Development of Ceramic Interconnect Materials for SOFCs

Kyung Joong Yoon, Jeffry W. Stevenson, and Olga A. Marina

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Motivation

Challenges of Acceptor-doped Lanthanum Chromite
- Inferior Sintering Behavior
- Reactivity with YSZ Electrolyte (Formation of Lanthanum Zirconate)

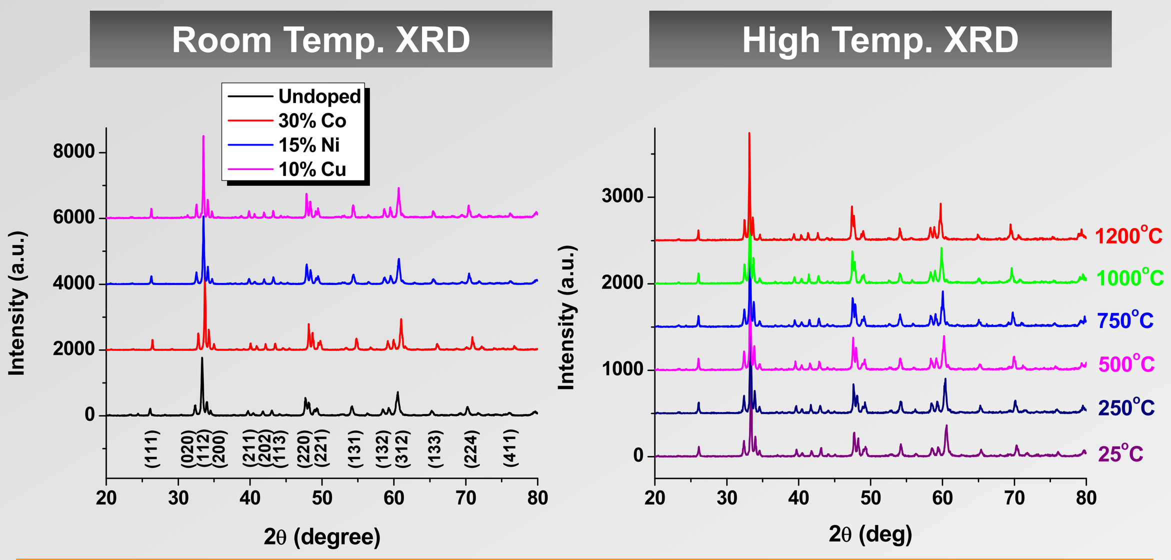
Goals

Develop Ceramic Interconnect Materials with
- Chemical Stability
- High Electronic Conductivity
- Low Ionic Conductivity
- Improved Sintering Behavior
- Thermal Expansion Match
- Dimensional Stability
- Chemical Compatibility with Other Components

Through Doping Yttrium Chromite with calcium on A-site and Transition Metals on B-site

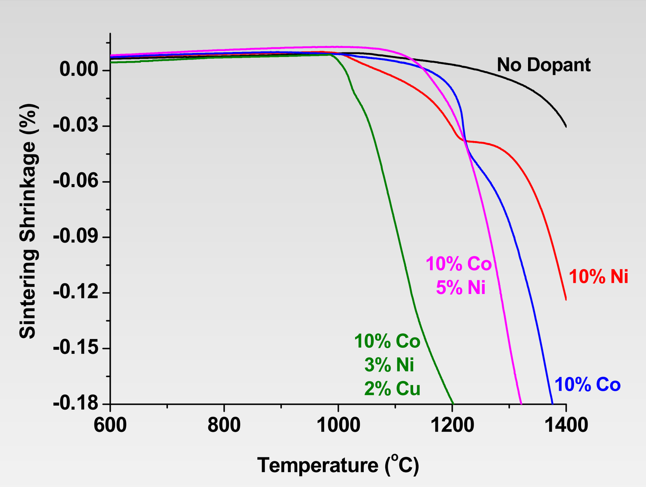
Chemical Stability

Room Temp. XRD | High Temp. XRD



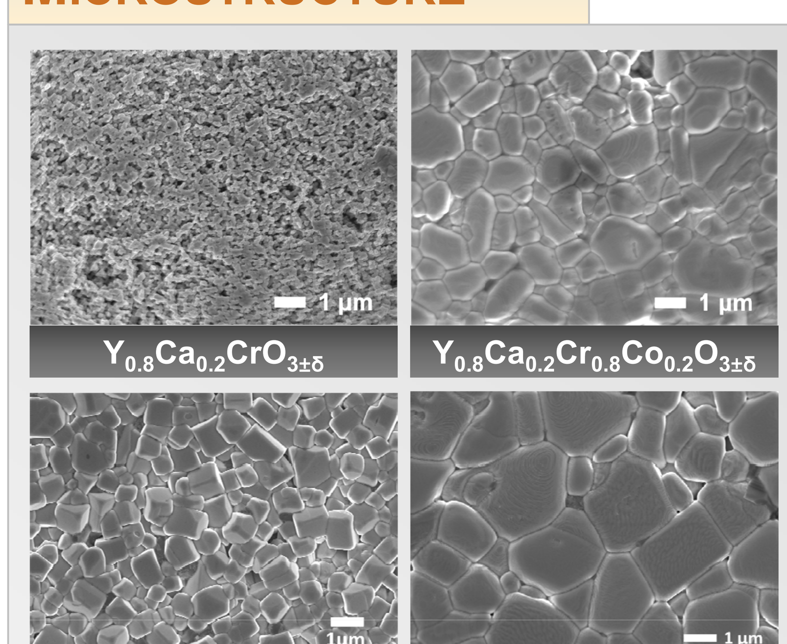
- Single Phase Orthorhombic Perovskite Structure ($25^oC<T<1200^oC$, $10^{-20}atm<p_{O2}<1atm$)

Sintering Behavior



- Measured with Dilatometer
- Co- and Ni-doping improves sinterability.
- Small addition of Cu (~2%) remarkably enhances sinterability.

Microstructure



$Y_{0.8}Ca_{0.2}CrO_{3\pm\delta}$ | $Y_{0.8}Ca_{0.2}Cr_{0.8}Co_{0.2}O_{3\pm\delta}$ | $Y_{0.8}Ca_{0.2}Cr_{0.85}Ni_{0.15}O_{3\pm\delta}$ | $Y_{0.8}Ca_{0.2}Cr_{0.9}Cu_{0.1}O_{3\pm\delta}$

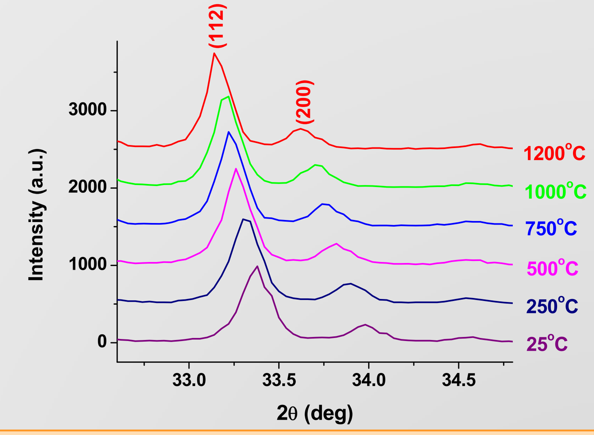
- Sintering : 1400°C
- Thermal Etching : 1375°C

- Cu, Co-, and Ni-doping : Open Porosity ↓ / Grain Size ↑

Thermal Expansion

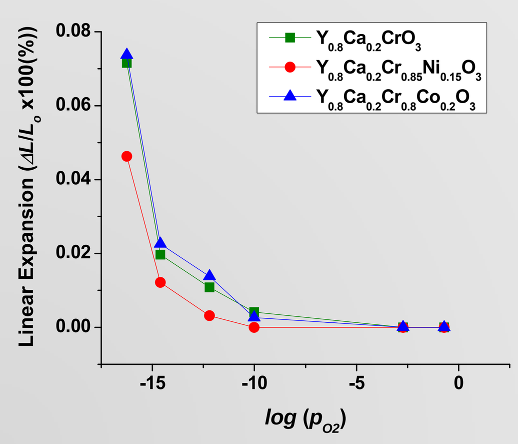
Composition	TEC (X10⁶)
No Dopant	9.7
10% Co	10.8
10% Ni	10.0
10% Co, 5% Ni	12.2
10% Co, 3% Ni, 2% Cu	11.7
15% Co, 10% Ni, 2% Cu	13.8
$La_{0.8}Ca_{0.2}CrO_3$*	10.05
8 mol% YSZ**	10.9

High Temp. XRD



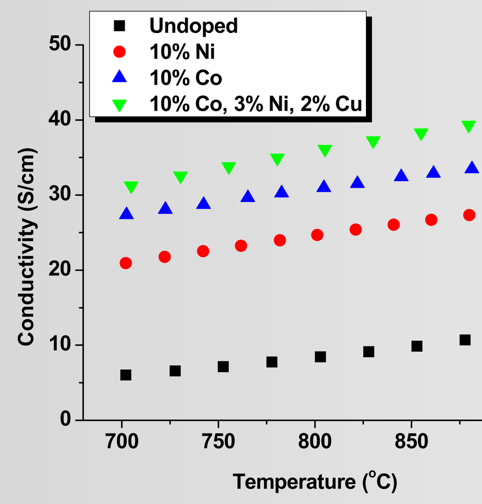
- Dilatometry measurements agree well with high temperature XRD fitting.
- Co- and Ni-doping increases TEC.
- TEC → Controlled by adjusting amount of B-site dopants.

Chemical Expansion



- T=900°C
- p_{O2} = 10^{-18} ~ 0.21 atm
- Ni-doping: Expansion ↓
- Co-doping: Insignificant Effect

Electrical Conductivity



- Co- and Ni-doping improves conductivity.
- Increase of Charge Density was confirmed by Seebeck measurements.

Point Defect Model

Oxygen Exchange Reaction

$$O_O^X + 2Cr_{Cr}^{\bullet} \leftrightarrow V_O^{\bullet\bullet} + 2Cr_{Cr}^X + \frac{1}{2}O_2$$

Equilibrium Constant

$$K = \frac{[V_O^{\bullet\bullet}][Cr_{Cr}^X]^2 p_{O2}^{1/2}}{[O_O^X][Cr_{Cr}^{\bullet}]^2}$$

Electrical Conductivity

$$\sigma = \frac{[Cr_{Cr}^{\bullet}]}{V} q\mu_p$$

$Y_{0.8}Ca_{0.2}CrO_{3\pm\delta}$

- Charge Neutrality

$$[Cr_{Cr}^{\bullet}] + 2[V_O^{\bullet\bullet}] = [Ca_Y']$$

- Site Conservation
  - A-site: $[Y_Y^x]+[Ca_Y']=1$
  - B-site: $[Cr_{Cr}^X]+[Cr_{Cr}^{\bullet}]=1$
  - O-site: $[O_O^X]+[V_O^{\bullet\bullet}]=3$
- Conductivity vs. p_{O2}

$$K_1 = \frac{(1-\frac{V}{q\mu_p}\sigma)^2([Ca_Y']-\frac{V}{q\mu_p}\sigma)}{(6-[Ca_Y']+\frac{V}{q\mu_p}\sigma)(\frac{V}{q\mu_p}\sigma)^2} p_{O2}^{1/2}$$

$Y_{0.8}Ca_{0.2}Cr_{0.85}Ni_{0.15}O_{3\pm\delta}$

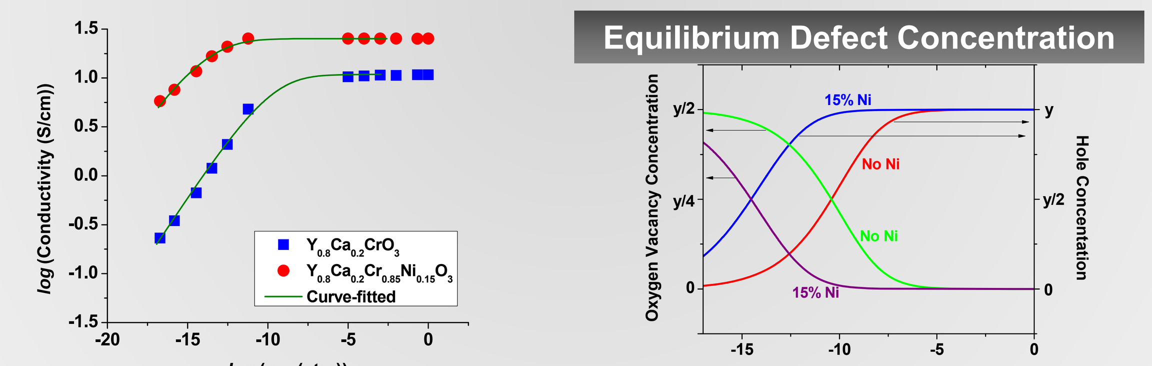
- Charge Neutrality

$$[Cr_{Cr}^{\bullet}] + 2[V_O^{\bullet\bullet}] = [Ca_Y'] + [Ni_{Cr}']$$

- Site Conservation
  - A-site: $[Y_Y^x]+[Ca_Y']=1$
  - B-site: $[Cr_{Cr}^X]+[Cr_{Cr}^{\bullet}]+[Ni_{Cr}']=1$
  - O-site: $]+[V_O^{\bullet\bullet}]=3$
- Conductivity vs. p_{O2}

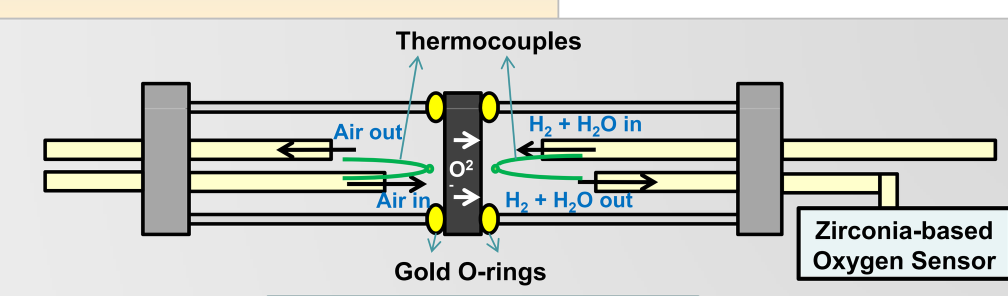
$$K_2 = \frac{(1-[Ni_{Cr}']-\frac{V}{q\mu_p}\sigma)^2([Ca_Y']+[Ni_{Cr}']-\frac{V}{q\mu_p}\sigma)}{(6-[Ca_Y']-[Ni_{Cr}']+\frac{V}{q\mu_p}\sigma)(\frac{V}{q\mu_p}\sigma)^2} p_{O2}^{1/2}$$

Equilibrium Defect Concentration



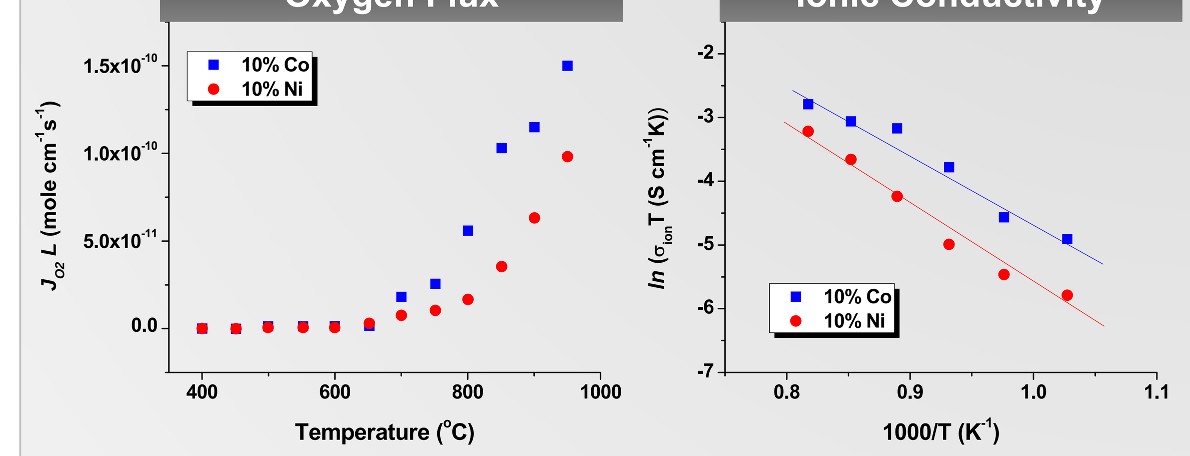
- Conductivity data fits well to defect model.
- Nickel doping improves stability toward reduction.
- Consistency in Oxygen Vacancy Concentration, Electrical Conductivity, and Chemical Expansion

Oxygen Permeation



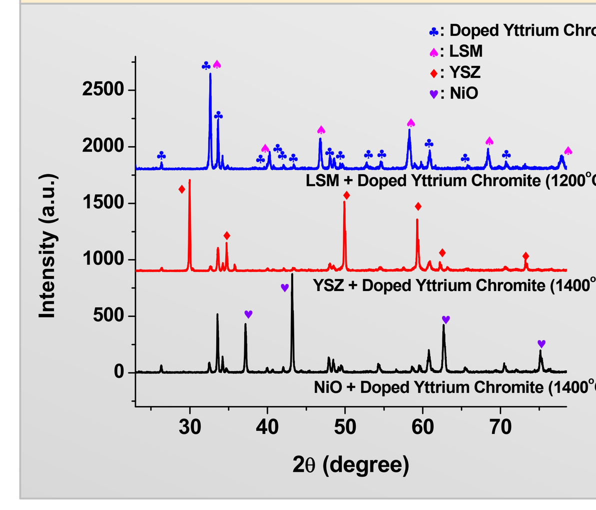
$$\sigma_{ion} = \frac{j_{O2} 4^2 F^2 L}{RT} \ln\left(\frac{p_{O2}^{(feed)}}{p_{O2}^{(sweep)}}\right)$$

Oxygen Flux | Ionic Conductivity



- Estimated Leakage Current Density < 5 mA/cm² (800°C, $10^{-20}<p_{O2}<0.21$, 20 μm thick Interconnect)

Chemical Compatibility



- Chemically Compatible with
  - YSZ and NiO at 1400°C
  - LSM at 1200°C

Summary

Calcium- and Transition Metal-doped $YCrO_{3\pm\delta}$
- Glycine-Nitrate Process
- Orthorhombic Perovskite Structure
- Cu-doping significantly improves sinterability.
- TEC can be controlled through B-site doping.
- Conductivity is improved by Co- and Ni-doping.
- Ni-doping improves stability toward reduction.
- Oxygen ionic leakage current is sufficiently low.
- Chemically compatible with YSZ, NiO, and LSM.

Future Works

- Optimize composition of multiple dopants.
- Investigate sintering behavior of thin interconnect on electrolyte and anode.

Acknowledgement

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About Pacific Northwest National Laboratory

The Pacific Northwest National Laboratory, located in southeastern Washington State, is a U.S. Department of Energy Office of Science laboratory that solves complex problems in energy, national security and the environment, and advances scientific frontiers in the chemical, biological, materials, environmental and computational sciences. The Laboratory employs 4,000 staff members, has a $760 million annual budget, and has been managed by Ohio-based Battelle since 1965.

For more information about the science you see here, please contact:

Kyung Joong Yoon
Pacific Northwest National Laboratory
P.O. Box 999, MS-NO
Richland, WA 99352
(509) 372-4255
kyungjoong.yoon@pnl.gov