## Role of Porosity in Impedancemetric NO<sub>x</sub> Gas Sensors Using Yttria-Stabilized Zirconia (YSZ) Electrolyte and Au-based Electrodes

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 $NO_x$  compounds, in particular NO and  $NO_2$ , contribute to poor air quality, acting as both pollutants and potent greenhouse gases. Therefore, diesel vehicles require  $NO_x$  sensors to monitor and control the exhaust after-treatment systems. There exists a commercially available sensor technology; however, this technology is expensive owing to both a complicated design with multiple cells as well as the need for precision electronic measurement circuitry capable of performing low current amperometry. Future government regulations will effectively mandate automobile manufacturers to develop  $NO_x$  control systems that limit emissions at single ppm levels. The development of affordable, sensitive, and compact  $NO_x$  sensors is needed for this application.

For high-temperature diesel exhaust, electrochemical solid-state sensors are well suited for the harsh conditions. Conventional sensor operation typically uses direct current (dc) methods, either amperometric (current based) or potentiometric (potential based) signals. In this work an alternating current (ac) impedance-based (i.e., impedancemetric) method is used, which has shown advantages over dc operational modes<sup>1-4</sup>, including better stability and a more simple, low-cost, single-cell design.

Non-equilibrium interfacial redox processes and surface catalysis seem to influence the impedancemetric sensing mechanism. Sensor response is dependent on multiple concurrent redox reactions with different kinetics at the electrode/electrolyte interface, and electrodes that are poor  $O_2$  catalysts result in effective sensors.<sup>1-3</sup> In this work, recently developed sensor designs using Au-based electrodes and alumina substrates were evaluated using two different porous YSZ electrolyte microstructures. In addition, new low-cost electronics were developed for operating impedancemetric sensors.

Figure 1 shows scanning electron microscopy (SEM) pictures of the two different porous YSZ microstructures. Porous YSZ was fabricated using a slurry of YSZ powder (8 mol %  $Y_2O_3$ -doped ZrO<sub>2</sub>), mixed with distilled water, dispersant, and binders. In addition, graphite pore formers were added to the slurry before firing in some samples. Figure 1a shows the resulting YSZ microstructure obtained with the addition of graphite pore formers after sintering in air at 1550°C. Figure 1b shows the resulting microstructure obtained without the addition of graphite pore formers, after sintering in air at 1000°C.

Figure 2 shows the Nyquist behavior for NO<sub>x</sub> sensors made with the two different porous YSZ electrolytes, both using Au-based electrodes, at 650°C in 10.5% O<sub>2</sub>, 10.5% O<sub>2</sub> + 100 ppm NO, and 18.9% O<sub>2</sub>. Both cells demonstrated reductions in low-frequency impedance when either adding 100 ppm NO or increasing the O<sub>2</sub> concentration. Much lower overall impedance (25 kohms) was obtained for YSZ with pore formers in comparison with the YSZ electrolyte obtained without the use of pore formers (130 kohms). The impacts of porosity on sensor performance will be discussed as well as implications for manufacturable sensor platforms and geometries. Simple, low-cost digital electronics were developed that showed effective operation of impedancemetric sensors and will also be discussed.

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Figure 1. SEM picture of porous YSZ electrolyte after (a) adding graphite pore formers and firing to 1550°C and (b) without the addition of graphite pore formers after firing to 1000°C.



Figure 2. Nyquist plot of NO<sub>x</sub> sensor at 650°C in 10.5% O<sub>2</sub>, 10.5% O<sub>2</sub> + 100 ppm NO, and 18.9% O<sub>2</sub> for porous YSZ (a) with pore formers after firing at 1550°C and (b) without pore formers after firing at 1000°C. Numbers corresponding to darkened points represent log of frequency in hertz.