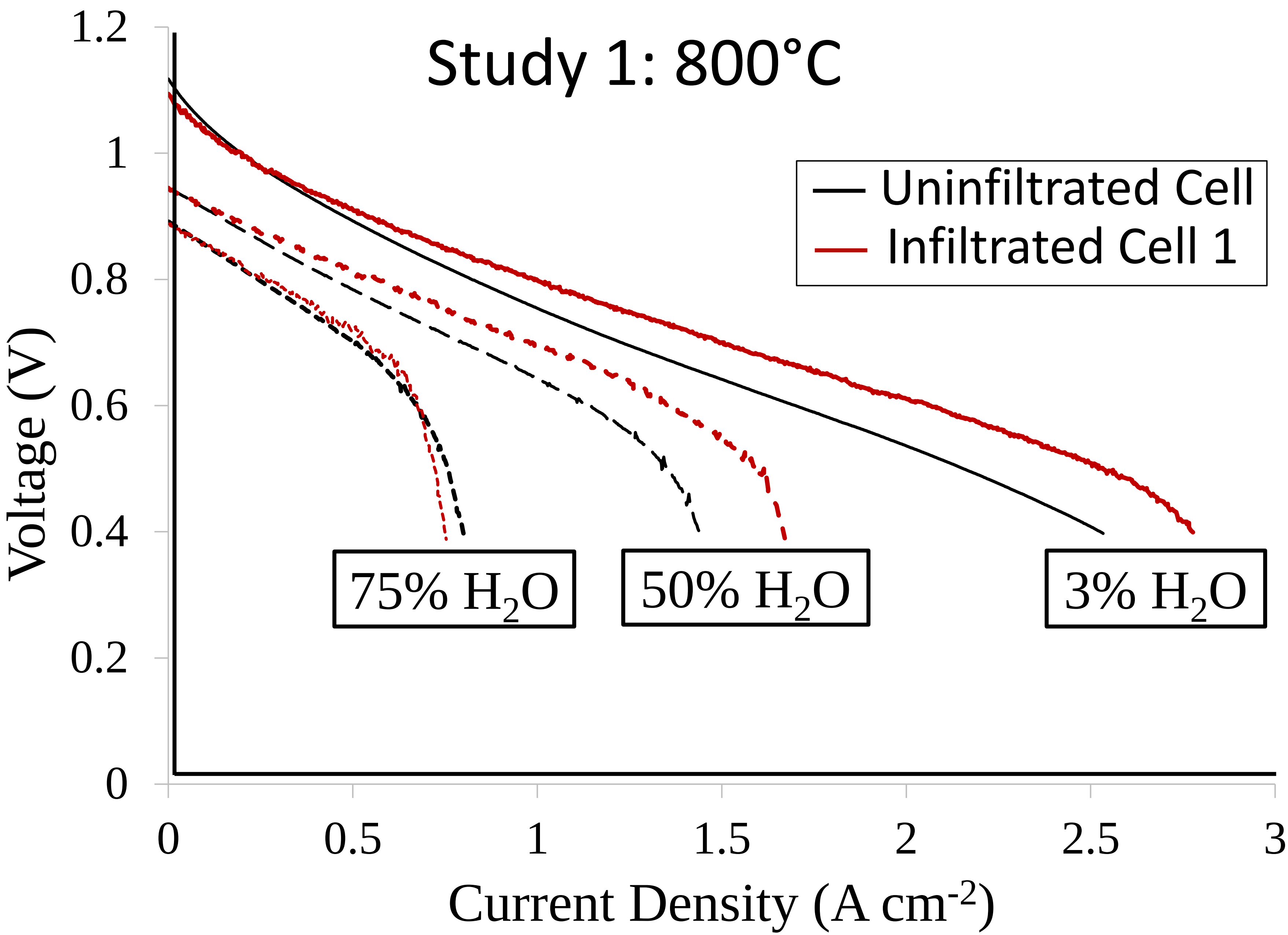
Cell Nomenclature for I-V Tests

STUDY 1	Cell Nomenclature		
Test Temperature	Uninfiltrated Cell 1	Infiltrated Cell 1	Infiltrated Cell 2
800° C	X	X	
700° C	X		X
600° C	X		X

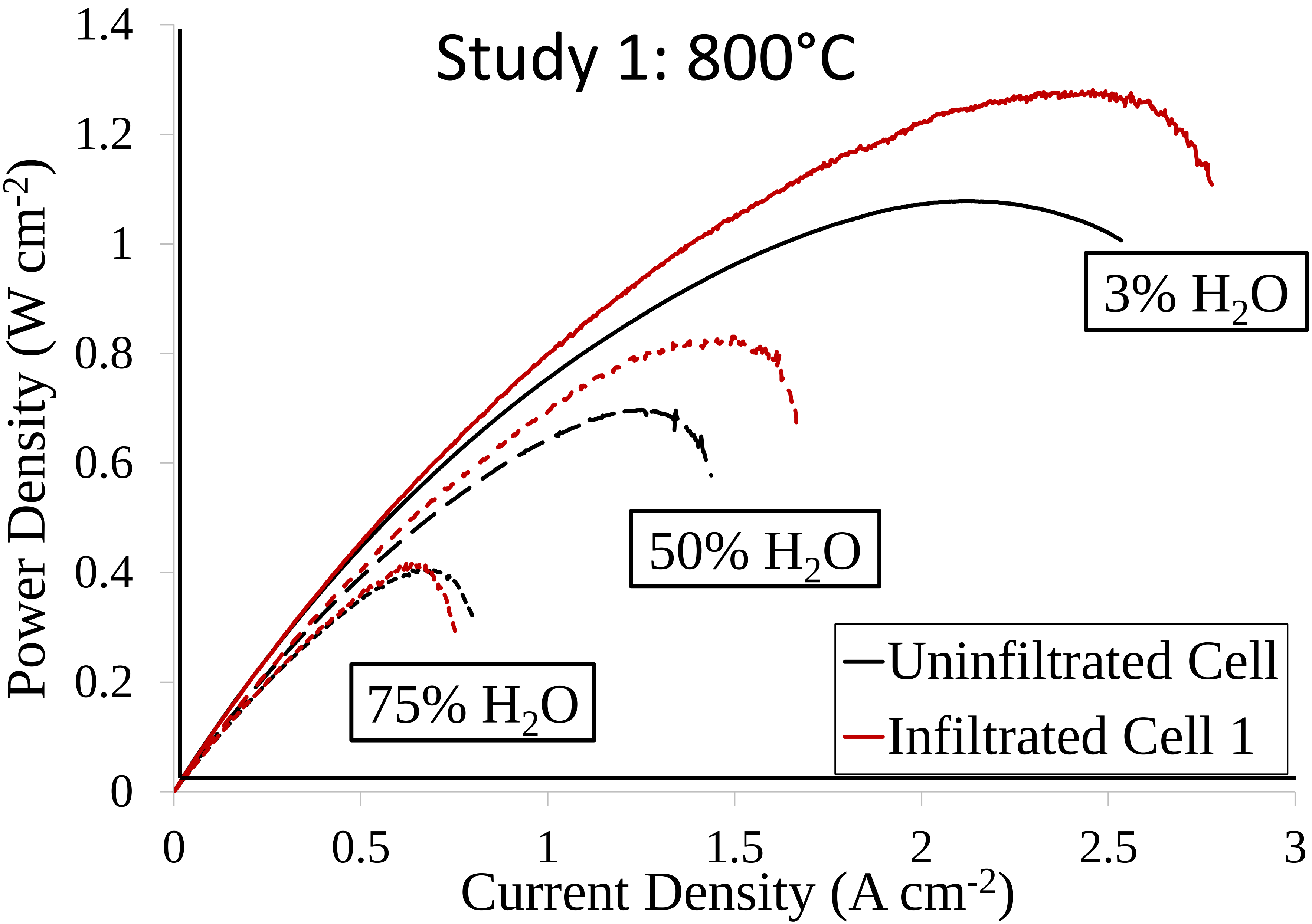
STUDY 2	Cell Nomenclature		
Test Temperature	Uninfiltrated Cell 2	Infiltrated Cell 3	Infiltrated Cell 4
750° C	X	X	
700° C	X		X
650° C	X		X

- Cells were tested in pure O_2 on cathode side under various anode atmospheres and temperatures
- Cathode atmosphere was switched to dry air without cooling and tested under various anode atmospheres and temperatures (results are discussed)
- **STUDY 1:** Cells were tested to high current densities and low potentials (well into concentration polarization conditions).
- **STUDY 2**: Cells were tested to low current densities and high potentials (concentration polarization conditions never reached).

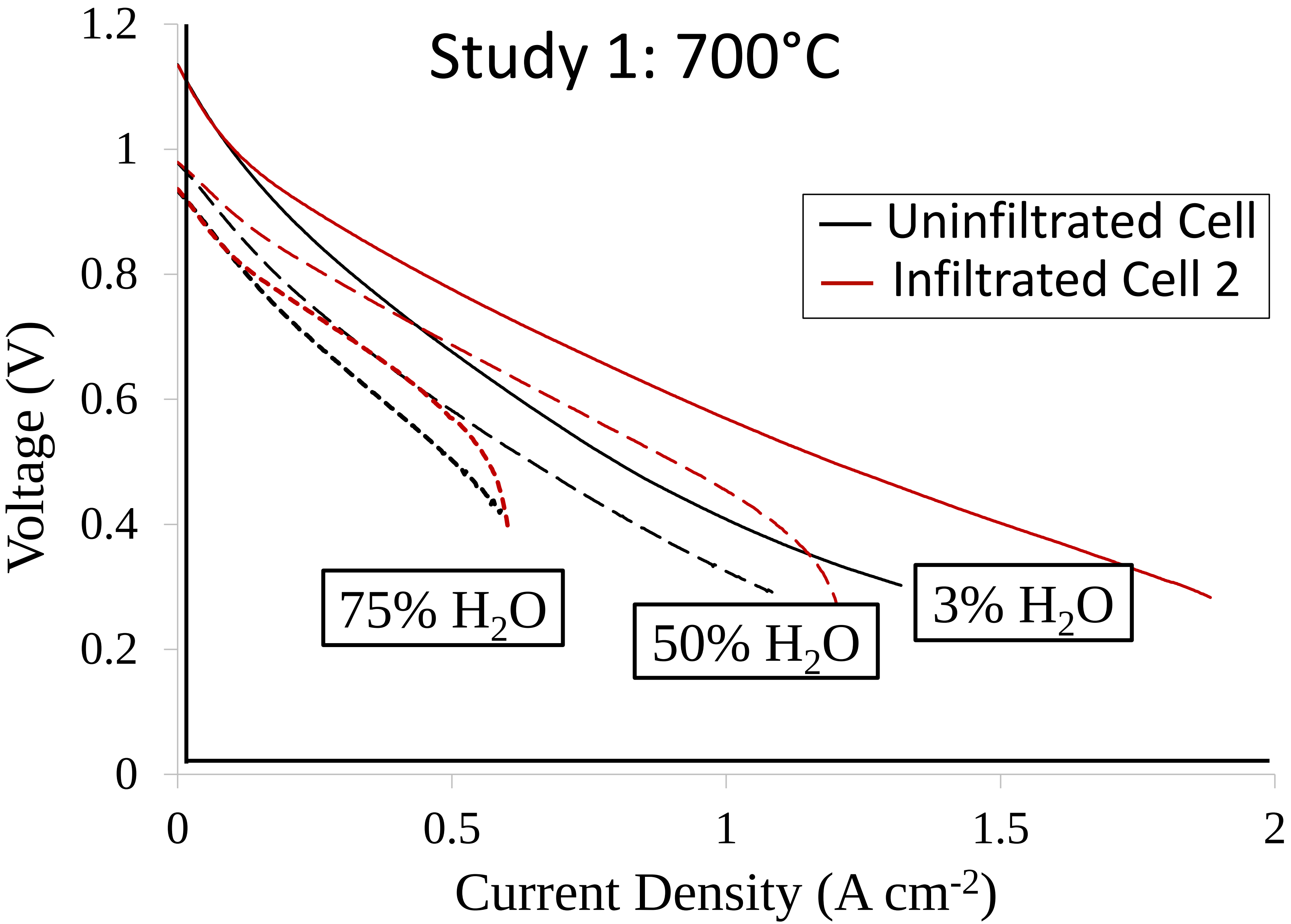
Electrochemical Test Results



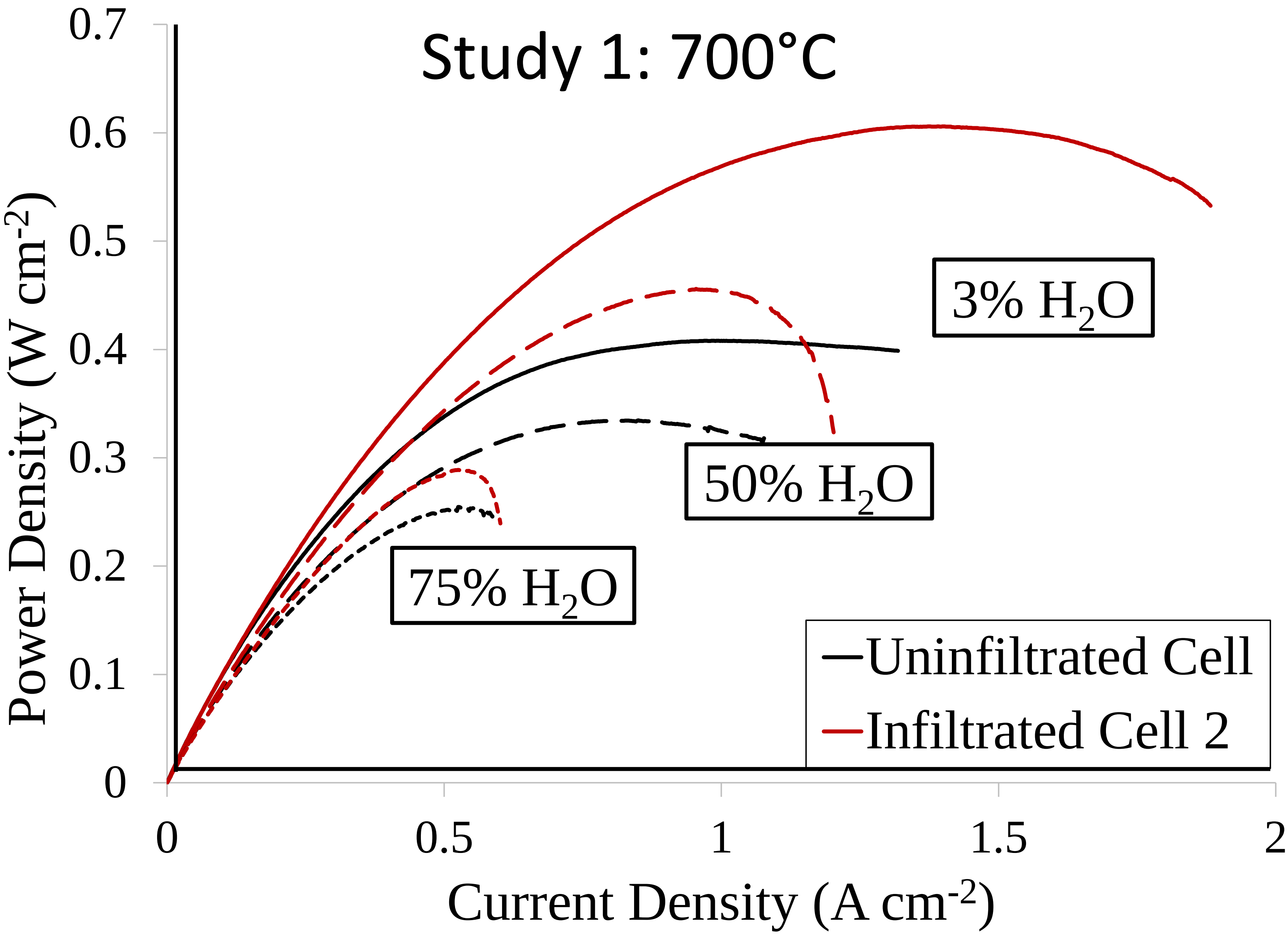
Electrochemical Test Results



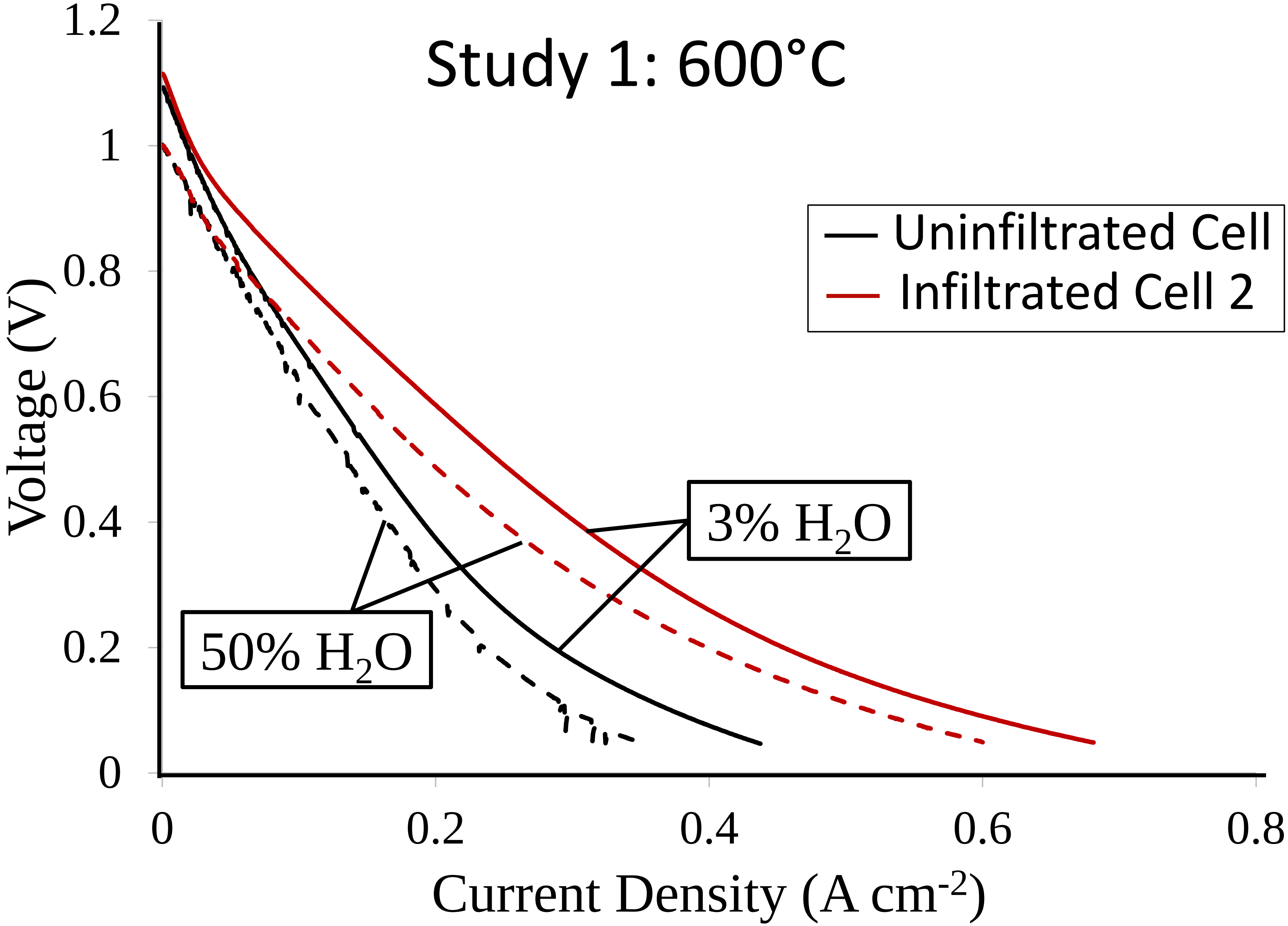
Electrochemical Test Results



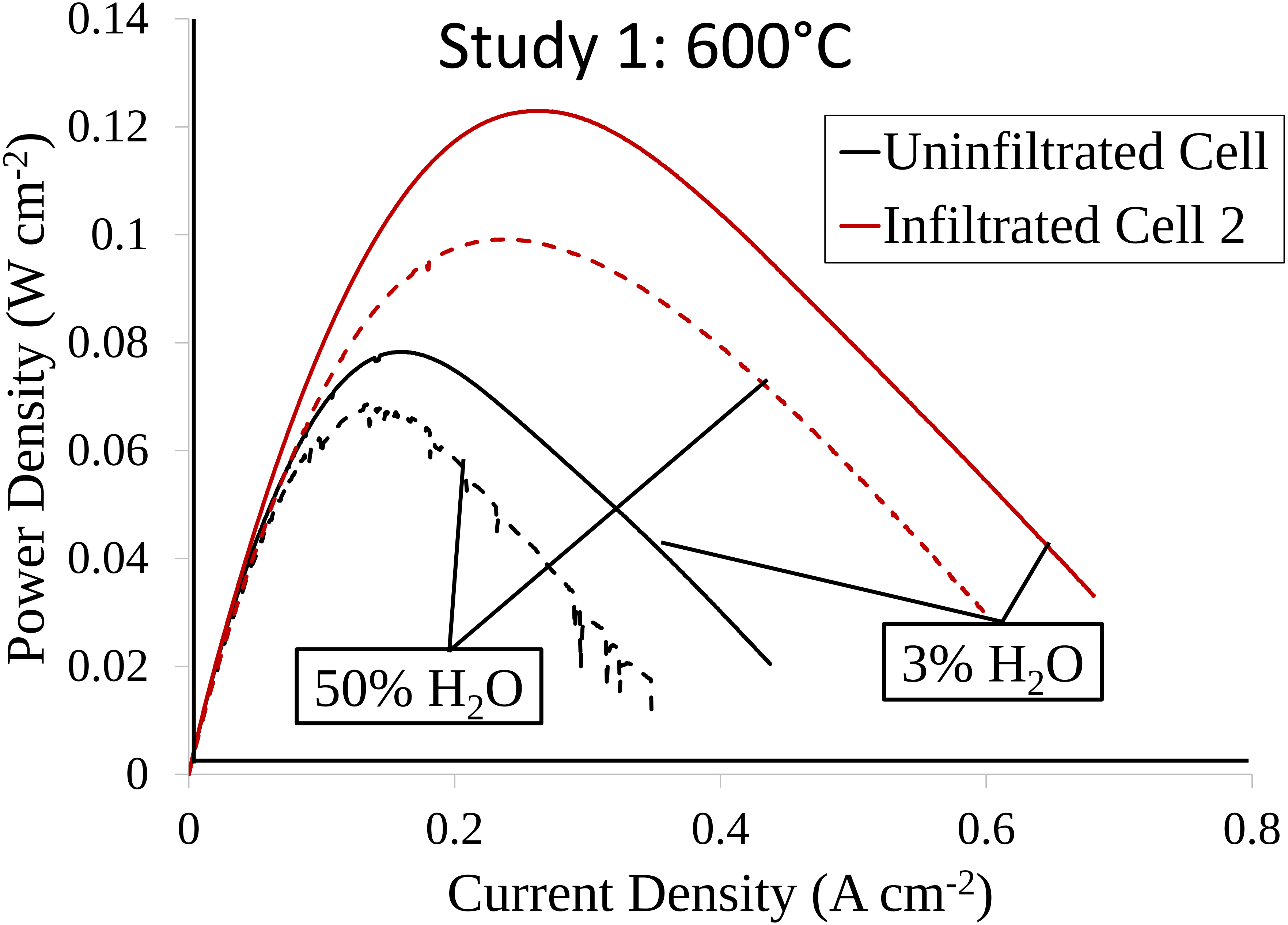
Electrochemical Test Results



Electrochemical Test Results



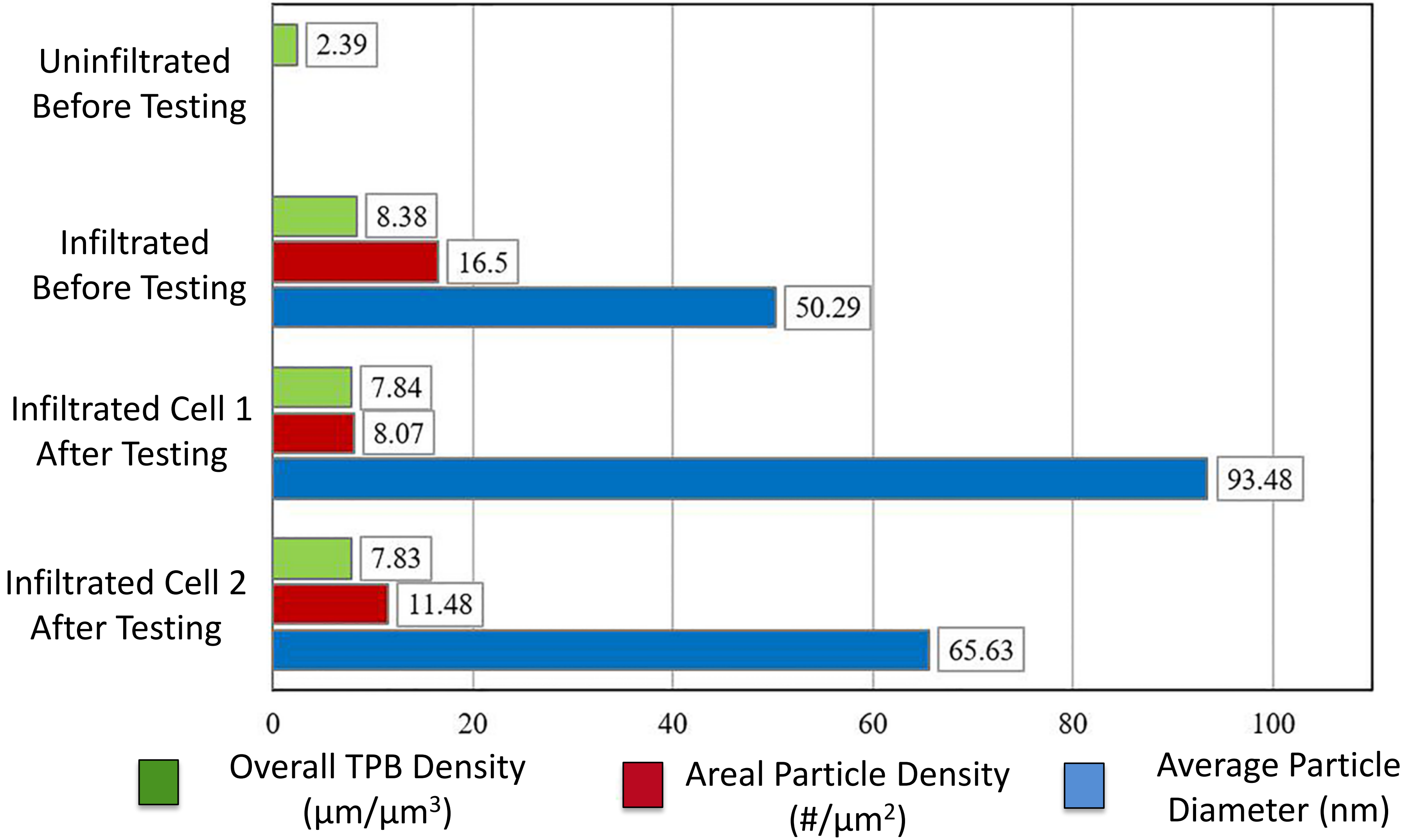
Electrochemical Test Results



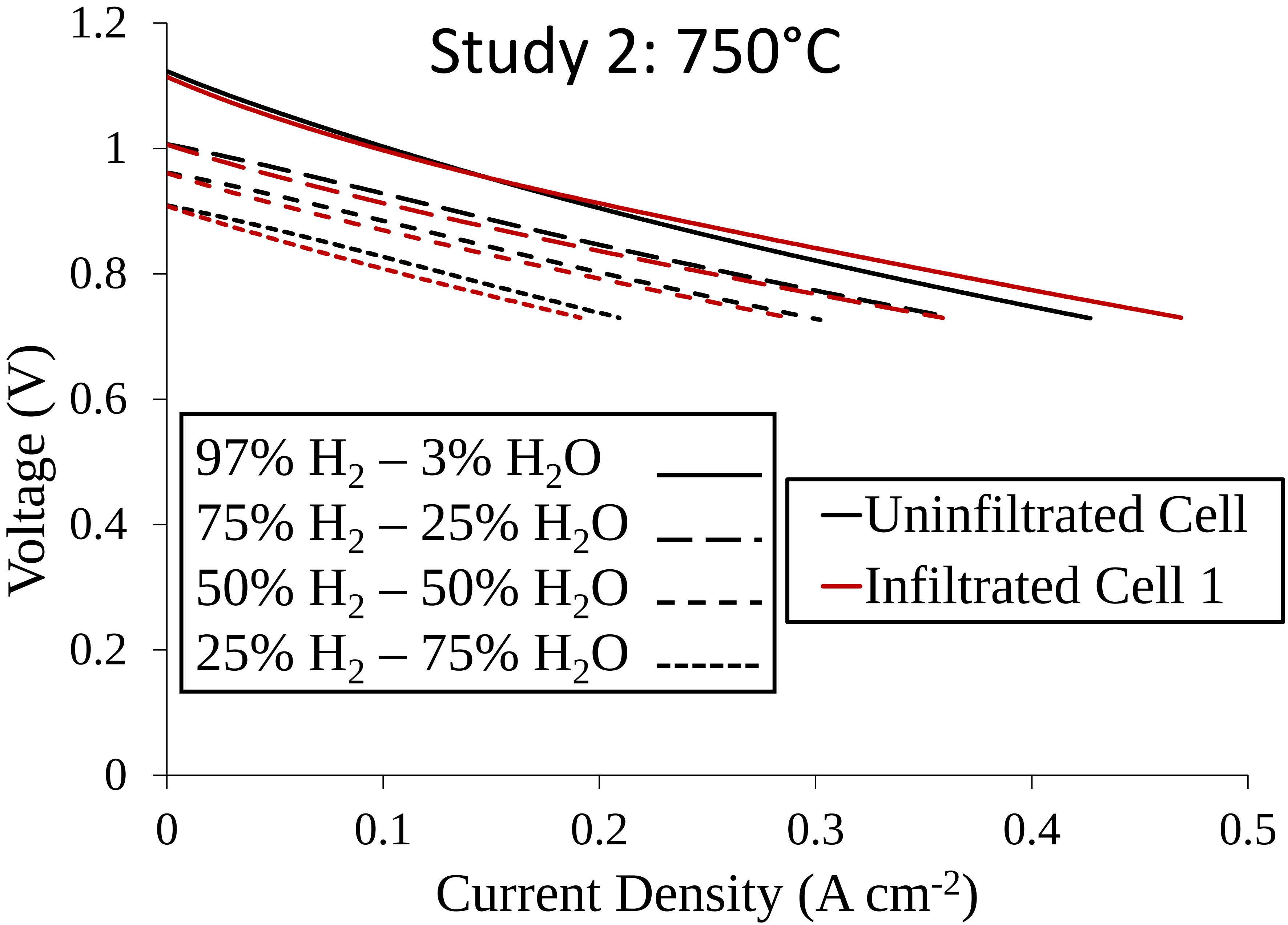
Summary of Study 1 Results

Testing Temperature	Cell	Maximum Power Density (W cm^{-2}) at Different Anode Gas Mixtures		
		3% H_2O – 97% H_2	50% H_2O – 50% H_2	75% H_2O – 25% H_2
800° C	Uninfiltrated	1.078	0.701	0.408
	Infiltrated Cell 1	1.281	0.831	0.414
	Change	+18.8%	+18.5%	+1.5%
700° C	Uninfiltrated	0.408	0.335	0.255
	Infiltrated Cell 2	0.606	0.455	0.289
	Change	+48.5%	+35.8%	+13.3%
600° C	Uninfiltrated	0.078	0.068	n/a
	Infiltrated Cell 2	0.123	0.099	n/a
	Change	+57.7%	+45.6%	n/a

Particle Statistics in Study 1



Electrochemical Test Results



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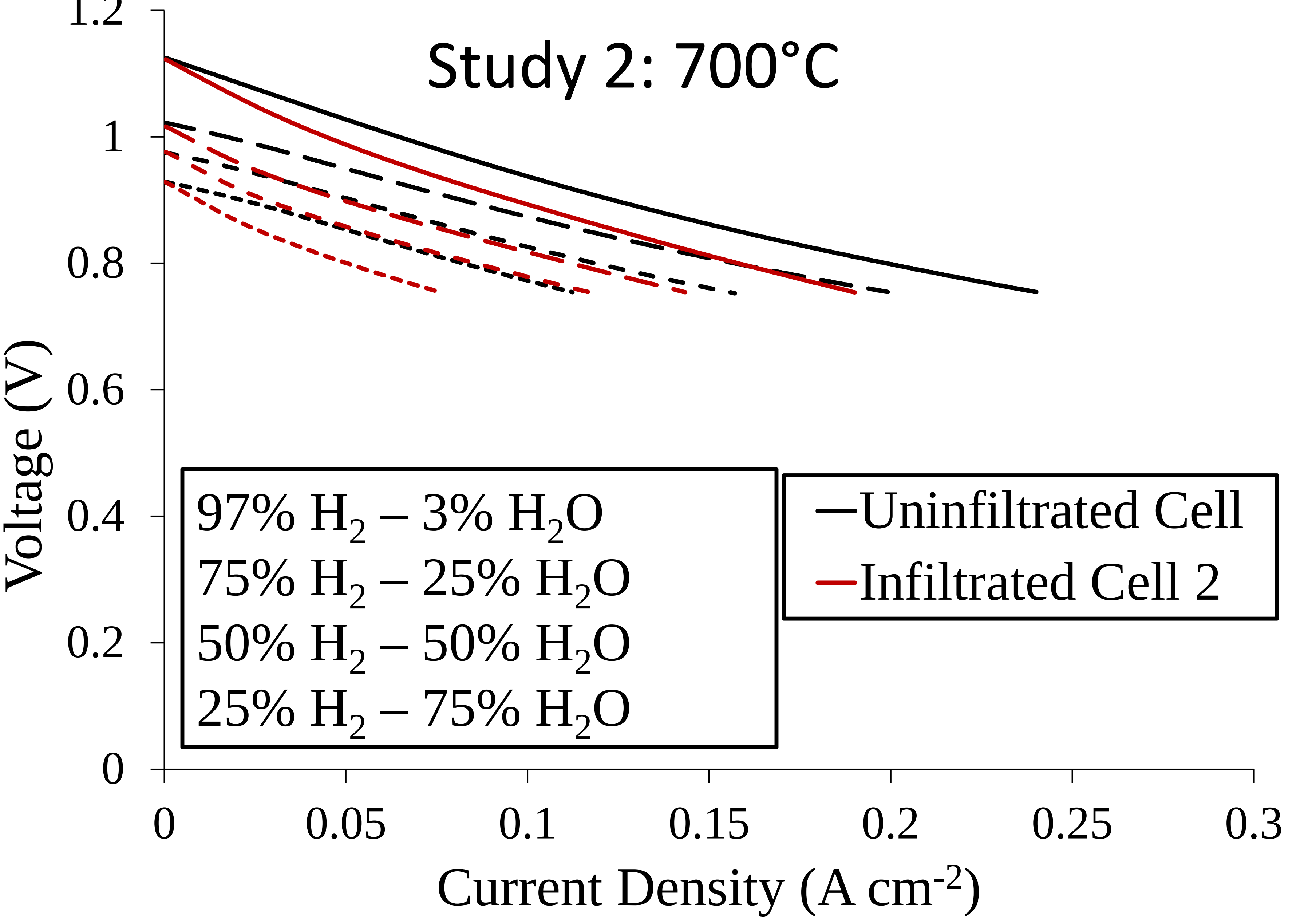
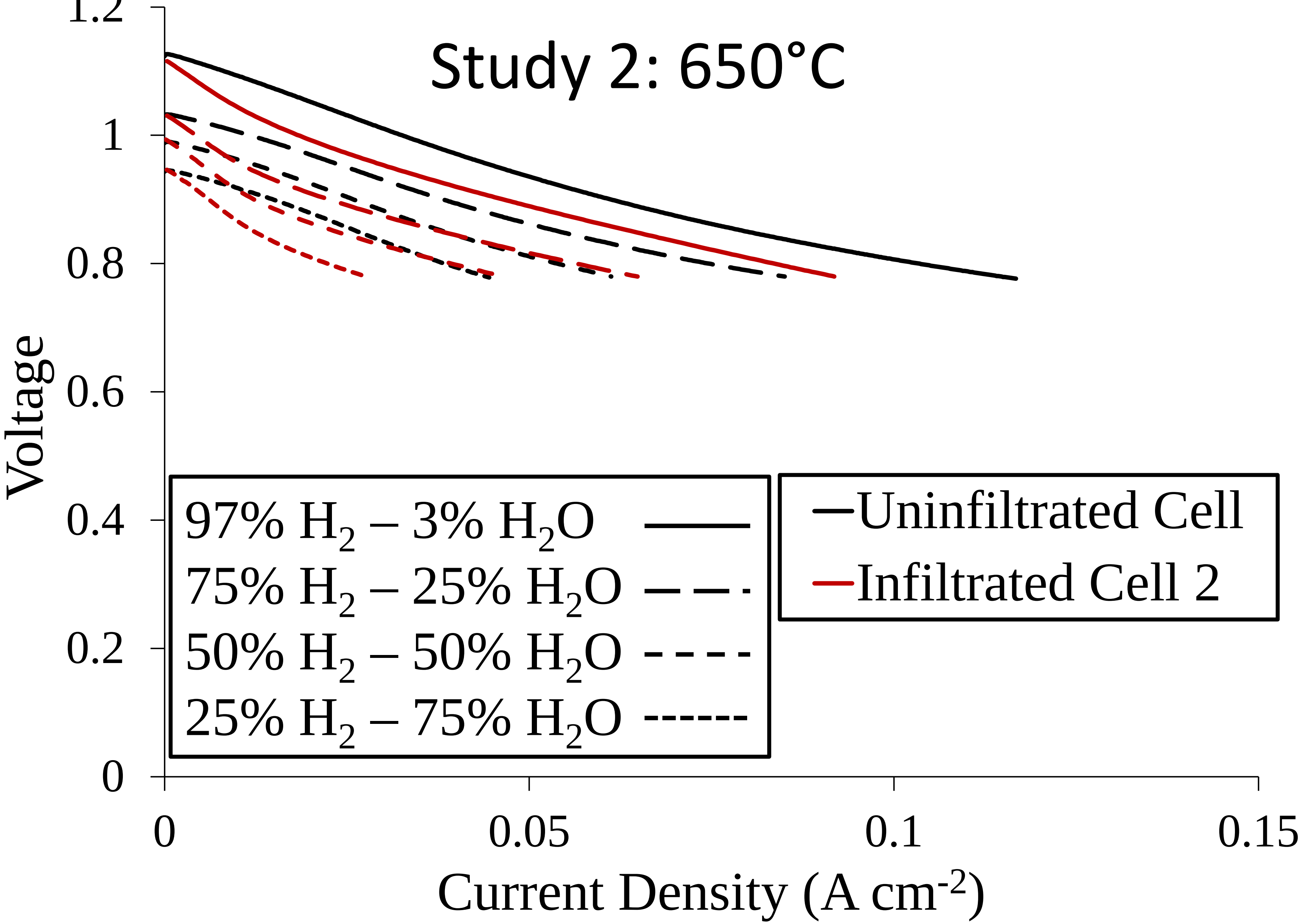
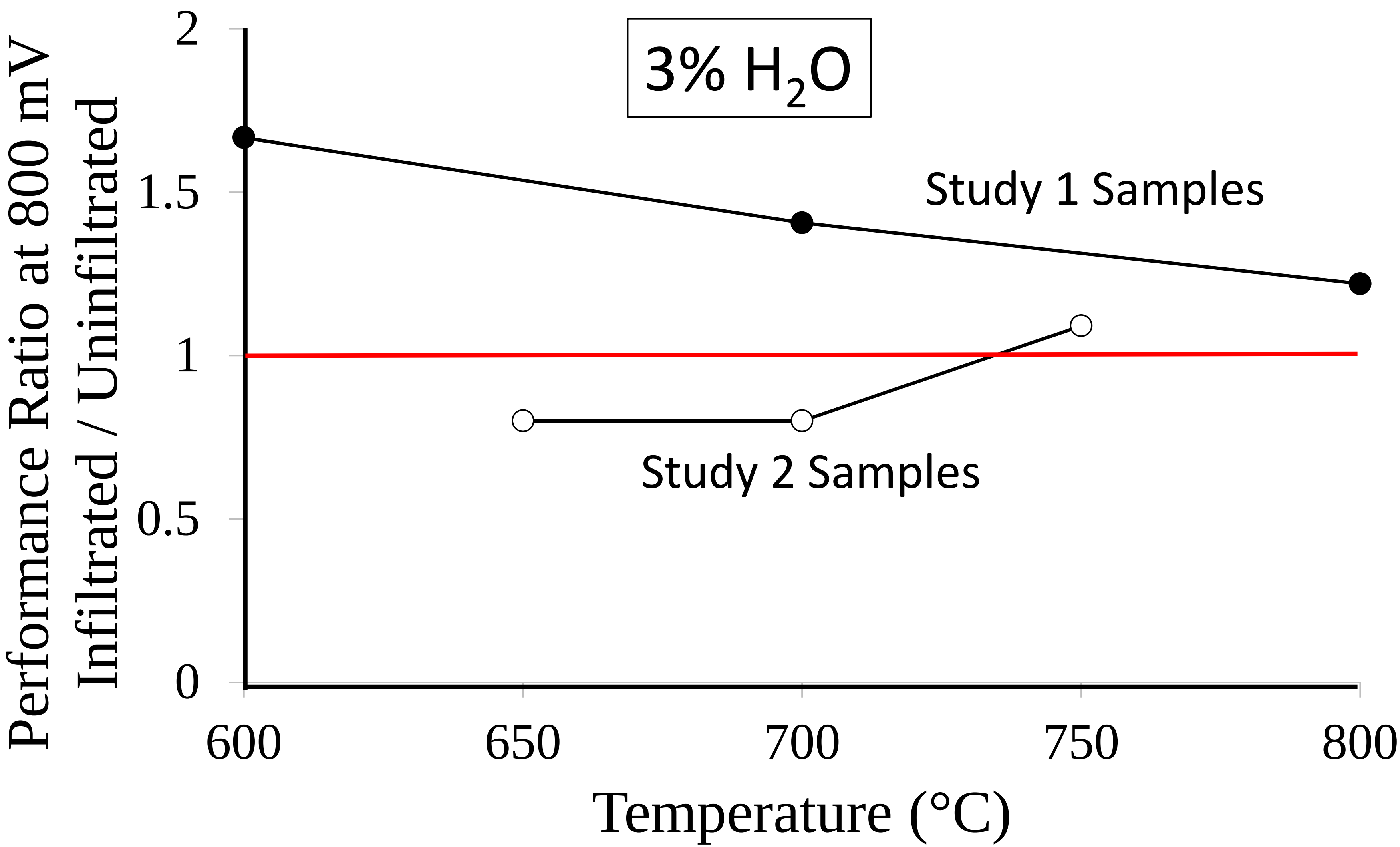


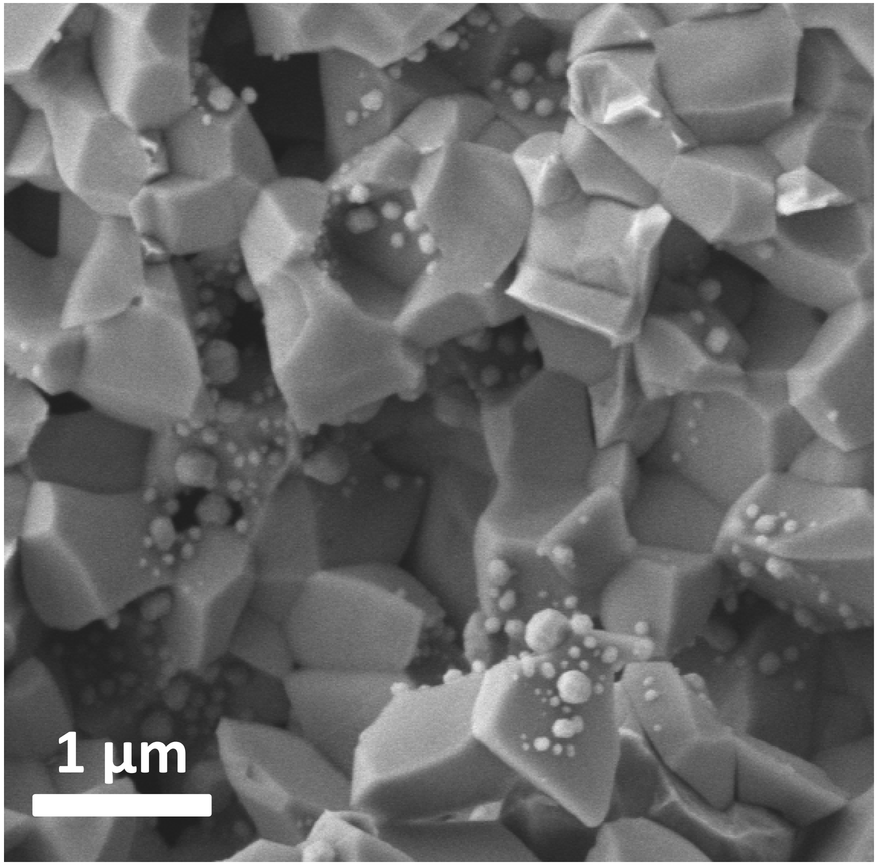
Electrochemical Test Results



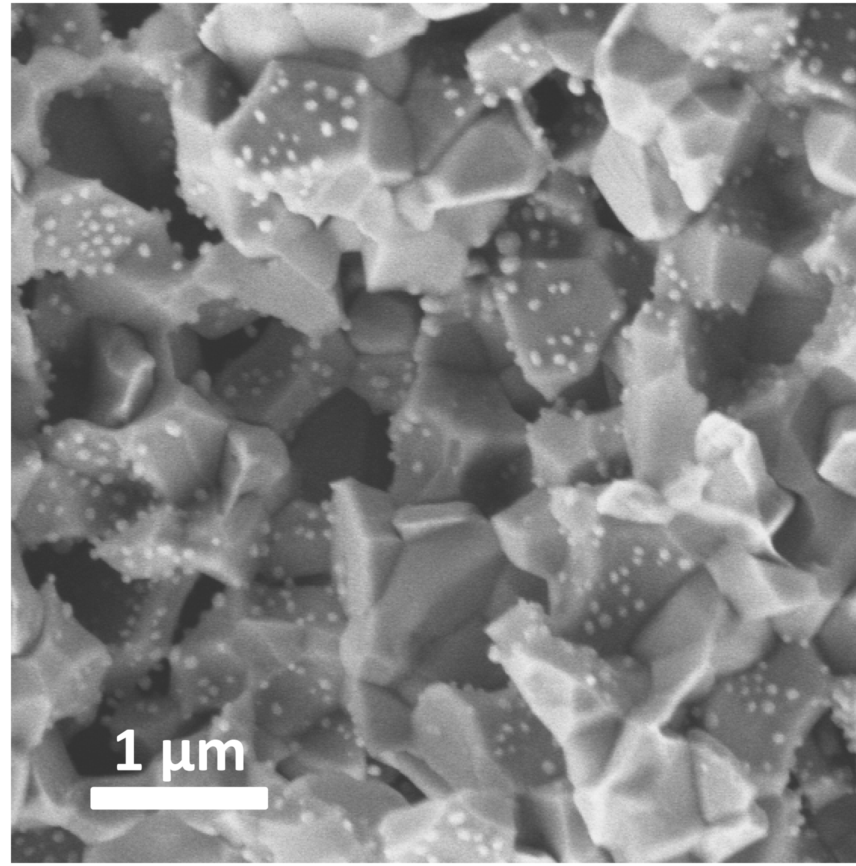
Comparison of Study 1 and Study 2 Samples



Nanoparticle Percolation versus Coarsening



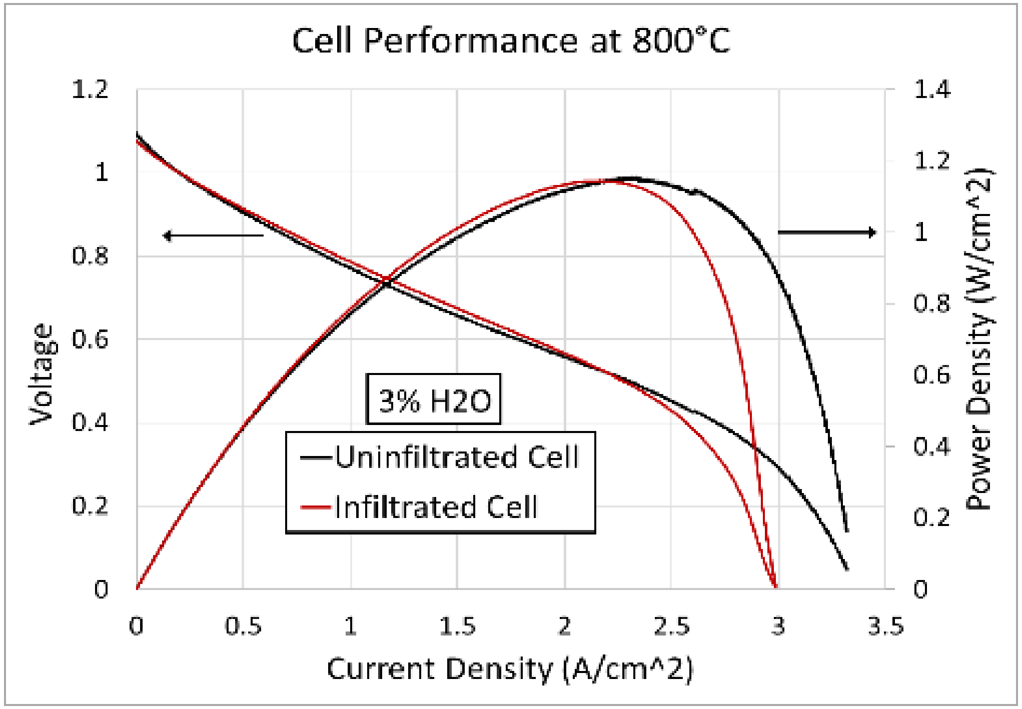
Infiltrated Cell 1 - 700°C
(High Current)



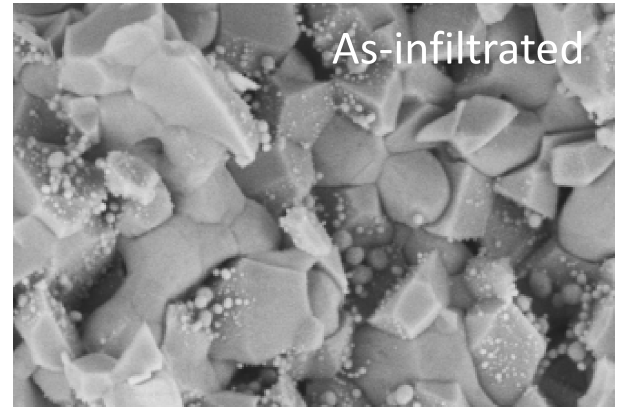
Infiltrated cell 3 – 750°CC
(Low Current)

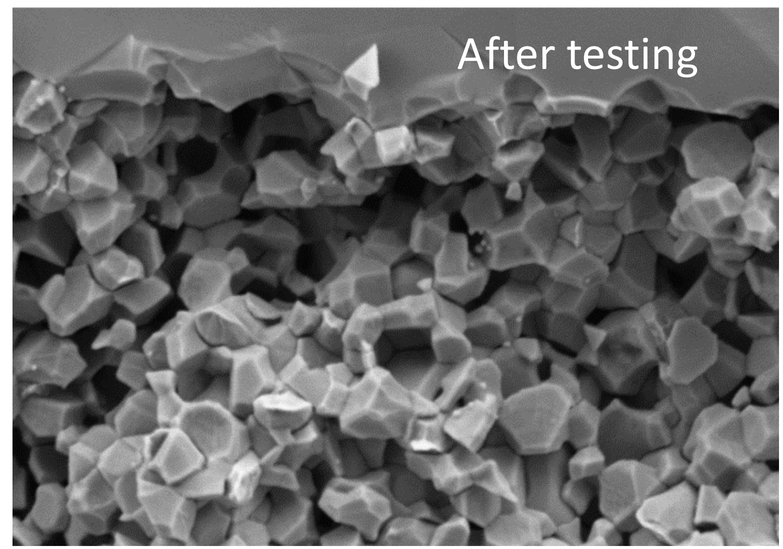
Nanoparticle connectivity can lead to coarsening

Ni Nanoparticle Instability at 800°C



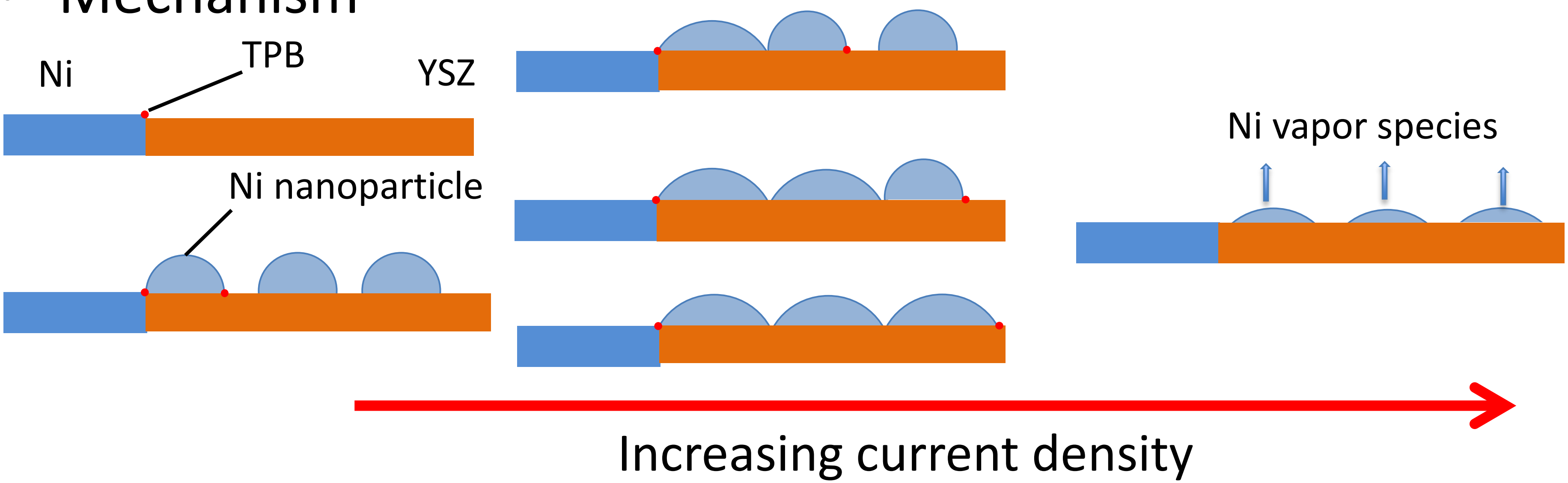
Ni nanoparticles disappeared from the AAL at extremely high current densities





Conclusions

- Mechanism



- An initial exposure to anodic concentration polarization conditions, followed by normal cell operation should preserve the percolated Ni nanoparticles and maintain improved cell performance.
- Exposure to very high current densities should be avoided.

Acknowledgements

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