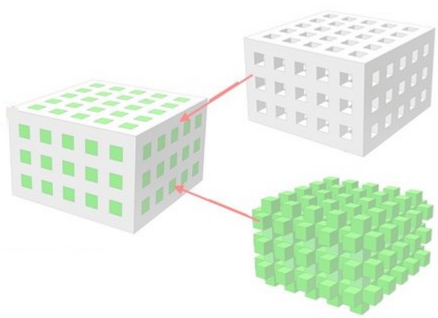
2023 FECM / NETL Spring R&D Project Review Meeting
April 18-20, 2023
Pittsburgh, PA

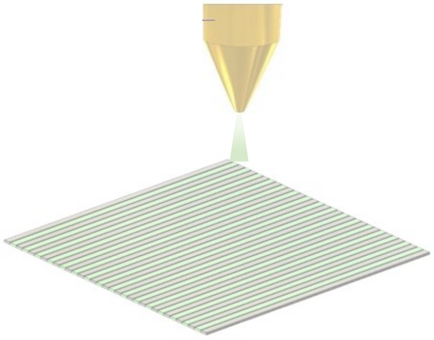
Development of Novel 3D Cell Structure and Manufacturing Processes for Highly Efficient, Durable, and Redox Resistant Solid Oxide Electrolysis Cells

DE-FE 0032107

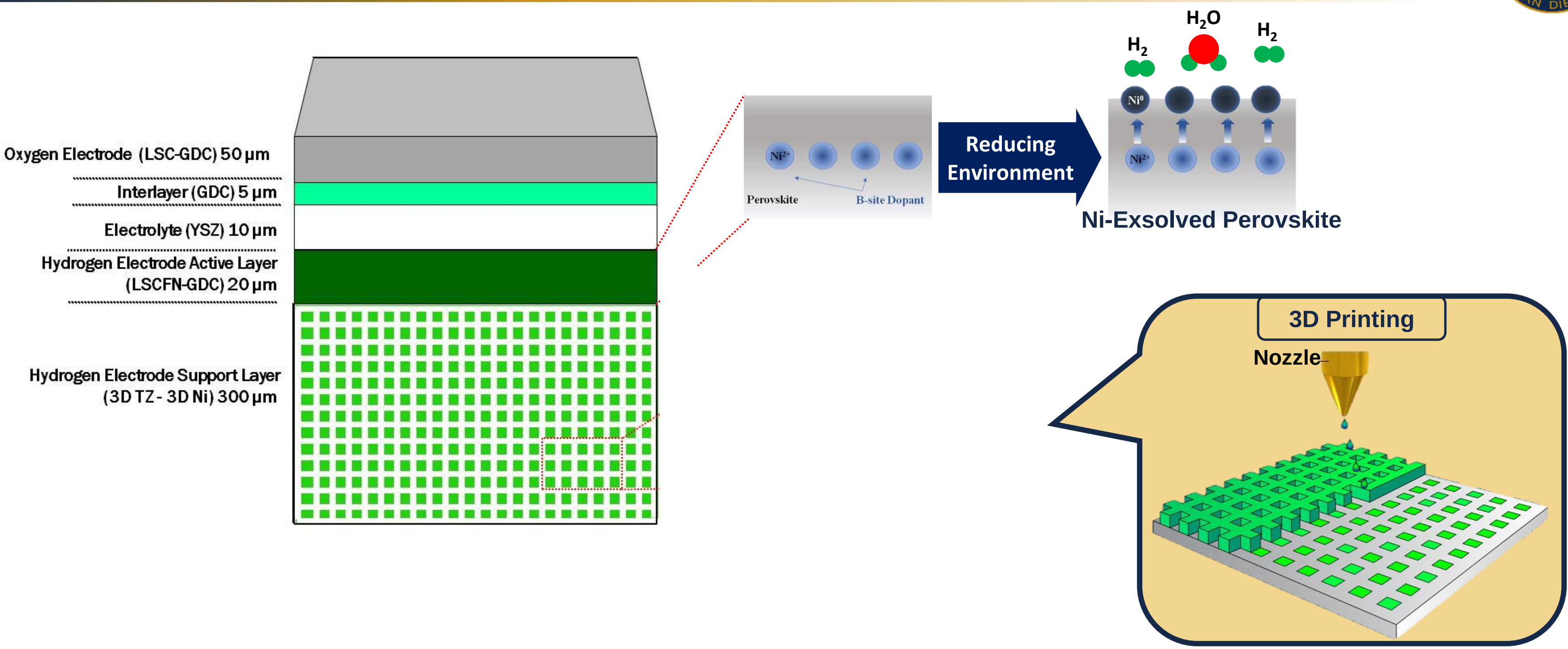


Sanghoon Lee, Ph.D.
Center for Energy Research
University of California, San Diego

PI: Dr. Nguyen Q. Minh



Project Overview



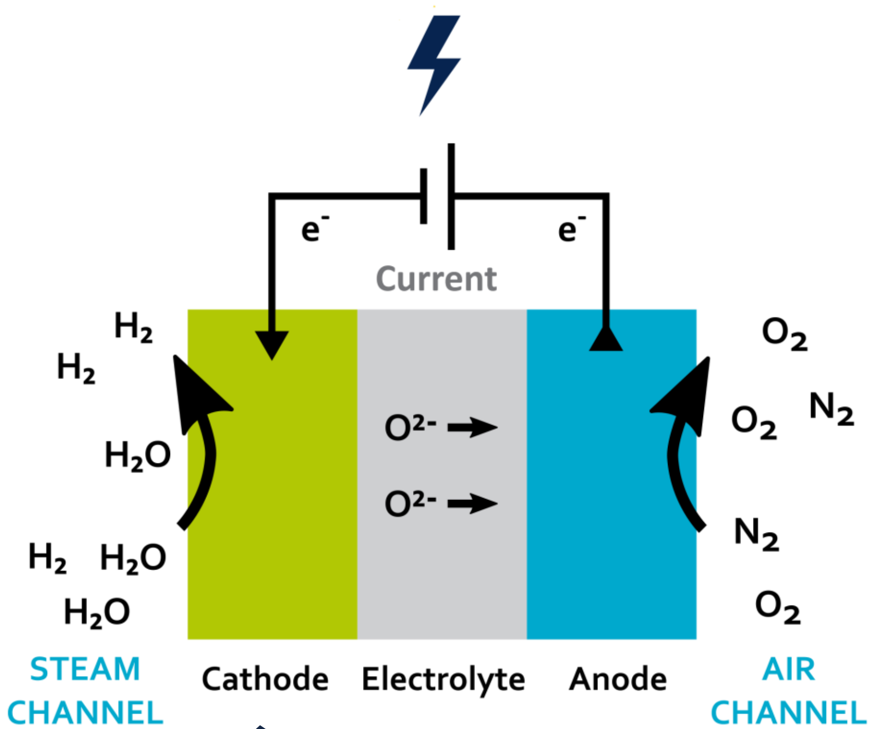
- **Objective**

  Develop and demonstrate highly efficient, durable, and redox resistant solid oxide electrolysis cells (SOECs) with a focus on

  1) **A cell design** with the <u>hydrogen electrode composed of two layers</u> – a 3D hydrogen electrode support layer and an exsolved perovskite hydrogen electrode active layer

  2) **A manufacturing scheme** incorporating <u>advanced 3D printing</u> for fabrication of the cell configuration

SOEC and Hydrogen Electrode



Hydrogen Electrode (ex., Ni-YSZ, etc.)

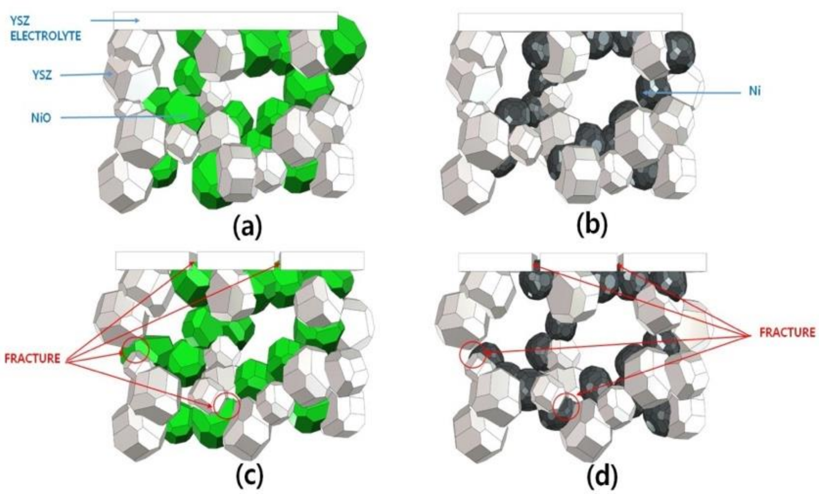
- Redox-tolerance
- Performance degradation

Ni-YSZ Hydrogen Electrode

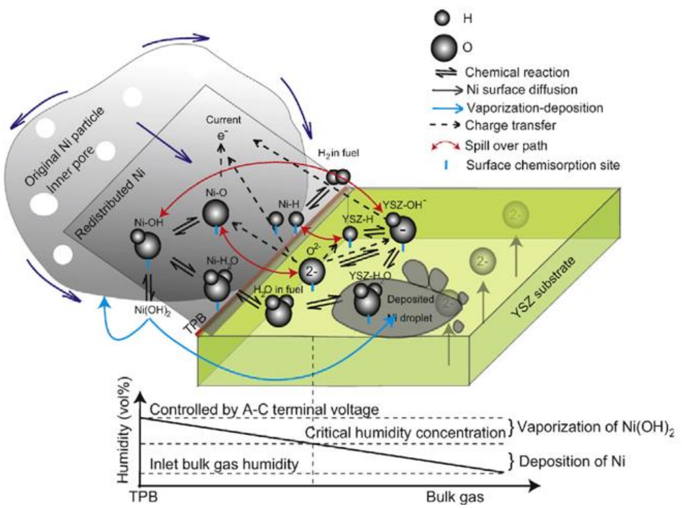
Merits of Ni-YSZ

- Great catalytic activity & electric conductivity
- Thermal stability & good compatibility
- Non-noble metal

Challenge 1) Redox-instability

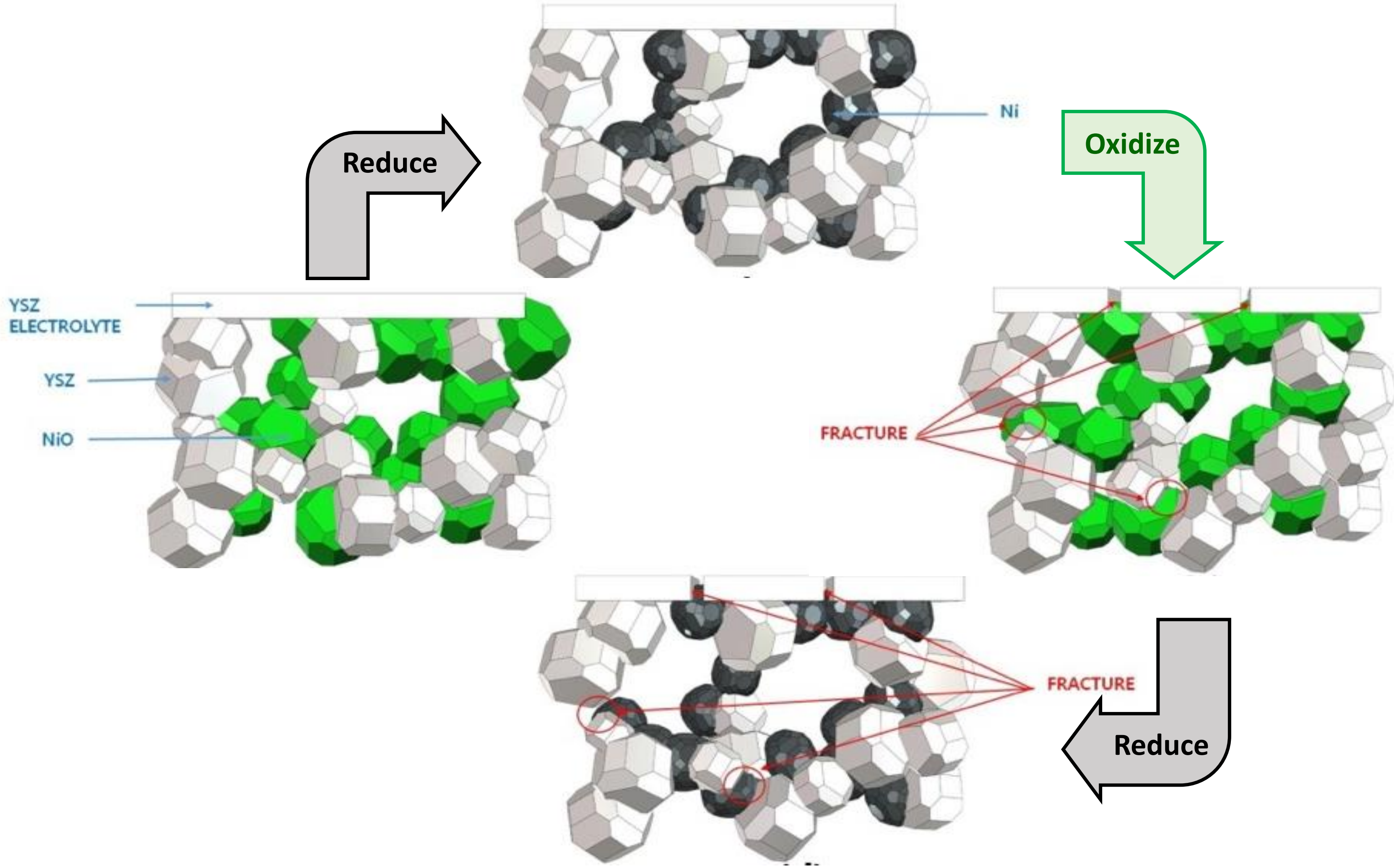


Challenge 2) Nickel agglomeration/migration



M.S. Khan et al., Ceramics International 42 (2016) 35–48

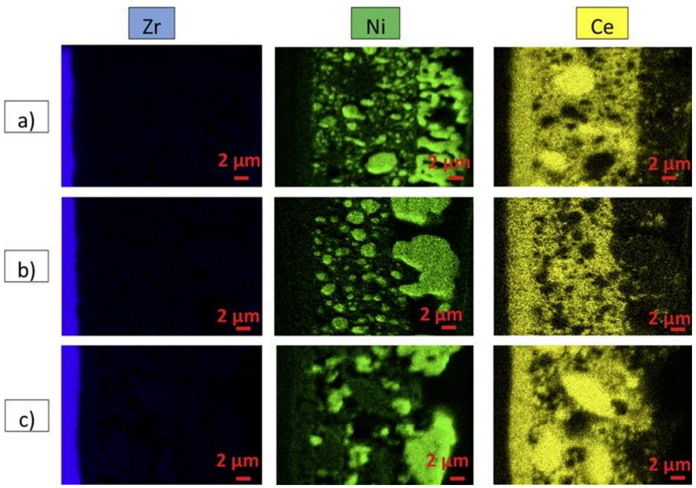
Redox-Instability



- Made with conventional ceramic forming techniques (ex., tape-casting)
  - Dramatic volume expansion/shrinkage

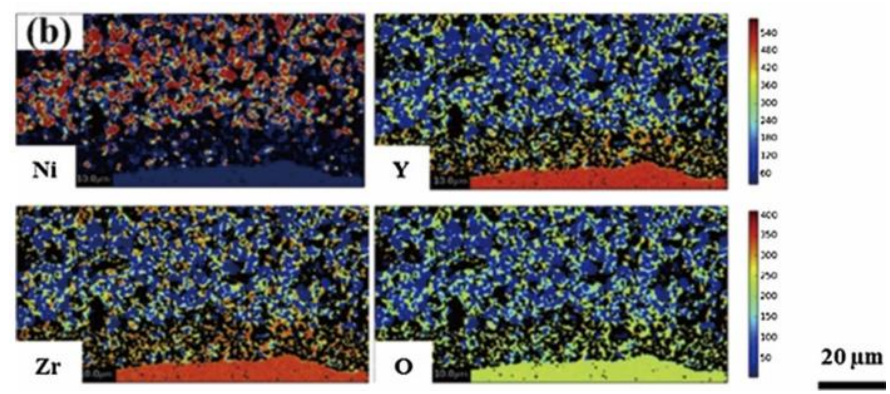
Nickel Agglomeration/Migration

Nickel particle agglomeration



A. Zekri et al., Fuel Cells, 17 (2017) 359-366

Nickel migration/depletion

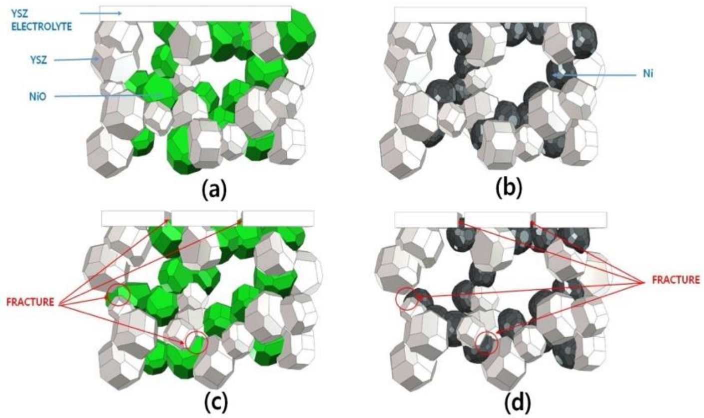


J. C. De Vero et al., J. Electrochem. Soc. 163 (2016) F1463–F1470

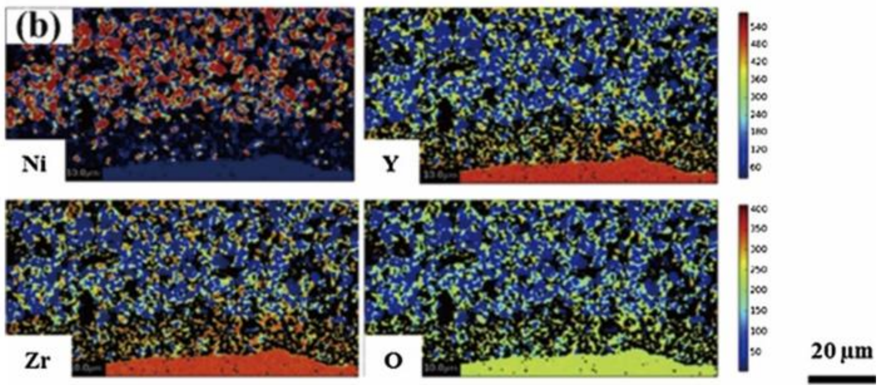
- Loss of **electrical conductivity** of the hydrogen electrode
- A reduction of available triple phase boundaries (TPBs)

Proposed Approach

Redox-instability

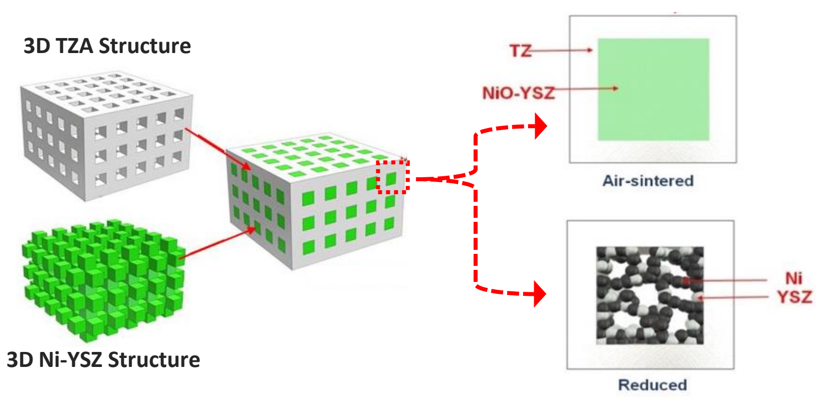


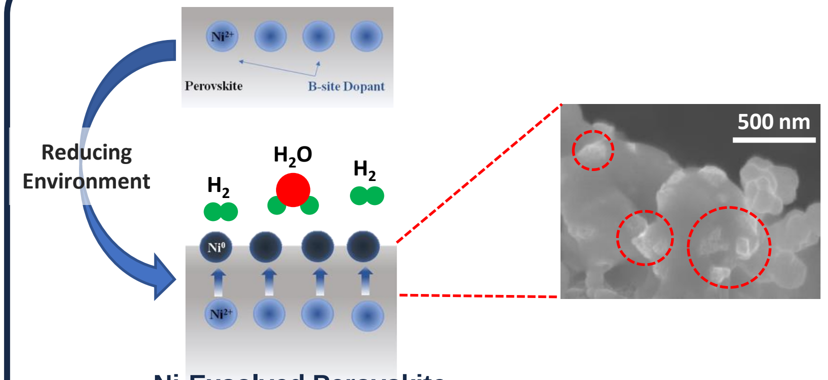
Nickel agglomeration/migration



3D Hydrogen-electrode Support Structure

Ni-substituted Perovskite

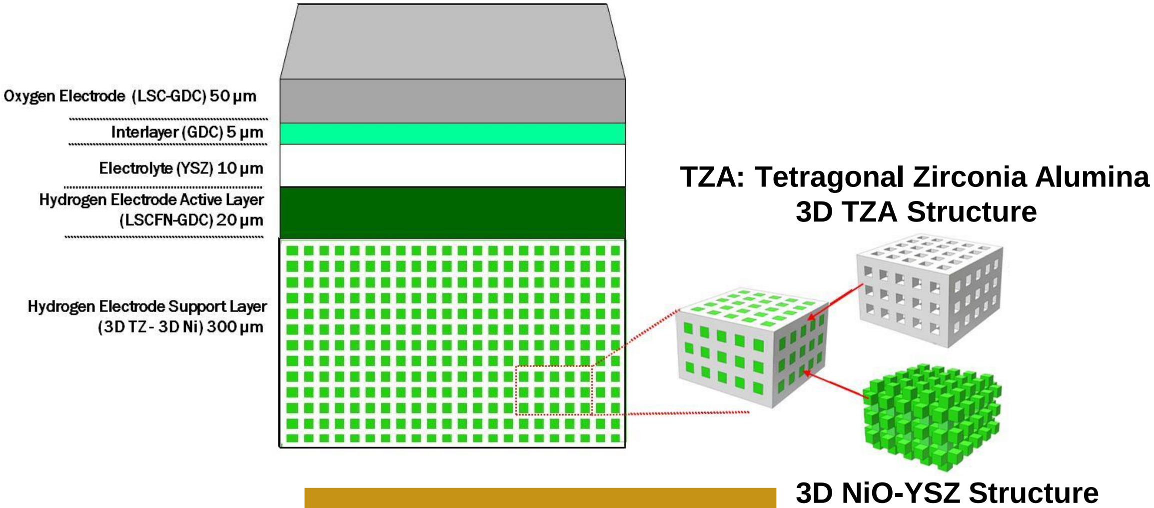




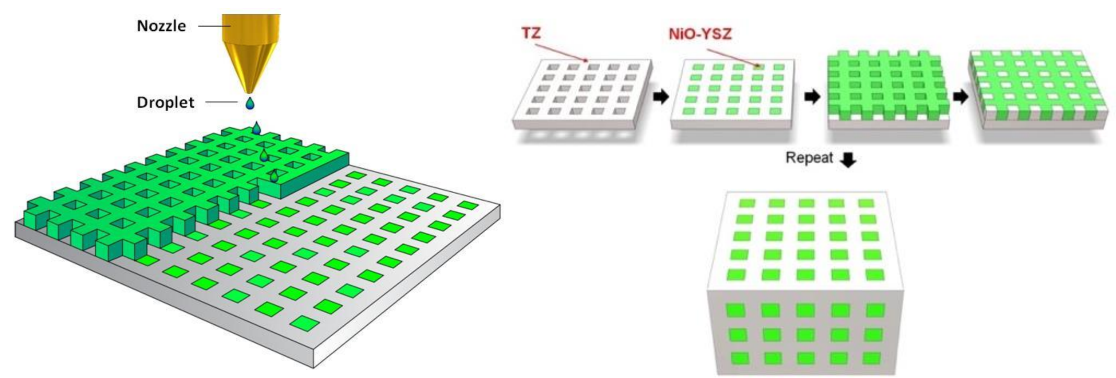
J. C. De Vero et al., J. Electrochem. Soc. 163 (2016) F1463–F1470

3D Hydrogen Electrode Support

3D Hydrogen Electrode Structure



3D Printing



What Do We Need for 3D Printing?

Ink

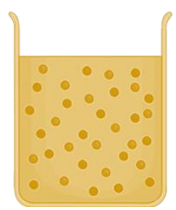
- Rheology
- Stability

Printing Equipment

- Jetting voltage
- Frequency
- Drop

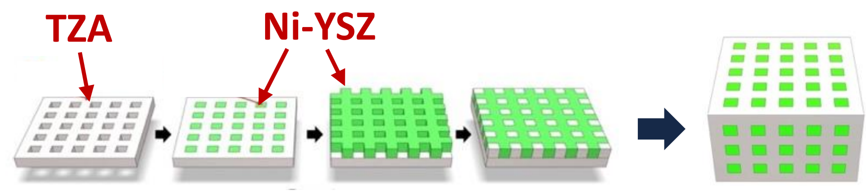
Ink Vehicle (Let down)

Aqueous Dispersion

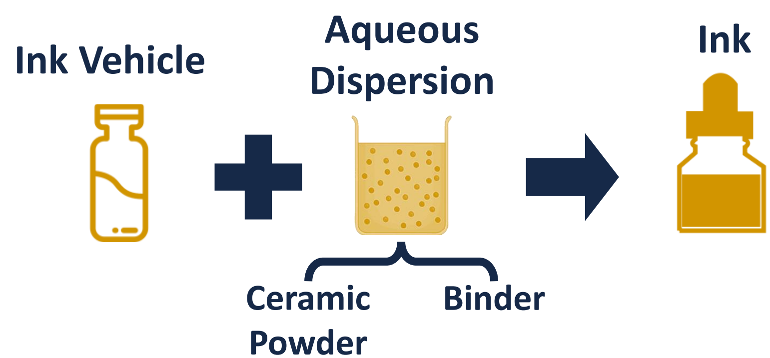


Ink Rheology

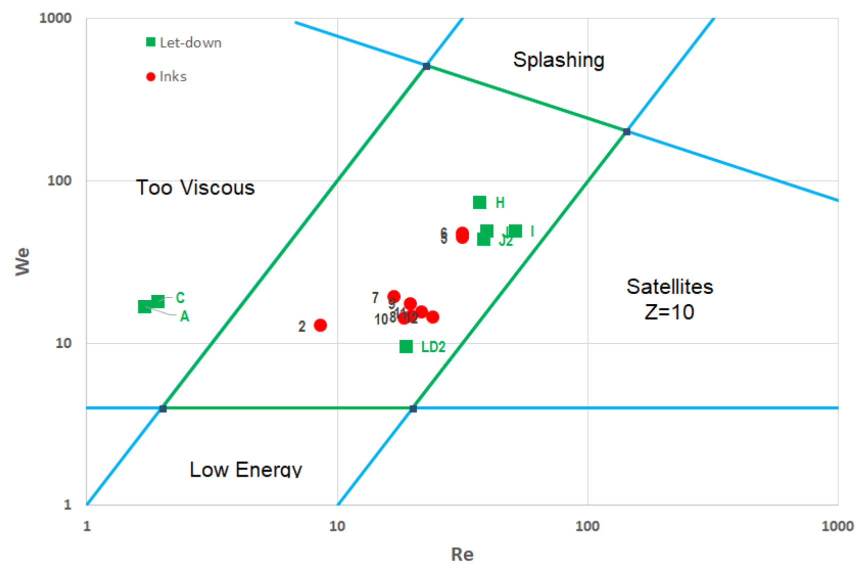
- Two Inks for Inkjet printing of 3D Ni-YSZ Support



- Ink Formulation



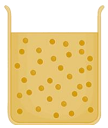
- Viscosity / Surface tension
  Re We



Ink Stability

Solid Loading of Ink

Aqueous Dispersion



Ceramic Powder

Binder

$$\text{Solid Loading} = \frac{W_{ceramic}}{W_{tot}}$$

TZA dispersion: up to 40% (w/w) (= 20% for ink)

NiO-YSZ dispersion: up to 20% (w/w) (= 10% ink)

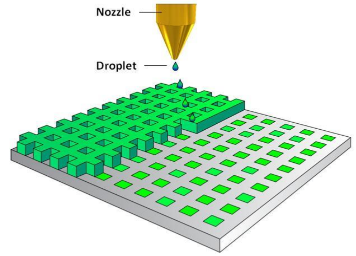
Dispersion Stability

300 hr Passed

TZA dispersions: several months

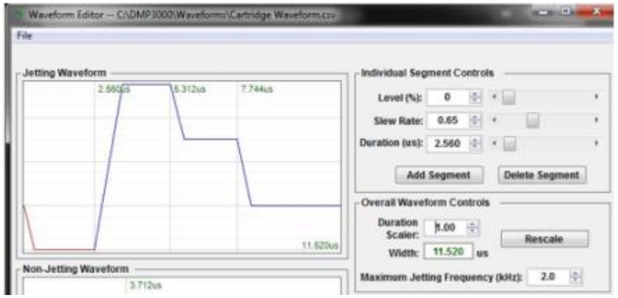
NiO-YSZ dispersions: over 1 month

3D Printing Parameters

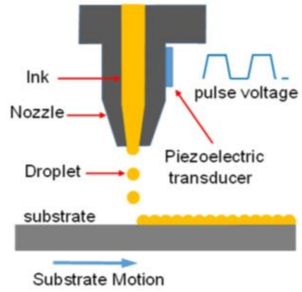


Printing Parameters

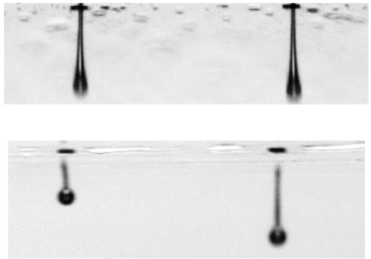
Jetting Voltage Waveform



Frequency & Drop Spacing



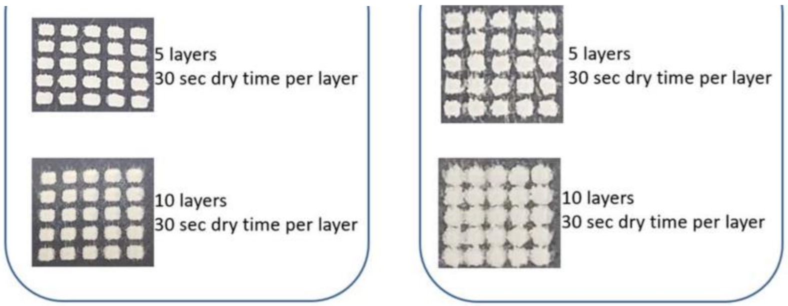
Ink Property



3D Printing Examples

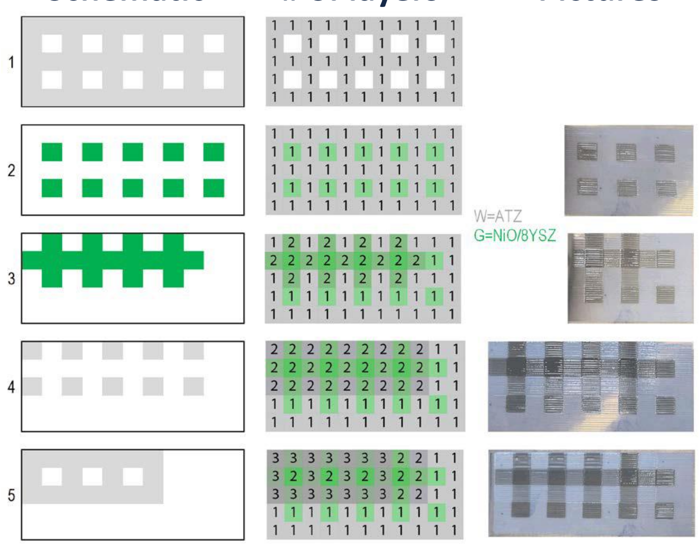
Example of Spacing and Resolution

1mm squares/1mm spacing | 0.5mm squares/0.5mm spacing

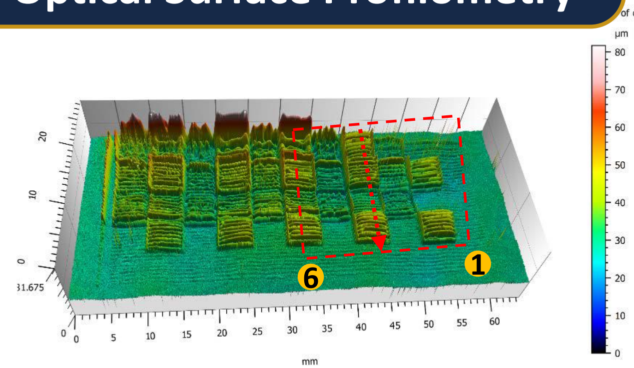


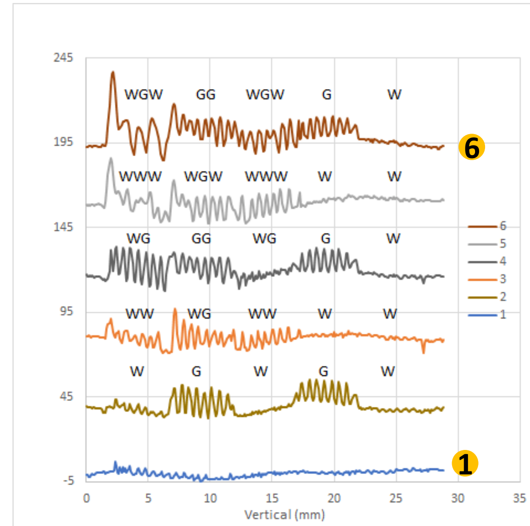
Layer Printing Strategy

Schematic | # of layers | Pictures



Optical Surface Profilometry





Parameters for Firing

After firing, the defined 3D structure must be maintained.

What parameters do matter for firing?

Ink Solid Loading

Ink Stability

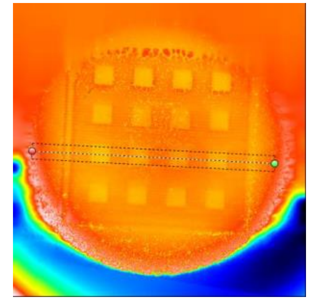
Firing of 3D Hydrogen Electrode

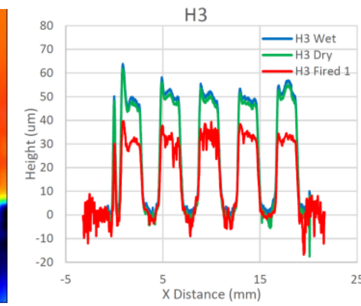
TZA-only

Before Firing

After Firing

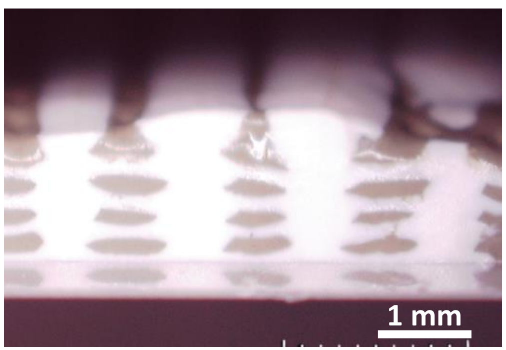
Profilometry



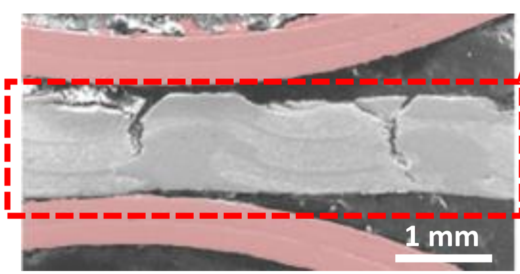


TZA-Ni/YSZ Two-phase

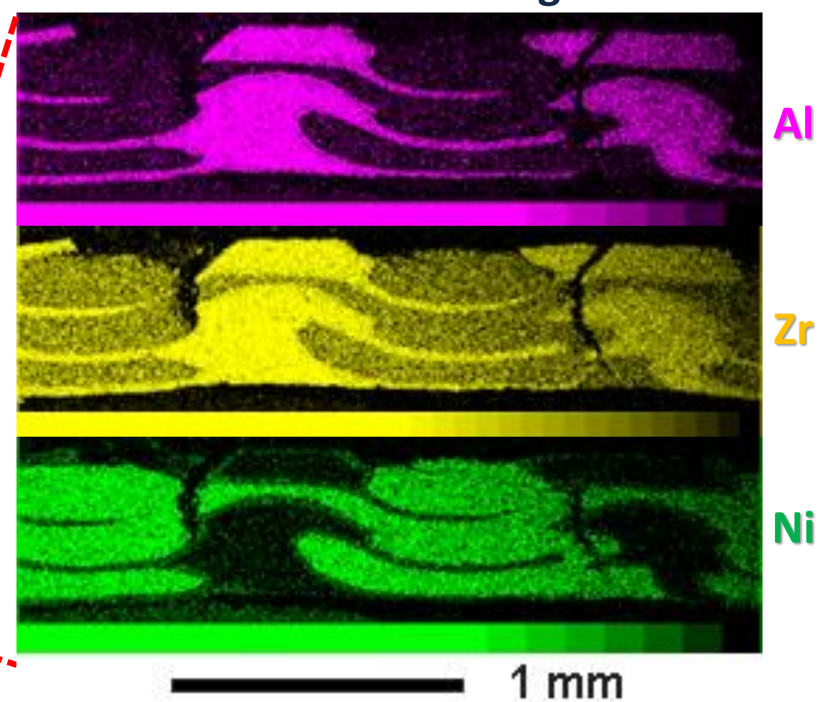
Before Firing



After Firing



EDX After Firing



Near-term Plans

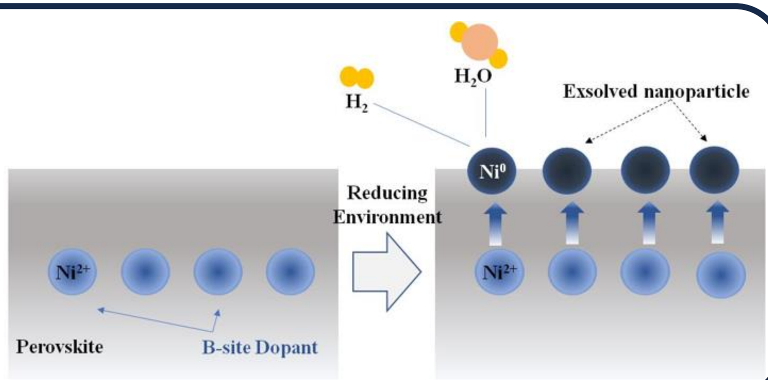
- Co-firing of TZA + NiO-YSZ / LSCFN-GDC / YSZ
- 3D Printing parameters optimization
- Refining firing process to avoid delamination and breakage
- Mechanical & electrochemical evaluation of 3D hydrogen electrode structure

Ni-Substituted Perovskite for Hydrogen Electrode Active Layer

What is Ni-Exsolved Perovskite?

LSCFN

- $La_{0.9-x}Sr_x Co_{0.2}Fe_{0.8-y}Ni_yO_{3-\delta}$ (LSCFN)
- Exsolution of Ni in reducing environment

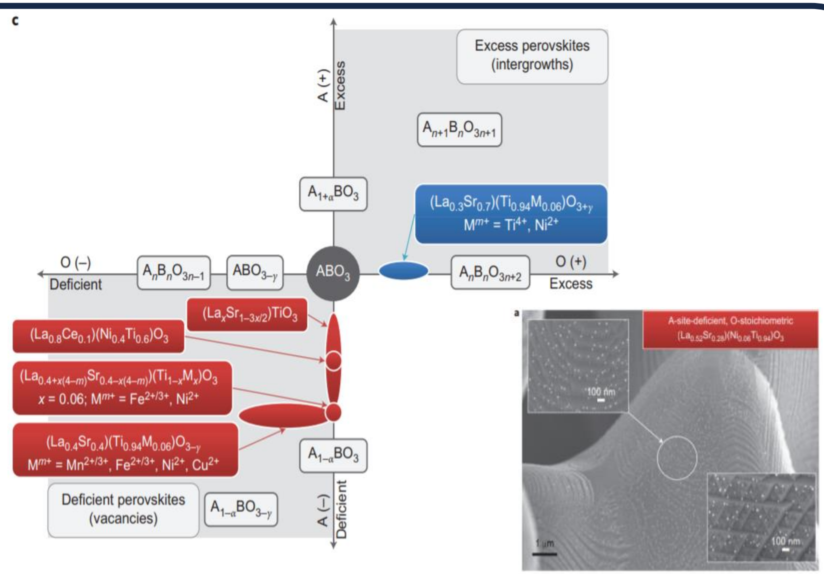


Principle of Exsolution

- $A_{1-\alpha}BO_{3-\delta}$ ➔ A-site deficiency
- Exsolution of B-site metals

$$A_{1-\alpha}BO_{3-\delta} \xrightarrow{\text{Exsolution}} (1-\alpha)ABO_{3-\delta'} + \alpha B \qquad (1)$$

$$ABO_{3-\delta} \xrightarrow{\text{Exsolution}} (1-\alpha)ABO_{3-\delta''} + \alpha AO + \alpha B \qquad (2)$$

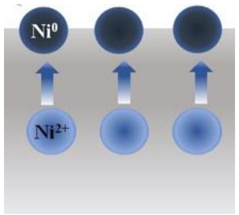


D. Neagu et al., Nat. chem., 5, (2013): 916-923.

Why Ni-Exsolved Perovskite?

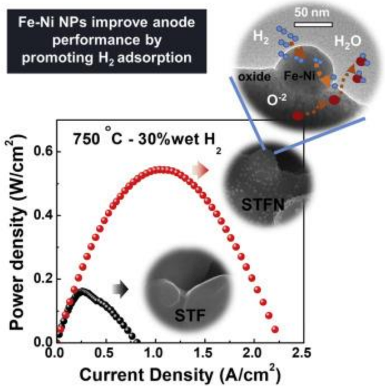
Material Property

- Ni: Excellent catalytic activity, non-noble metal
- Stable in reducing environment
- Anchored structure to prevent agglomeration/migration → exsolution
- Exsolved nanoparticle: increase catalyst surface area



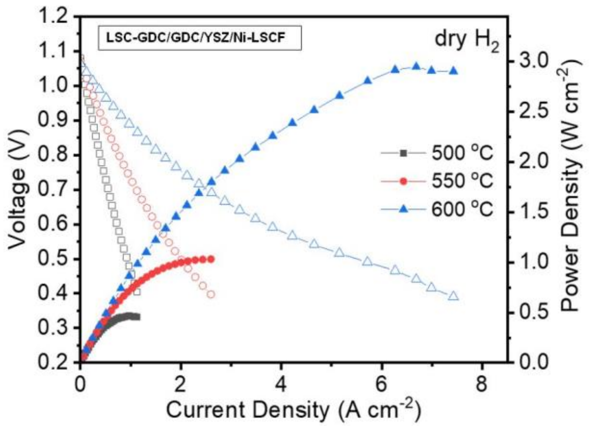
Preceding Research

- Great solution for Ni agglomeration issues



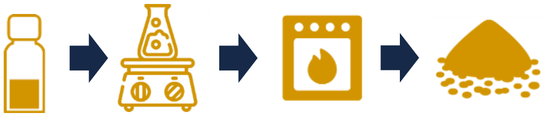
T. Zhu et al., Joule, 2 (2018) 478-496

- Preliminary Study at UCSD



How?

- **Fabrication: Sol-gel method**

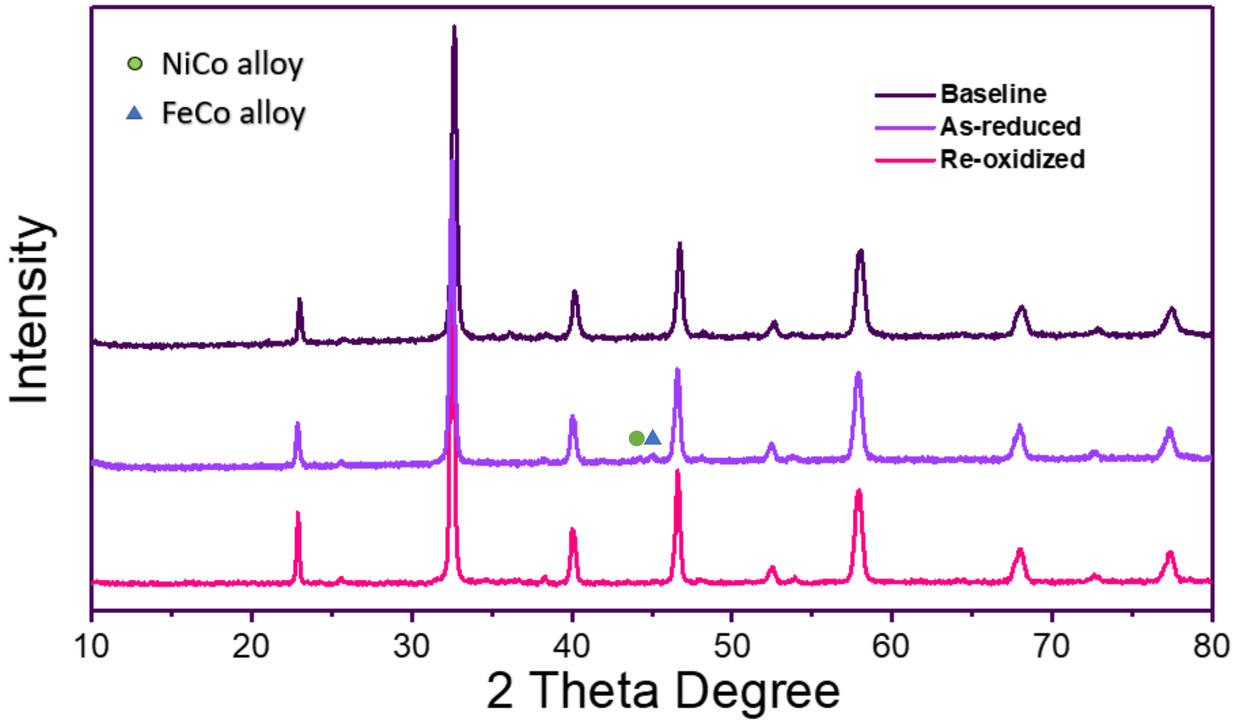


- **Characterization**

XRD	**Crystal Structure, Exsolved metal crystals**
FESEM	**Observation of exsolved nanoparticles**
Conductivity Test	**Pelletization & Van der Pauw method**
Electrochemical Characterization	**EIS Nyquist plot, i-V curve**

Characterization - XRD

As-synthesized, Reduced and re-oxidized LSCFN

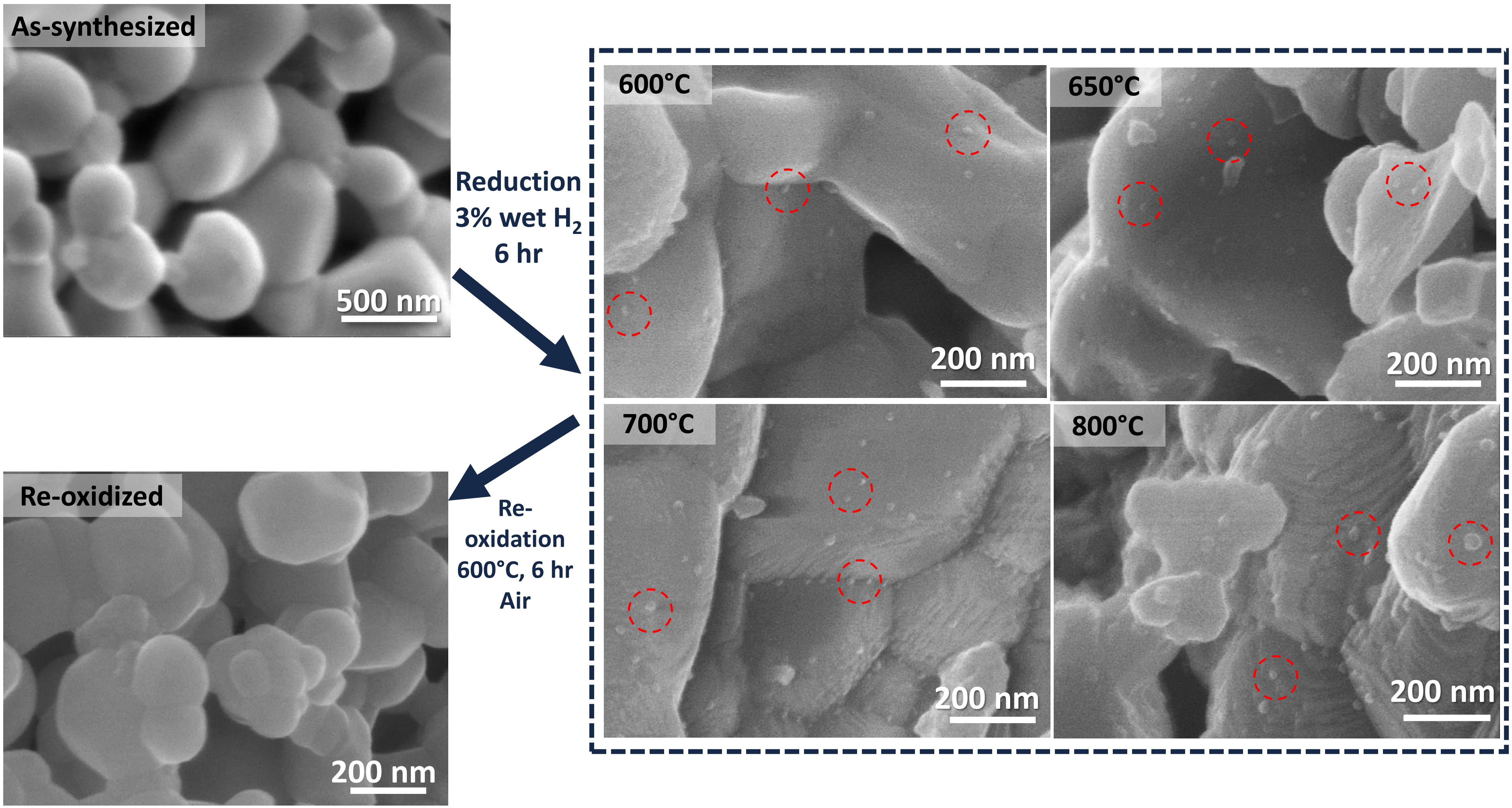


- **Reduction: Flow of dry hydrogen at 600°C with for 6 hr**
- **Reoxidation: Air-breathing at 600°C for 6 hr**

Capable of Exsolution/Dissolution

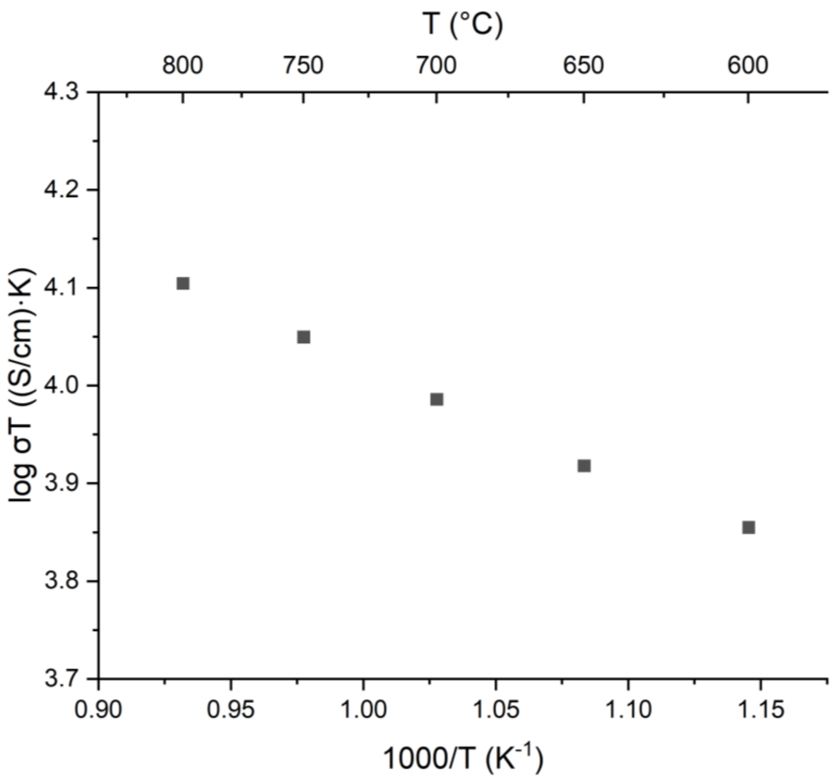
Characterization - FESEM

- Fully reversible exsolution of Ni particles



Characterization – Electronic Conductivity

- **Van der Pauw method**
- **Measured in air environment at 600-800°C**
- **Consistent with conductivity of LSCF with the same stoichiometry**



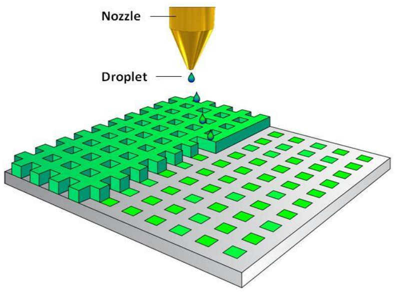
Near-term Plans

- **Electrochemical Test**
  - Symmetric cell test: LSCFN-GDC vs. LSCF-GDC vs. Ni-YSZ
  - Full SOEC test to determine iV curve and current density at 1.3V
- **Exsolution Study**
  - Long-term Study: Stability and growth of exsolved particles
  - Properties in Redox cycling

Highlights

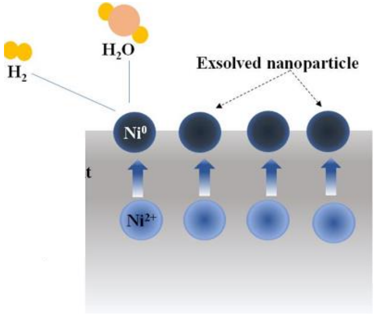
3D Hydrogen Electrode

- Ink and printing parameters defined
- Ink developed with sufficient stability
- Demonstrated printing and firing of defined structure



Ni-substituted Perovskite

- Reversible exsolution has been confirmed by XRD and FESEM
- Electronic Conductivity in air condition demonstrated
- Further detailed exsolution study planned



Acknowledgment

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

Project Manager: Sarah Michalik

UC San Diego

Dr. Nguyen Q. Minh (PI)

Prof. Ping Liu

Haichen Lin

RocCera

Dr. Sam Ghosh

Arkady Malakhov

Dr. Bruce Kahn (currently a professor at RIT)

RIT | Rochester Institute of Technology

Prof. Denis Cormier

Dr. Zhiheng Xu

Bobby Kovach

Thank You for Listening