Development of Novel 3D Cell Structure and Manufacturing Processes for Highly Efficient, Durable and Redox Resistant Solid Oxide Electrolysis Cells

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Project Overview

- Project: Development of 3D Cell Structure and Manufacturing Processes for Highly Efficient, Durable and Redox Resistant Solid Oxide Electrolysis Cells (DE-FE0032107)

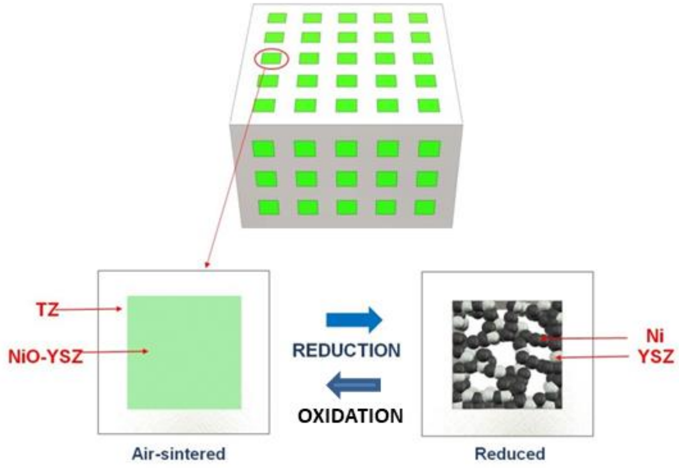
- Project Objective: Develop and demonstrate highly efficient, durable and redox resistant solid oxide electrolysis cells (SOECs) with a focus on
  - (i) A cell design with the hydrogen electrode composed of two layers – a 3D hydrogen electrode support layer and an exsolved perovskite hydrogen electrode active layer
  - (ii) A manufacturing scheme incorporating advanced 3D printing and photonic sintering for fabrication of the cell configuration

- DOE/NETL Project Manager: Ms. Sarah Michalik

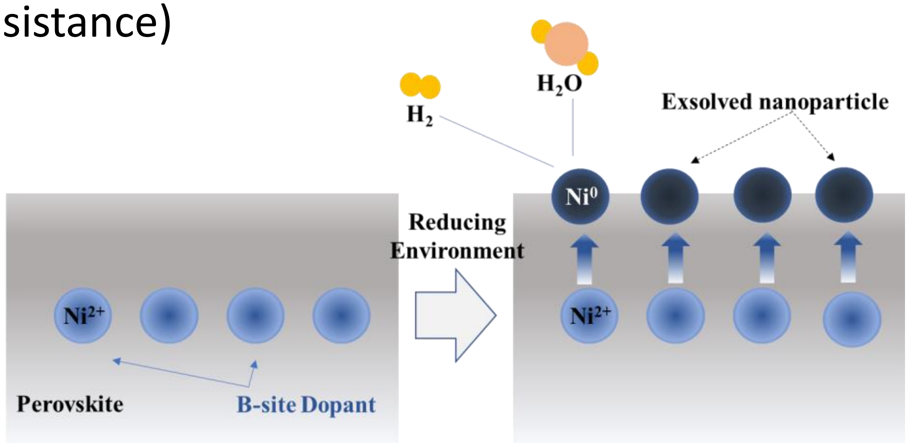
- Project Team:
  - ❑ University of California San Diego (UCSD)
  - ❑ RocCera LLC (RocCera)
  - ❑ Rochester Institute of Technology (RIT)

Motivation

- 3D hydrogen electrode support for redox resistance

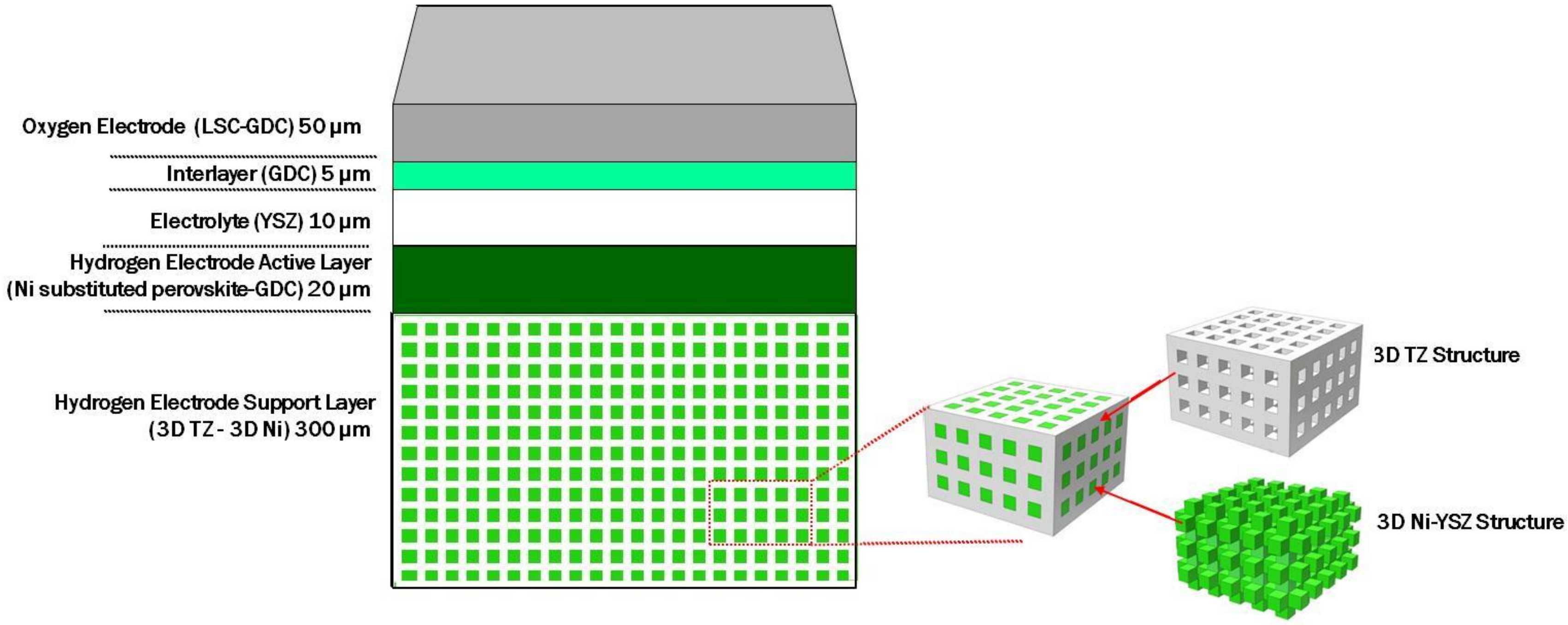


- Exsolved perovskite hydrogen electrode active layer (high performance, improved stability, redox resistance)



Cell Design

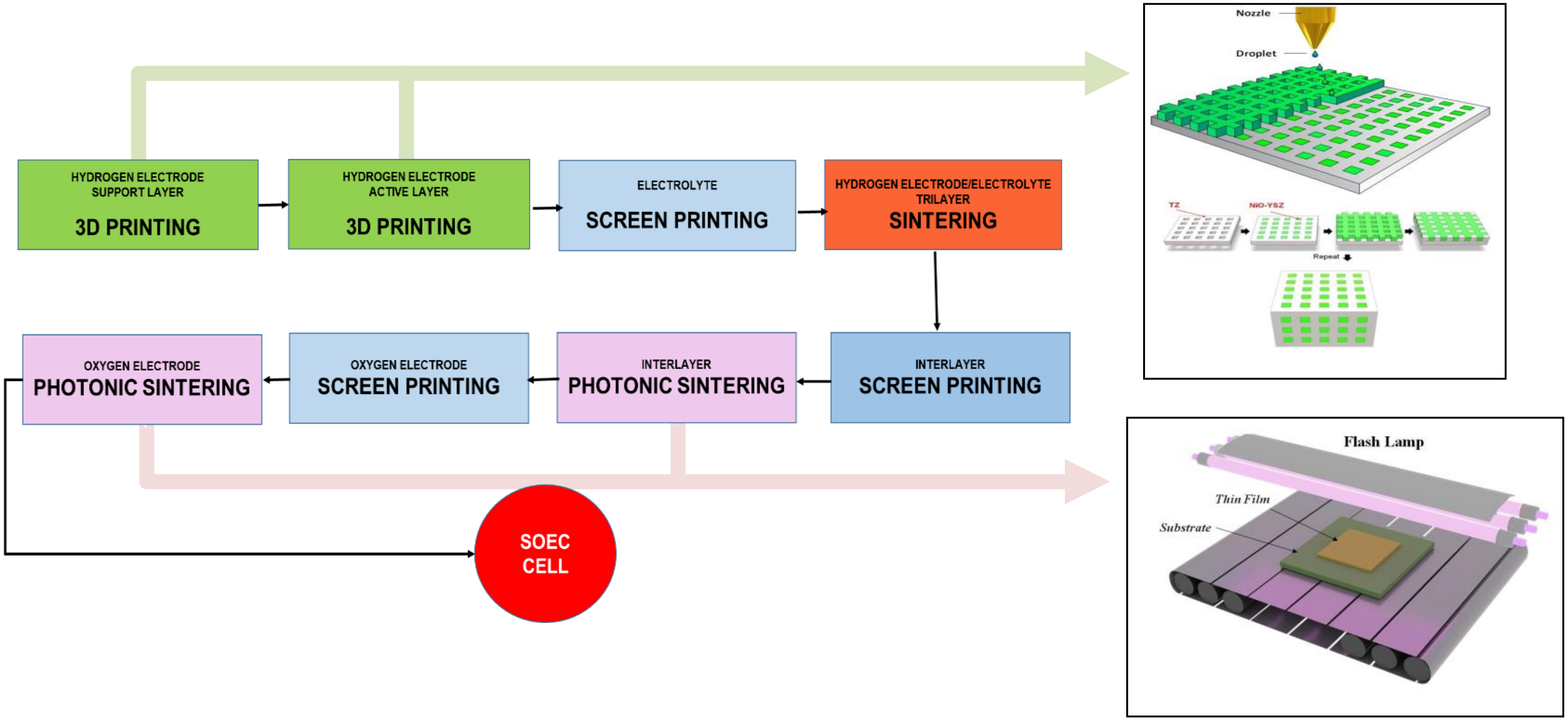
- **Design features**:
  - Hydrogen electrode supported configuration
  - Unique hydrogen electrode concept – a support layer with 3D structural geometry coupled with an exsolved perovskite active layer



LSC: Lanthanum strontium cobalt perovskite
GDC: Gadolinium doped ceria
YSZ: Yttria stabilized zirconia
TZ: Tetragonal zirconia

Fabrication Process

- Similar to, but different from the conventional process in two areas:
  - 3D printing (instead of tape casting) for the hydrogen electrode support
  - Photonic sintering (instead of conventional firing) for the interlayer and oxygen electrode



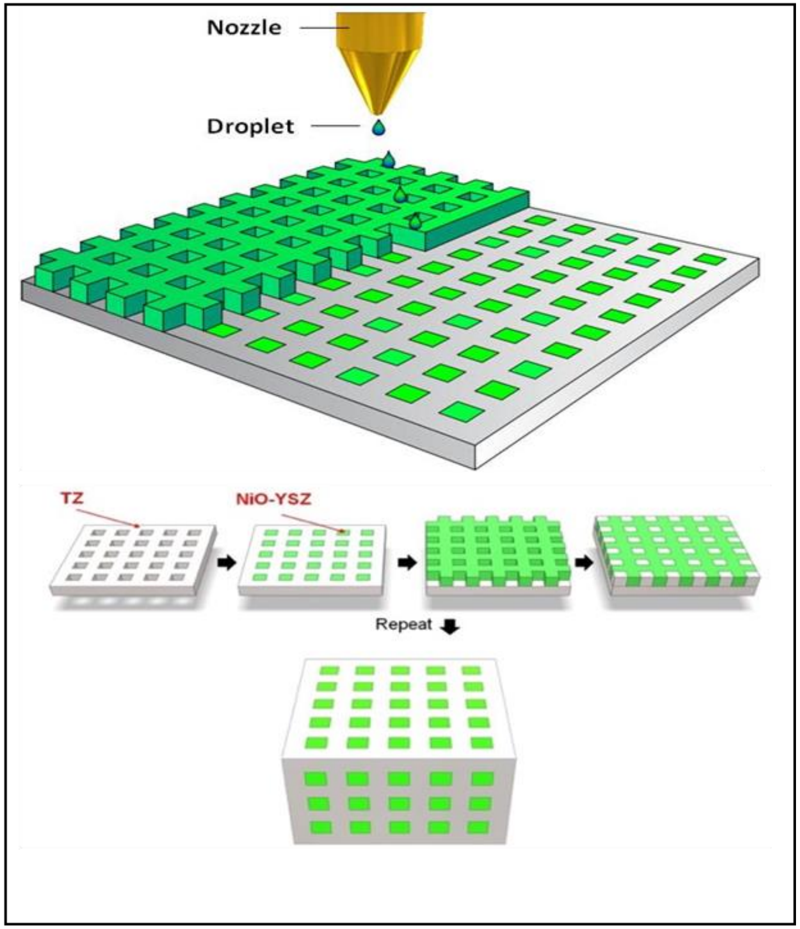
Project Activities
Discussed in this Presentation

- Fabrication development of 3D hydrogen electrode support by 3D printing and co-firing

- Evaluation of Ni-substituted perovskite for hydrogen electrode active layer

3D Printing

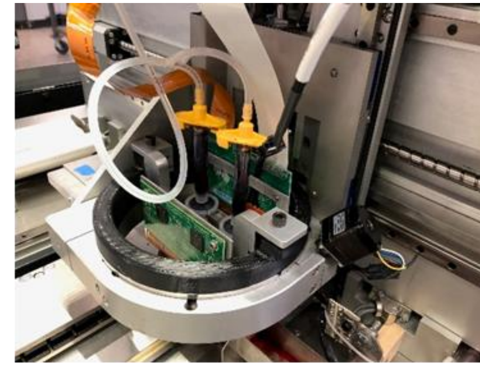
- Multi-Material 3D Printing
  - Use two or more deposition tools to digitally deposit the desired material at each voxel (volumetric pixel) location
  - Techniques can include inkjet printing, micro-extrusion, aerosol printing, and others
  - Each method imposes unique requirements on raw material formulation to ensure printability and part quality
- 3D Printed Support Structure
  - Unique "3D checkerboard" structure made possible by multi-material 3D printing

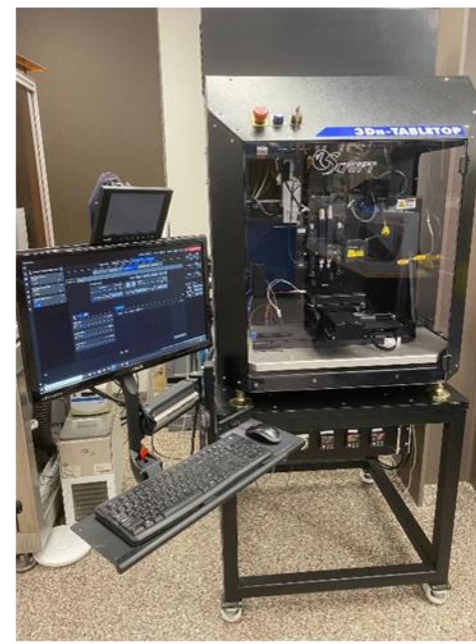


Fabrication of 3D Hydrogen Electrode Support by 3D Printing

- **Inkjet Printing (Dimatix with progression to industrial grade inkjet material deposition)**
  - Readily able to print multiple materials
  - Moderate feature resolution in lateral plane (high 10's of µm), but able to print extremely thin layers (1 µm or even less)
  - Requires low viscosity ink with relatively low solid loading
  - Nozzle clogging with non-optimized inks is a challenge

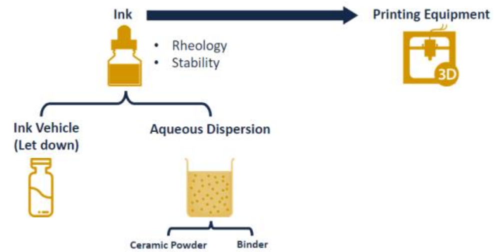
- **Micro-extrusion Printing (nScrypt)**
  - Able to print high solid loading viscous pastes
  - Can print multiple materials dual-extrusion configurations
  - Moderate feature resolution in lateral plane (similar to inkjet), but relatively thick layers (high 10's of µm and up)



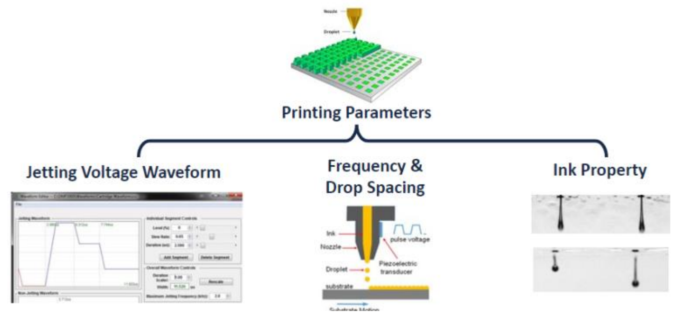


Process Specification Development

- Ink formulations



- Printing parameters

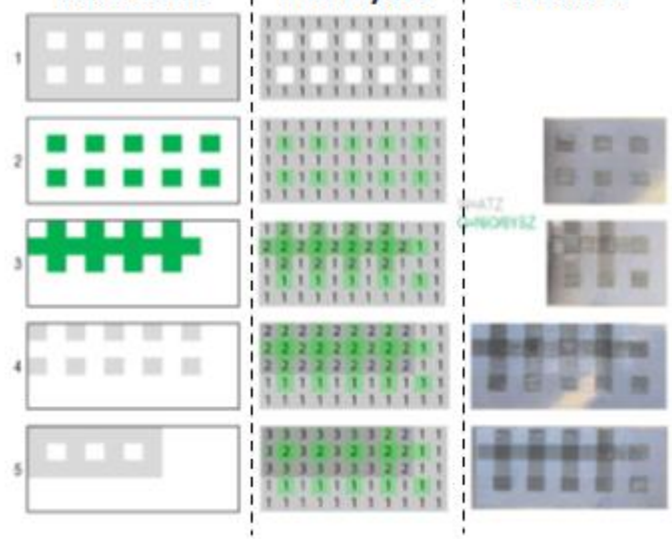


- Drying parameters

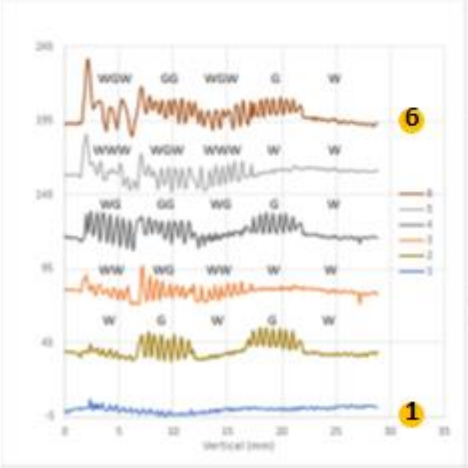
- Firing parameters

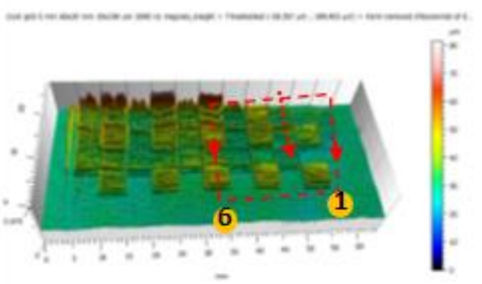
Inkjet Printed 3D Hydrogen Electrode

Layer Printing Strategy



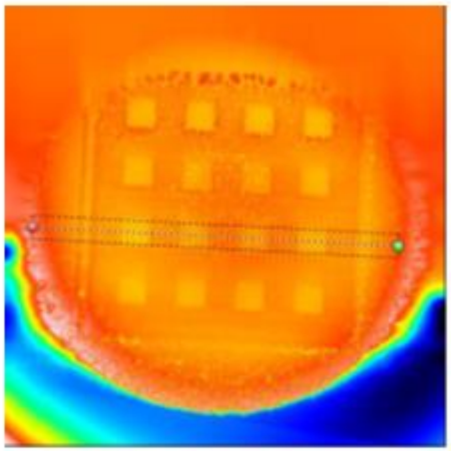
Optical Surface Profilometry

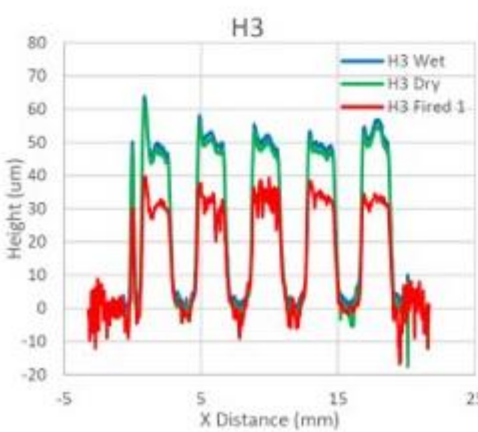




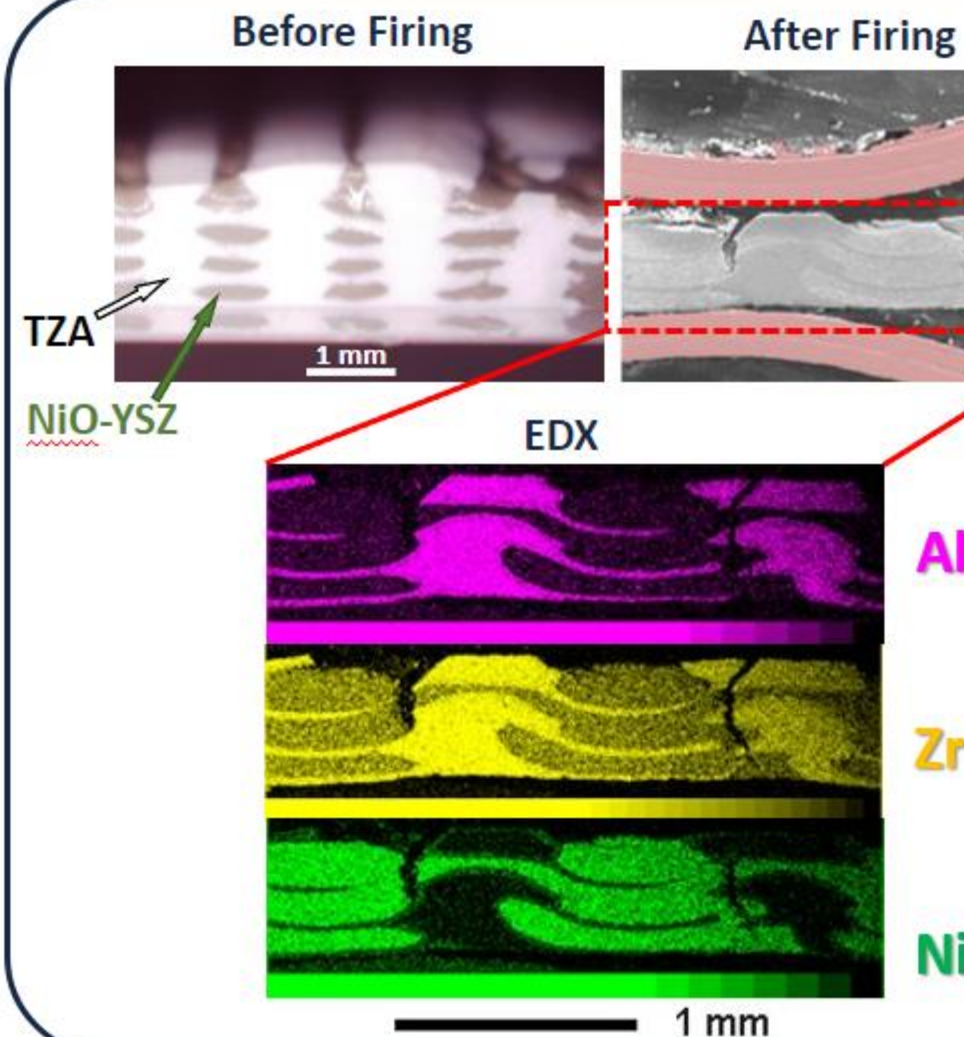
Characterization of Sintered Inkjet Printed Sample

Surface Profilometry





FESEM/EDX



Micro-Extrusion Printing

nScrypt Printing Parameters

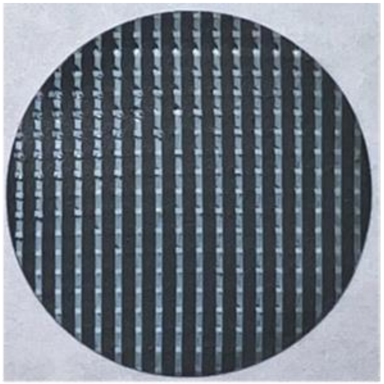
Parameter	Value
Substrate Material	PTFE
Dispensing Tip Size (Gauge/Inner Diameter)	23 / 564 µm
Pneumatic Dispensing Pressure	7.5 psi
Layer Thickness	100 µm
Valve Open Wait Time	0.05 s
Print Speed	50 mm/s
Valve Open Speed	0.5 mm/s
Valve Close Speed	12 mm/s

5-Layer Sample

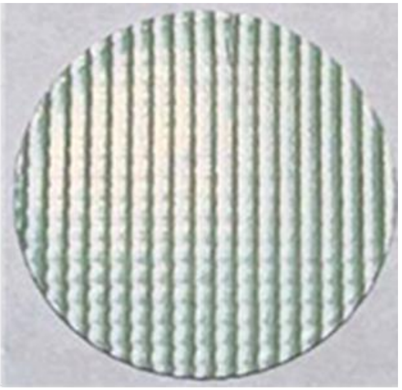
Firing and Shrinkage of Micro-Extrusion Printed Sample

As-Printed nScrypt Sample

Laser Cut Sample

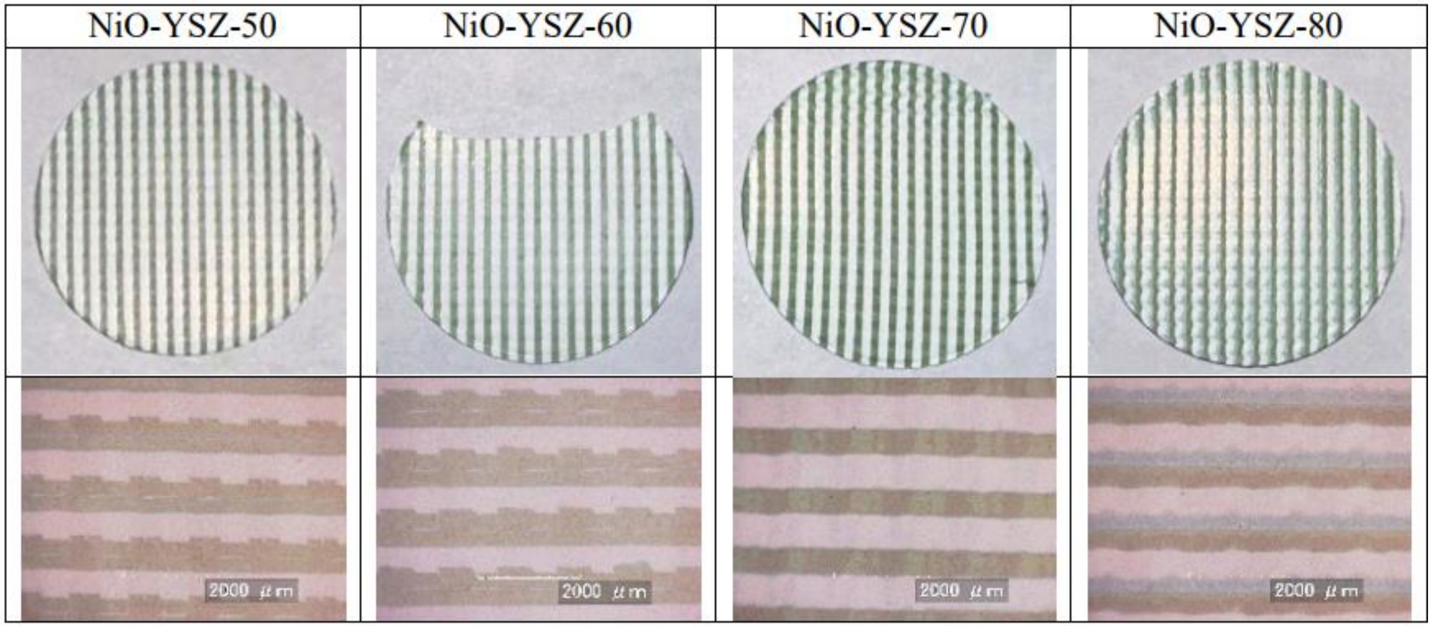


Stand-Alone Laser Cut Sample Prior to Sintering (25 mm diameter)

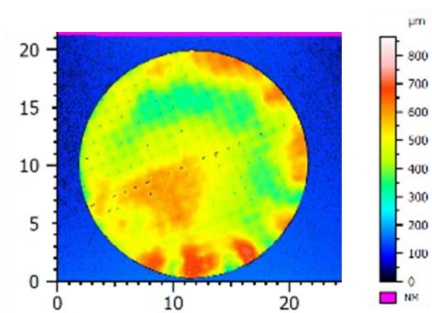


Sintered Disk (19.5 mm diameter)

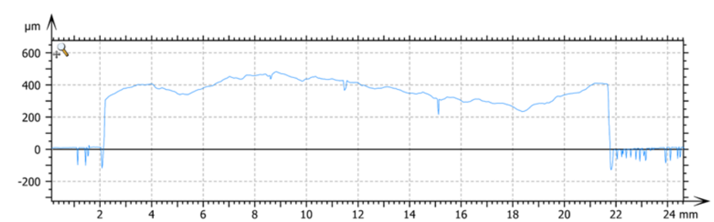
Characterization of Sintered Micro-Extrusion Printed Samples



The sintered sample did not exhibit any cracks;



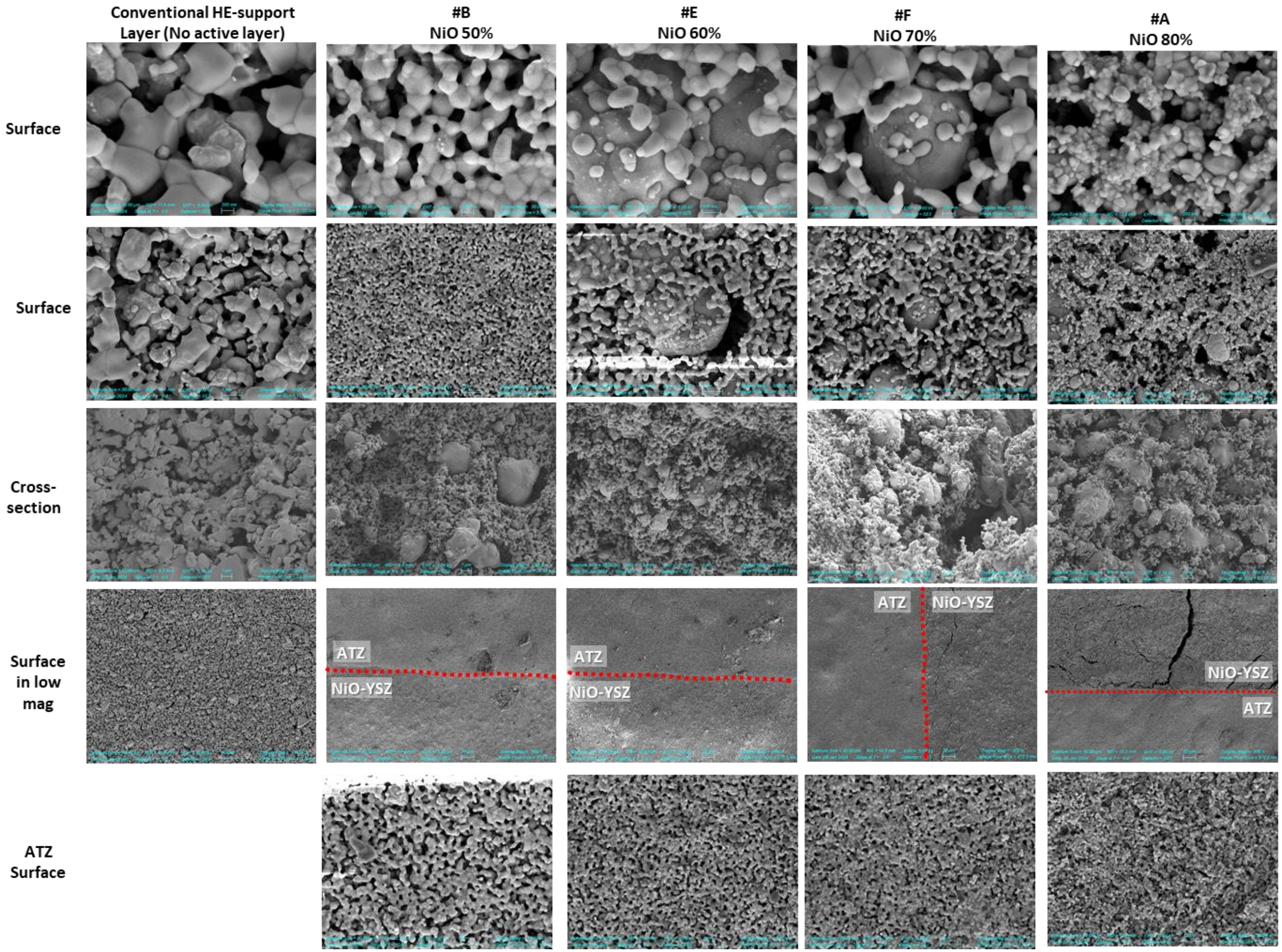
Sintered Part Thickness = 400 µm for a 5 layer sample

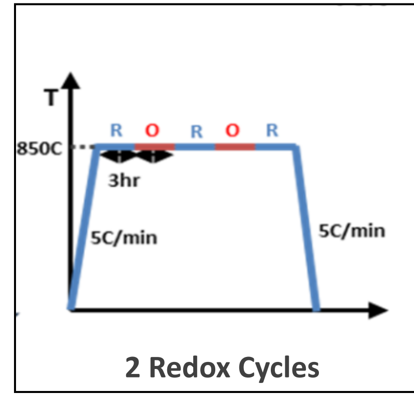


Flatness of the sintered cell

Fabrication Development of Hydrogen Electrode Support 3D Structure

Redox Cycle Testing

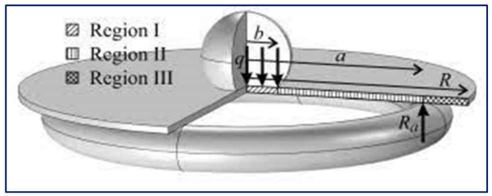


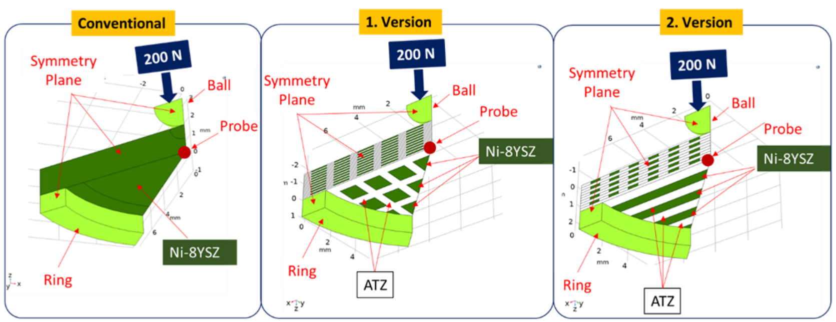


No cracks in the ATZ structure

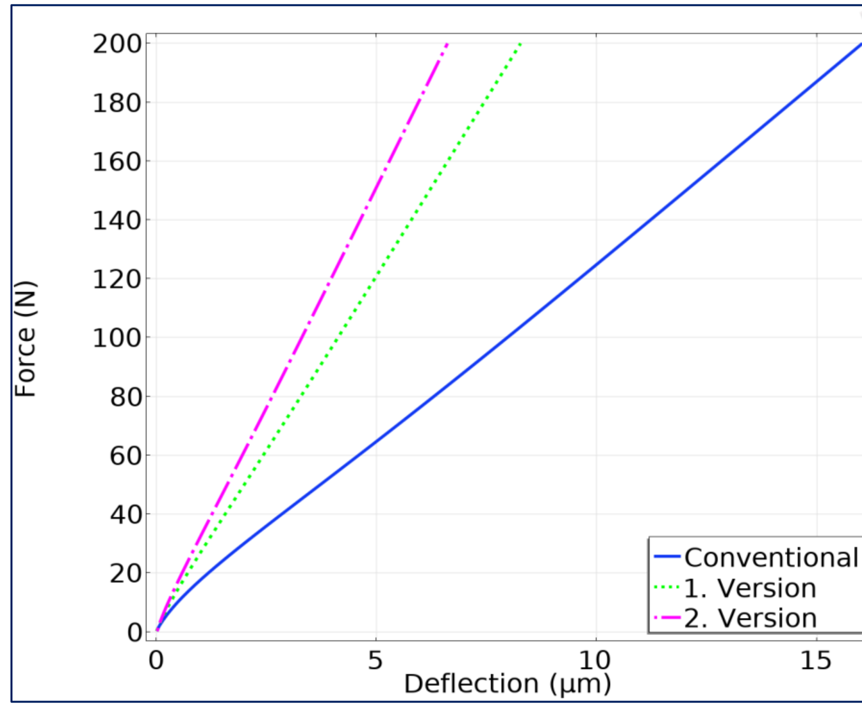
3D Structure Rupture Strength Simulation

Ball-on-Ring Setup





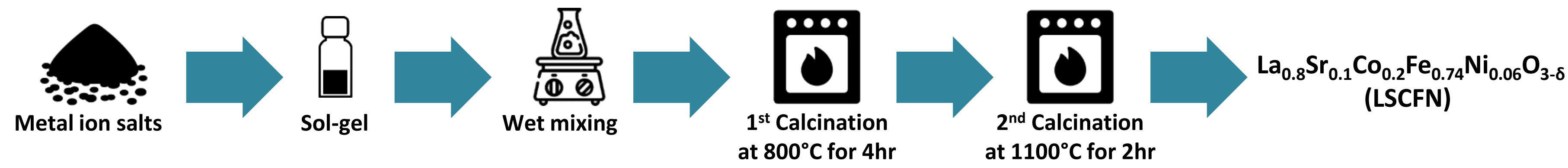
Transverse Rupture Strength Simulation



Simulated Deflection of Hydrogen Electrode Supports under Increasing Load

Synthesis of Ni-Substituted LSCF (LSCFN)

Synthesis Process

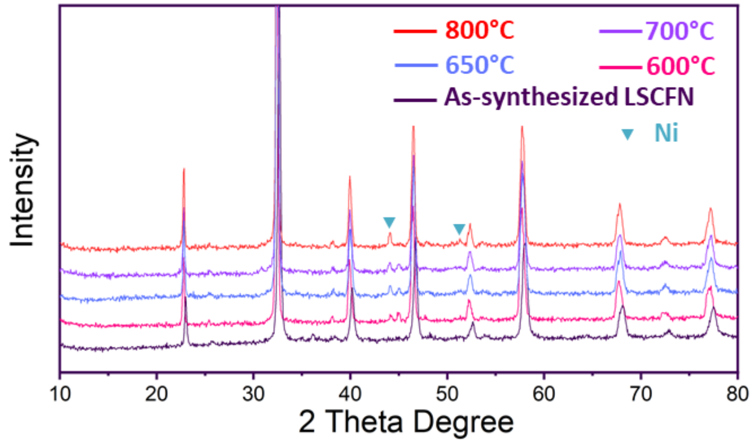


- **Sol-gel Process**

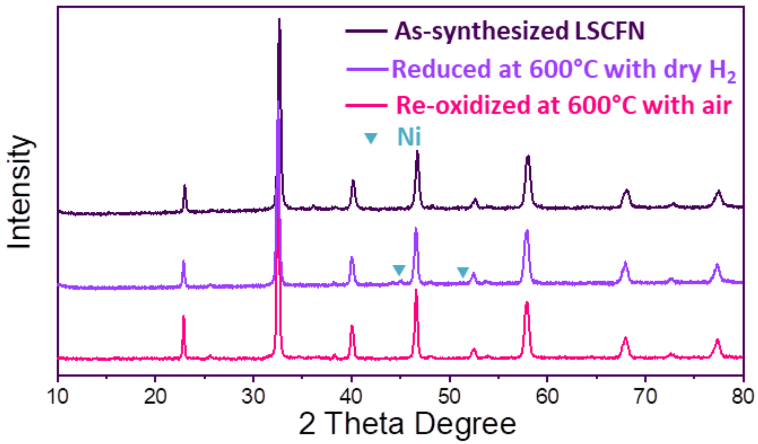
- **Metal Ion Precursors**
  - $La(NO_3)_3 \cdot 6H_2O$
  - $Sr(NO_3)_2$
  - $Co(NO_3)_2 \cdot 6H_2O$
  - $Fe(NO_3)_3 \cdot 9H_2O$
  - $Ni(NO_3)_2$

Characterization of LSCFN Powder - XRD

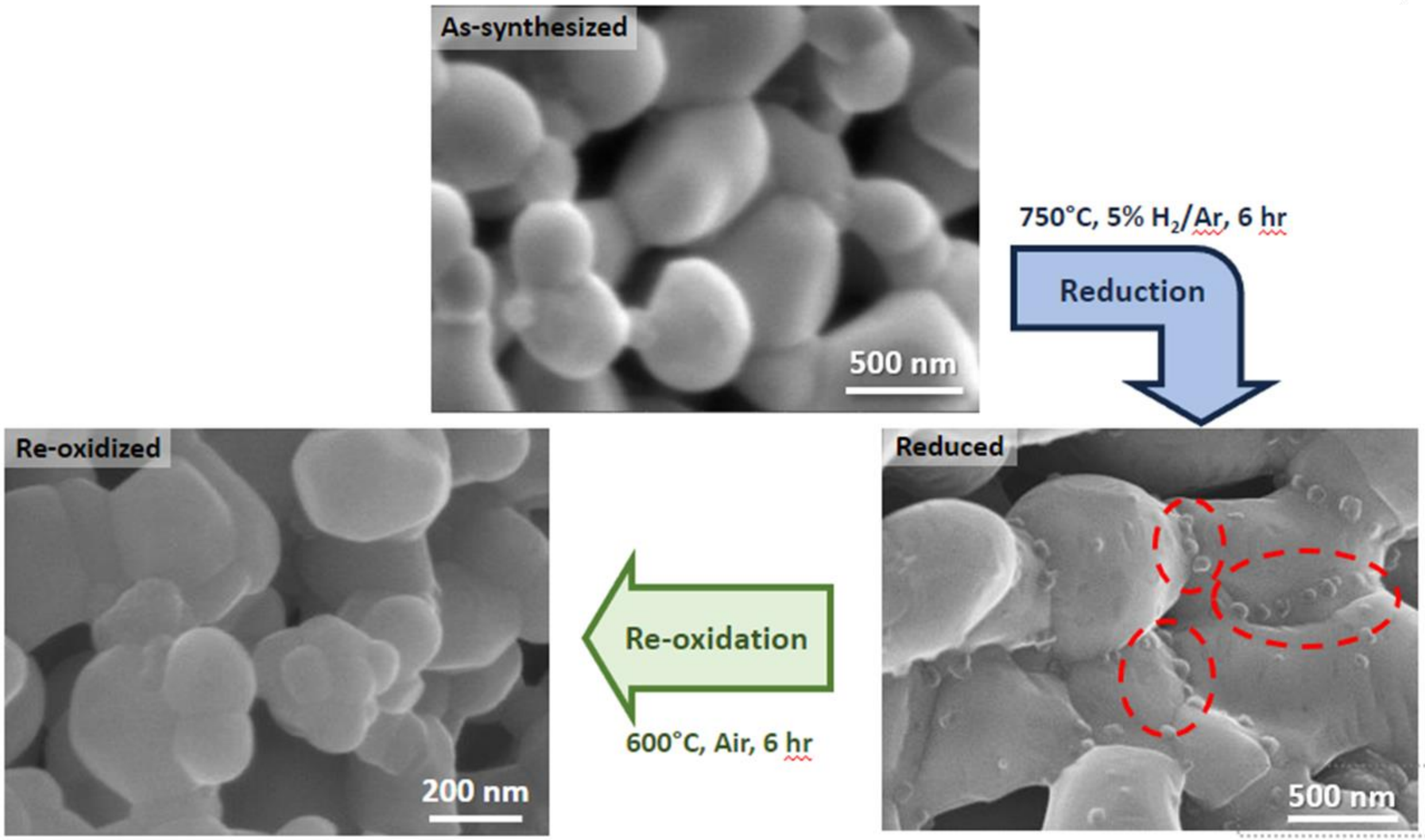
- **Reduced LSCFN at different temperature with 50% H_2-50% H_2O**
  - No impurities observed
  - Ni peaks at 44° and 52°, more prominent as temperature increases



- **Re-oxidation of LSCFN**
  - No secondary phase observed
  - Ni peaks completely disappeared after re-oxidation



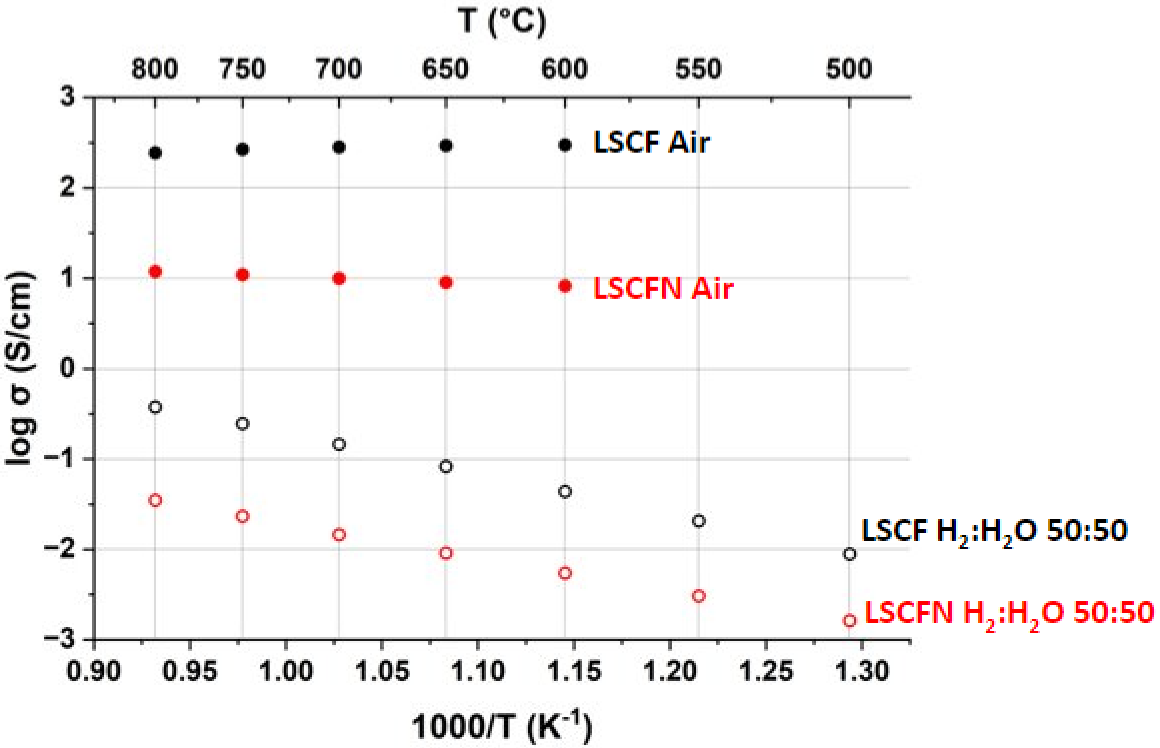
Characterization of LSCFN Powder -FESEM



Reversible Exsolution
No Trace of Exsolution

Characterization of LSCFN Powder - Conductivity

- Commercial LSCF: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$
- Synthesized LSCFN: $La_{0.8}Sr_{0.1}Co_{0.2}Fe_{0.74}Ni_{0.06}O_{3-\delta}$



Ni-Substituted Perovskite Hydrogen Electrode Active Layer

Reduction of New Stoichiometry LSCFN -FESEM

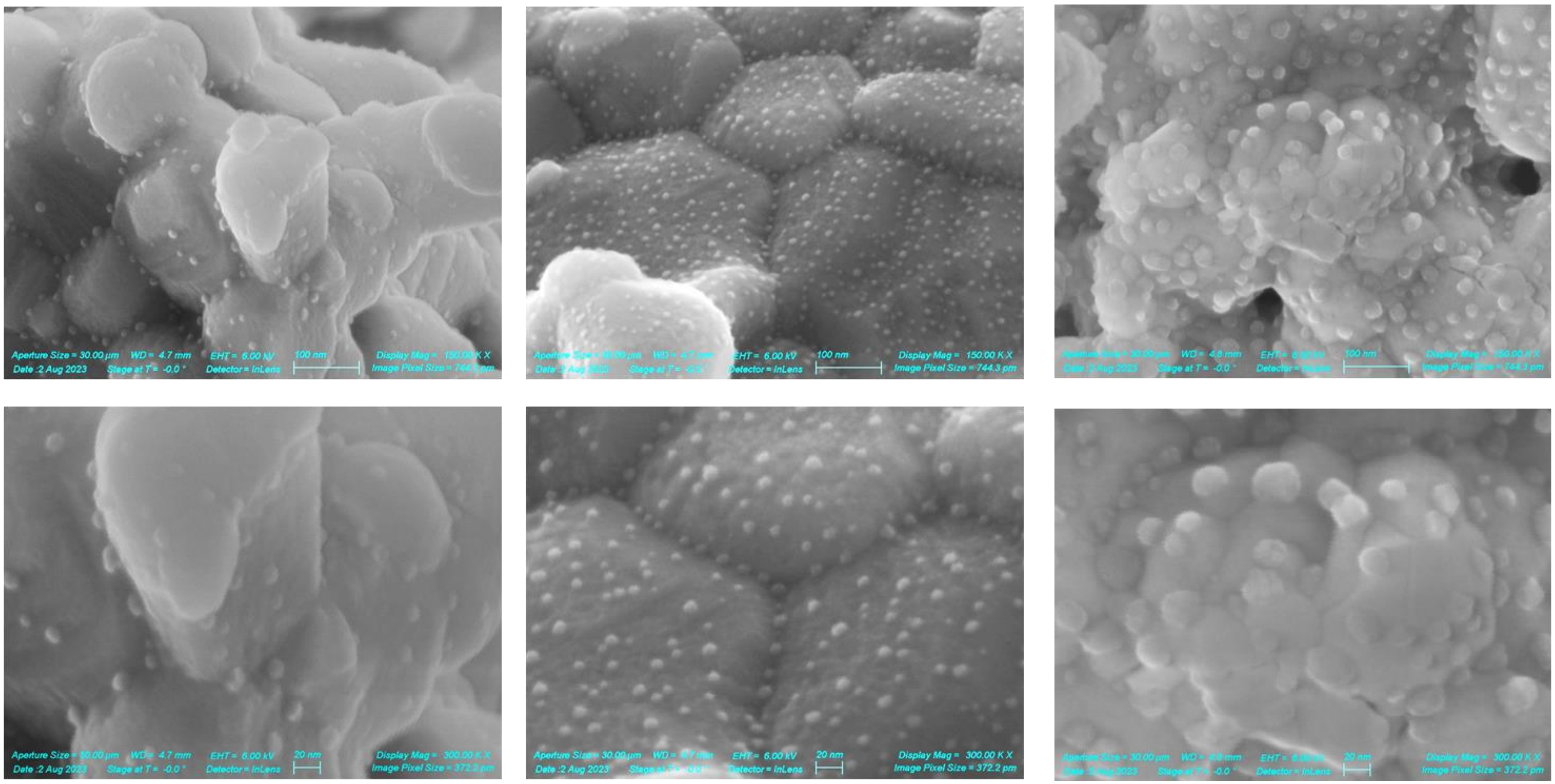
$(La_{0.6}Sr_{0.4})_{0.9}Co_{0.2}Fe_{0.74}Ni_{0.06}O_3$ (A-site deficient)

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.74}Ni_{0.06}O_3$ (A-site balanced)

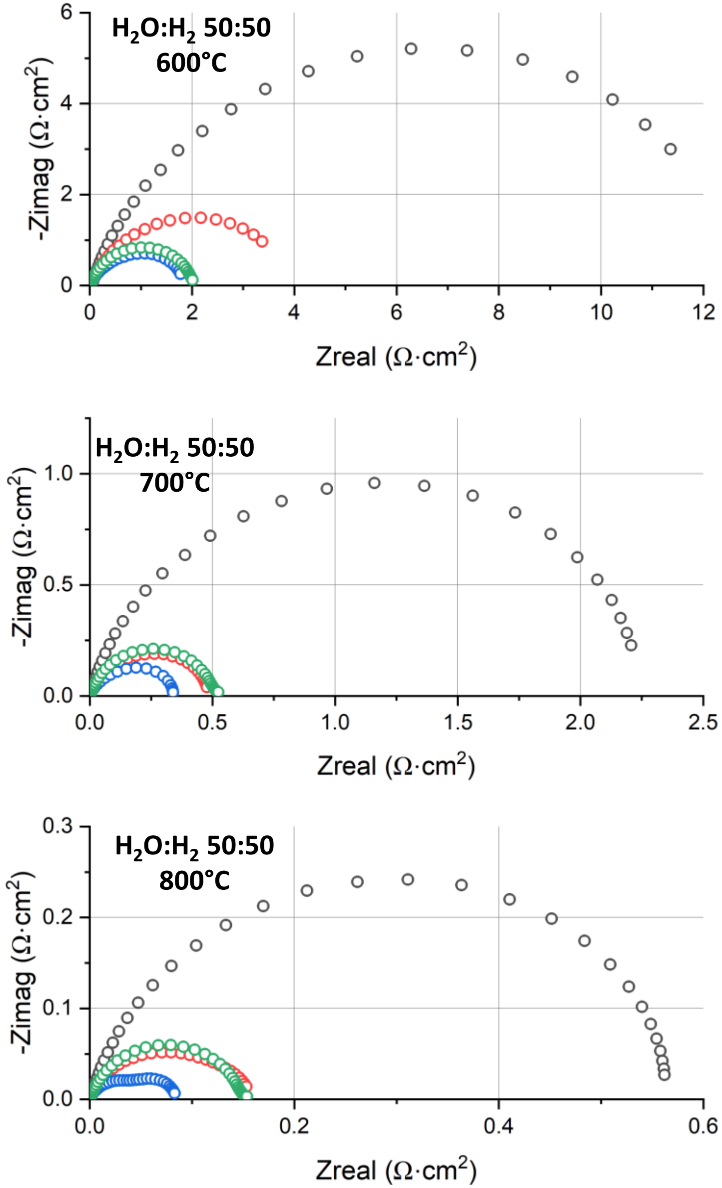
600°C A-site deficient

600°C A-site balanced

700°C A-site balanced



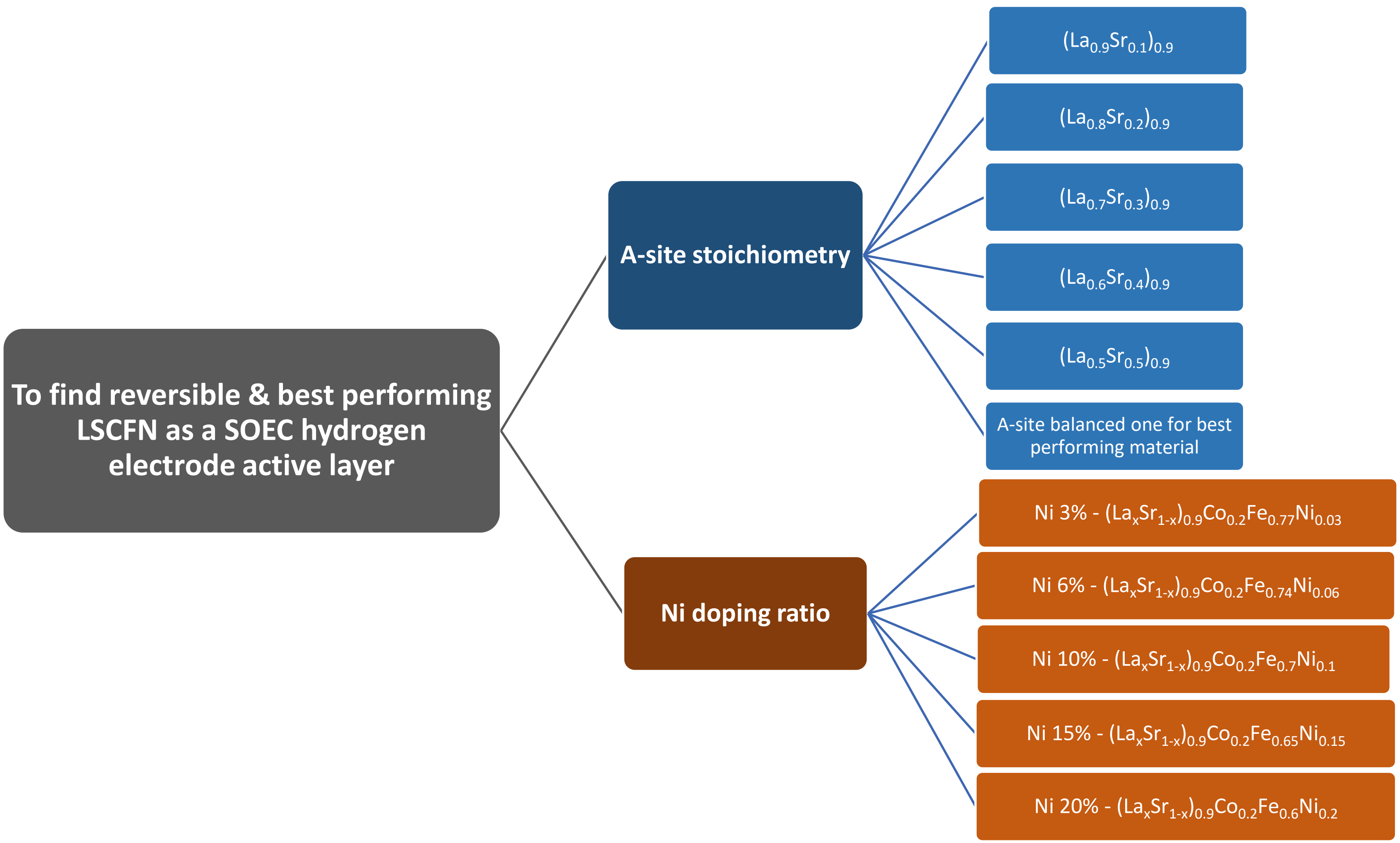
Electrochemical Characterization of LSCFN



- **Symmetrical cell AC Impedance**
  - LSCFN7328 showed the least polarization resistance

○ **Commercial LSCF-GDC**
○ **LSCFN 6428 - GDC ($(La_{0.6}Sr_{0.4})_{0.9}Co_{0.2}Fe_{0.7}Ni_{0.1}$)**
○ **LSCFN 7328 - GDC ($(La_{0.7}Sr_{0.3})_{0.9}Co_{0.2}Fe_{0.7}Ni_{0.1}$)**
○ **LSCFN 8228 - GDC ($(La_{0.8}Sr_{0.2})_{0.9}Co_{0.2}Fe_{0.7}Ni_{0.1}$)**

Blueprint for LSCFN Research



Highlights

- **Fabrication of 3D hydrogen electrode supports**
  - Inkjet printing and micro-extrusion processes for 3D structure fabrication
  - Demonstration of fabrication of hydrogen electrode support 3D structures
  - Demonstration of redox resistance
- **Metal exsolution of substituted perovskite for hydrogen electrode active layer**
  - Reversible exsolution/dissolution
  - Nickel exsolution, electrical and electrochemical characteristics

Acknowledgments

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