Development and Characterization of High Performance and Robust Mixed Conducting Cathodes Supportive of Lower Cost SOFCs

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Personnel at LG Fuel Cell Systems Inc.

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Zhien Liu	Senior Investigator
Rich Goettler	Senior Investigator

Summary of Our Preliminary and Year 1 Research

Results and Technical Approaches

Identifying a series of nickelates with an active performance

(+) High D and k in a wide temp region (+) Cr resistance; (-) Phase decomposition

Identifying a series of nickelates with a stable and active performance (LGFCS proprietary work)

Thermal Stable Compounds:

Doped PNNO5050, PNNO2575, and doped PNNO2575

Electrochemically Stable Compounds:

To be reported

Testing methodology

Reproducibility and reliability

Multiple cells; statistic distribution of data

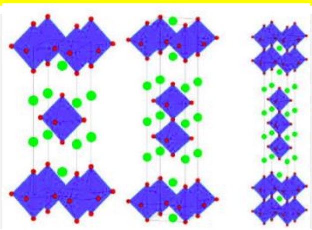
Quantification of Phase Evolution in a Single Cell

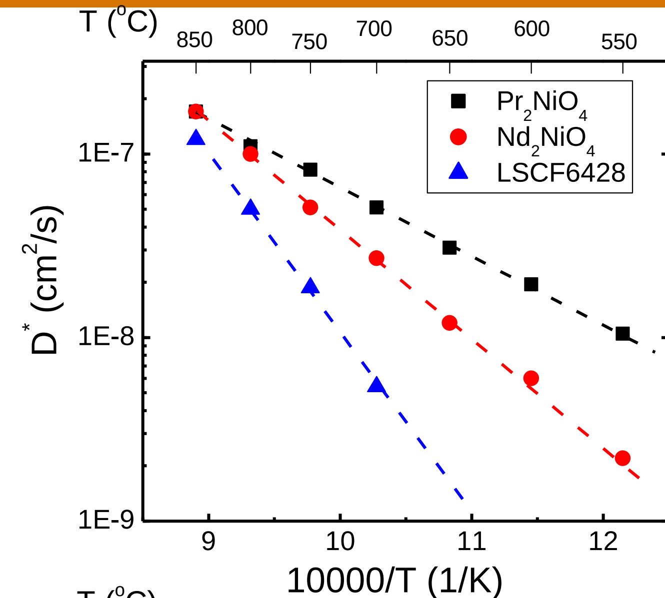
Standard and Au grid electrode

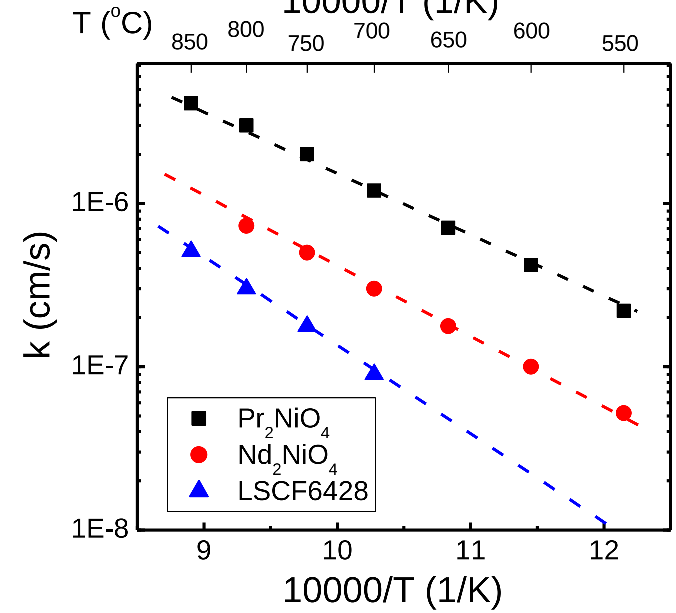
Accelerated Testing Protocols

Theoretical analysis and methods

Comparison between Nickelates and Perovskite Cathodes

Nickelatess	Advantage	1. Superior D and k 600°C: $D = 2\times10^{-8}$ cm²/s; $k = 4.2\times10^{-7}$ cm/s 800°C: $D = 1.1\times10^{-7}$ cm²/s; $k = 3\times10^{-6}$ cm/s 2. Active over wide range of temperatures 3. Thermal expansion matching with electrolytes 4. Absence of Sr and kinetic demixing
	Disad-vantage	Phase transition in $A_{n-1}A_2'B_nO_{3n+1}$, from n=1 to n>1. 
LSCF	Advantage	1. Extensive research has been carried out 2. Active electrode 600°C: $D = 4\times10^{-10}$ cm²/s; $k = 5\times10^{-8}$ cm/s 800°C: $D = 5\times10^{-8}$ cm²/s; $k = 3\times10^{-7}$ cm/s 3. Long-term operation has been demonstrated at multiple institutions.
	Disad-vantage	1. Sr segregation 2. Volatile Co densification 3. Demixing





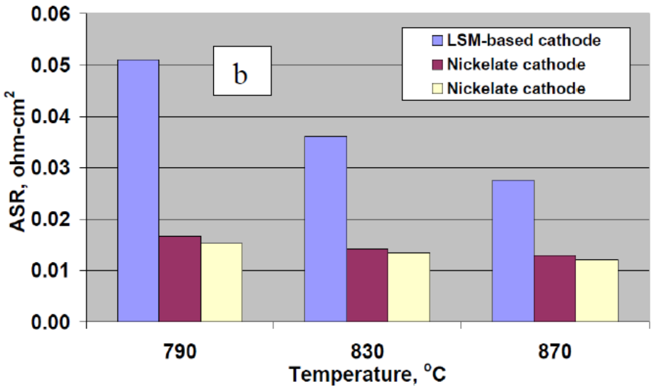
(Boehm et al., SSI, 176, 2005)

Developing Cathode Materials with Low Polarization Resistance

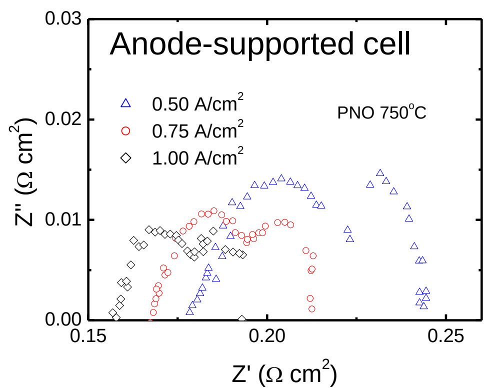
Rationales

1. Rapid surface exchange and oxygen ion diffusion in Pr_2NiO_4 – based oxides
2. Activity of nickelates over a wide temperature region (550 – 900ºC)
3. CTE Compatibility between nickelates and electrolytes (doped ceria or zirconia)

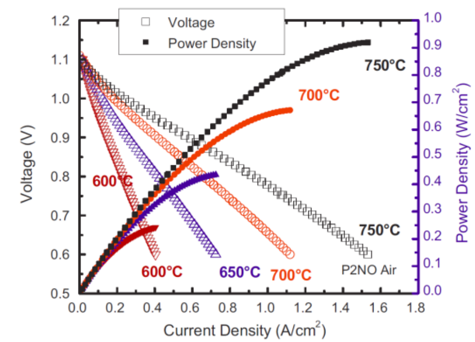
Current Status

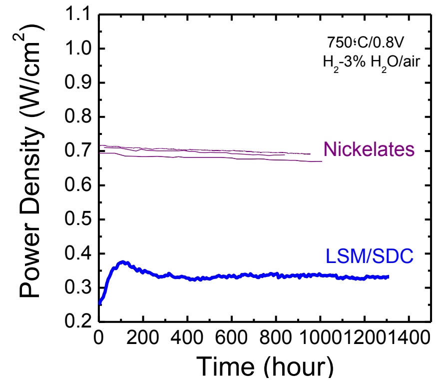


LGFCS, SECA workshop 2013



Zhou, Templeton, Nie, Chen, Stevenson, Pederson, *Electrochim Acta* **71**, 44-49 (2012)





Approaches

1. Compositions:
   - $(Pr_{0.50}Nd_{0.50})_2NiO_4$ – PNNO5050
   - $(Pr_{0.25}Nd_{0.75})_2NiO_4$ – PNNO2575
   - Substituted PNNO (LGFCS proprietary work)

2. Measurements
   - Half-cell measurements: ScSZ as the electrolyte measured at 750, 790, 830, and 870ºC
   - Full-cell measurements: ScSZ electrolyte-supported and anode-supported cells
   - Durability (250 – 4000 hours) and reproducibility (3-5 cells per condition)
   - Current-potential sweep, impedance/differential relaxation time analysis, pO_2

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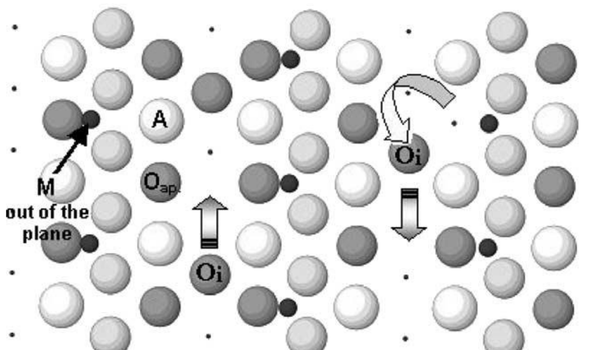
Stabilize the Structure
What are the roles of substituting elements?

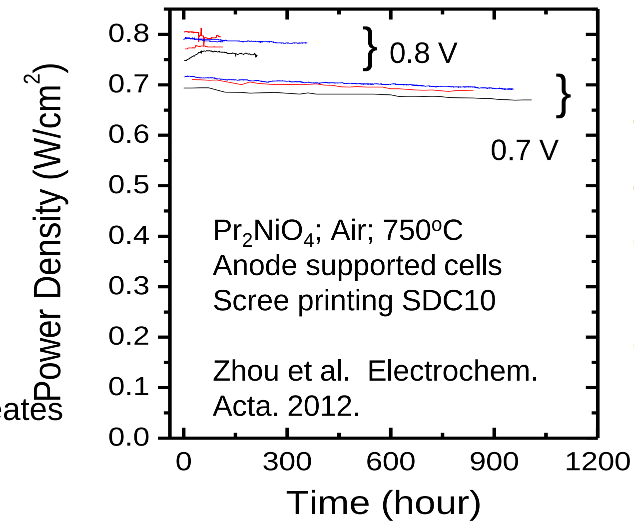
Rationale

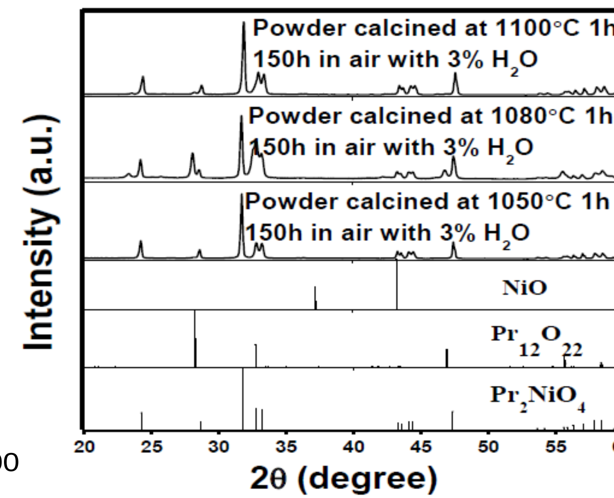
1. It is unknown why the performance of Pr_2NiO_4 is stable, but the phase transition from Pr_2NiO_4 to Pr_6O_{11} and higher ordered phases (e.g. $Pr_3Ni_2O_7$ and $Pr_4Ni_3O_{10}$) was observed.
2. Why are some compositions more stable than the others?
3. Charge/valance ratio and strain effects on the structural stability at A-site are contributing factors.

Current Status



Migration of oxygen ion to interstitial site creates vacancy available for adsorption of oxygen (Boehm et al., SSI, 176, 2005)





Approaches

1. Electrochemical measurements of doped PNNO5050 and PNNO2575
2. Phase stability in doped $(Pr_{0.25}Nd_{0.75})_2NiO_4$ – PNNO2575 calcined at various temperatures and measured at 790 and 870ºC for a long duration.
3. A-site deficient compounds has shown improved activity, but its durability is unknown. The chemical potential of A-site element will influence the formation of Pr_6O_{11} or Nd_2O_3, thus controlling the phase stability.

Ionic Radii (3+ and CO#: 8)

La: 1.16 Å; Nd: 1.11 Å
Pr: 1.13 Å; Pr (4+): 0.96 Å
Sm: 1.08 Å; Sm (2+): 1.27 Å

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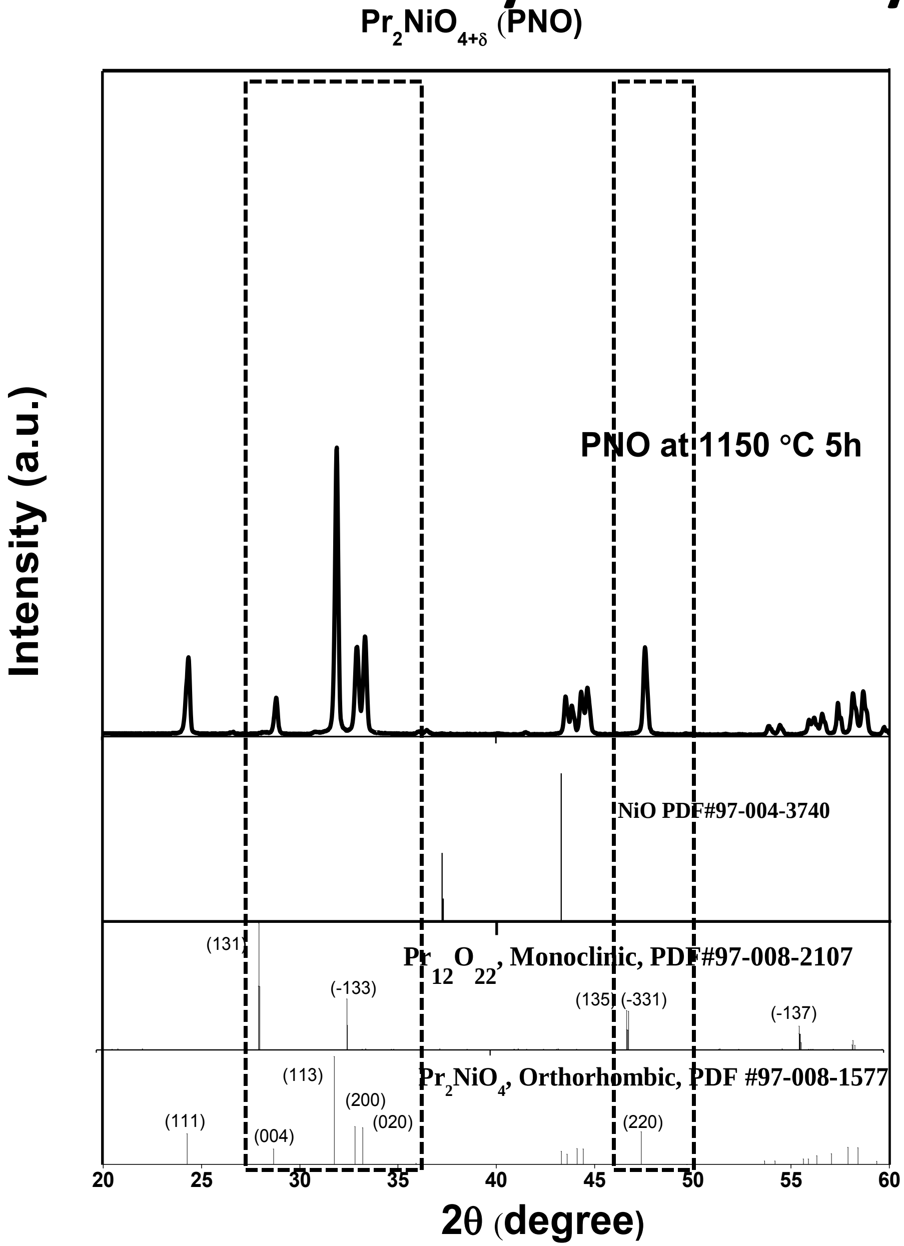
Phase Purity and Stability of PNNO

Phase Purity And Stability Challenges in R-P Nickelates



Preliminary work under LGFCS Phase II subcontract

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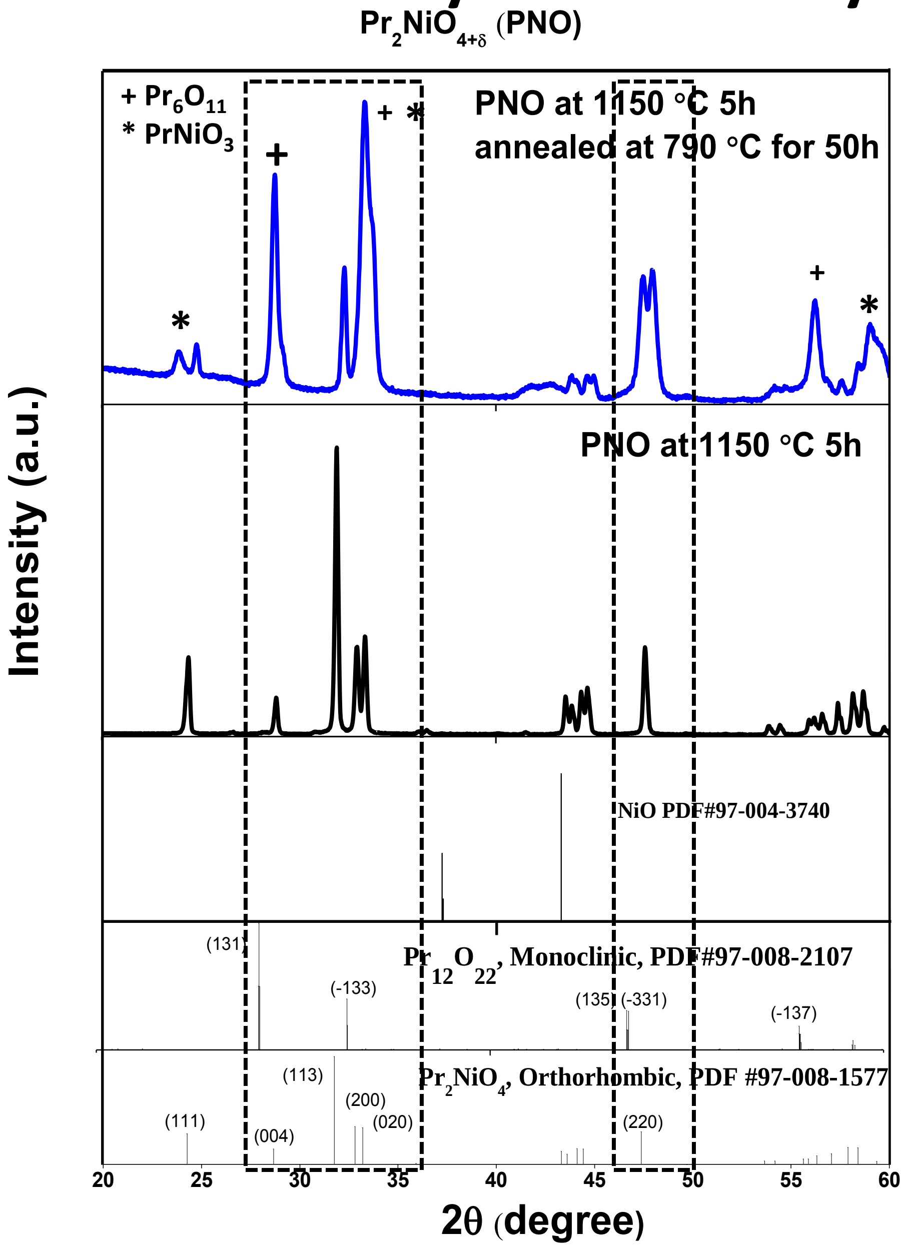

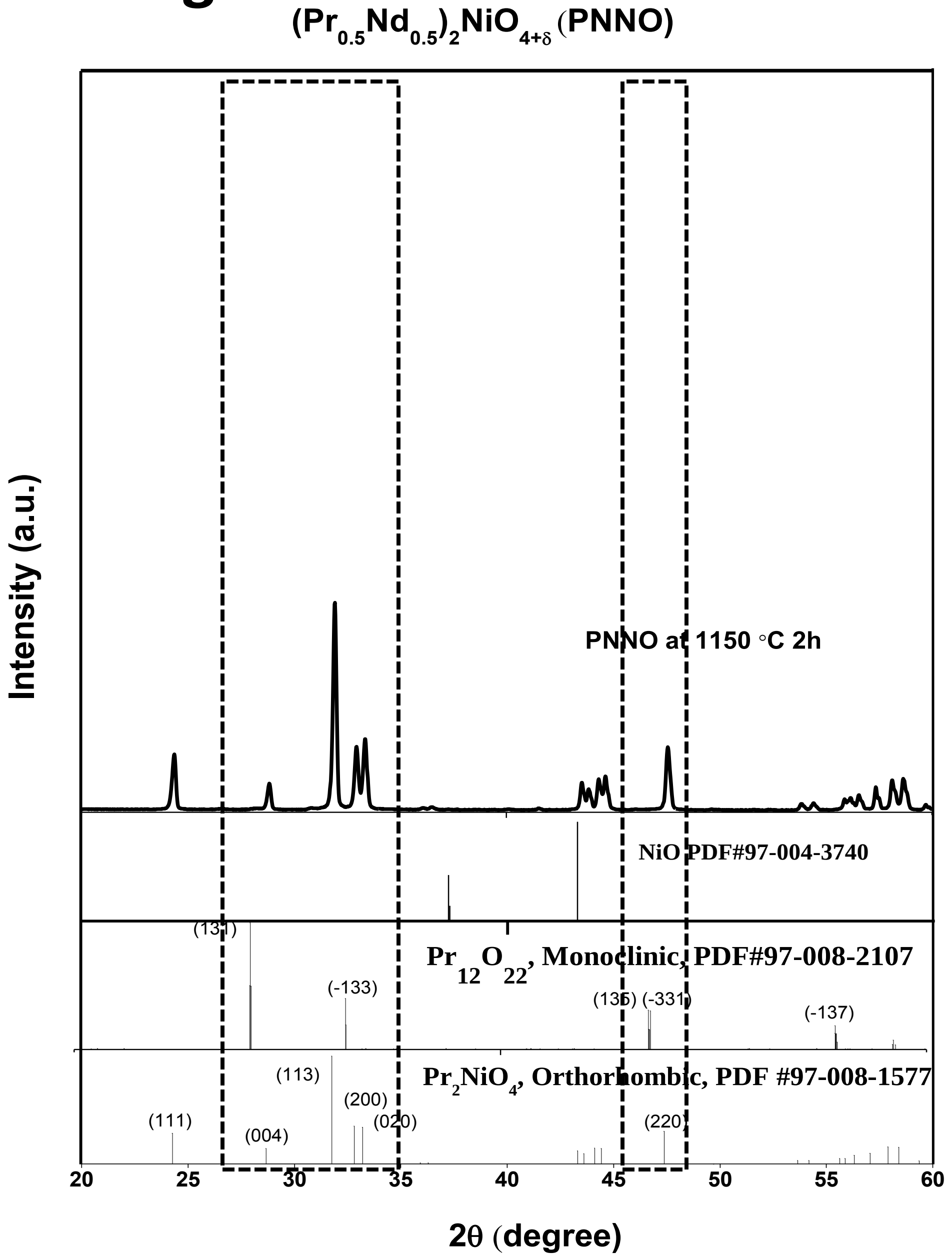

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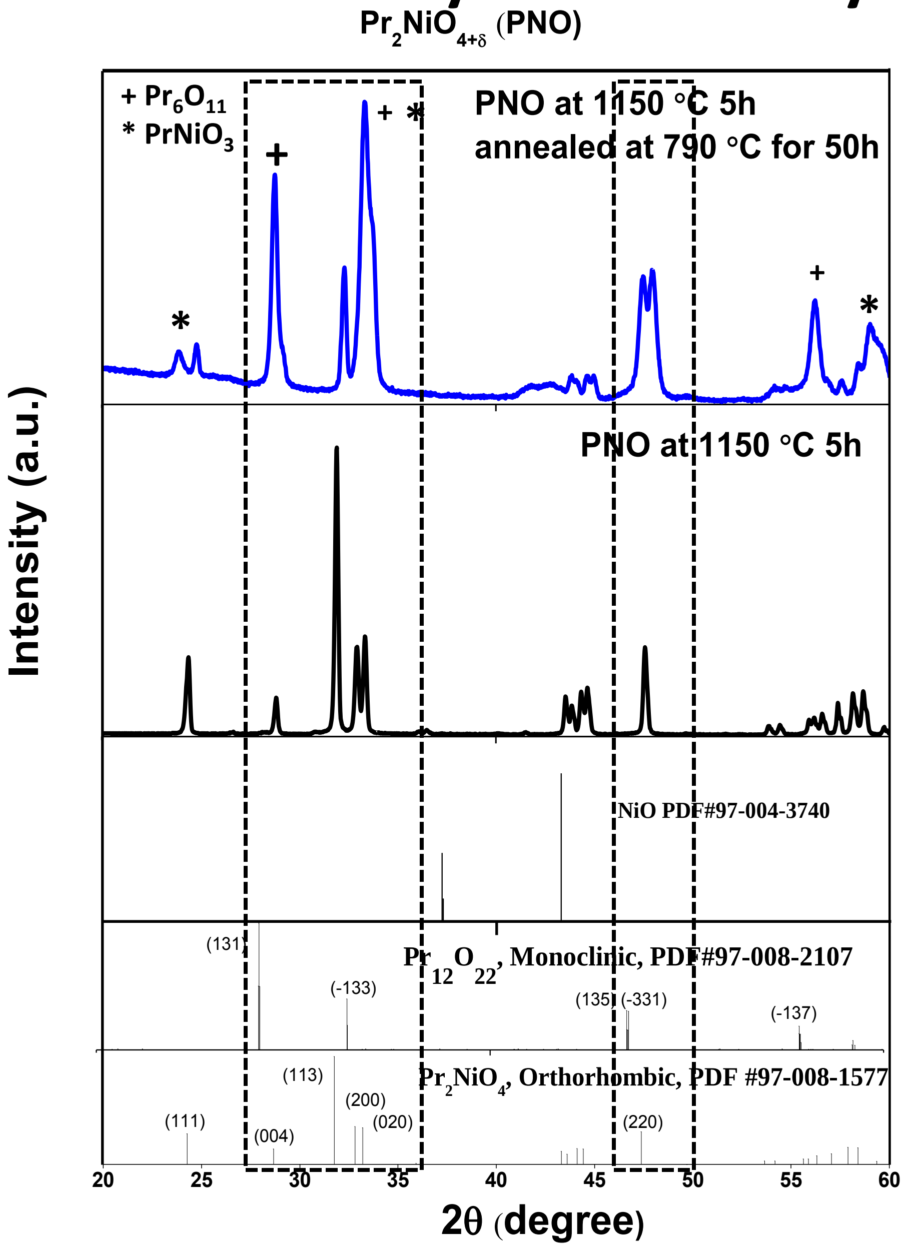

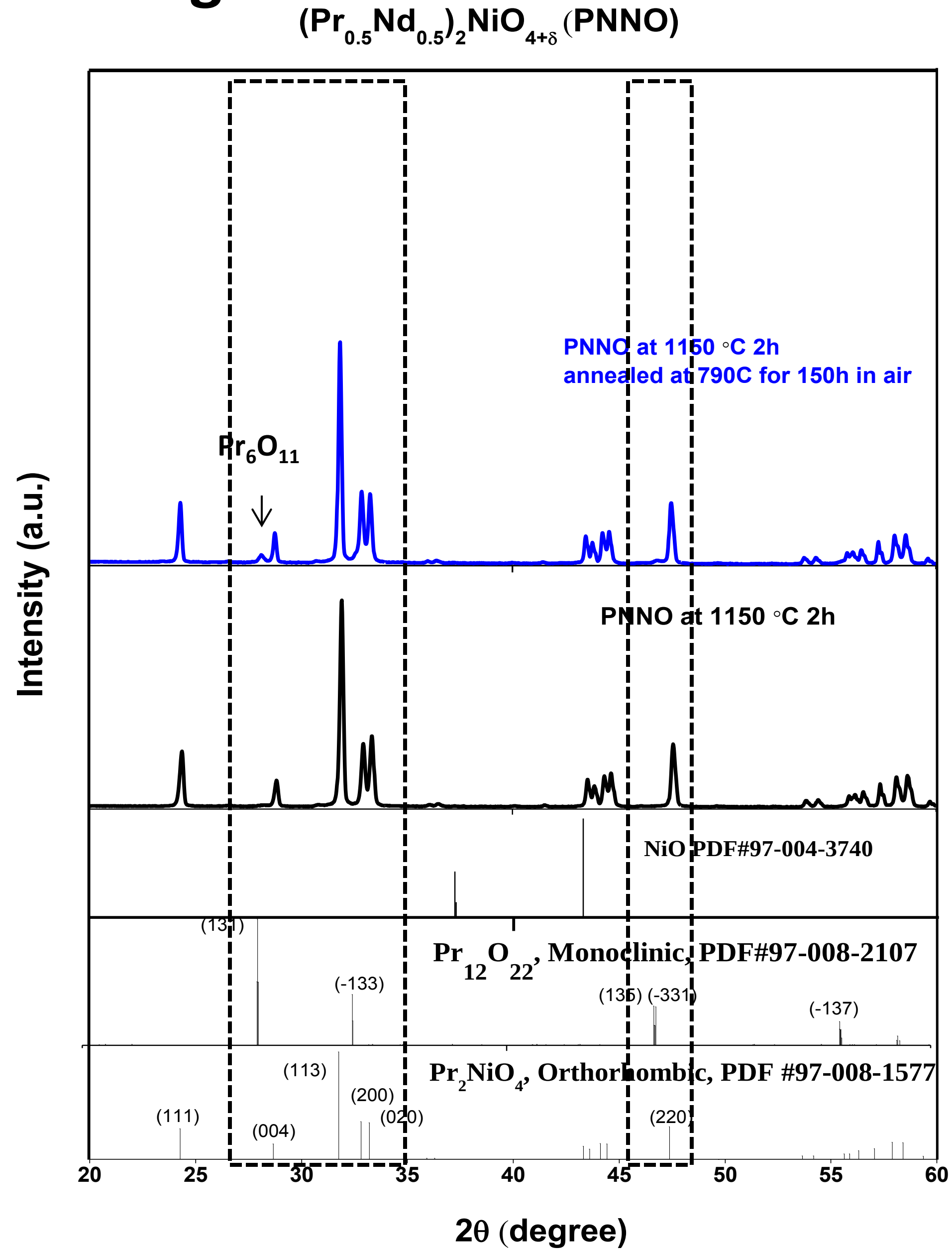

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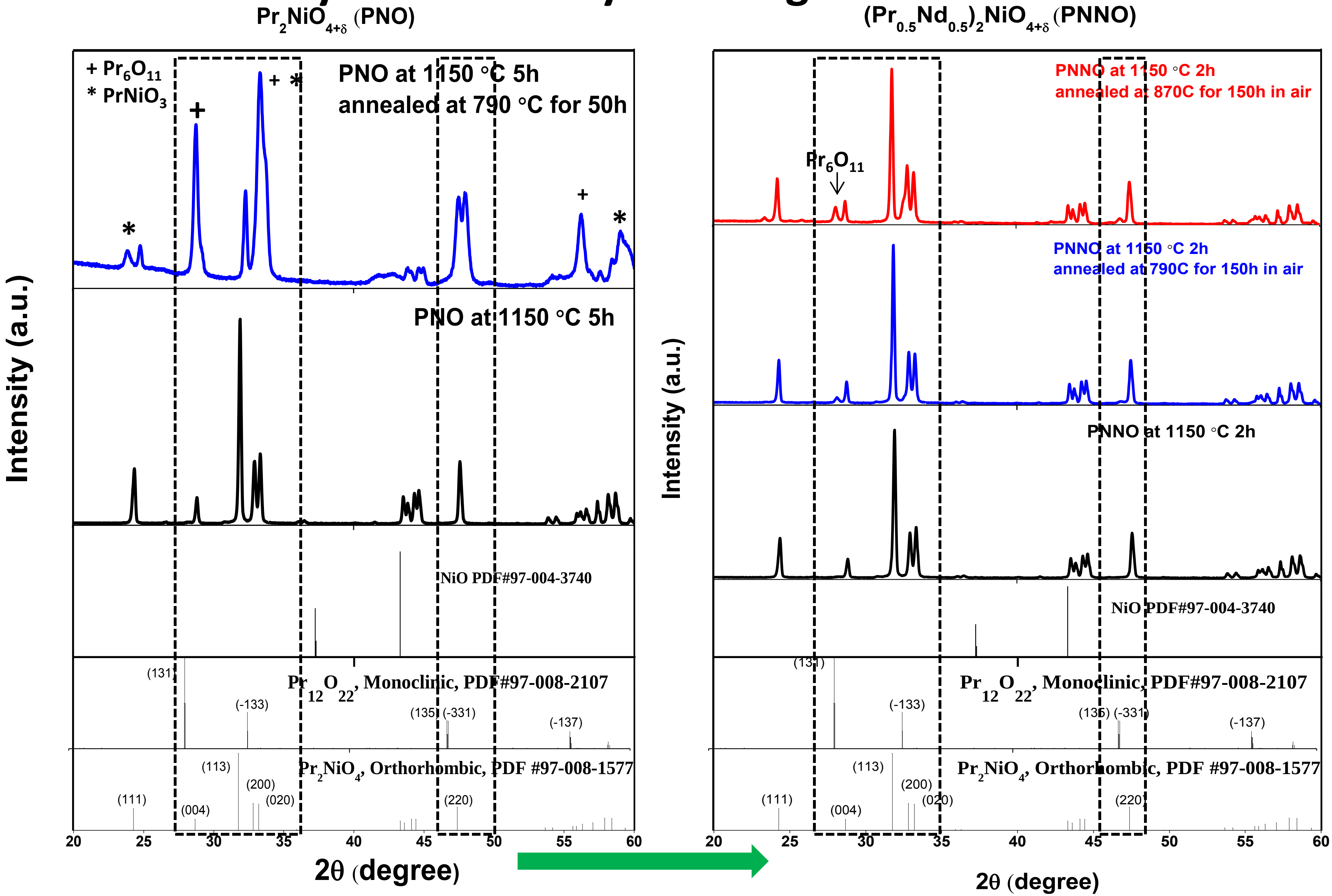
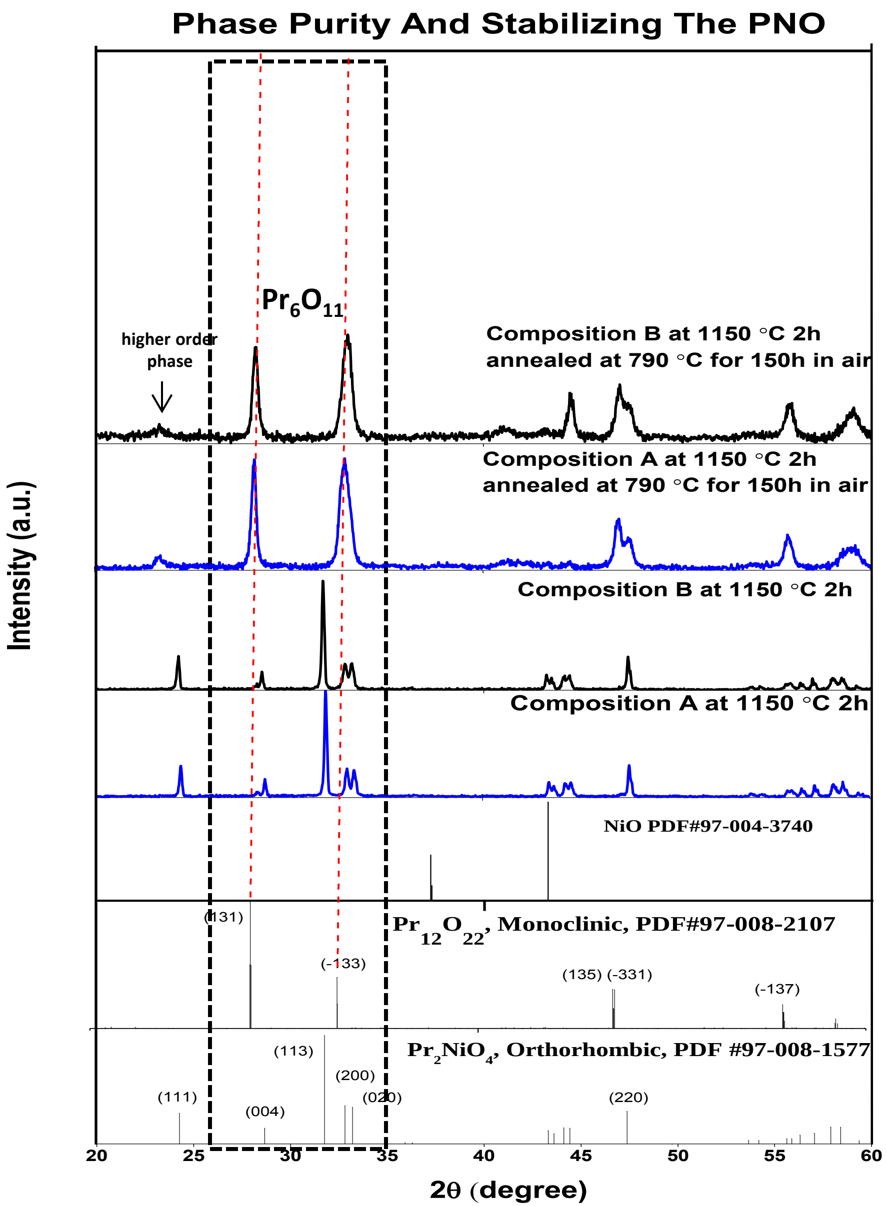


50% Nd-substitution does not stabilize R-P Structure

Preliminary work under LGFCS Phase II subcontract

Stabilizing The R-P Structure



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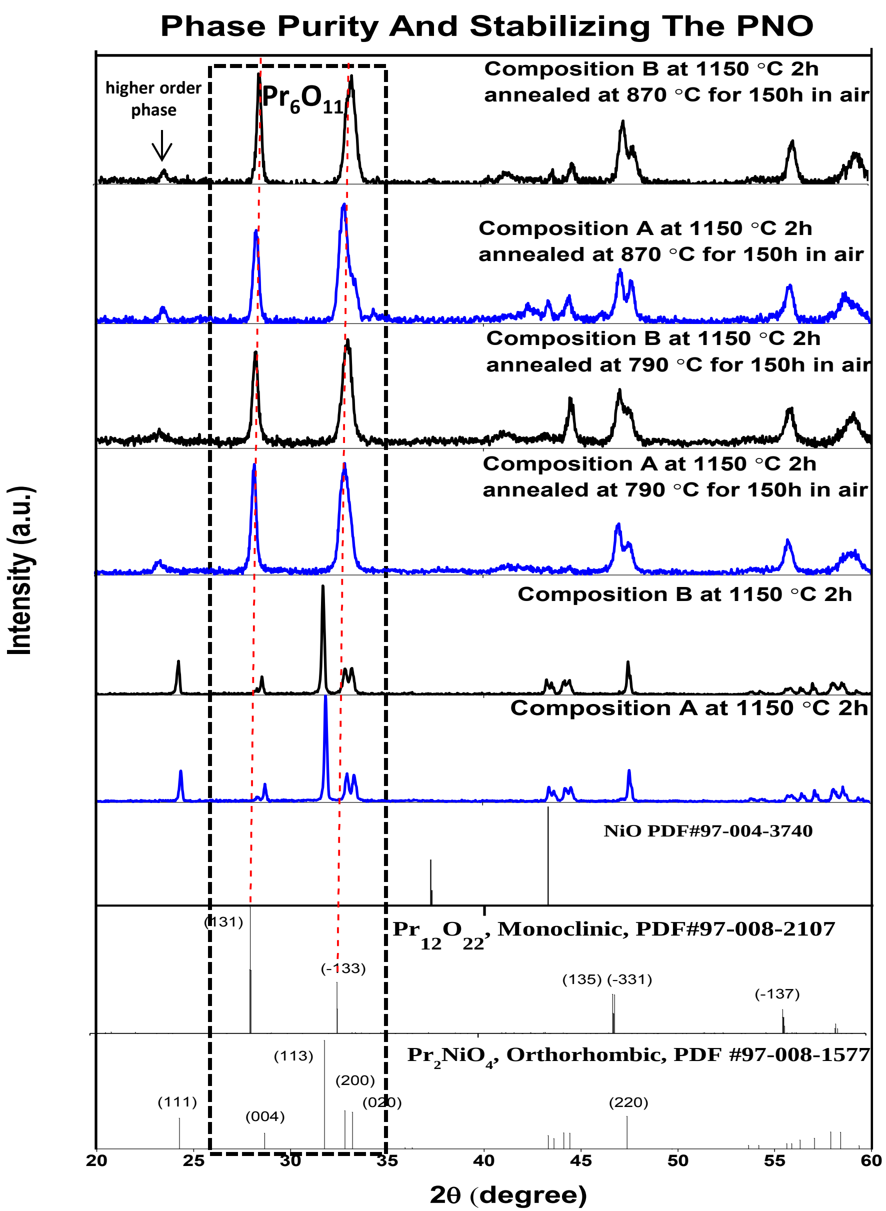

LGFCS proprietary work

Preliminary work under LGFCS Phase II subcontract

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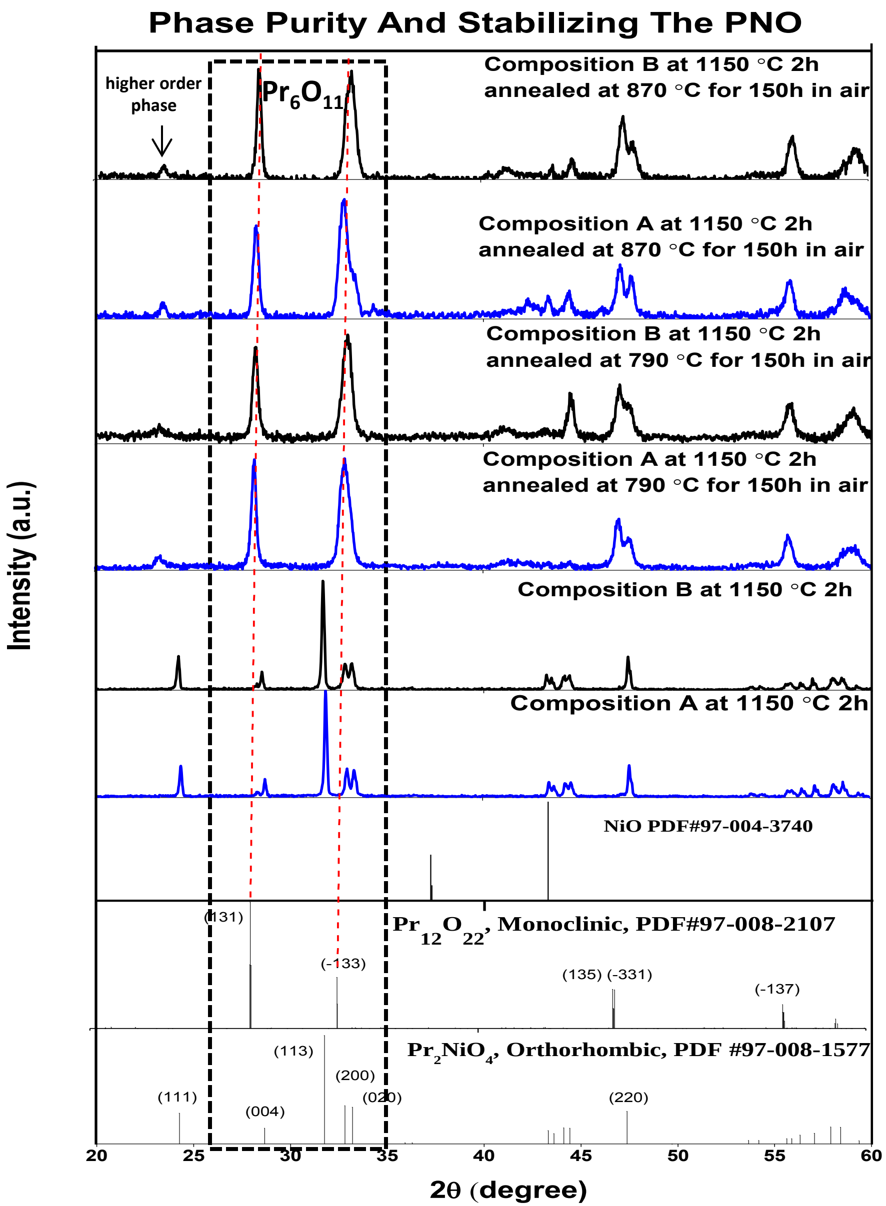

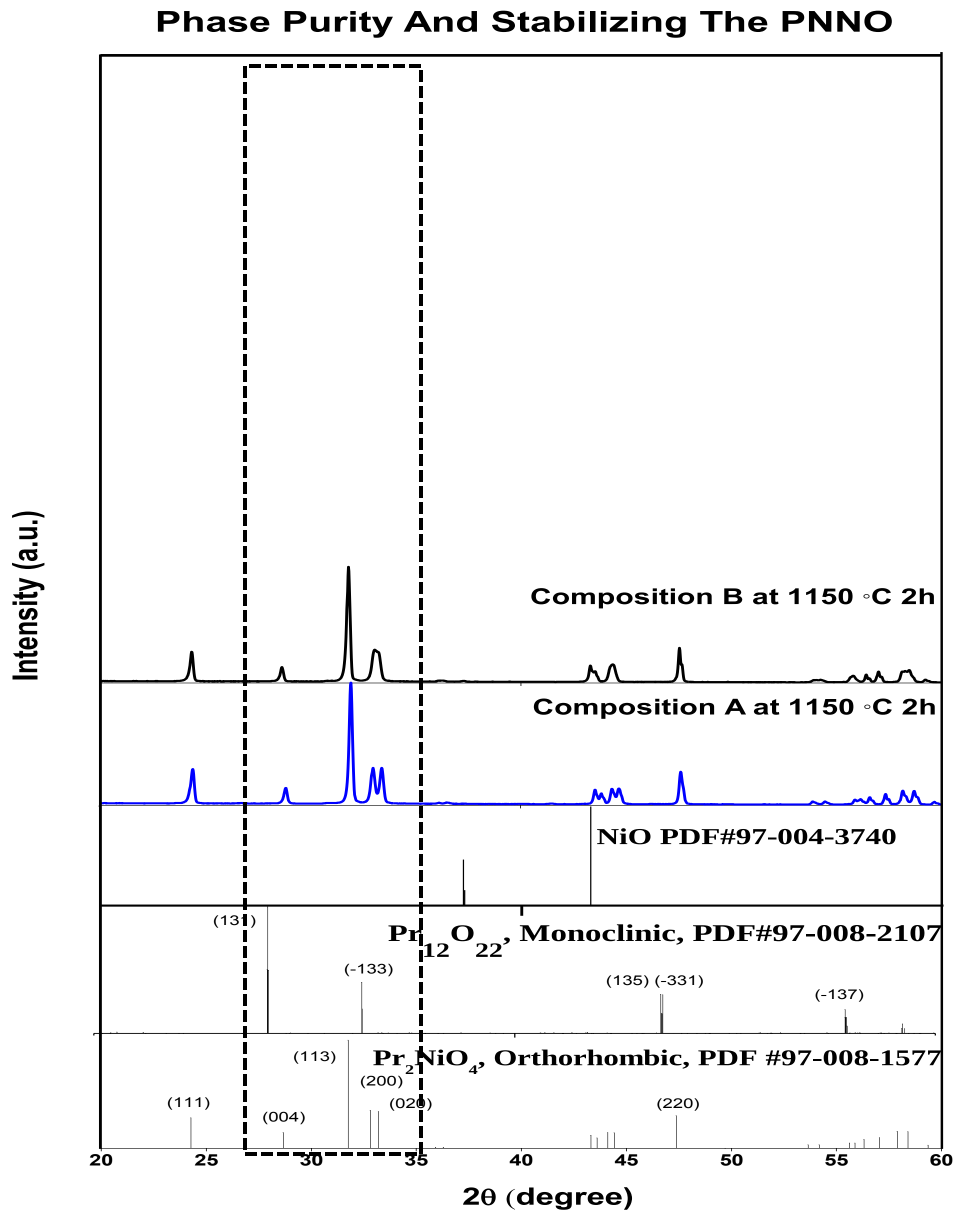

Stabilizing The R-P Structure

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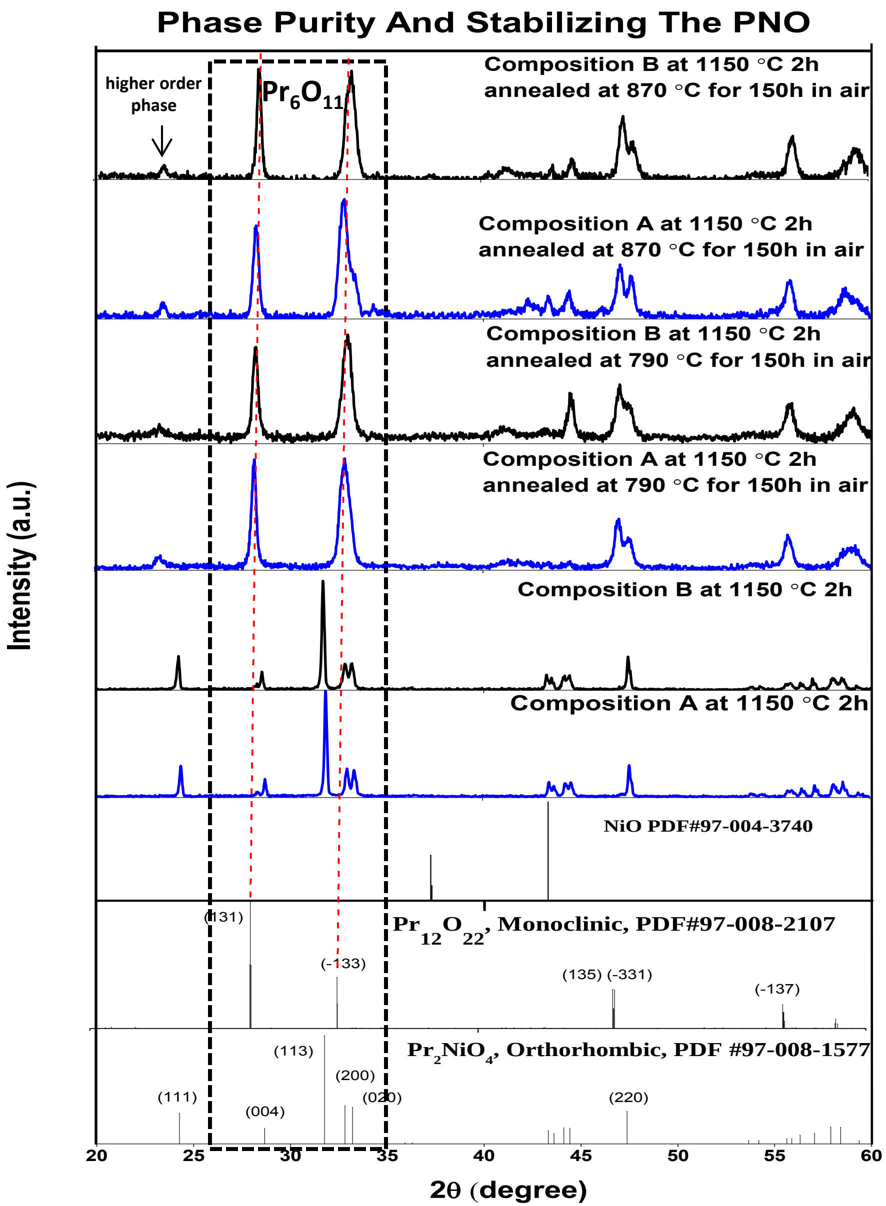

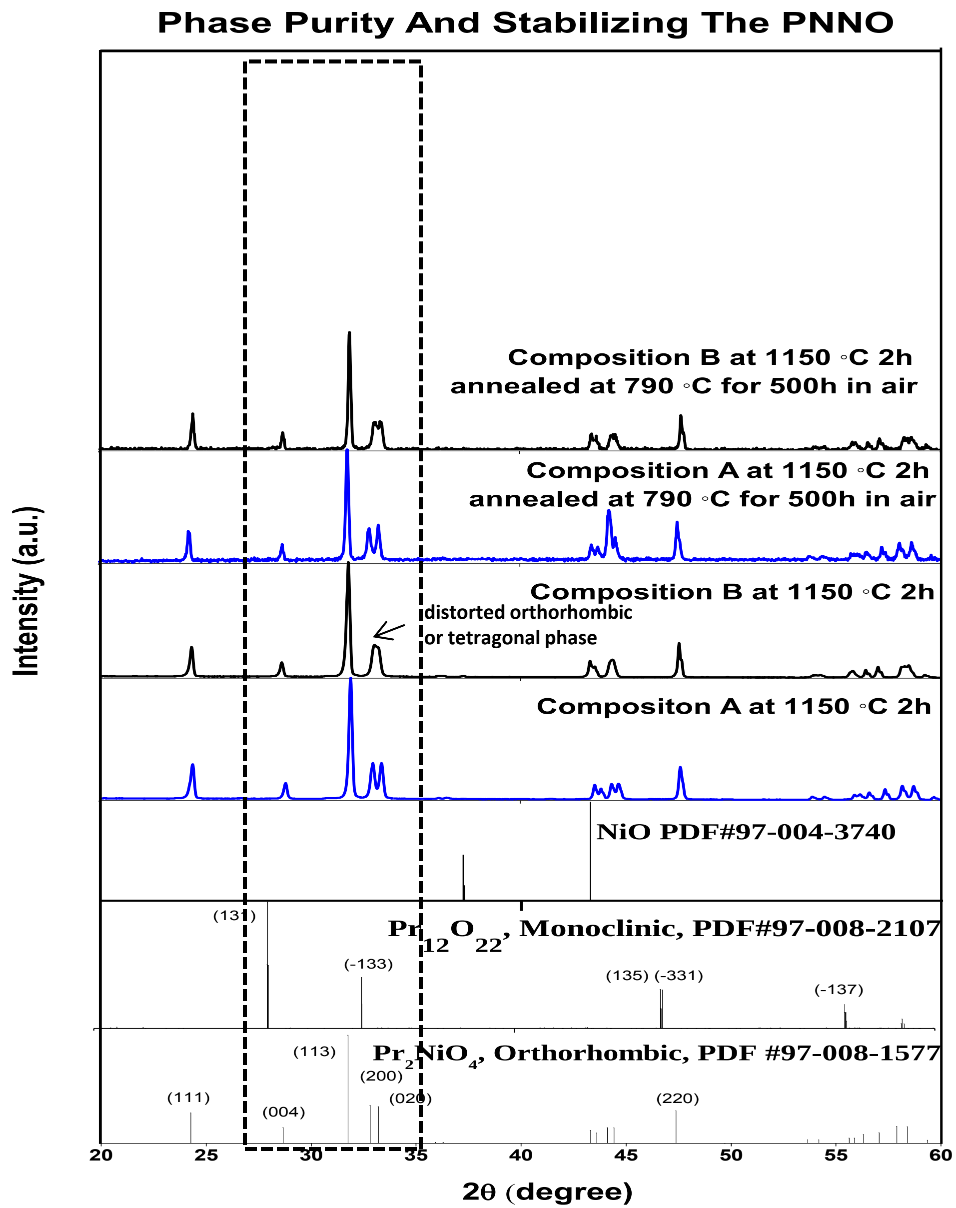

LGFCS proprietary work

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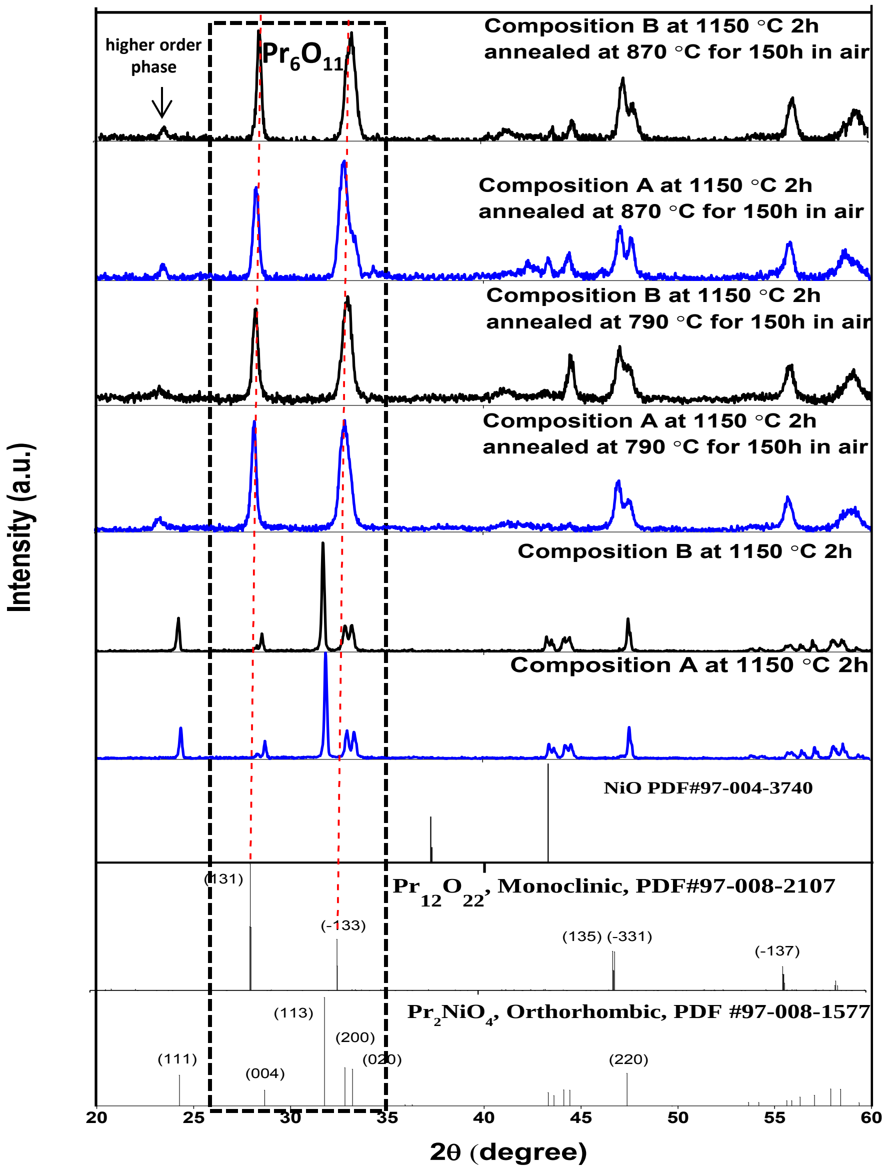
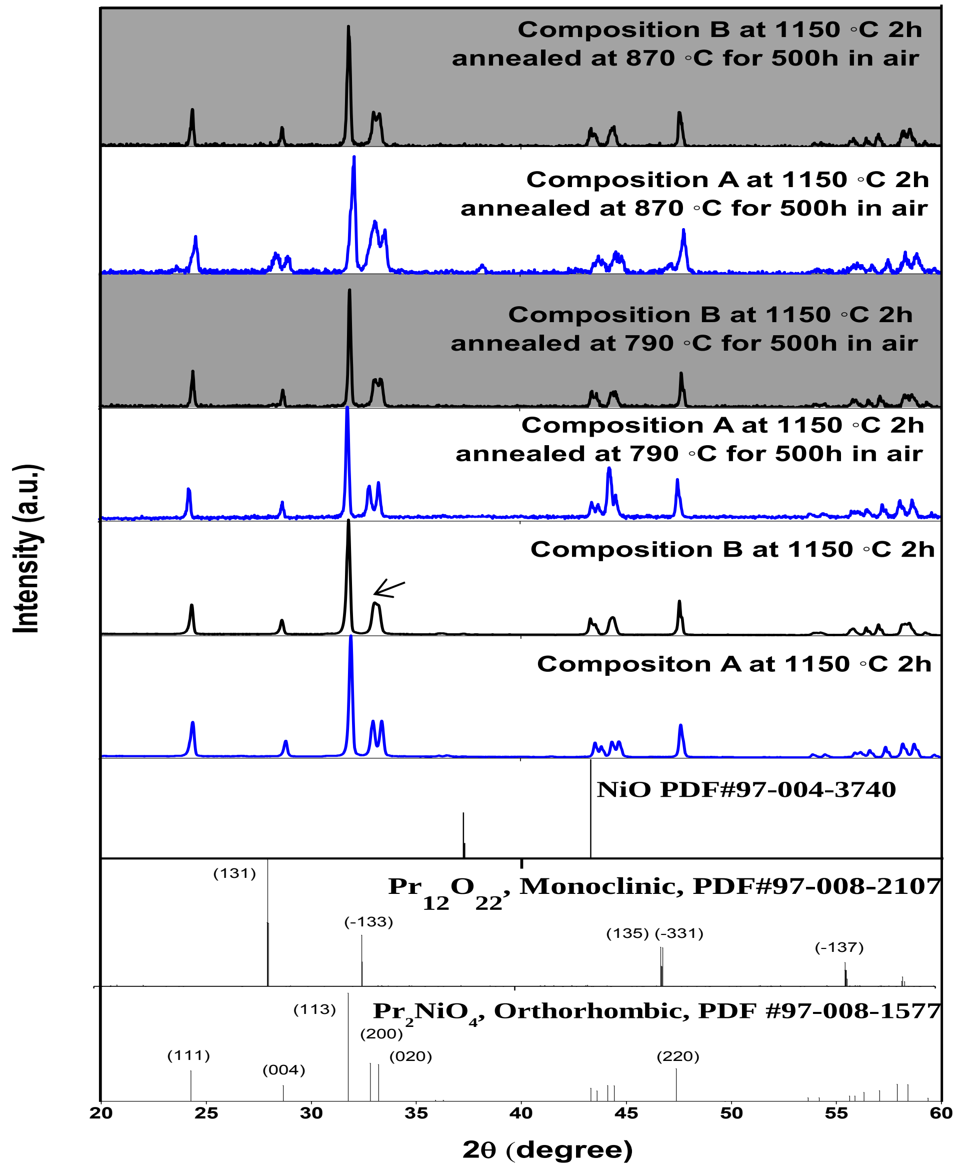
Stabilizing The R-P Structure

Phase Purity And Stabilizing The PNO

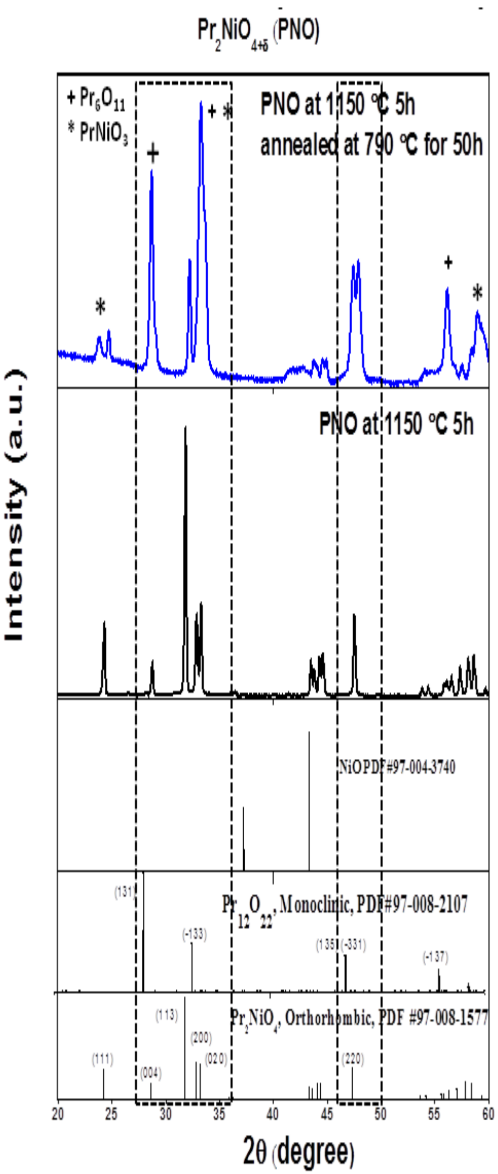


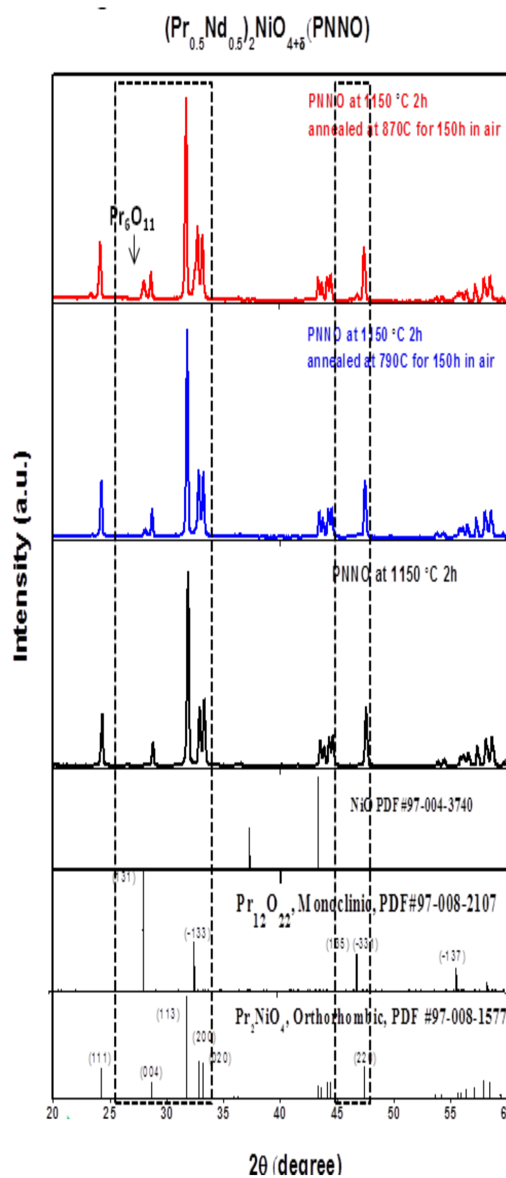
Phase Purity And Stabilizing The PNNO

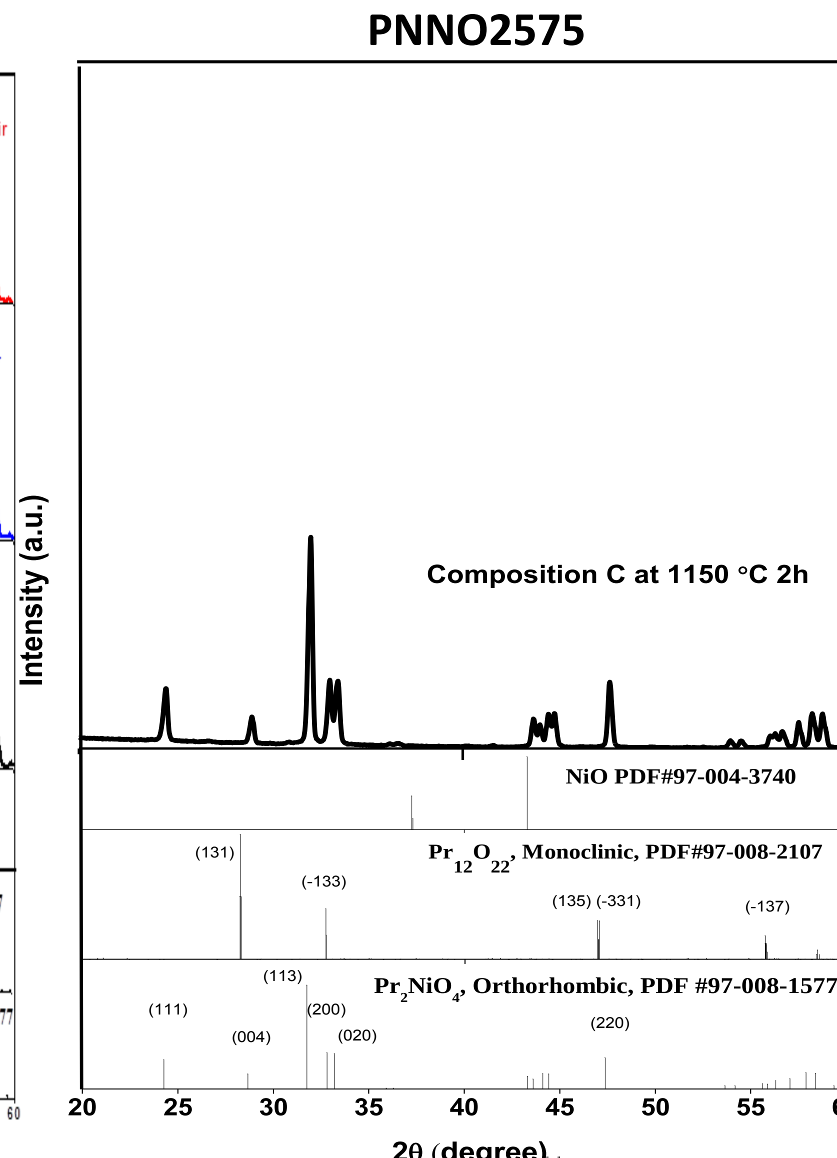


Phase Stabilized with Combination of A and B site Substitution and Doping

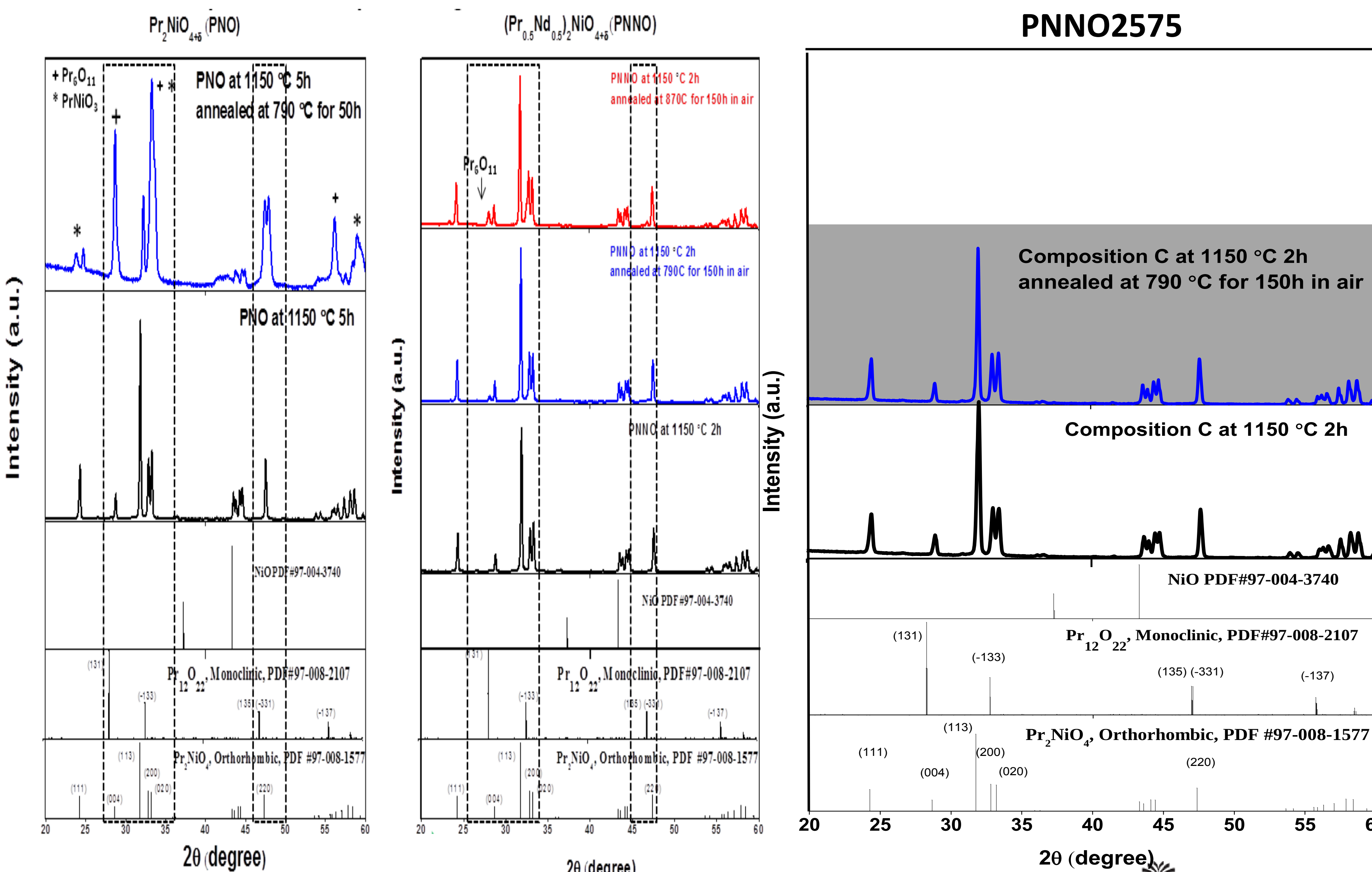
Fully Stabilizing the R-P Structure via A-site Doping







Fully Stabilizing the R-P Structure via A-site Doping



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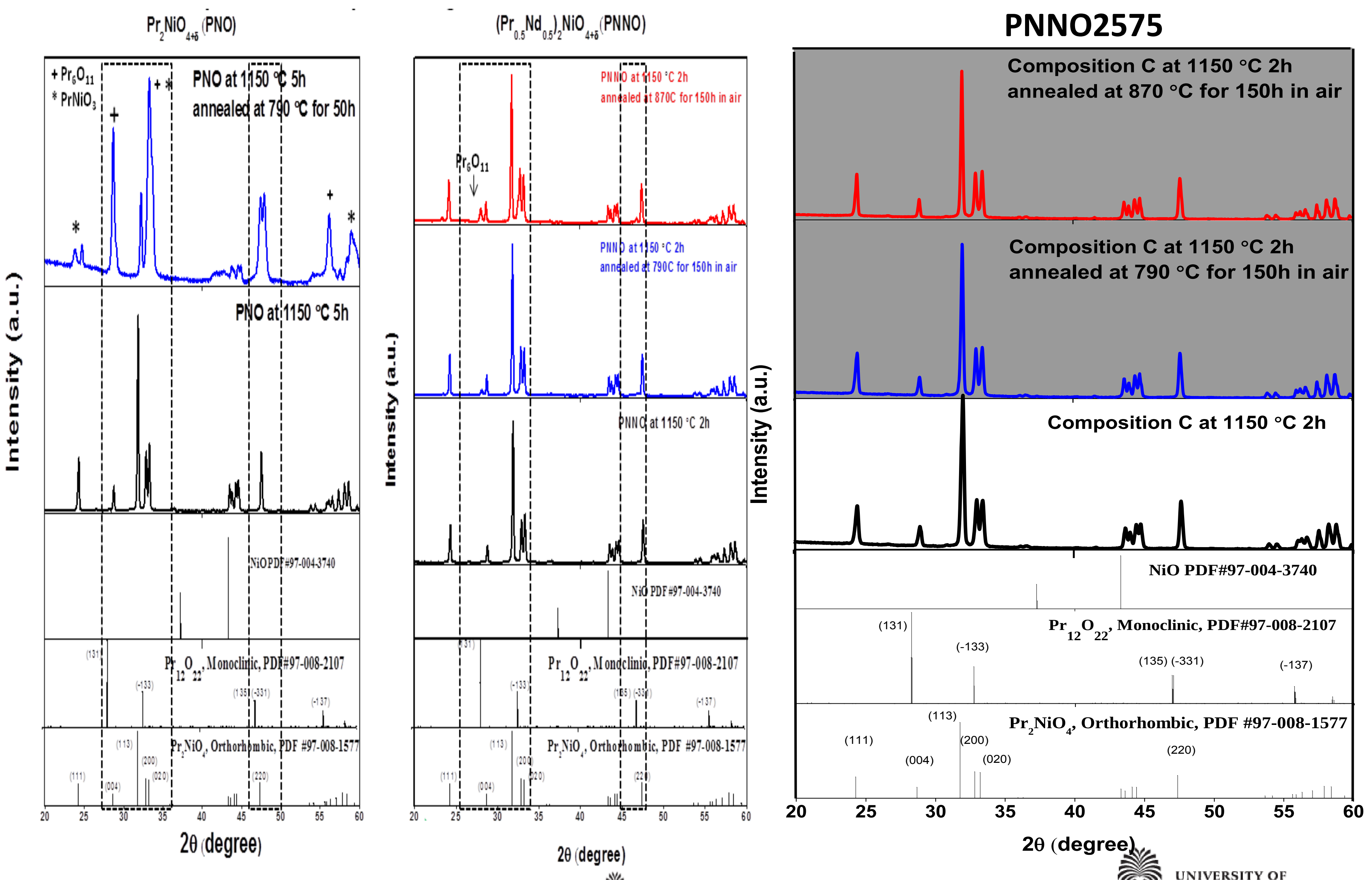

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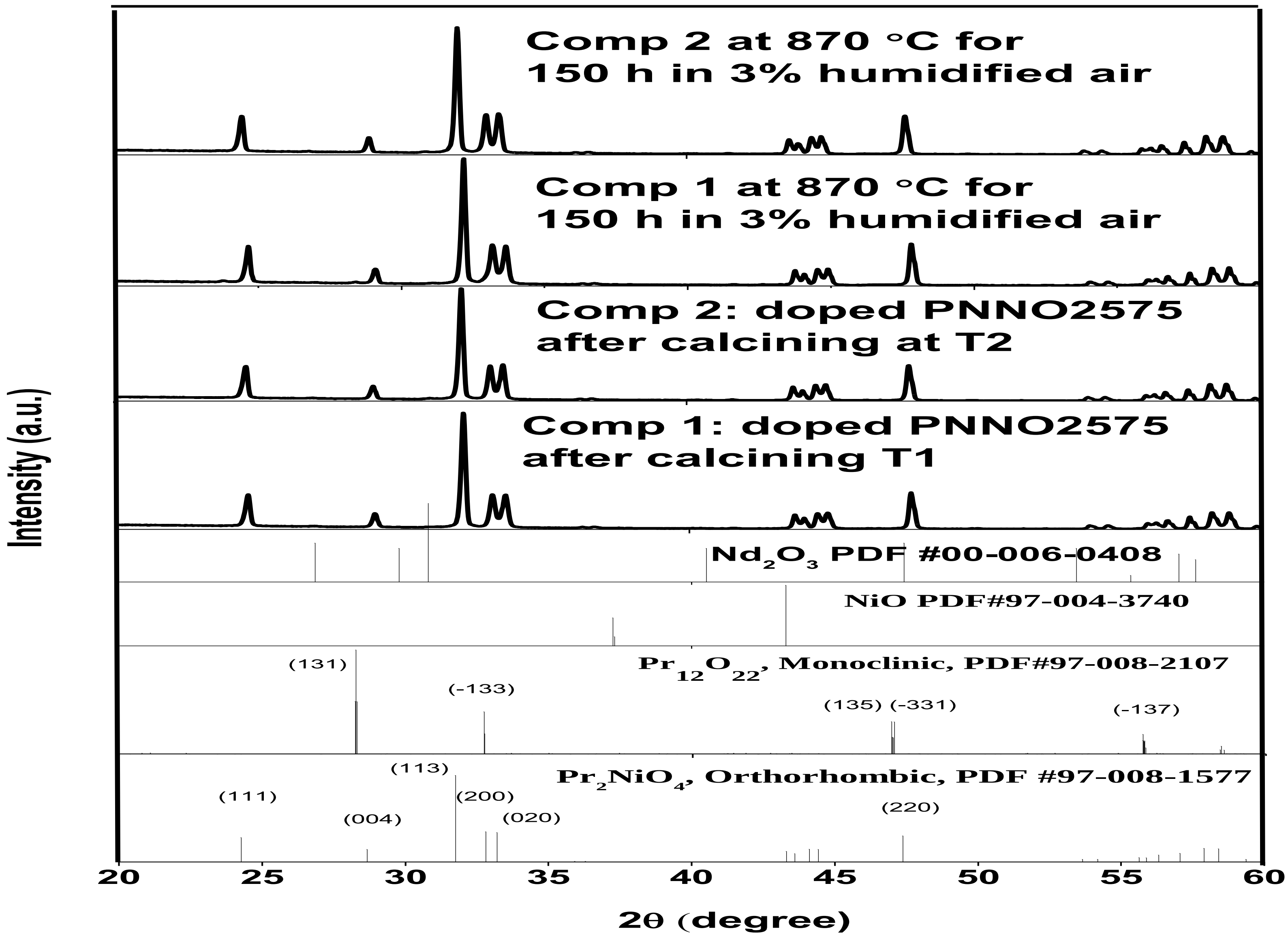
Substituted PNNO2575

Phase Stable: 790 and 870 °C, 3% H_2O, dopant%, and $T_{calcining}$



Quantification of Cathode Durability

Quantification of Phase Evolution during Operation (Nickelates and LSCF)

Quantification of phase evolution is **necessary**

1. to investigate the kinetics for phase decomposition (in LSCF) and phase transition (in nickelates).
2. to predict the durability of the cathodes.

Quantification is very **challenging** because of

1. the overlapping of XRD reflections and possible interactions between the cathode and its current collector (e.g. LSC, LNF).
2. the cathode thickness (30 μm), which might be too much for XRD analysis to study the cathode evolution occurring at the cathode/electrolyte interfaces.
3. the slow kinetics of phase evolution (could take 1000s-hours), which necessitate the development of accelerated test protocols.

Requirements and Cell Designs for Quantifications

Requirements for Current Collector

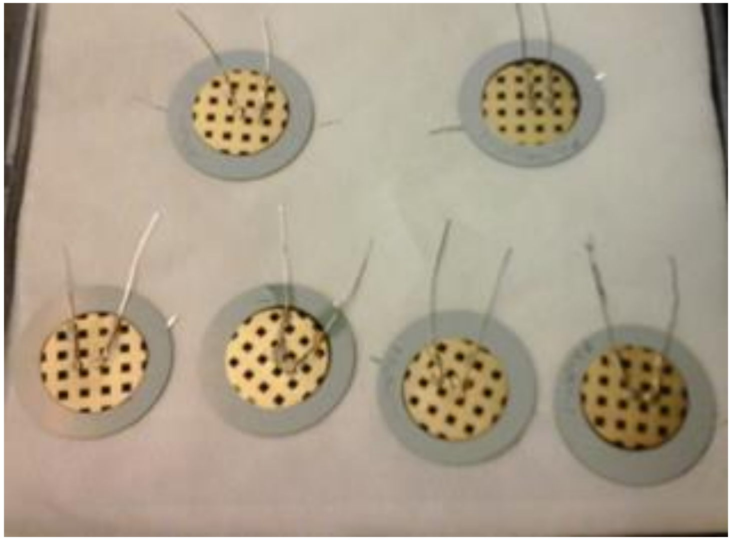
1. Chemically and mechanically compatible with the cathode
2. Chemically stable during operation
3. Electrically conducting
4. Its XRD reflections don’t overlap with major cathodes
5. Don’t interfere (deteriorate or enhance) cathode performance
6. Stable and reproducible XRD reflections before and after measurements to provide a **baseline**.

Cell Designs by using Au Current Collector

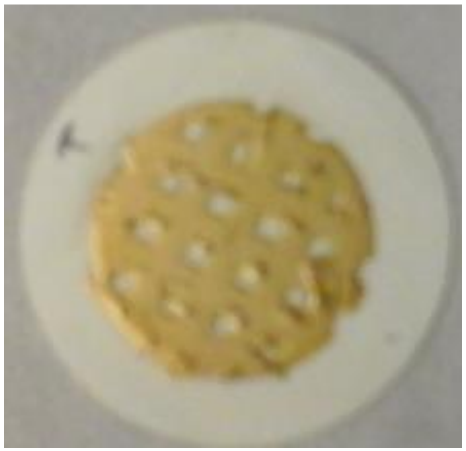
1. Design a series of Au grids with various open areas and grid width, which are used as current collector and baseline reference
2. **Questions to be addressed**: (1) which is the optimized thickness of Au grid (2) Au intensity and peak area vs. operation conditions.

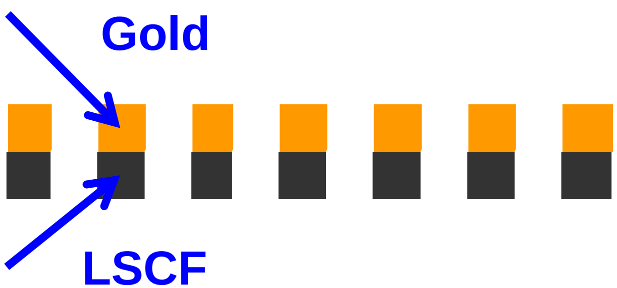
From oxide current collector

to gold collector



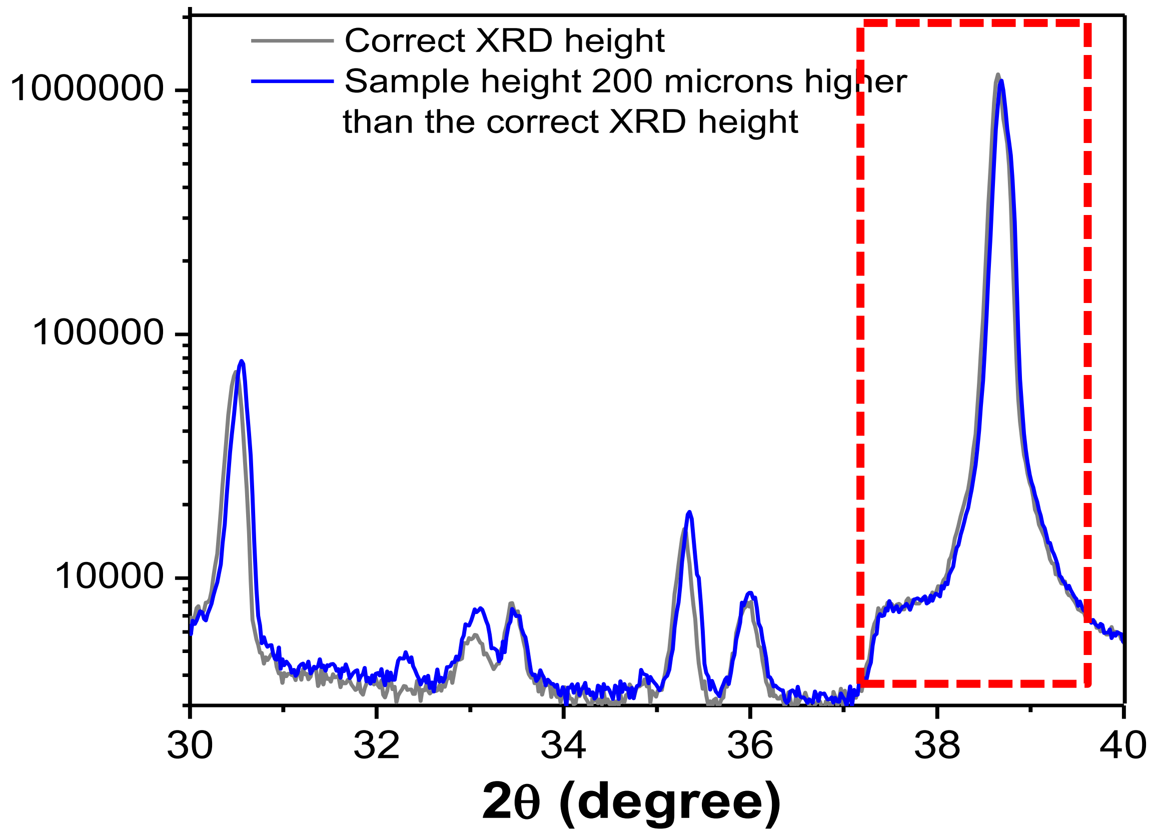
Validation of Stable and Reproducible Au Intensity





Au/LSCF/GDC/YSZ

(LSCF and Au were printed with the same grid, so Au covered all LSCF)



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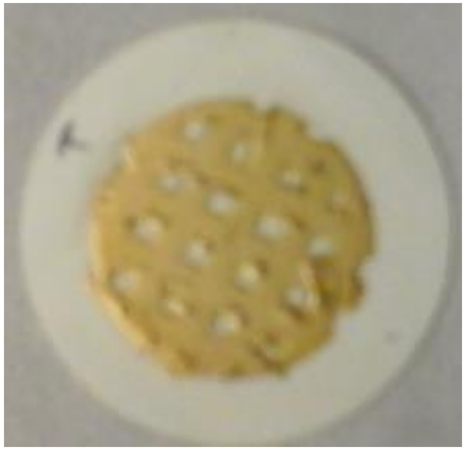

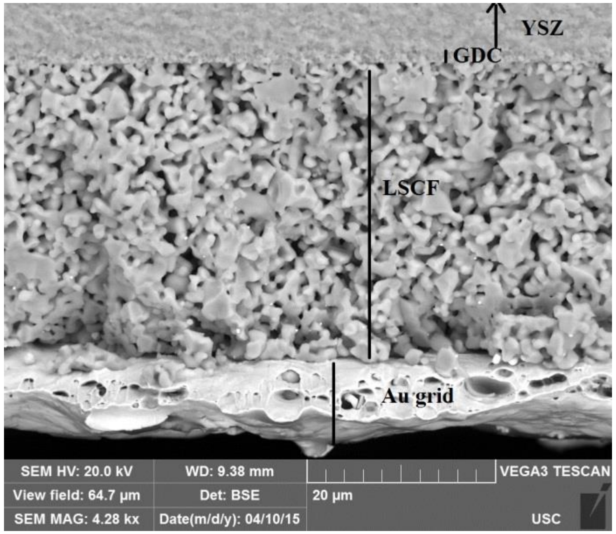

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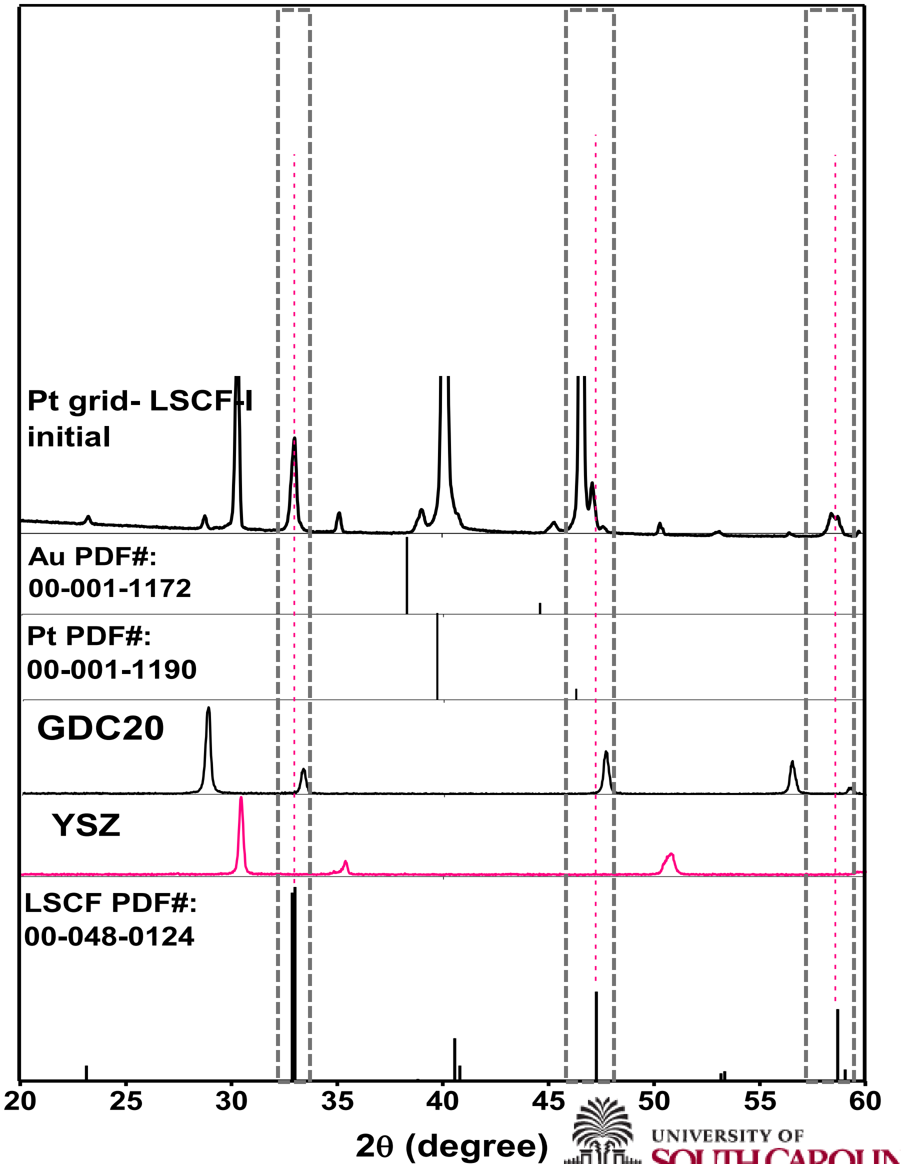

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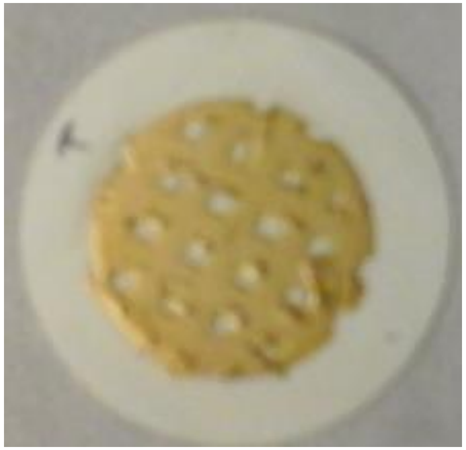

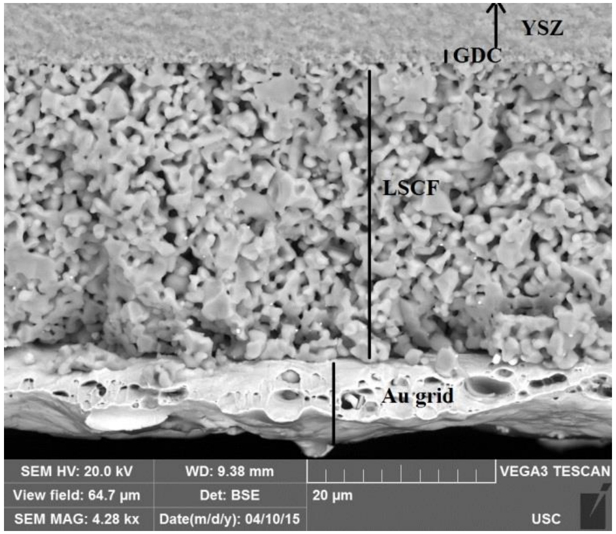

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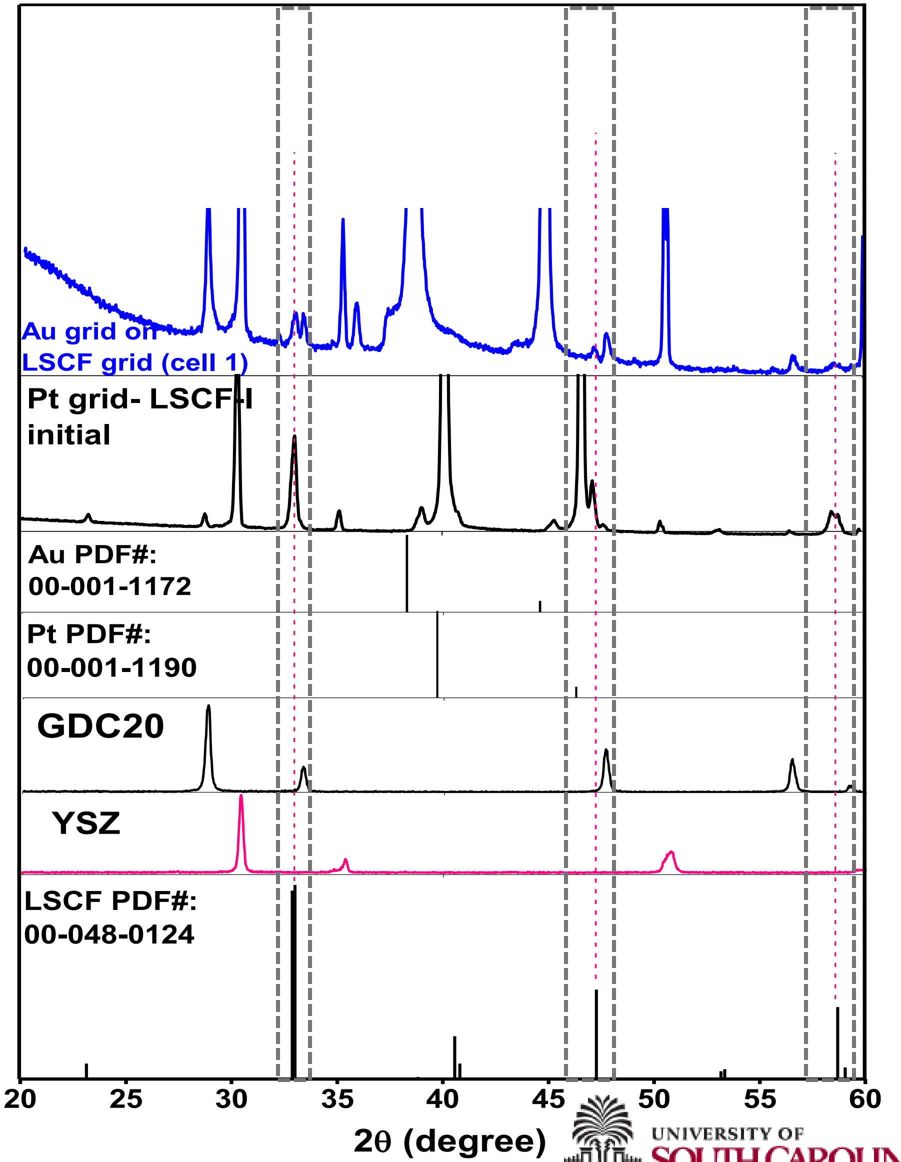

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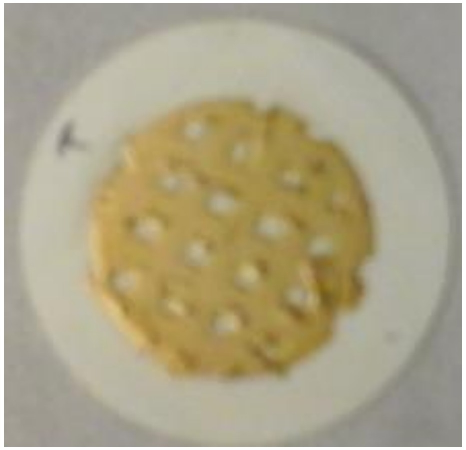

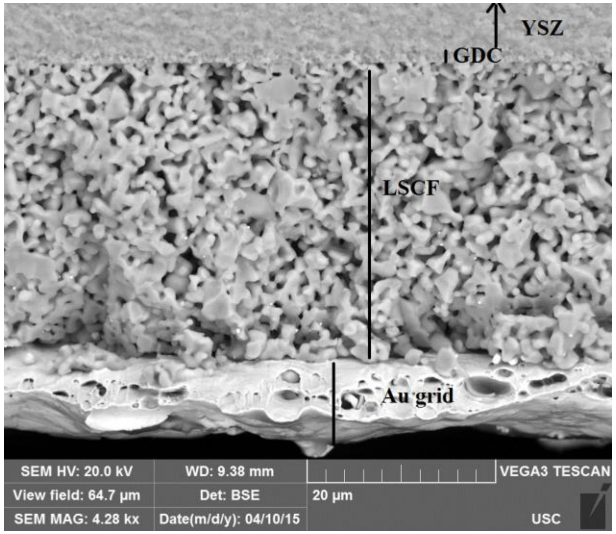

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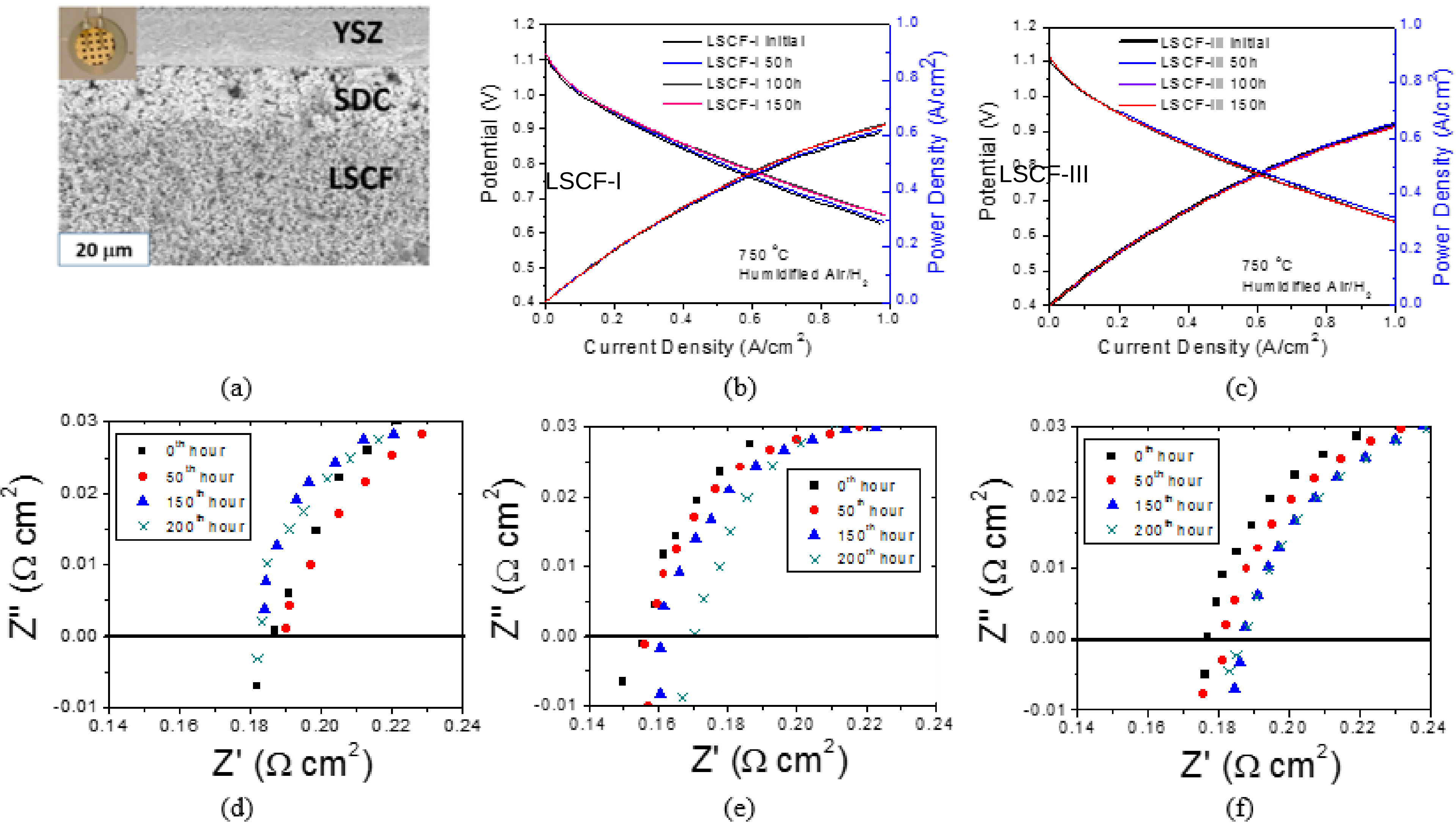
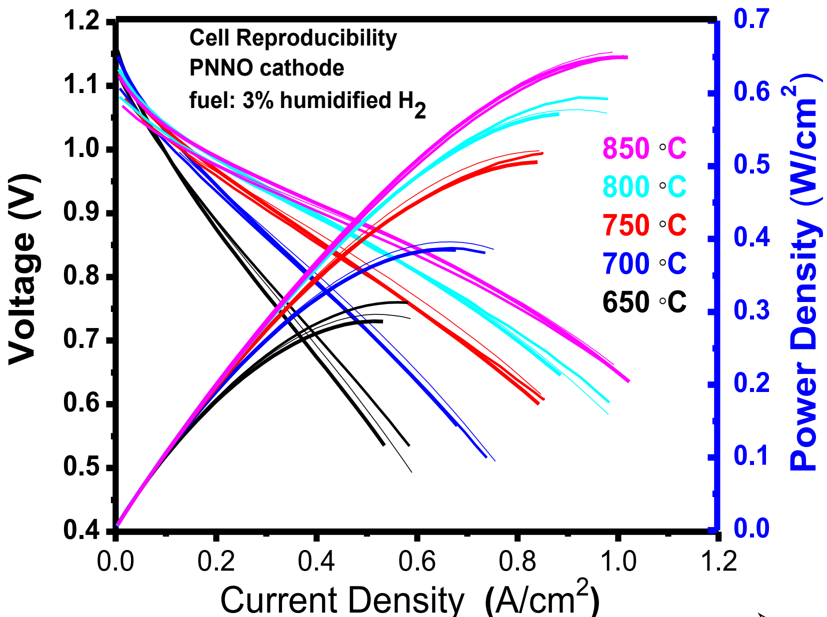
Electrochemical Measurements

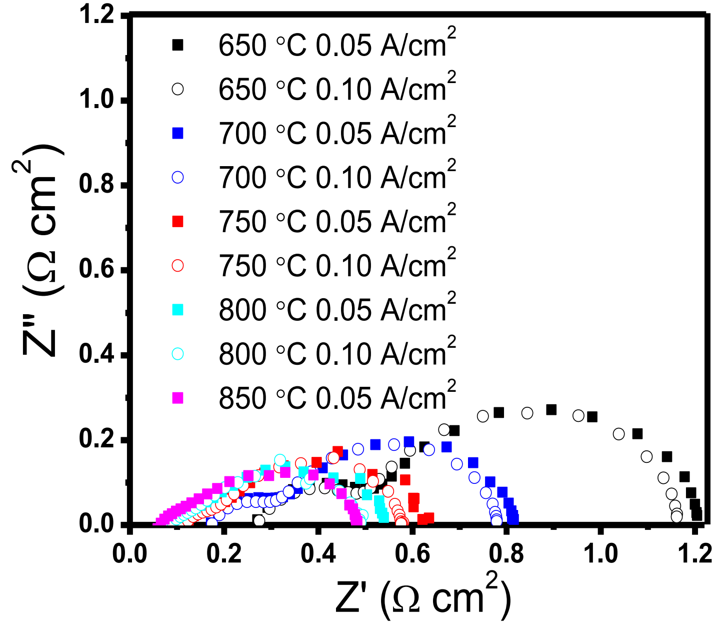
(Accelerated Test)

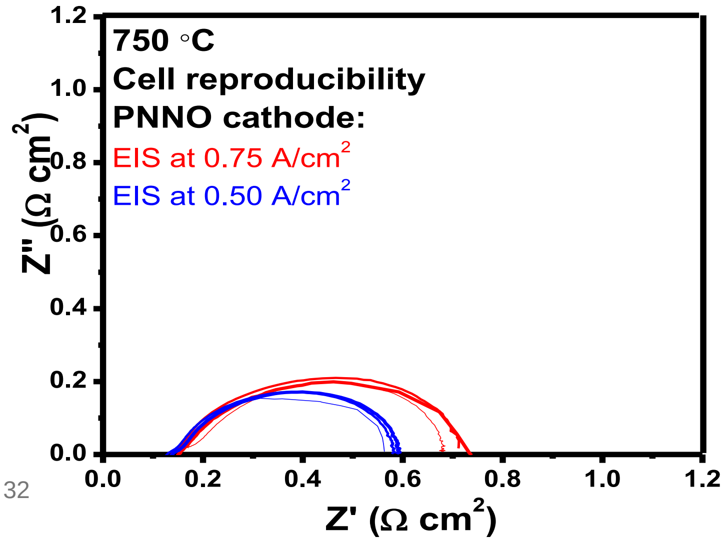
Accelerated Test: LSCF



Performance of PNNO5050 and Substituted PNNO5050





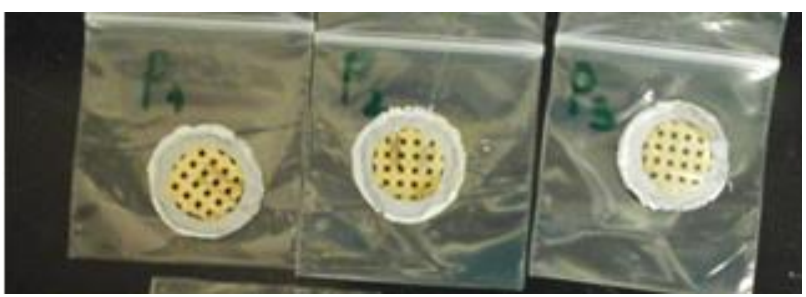


- Cell performances are reproducible. Au was used as the current collector to quantify the kinetics of phase evolution.
- The ohmic loss is small at all temperatures even though the electrolyte is ~ 20 μm. The cathodic resistance for gas diffusion seems large, which can be reduced by using LSC or LNF. But the reason why it was not observed in LSCF is unknown.
- R_{ohm} is 0.12 Ω cm^2 at 750 °C decreasing to 0.06 Ω cm^2 at 850 °C.

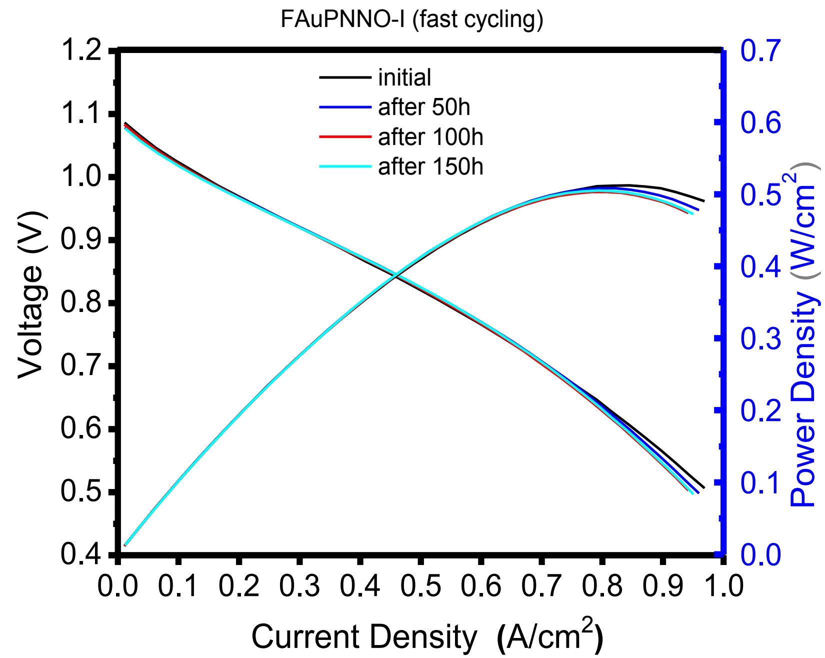
Accelerated Test Protocols Nickelates

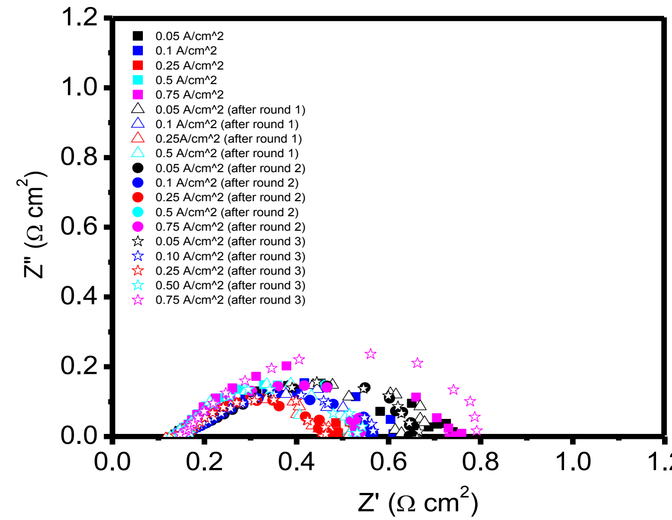
1. Is Au peak area consistent among the cells?
2. Does Au peak area change after accelerated test, if so by how much and why?
3. Can the crystal phase changes in the cathode be quantified in a reliable way?

- ➢ Cathode phase evolution can be calculated with respect to Au reference peak
- ➢ Average Au peak area before and after the measurements can be used directly to calculate the percentage of cathode phases.



Full cells with Au grid after the measurements.





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Identifying a series of nickelates with a stable and active performance (LGFCS proprietary work)

Thermally Stable Compounds:

Doped PNNO5050, PNNO2575, and doped PNNO2575

Electrochemically Stable Compounds:

To be reported

Testing methodology

Reproducibility and reliability

Multiple cells; statistic distribution of data

Quantification of Phase Evolution in a Single Cell

Standard and Au grid electrode

Accelerated Testing Protocols

Theoretical analysis and methods