Impregnation of nanoparticle scaffolds for syngas-fed solid oxide fuel cell anodes

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A strategy for fabrication of solid oxide fuel cell anodes with improved porosity and lower sintering temperatures by impregnation of nanoparticle-containing porous scaffolds of ceria-gadolinia (CGO) has been developed. The CGO scaffolds are fabricated using a screen-printed ink containing nanoparticles and commercial particles of CGO and polymeric pore formers. Scanning electron microscopy and *in situ* ultra-small angle X-ray scattering show that incorporation of nanoparticles increases the porosity by allowing a reduction in sintering temperature. Electrochemical characterisation of symmetrical cells shows that the cells sintered at 1000 °C possess similar electrode polarisation compared to those sintered at 1300 °C. Button cell testing showed that reducing the sintering temperature produced cells which perform better at 700 °C and below in hydrogen, and performed better at all temperatures using syngas. This approach has the potential to allow the use of a wider range of nanomaterials, giving a finer control over microstructure.

Introduction

Incorporation of nanomaterials into devices such as solid oxide fuel cell (SOFC) electrodes has the potential to improve surface areas, lower heat-treatment temperatures, allow finer control over microstructure and could give access to new functionality. However, the use of inorganic nanomaterials has been hampered by the difficulties of fabricating devices using traditional processing techniques such as screen printing or tapecasting(1). In a typical ceramic fabrication process, an ink is formulated by suspending the ceramic particles in a liquid containing dispersants and binders(2). When dried, this ink can form a monolith if tape cast or a film on a support if screen printed. The difficulty with using nanomaterials has been to maintain a workable viscosity for the ink while increasing the solid loading to levels which are linked to important properties in the final product such as increased density, better particle interconnectedness, and potentially increased adhesion to the substrate and uniformity(3-5).

Typically, SOFC anodes are three-dimensionally-percolating mixtures of an electron-conducting metal and an oxide-conducting ceramic, with electrochemical reactions taking place at the interface between metal, ceramic and gas, known as the triple phase boundary (TPB). Maximising the TPB length should improve the performance of the electrode.

Good adhesion to the current collector and electrolyte are also required to reduce ohmic losses. Normally an ink of nickel oxide and doped ceria or zirconia will be used, and this will need to be heat-treated at 1300 °C or higher to produce well-adhered and physically-stable electrodes.

A fabrication method which may help improve triple phase boundary length is impregnation (also known as infiltration) of porous scaffolds, where the ceramic component of the anode is printed as an ink, forming a porous scaffold after heat-treatment. The metal component is added afterwards by impregnation of metal nitrate solution into the scaffold(6-7). Hitherto, this method has only used conventional ($>1\text{ }\mu\text{m}$) sized particles for the scaffold. The use of nanomaterials may be able to produce finer microstructures, increase the TPB length further and allow use of new materials.

In this study we report on the fabrication of CGO scaffolds using a mixture of nano and larger commercial particles, with pore formers. We demonstrate that the incorporation of the nanoparticles results in physically-stable electrodes after sintering at only 1000 °C, giving electrodes with significantly higher porosity and producing cells with superior low temperature performance compared to cells produced using a standard heat-treatment temperature of 1300 °C in hydrogen and at all temperatures in syngas fuel.

Experimental

Inks were formulated from a mixture of commercial gadolinia-doped ceria ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.97}$, CGO, particle size = $0.5\text{ }\mu\text{m}$) from Praxair, nanoparticle CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.97}$, particle size = 5 nm from TEM) produced by continuous hydrothermal flow synthesis (CHFS), polymer microbeads ($6\text{ }\mu\text{m}$, Microbeads AS, Spheromers CA6), terpeneol as a solvent, Hypermer KD15 as a dispersant and an ethylcellulose binder (Hercules EC N-7). The CGO nanopowders were produced by continuous hydrothermal flow synthesis using a pilot plant at University College London as described elsewhere(8). CHFS has previously been used to make samaria-doped ceria(9), ceria-zirconia solid solutions(10-11), an entire phase diagram of 66 ceria-zirconia-yttria samples(12) and a range of other metal oxides(13-14) and phosphates(15) with typically sub 50 nm diameter. In CHFS, an aqueous mixture of cerium ammonium nitrate and gadolinium nitrate solution was continuously mixed with a stream of superheated water at $450\text{ }^{\circ}\text{C}$ and 22.1 MPa in a patented confined jet mixer(16). Particles were then cooled (via a pipe cooler) and then collected as an aqueous slurry at the exit of the back-pressure regulator.

For preparation of scaffolds, the solvent (0.653 g), dispersant (0.265 g) and binder (0.040 g) were mixed together until the binder had fully dissolved. Next, with stirring in an ultrasonic bath, each solid component was added sequentially in two or three aliquots, starting with the dried CGO nanoparticles (0.751 g), followed by the commercial CGO (1.047 g), and finally the polymer microbeads (0.153 g). The ultrasonication and stirring is effective in suspending the nanoparticles. This gave an ink with ca. $26\text{ vol\%}$ solids content, which was an acceptable level for a screen printing ink(3).

The inks were screen printed onto $200\text{ }\mu\text{m}$ thick yttria-stabilised zirconia (YSZ) electrolytes. In the case of fuel cells, the procedure differed slightly between cells with different sintering temperatures for the anode. In the cells with scaffolds sintered at $1300\text{ }^{\circ}\text{C}$, one side was printed with the scaffold ink, while the other was printed with a

thin layer of a CGO ink (this is to prevent reactions between the cathode material and the YSZ electrolyte). The printed pellets were then heat-treated at 1300 °C for one hour, with a 1 °C/min ramp rate during heating and cooling. The LSCF-CGO cathode (ink purchased from Fuel Cell Materials, Columbus, OH, USA) was then screen-printed, and the cell heat-treated at 1100 °C for three hours with a 5 °C/min ramp rate during heating and cooling. The process for the cells with scaffolds heat-treated at 1000 °C was identical except the order of printing and sintering was a protective CGO layer first, followed by cathode and finally by the CGO scaffold. Cells with one, two or three layers of CGO scaffold were produced. The scaffold was dried in an oven at ~80 °C in between each printing cycle.

Next, the CGO scaffolds were impregnated with a nickel salt. The impregnation solution was prepared from 0.125 g of nickel nitrate hexahydrate in 200 µL of absolute ethanol. The solution was dropped onto the scaffold using a 1 – 20 µL pipette, with the volumes used determined empirically by visually observing whether the drop spread beyond the edge of the scaffold. If it did, then the volume of the following impregnation was reduced. The first volume used was determined by dropping pure ethanol onto the scaffold. In between each impregnation, the pellets were placed into a furnace directly at 500 °C for 5 mins. This cycle was then repeated ten times. After the final impregnation, the pellets were placed into this furnace, and the temperature was increased to 800 °C at 5 °C/min and held for eight hours before cooling at 5 °C/min. The NiO loading was determined by weighing.

Four symmetrical cells were produced: a single layer cell heat-treated at 1300 °C; a single layer cell heat-treated at 1000 °C; a double layer cell heat-treated at 1000 °C and a triple layer cell heat-treated at 1000 °C. In addition, four button cells for fuel cell testing were produced from single and double layer CGO scaffolds heat-treated at 1000 °C, and the same heat-treated at 1300 °C.

The scaffolds were studied by Ultra Small Angle X-ray Scattering (USAXS) to obtain information about the pore structure, while the *in situ* measurements allowed us to monitor the development of the microstructure with temperature(17). For the USAXS measurements, single layered samples were printed onto MgO substrates (used instead of YSZ as it is less absorbing of X-rays) for analysis by USAXS. The USAXS data were taken at sector 15, Advanced Photon Source, Argonne National Laboratory. Briefly, small angle scattering intensities around the direct beam was measured using channel cut Si crystal monochrometers in a Bonse-Hart configuration. The x-ray energy was 16.8 keV and the beam size was 1.5 x 0.4 mm. The sample was mounted in a LinkAm heater for the *in situ* USAXS measurements. The USAXS intensity is plotted as a function of the scattering vector $q = 4\sin(\theta)/\lambda$ where λ is the x-ray wavelength and θ is the scattering angle. The USAXS spectra can be viewed as the autocorrelation of the electron density fluctuations inside the sample, resulting from contrast between the pores and the powders. The USAXS is normally plotted in a log-log plot, and at low q Guinier approximation is valid so the USAXS intensity shows an inflection proportional to $-\exp(q^2 R_g^2/3)$ where R_g is the radius of gyration. At higher q values, the USAXS intensity follows a power law slope with an exponent of -3, as expected from Porod's law from slit-smeared USAXS. Our USAXS could not resolve the Guinier inflection from the large pores made by polymer microbeads, so we used a combination of a powder law slope and a log-normal

size distribution of spherical pores to model the USAXS intensity for non-linear least squares fitting.

Electrochemical measurements were carried out with an Autolab PGSTAT. Symmetrical cell tests were carried out under humidified hydrogen in nitrogen, while fuel cell tests were carried out under humidified hydrogen in nitrogen and humidified syngas in nitrogen (15 % H₂, 25 % CO, 60 % N₂). For the syngas tests the cells were put under load in 50% H₂ in N₂ before switching to syngas and carrying out the measurements. This avoids the carbon deposition caused by direct exposure to syngas at OCV. In all cases the same procedure for reducing the anode was employed; the cells were heated under dry nitrogen to 765 °C at 5 °C min⁻¹ before switching to humidified 10 % hydrogen in nitrogen for one hour before cooling to the operating temperature. In all cases in this report, the humidification was carried out at 20 °C, giving a humidity of 2.3%, while the gas compositions given refer to the gas compositions prior to humidification.

Results and discussion

Scaffolds heat-treated at both 1000 and 1300 °C were not removed by placing and removing Sellotape from the scaffold, indicating that they were physically stable and adhered to the electrolyte. Scaffolds produced from CGO are not normally stable after heat-treatment at 1000 °C, a fact which was confirmed by producing a similar ink but with the nanoparticle portion replaced with extra commercial CGO. Scaffolds produced from this ink and heat-treated at 1000 °C were not stable and could be removed even by the slight breeze caused by opening the furnace after heat-treatment. This indicates that the nanoparticle CGO is acting as a sintering aid, binding together the commercial CGO particles and adhering the scaffold to the electrolyte.

SEM imaging of the scaffolds (figure 1) showed differences between the structures, with the finer microstructure of the scaffold heat-treated at 1000 °C obvious. The microstructure of the scaffold heat-treated at 1300 °C appeared typical of ceria heat-treated at such a temperature, with no obvious indication of the influence of the nanoparticles. Both scaffolds showed pores of ca. 6 µm caused by the removal of the pore formers, and both showed a thickness of ca. 10 µm.

Figure 1. Porous CGO scaffolds heat-treated at 1000 °C (a) and 1300 °C (b) at 15k magnification

In situ USAXS carried out during the heat-treatment of a scaffold (figure 2) shows the development of the pore structure with temperature. At lower temperatures there is a bimodal pore size distribution. The smaller pores begin to increase in size and decrease in volume fraction between 766 and 927 °C, completely disappearing by 1150 °C. The larger pores do not show similar changes until above 1100 °C. These results indicate that the nanoparticles begin sintering below 927 °C, and must be mostly responsible for the physical stability of the scaffolds calcined at 1000 °C.

Figure 2. Pore size and volume against temperature derived from *in situ* USAXS data.

The final step in the fabrication of the anodes is impregnation of nickel nitrate solution, which is converted to nickel oxide on exposure to air. Because of the difference in density between the nickel nitrate solution and solid nickel oxide, the scaffolds need to be impregnated multiple times to obtain a percolating coverage of nickel oxide(18). In all cases the theoretical mass of impregnated nickel oxide was close to the measured mass. Because the volume of nickel nitrate solution added was determined empirically, from observation of whether or not the previous impregnation was fully absorbed, the nickel oxide loading is not identical between cells. The loading of nickel oxide is lower in multi-layered cells, probably due to the reduced ability of the nickel nitrate solution to fully absorb into the deeper scaffolds.

Impregnated symmetrical cells were tested using impedance spectroscopy in order to assess the effects of scaffold calcination temperature and thickness of scaffold. Three cells heat-treated at 1000 °C were tested: single layer, double layer and triple layer. These were compared to a single layer cell produced using the same ink but calcined at 1300 °C in order to assess the differences between the scaffolds calcined at different temperatures.

Figure 3 shows the impedance spectrum at 500 °C for the single layer cells as an example. All four cells show the two semi-circles typical of Ni-CGO anodes, with the high frequency response normally assigned to charge transfer processes and the low frequency response is normally assigned to diffusion processes. Modelling these cells as equivalent circuits (inset of figure 3) shows that in this case, the assignments are consistent with this, as the high frequency response decreases in size exponentially with increasing temperature as expected from a thermally-activated charge transfer process, while the lower frequency response decreases in size with increasing hydrogen concentration, as expected from a diffusion-based process. For the low frequency response, the changes with hydrogen concentration are much less pronounced for the cells heat-treated at 1000 °C.

Figure 3. Impedance spectra for symmetrical cells tested at 500 °C produced from scaffolds heat-treated at 1300 °C (top) and 1000 °C (bottom). The characteristic frequencies of each response are displayed on the plot for the 10% H₂ single layer samples only. The inset shows the equivalent circuit used for modelling.

By examining the higher frequency response the authors have assigned as related to charge transfer, some differences between the anodes could be observed. For the cells with scaffolds heat-treated at 1000 °C, the activation energy decreased as the number of layers increased, from 120 kJmol⁻¹ for one layer, 111 kJmol⁻¹ for two layers and 97.4 kJmol⁻¹ for three. For the sample with a scaffold heat-treated at 1300 °C, the calculated activation energy of 128 kJmol⁻¹ was comparable to the single layered cell heat-treated at 1000 °C.

The samples heat-treated at 1000 °C showed much smaller polarisation in the low frequency response than the sample heat-treated at 1300 °C, which is consistent with the higher level of porosity demonstrated by USAXS and SEM. The scaffolds heat-treated at 1000 °C all possessed lower resistances for the electrode component of the resistance than the scaffold heat-treated at 1300 °C. The ohmic component of the resistance (the intercept with the x-axis at the high frequency end) was larger by up to 50 % in all the samples heat-treated at 1000 °C, which suggests that the electrical contacts were poorer. Previous work on infiltrated electrodes using FIB-SEM

tomography(18) has shown that the level of percolation of nickel is sensitive to the loading of nickel, it may be that the higher porosity of the lower temperature samples results in a poorer connectivity of nickel at the loadings used in these samples. The electrode resistances decrease with increasing number of layers, indicating that the active electrochemical volume was increasing in size.

Fuel cells were fabricated from the two layer scaffolds. Despite the slightly better performance noted in the triple-layered symmetrical cells, these were not produced due to the increased complexity of printing the extra layer. The measured power densities in 50 % H₂ (Figure 4) showed that the cell produced using a scaffold heat-treated at 1300 °C outperformed the cell produced using a scaffolds heat-treated at 1000 °C (when tested at 800 °C). However, at lower testing temperatures, the cell made from a scaffold heat-treated at 1000 °C produced higher power densities. This is due to the difference in activation energy producing a different response to changing temperature.

Figure 4. Power density curves measured under 50 % H₂ for double layered scaffolds showing the effects of scaffold heat-treatment temperature. Scaffolds heat-treated at 1000 °C are circles while those heat-treated at 1300 °C are squares. Power densities are closed symbols, while voltages are open symbols.

These two cells were also tested in syngas (figure 5). In order to avoid exposing the cells to syngas at under conditions of low oxygen flux which may lead to carbon deposition, the cells were held at 0.5 V under 50% H₂ before switching to syngas and subsequently testing at 0.5 – 0.8 V. In these tests, the cell produced from the scaffold heat-treated at 1000 °C performed better under all conditions. The energy content of the syngas fuel used is around 80% of the energy content of the 50% H₂ fuel used in the previous test. While the cell produced from the scaffold heat-treated at 1300 °C indeed shows 80% of the power density comparing the syngas test to the hydrogen test, the cell produced from the scaffold heat-treated at 1000 °C produces a higher relative power density than this. This suggests that this cell is more efficient under syngas than under hydrogen.

Figure 5. Fuel cell tests under humidified 15% H₂, 25% CO syngas showing the effect of scaffold sintering temperature. The scaffold heat-treated at 1000 °C is in circles while the one heat-treated at 1300 °C is squares. Power densities are filled symbols while voltages are open symbols.

Conclusions

A strategy for incorporating nanoparticles into solid oxide fuel cell anodes has been demonstrated, and has been shown to confer benefits including lower onset of sintering temperatures, higher porosity and ultimately better performance at lower temperatures and under syngas. The nanoparticles used along with conventional micron-sized CGO particles appeared to act as a glue to enable the lower sintering temperatures. Low temperature routes towards solid oxide fuel cells should allow the use of more advanced catalysts, finer microstructure and materials which are not stable at higher temperatures.

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