LA-SiGMA

Louisiana Alliance for Simulation-Guided Materials Applications

Temperature Dependence of Porosity for Porous Electrolyte Based No_x Sensors

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Introduction

Goal: To develop more sensitive emission sensors for automotive exhaust systems

- NO and NO_2, collectively described as NO_x, are the primary pollutants
- Emissions and fuel economy controlled by the same system

NO_x Sensors

- Conventional sensors
  - Made of Yttria-Stabalized Zicronia (YSZ)
  - Operate at high temperatures
  - Dense microstructure

- Experimental sensors
  - Made of YSZ
  - Operate at high temperatures
  - Porous microstructure
  - Sensitivity depends on porosity
  - Porosity depends on fabrication temperature

Project Motivation

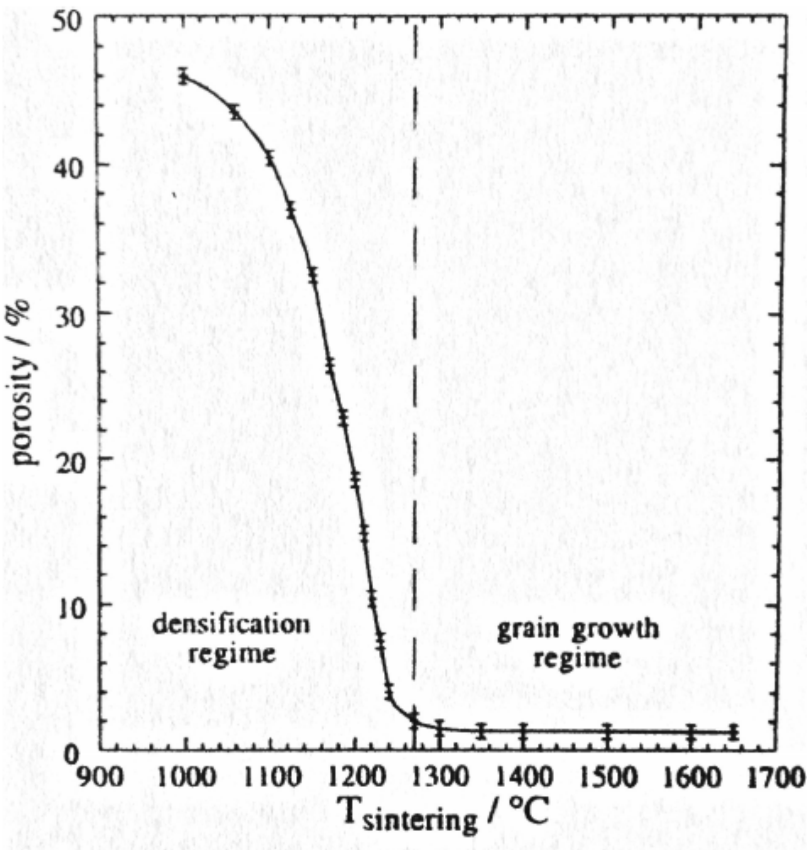


Figure 1. Porosity vs. Sintering Temperature

- We want to determine the porosity that yields the optimum sensitivity
  i. Cannot be too porous
  ii. Cannot be too dense

- Begin by investigating how pure 8% molar Tosoh™ YSZ behaves with temperature
  i. Steil and Thevenot[1] showed that porosity will decrease with temperature as seen in figure 1.

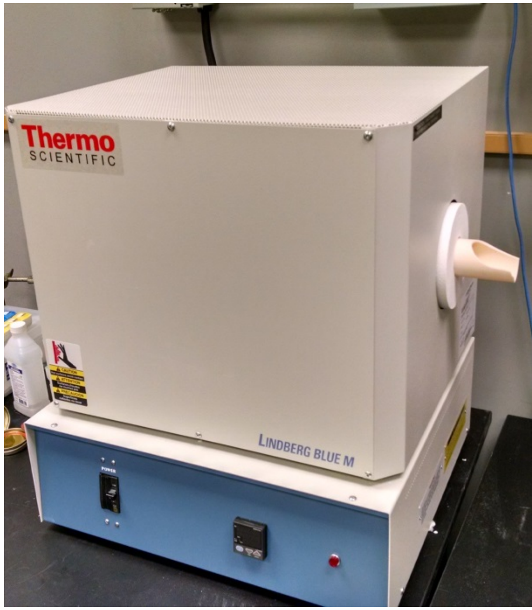
Sample Making

- 500 mg of YSZ was placed in a die press and pressed at approximately 200 Mpa

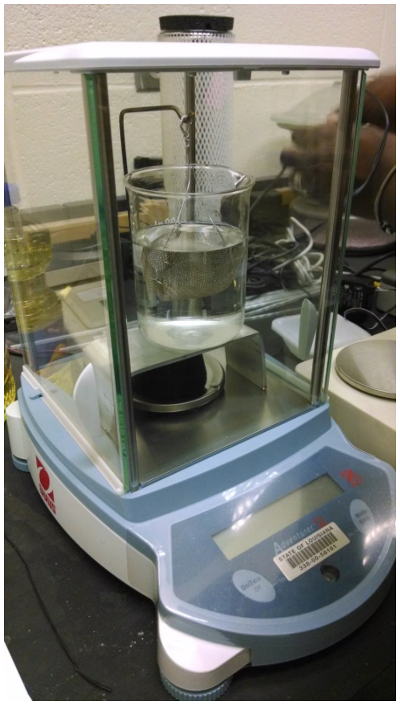
- Samples were fired at 950˚C, 1000˚C, 1050˚C, 1100˚C, 1150˚C, and 1200˚C for one hour.

- 5 Samples were made per temperature
  - 3 used for Archimedes porosity measurements
  - 1 for Scanning Electron Microscopy (SEM) imaging
  - 1 spare

- Mass at fabrication and press pressure have negligible effects on final porosity



Archimedes Porosity Measurements



- The Archimedes Principle was used to determine porosity using the following formula

$$Porosity = \frac{W_{wet} - W_{dry}}{W_{displaced}}$$

- Samples were soaked for approximately 20 hours to saturate pores
  - Samples were soaked for 1 hour between runs

- 3 Archimedes measurements were then taken at one hour intervals

SEM Imaging

- Samples had to be gold plated
- SEM images were taken at 3 different points for each sample
  - Each point had three different magnifications
  - Images intended to be representative (devoid of cracks, abnormal growths, etc. . .)
- A total of 54 pictures were taken and used for analysis

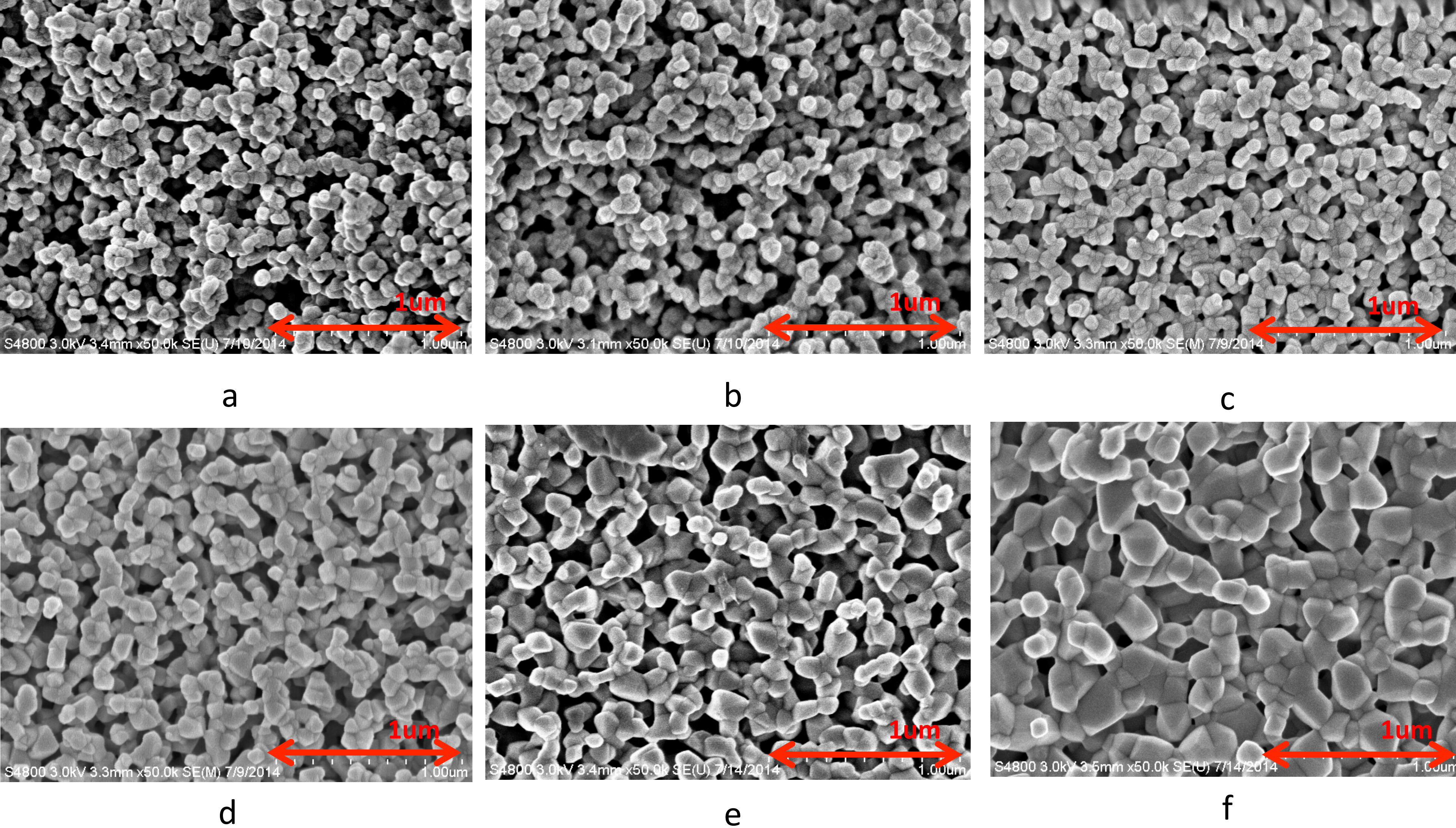


Figure _: Particle Coalescence for a.) 950˚C b.)1000˚C c.)1050˚C d.)1100˚C e.)1150˚C f.)1200˚C

Image Processing and Analysis

- Use MATLAB to analyze SEM images
  - Each pixel is assigned a brightness value between 0-255, 255 being white
  - Numerically integrate brightness values using the following formula

$$Porosity \approx 1 - \frac{\sum_{i=1}^{nx}\sum_{j=1}^{ny} f(x_i, y_j) - f_{\min}(nx\Delta x)(ny\Delta y)}{(f_{\max} - f_{\min})(nx)(ny)}$$

Archimedes Results

- Archimedes results agree with the trend predicted by Stein and Thevenot.
  - 3 runs of Archimedes obersved
  - Differences between this experiment and theory can be accounted for with how the samples were made
  - Runs 2 and 3 demonstrate error at 950˚C. This is most likely due to how brittle the sample is

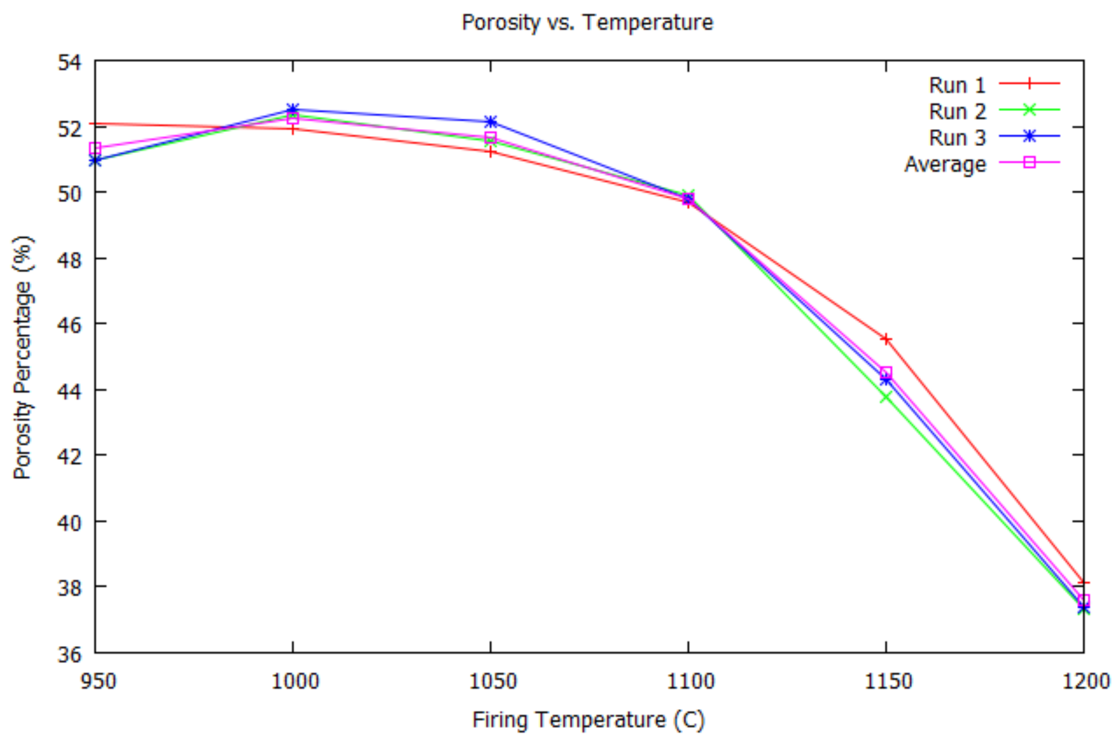
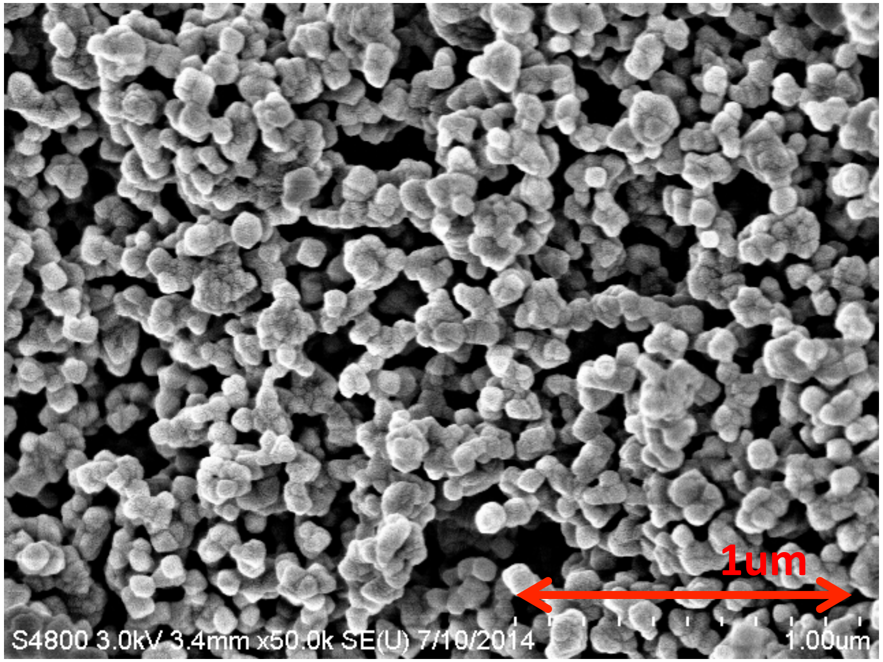
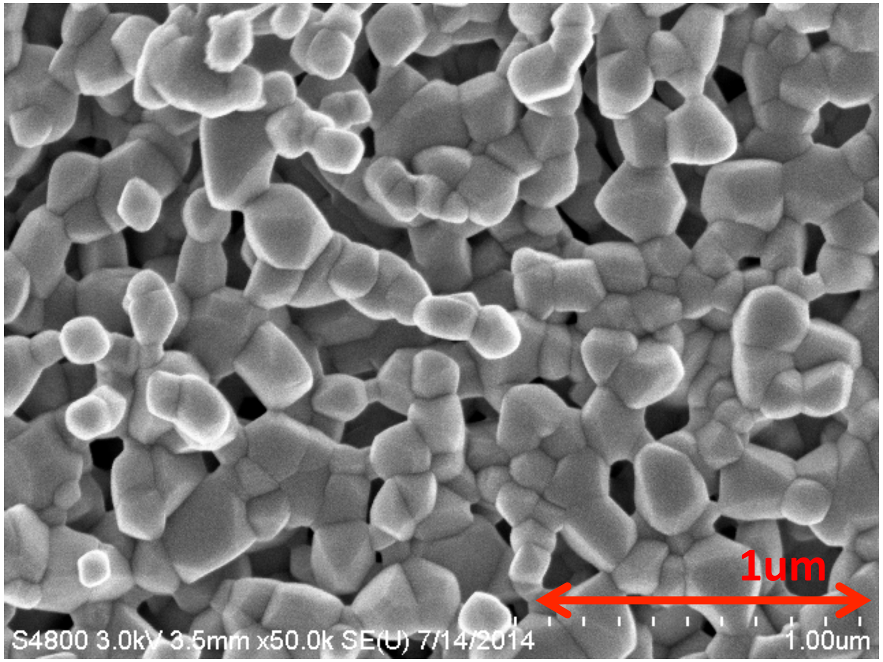


Image Processing Results





Temperature (˚C)	SEM Porosity %	Archimedes Porosity %
950	50.65	52.09
1200	44.36	38.13

Summary

- Samples were made with 500mg of YSZ
  - Fired at 950˚C, 1000˚C, 1050˚C, 1100˚C, 1150˚C, and 1200˚C for one hour.
- Archimedes results agree with results shown by Steil and Thevenot
- Simulation results appear to agree with Archimedes experiments.

Acknowledgements

- **This material is based upon work supported by the National Science Foundation under the NSF EPSCoR Cooperative Agreement No. EPS-1003897 with additional support from the Louisiana Board of Regents**

- **Thank you to Dr. Erica Murray, Dr. Weizhong Dai, and Ling Cui for their help and hospitality this summer. Special thanks is also given to Dr. Alfred Gunasekaran of the Institute for Micromanufacturing at Louisiana Tech for assisting in collecting the SEM images.**

- **Thank you to Dr. Naidu Seetala for his guidance in the Archimedes Porosity Measurement experimental set up**

- **Thank you to Louisiana Tech University and to LA-SiGMA for allowing me this opportunity.**

References

[1]Ling, C., Han F., Dai, W. and Murray, E.P. "Influence of Microstructure on the Sensing Behavior of NOx Exhaust Gas Sensors" *Journal of the Electrochemical Society*. Volume 161, Issue 3 (2014): B34-B38

[2]Steil, M. C. and Thevenot, F. "Densification of Yttria-Stabilized Zirconia." *Journal of the Electrochemical Society*. Volume 144, Issue 1 (1997): 390-398