Temperature Dependence of Porosity for Porous Electrolyte Based NO_x Sensors

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Abstract

New Environmental Protection Agency regulations call for reduced NO and NO_2 emissions from vehicles. Electrolyte based NO_x sensors composed of Yttria-stabilized Zirconia (YSZ), typically used to monitor vehicle emissions and diagnostics, must be made more sensitive in order to meet these more stringent regulations. YSZ based NO_x sensors, whose sensitivity depends on porosity[1], were investigated in order to determine the optimum porosity. The porosity of these sensors depends on the temperature at which they are fired. Several samples were made using Tosoh™ YSZ powder. For each sample approximately 500mg of YSZ powder was dry pressed at approximately 200 MPa. They were then fired at 950˚C, 1000˚C, 1050˚C, 1100˚C, 1150˚C, and 1200˚C. The porosities were then measured using Archimedes methods in conjunction with computer based contrast analysis of scanning electron microscopy images. Preliminary results confirm increasing firing temperature yields a decrease in porosity.

Archimedes Results

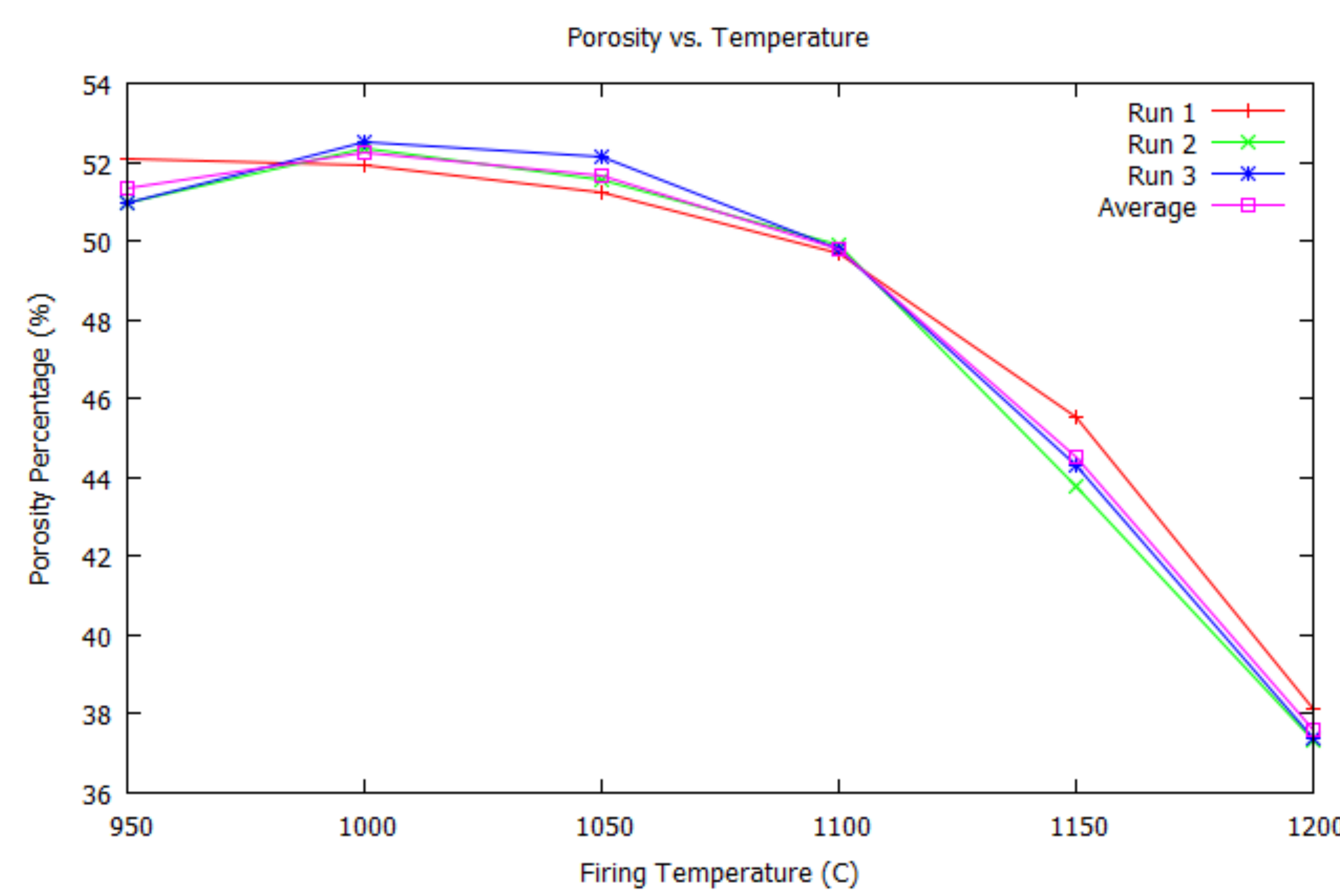

Figure 3: Archimedes results of samples fired at 950˚C, 1000˚C, 1050˚C, 1100˚C, 1150˚C, and 1200˚C

Figure 3 displays the results of all three runs and their average. Run 1 depicts a constantly decreasing porosity with temperature as predicted by Steil and Thevenot[2]. Runs 2 and 3 only depict this behavior after 1000˚C. This is most likely attributable to the fact that after Run 1 the samples would begin to chip around the edges and begin to lose mass and influencing future measurements. This error is most prominent at 950˚C as they are the most porous and therefore the most brittle.

Future work may be required to investigate the variance in porosity at 950˚C. Further investigation is also needed to confirm at what point the change in porosity diminishes.

$$Porosity = W_{wet} - W_{dry} / W_{displaced}$$

Summary

Based on Archimedes measurements it appears that pure YSZ behaves as predicted by Steil and Thevenot, meaning that porosity decreases with firing temperature. Image processing must still be carried out on S.E.M. images to more accurately determine porosity measurements. Computer modeling, based on the S.E.M. images will be used in conjunction with electrical measurements to determine the optimum porosity that contributes to NOx sensor sensitivity.

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Experimental Set Up

Samples of 500mg pure YSZ were pressed into pellets (See Fig.1) using the dry press methods at 200 MPa. The samples were then fired at 950˚C, 1000˚C, 1050˚C, 1100˚C, 1150˚C, and 1200˚C respectively. Five samples were created for each temperature. Three samples were used in Archimedes measurements, one sample in S.E.M. imaging, and the last served as a spare.

Archimedes samples were soaked for approximately 20 hours in deionized water in order to fully saturate all available pores. The porosities were then measured three separate times with each run being an hour apart.

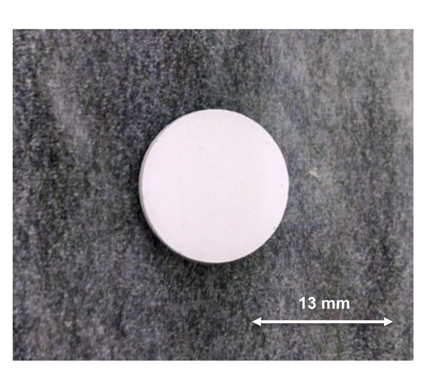

Fig.1

Fig.1) A typical YSZ pellet after firing (Fig 2.) The Archimedes measurement set up

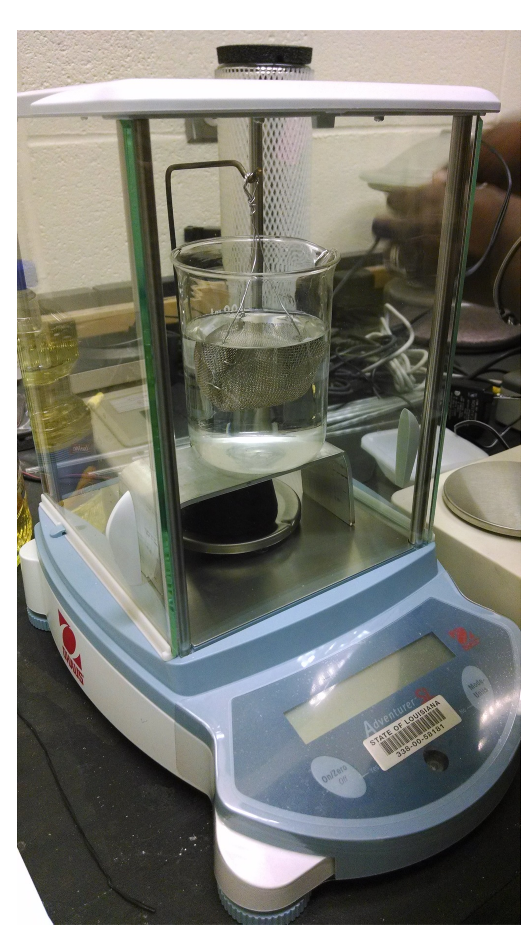

Fig. 2

Future Computational Work

The next step is to calculate porosity using computational methods, something most easily accomplished through image processing. Scanning Electron Microscopy (S.E.M.) images can be scanned onto a computer where each individual pixel is assigned a brightness value between 0 and 255. These values are then summed up and numerically integrated using the following formula to determine the porosity:

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

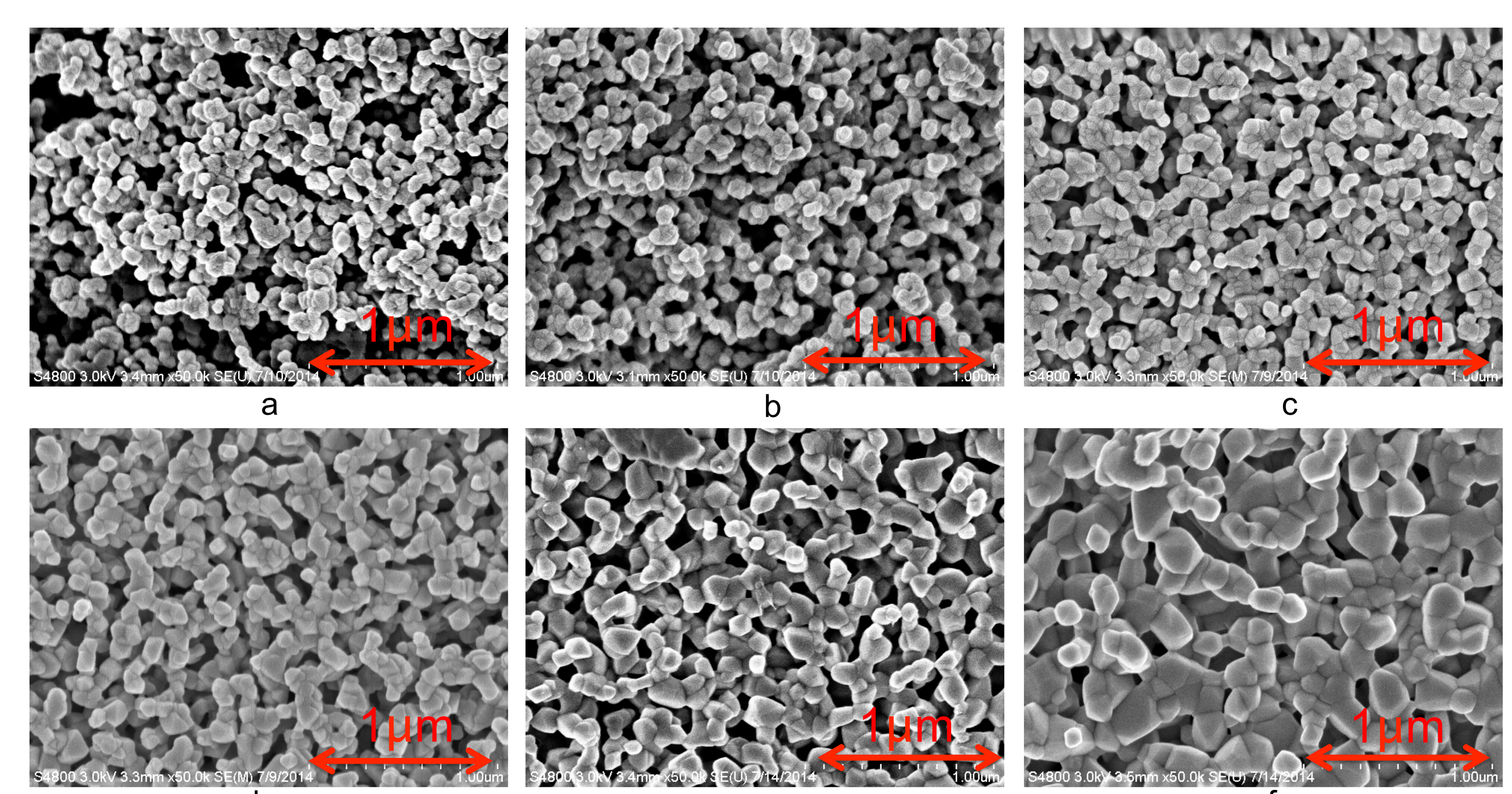

Figure 4: SEM images of samples fired at a.) 950˚C b.) 1000˚C c.) 1050˚C d.) 1100˚C e.) 1150˚C f.)1200˚C at 1 micron

References

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

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