Dramatic Improvement in Commercial LSM-YSZ Cathode Ohmic Resistance and Activity by YSZ Nanoparticles

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Introduction

Porous composites of lanthanum strontium manganite (LSM) and yttria-stabilized zirconia (YSZ) have been the most common SOFC cathodes. LSM provides electronic conductivity and YSZ provides oxide ion conductivity. However, the negligible ionic and electronic conductivity of LSM and YSZ, respectively, limit the active three-phase boundaries (TPB) at the interface of percolated networks of LSM and YSZ particles. That limitation results in a low active TPB density in LSM-YSZ cathodes. In this study, we report on a processing method that increased the TPB density in a commercial LSM-YSZ cathode, resulting in a dramatic cell performance improvement in both ohmic resistance and electrochemical activity. The method produces ultra-high surface area nanoYSZ, up to 115 $m^2 \cdot g^{-1}$, withing the cathode.[1] The nanoYSZ was generated by *in situ* carbon templating, a processing method that our lab has developed. The method produces high surface area mixed-metal-oxides by heating hybrid inorganic-organic materials to 850°C-1350°C in an inert atmosphere such as nitrogen or argon followed by oxidation at 700°C in air. [2-6] The nanoYSZ particles were expected to form an interconnected network of particles on the surface of both LSM and YSZ particles, providing additional active TPB sites and broader O^{2-} conduction pathways (Figure 1). The experimental results showed that the incorporated nanoYSZ indeed formed an interconnected layer of nanoparticles on the surface of LSM-YSZ porous scaffolds (Figure 3). This interconnected layer of nanoYSZ resulted in a reduction of both the polarization and ohmic resistances by 40% and 35%, respectively. The combination of both reductions resulted in a 90% maximum power density increase. For comparison, two cells were modified with mixed ionic electronic conductors (MIECs): $Pr_xBa_{1-x}Co_{3-\delta}$ (PBC) and $La_xSr_{1-x}Co_yFe_{1-y}O_{3-\delta}$ (LSCF). While the MIECs reduced the polarization resistance, they only marginally affected the ohmic resistance, which resulted in a lesser impact on power density than nanoYSZ. This work demonstrates that *in situ* carbon templating provides a pathway to improving commercial SOFC performance with nanomaterials.

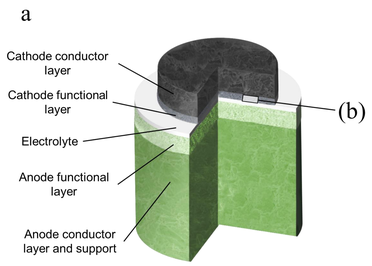

Figure 1. Schematic image of a) a commercial MSRI cell showing its different structural layers and b) the proposed effect of incorporating nanoYSZ into the cathode. [1]

Results

The highest maximum power density (628 $mW \cdot cm^{-2}$) was achieved with the cell modified with nanoYSZ (nYSZ), a 90% increase over the baseline cell (330 $mW \cdot cm^{-2}$), Figure 2a. Impedance spectroscopy, shown in Figure 2b, indicates that the dramatic power density increase is attributed to a combination of substantial improvement in both the polarization and ohmic resistance, which were reduced by 40% and 35%, respectively. Both PBC and LSCF reduced polarization resistance, but, unlike nYSZ, did not substantially impact the ohmic resistance (Figure 2b). The superior impact on ohmic resistance by nanoYSZ is attributed to its smaller particle size and better percolation than both PBC and LSCF (Figure 3).

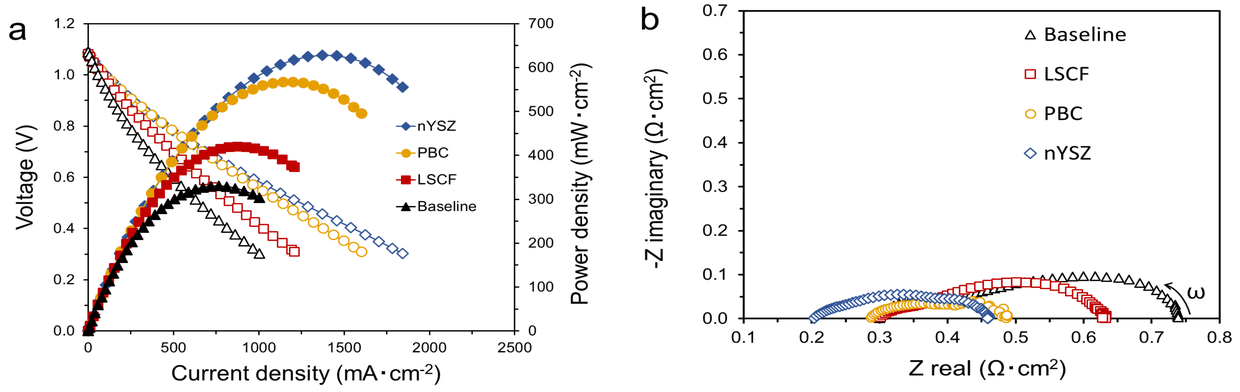

Figure 2. a) Fuel cell *i-V-P* performance and b) Nyquist plots of the studied cells. All fuel cell performance data were collected at 750°C after 24 hours of continuous fuel cell operation. [1]

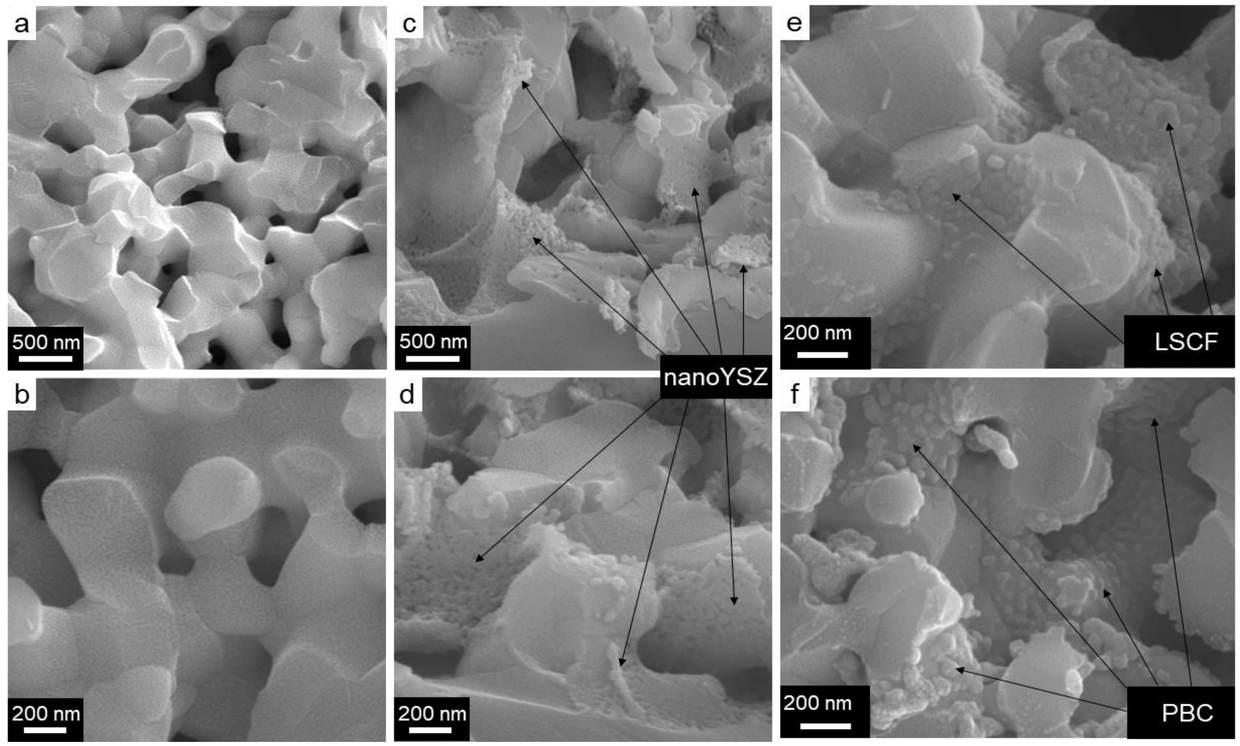

Figure 3. SEM images of commercial LSM-YSZ cathodes without modification (a and b), with nanoYSZ (c and d), with LSCF (e), and with PBC (f). [1]

Transmission electron microscopy (TEM) indicates that the generated nanoYSZ possessed discrete and small particles ranging between 5 nm and 10 nm (Figure 4b – 4c). TEM diffraction patterns indicate that an amorphous material forms upon heating in N_2 (Figure 4a), reflecting the presence of a high concentration of amorphous carbon. Upon oxidation of the amorphous carbon, a pure crystalline YSZ with a cubic structure forms (Figure 4b).

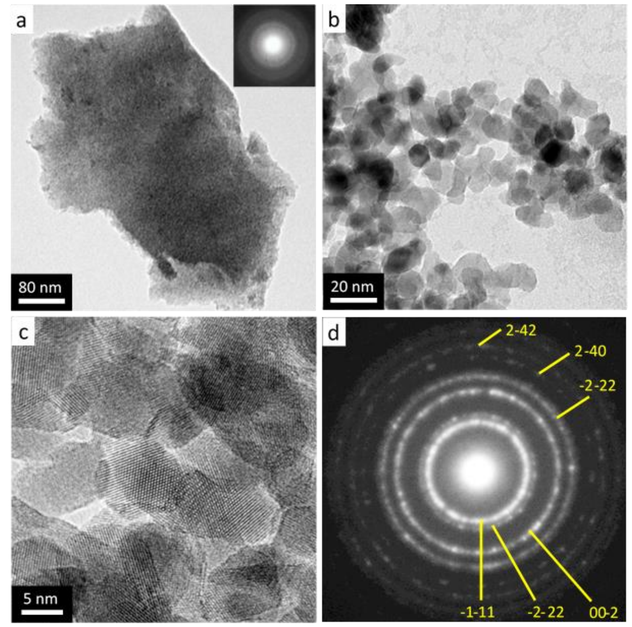

Figure 4. TEM images of YSZ hybrid material a) heated to 850°C in N_2 and b-c) subsequently calcined in air at 700°C. c) Zoomed in view of b). d) TEM electron diffraction ring of YSZ nanoparticles (depicted in c) with a cubic crystal. [1]

Conclusion

Ultra-high surface area crystalline nanoYSZ was successfully integrated into LSM-YSZ cathodes of commercial SOFCs via *in situ* carbon templating. The integration of nanoYSZ increased the cell maximum power density by 90%, outperforming cells modified with LSCF and PBC by 50 % and 11%, respectively. This remarkable improvement in power density is attributed to the interconnected networks of the YSZ nanoparticles, which enhanced the density of active TPB and enlarged O^{2-} conduction pathways. As a result, the polarization and ohmic resistance of the nYSZ cell were 40% and 35% lower than the baseline cell, respectively. The nanoparticles of the two MIECs, on the other hand, were larger and interconnected to a lesser degree than nanoYSZ. Thus, they impacted the cell ohmic resistance less extensively than nanoYSZ.

References:

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