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The effects of templating synthesis procedures on the microstructure of Yttria Stabilised Zirconia (YSZ) and NiO/YSZ templated thin films

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Abstract

The microstructure of the electrodes, in particular the anode, is of vast importance in the present stage of Solid Oxide Fuel Cell (SOFC) development. Templating methods provide well ordered, inverse opal, macroporous structures for small quantities of powder, scaling up the procedure to produce commercial quantities of powder remains a challenge. This study examined different synthesis conditions for producing larger amounts of high quality YSZ and NiO/YSZ electrodes using the templating technique and the effects of these on microstructure. The study revealed that as the quantity of the polystyrene (PS) spheres for the template is increased the microstructure quality is reduced, due to increasing difficulty in homogeneous permeation of the template. Thus the optimisation of the ratio of PS spheres to powder is of great importance and in this study was found to be around 2:1, however the addition of NiO has additional effects on the microstructure.

Keywords: Yttria Stabilised Zirconia (YSZ); SOFC anode; Microstructure; Templating; Polystyrene spheres; Humidity; Thin film

1. Introduction

The targeted control of porosity has been studied and used in a wide range of applications such as membranes for separation and purification, high surface area adsorbants [1], supports for sensors and catalyst [2], photonic crystals [3–5] and electrodes for fuel cells [6–10].

Hard templating methods using colloid crystalline templates [11], such as polystyrene or silica spheres, to produce three-dimensional ordered macroporous (3DOM) materials are becoming an increasingly popular way to synthesise a wide range of materials and have been extensively studied for materials such as silica [12], metals [13], semiconductors [3], metal oxides [14–17], carbon [18] and polymers [19,20].

Templating particles range in size from nanometres to micrometres and self-assemble in the correct synthesis conditions into cubic close packed arrays. Once infiltrated with precursor solution and then either chemically or thermally removed, the long range periodic ordering of spheres is replicated in a solid, inverse opal matrix, yielding materials with ordered pores. An advantage of the template method is that the dimensions of the pores in the final material are set by the size of the template, thus the microstructure can be readily tailored, with both the final porosity and the surface area determined by the size of the template particles.

Yttria Stabilised Zirconia (YSZ) is commonly used as an oxygen sensor and an oxygen pump in automotive and industrial applications, and is the choice electrolyte for commercial Solid Oxide Fuel Cell (SOFC) technology. YSZ is also a major component of the SOFC anode where it is typically mixed with 50 vol% NiO and then reduced at operating conditions to create a varyingly porous Ni/YSZ cermet electrode. The porosity is important in two regards: efficient gas transport through the electrode and high surface area for catalytic reactions. Thus optimising pore size and size distribution in the anode is necessary for achieving fast gas transport to and from all catalytically active sites, and will result in optimum electrochemical performance and even distribution of fuel.

To date the electrode porosity is only loosely controlled by the powder morphology, sintering conditions and the addition of pore formers, such as graphite powders [21]. In

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the SOFC anode further porosity is introduced with the change in Ni fraction due to NiO reduction to Ni metal. Whereas templating methods for SOFC electrode optimisation have been attempted for a limited number of materials, YSZ [10,14,17], $Ce_{0.9}Gd_{0.1}O_{1.95}$ [6], $Sm_{0.5}Sr_{0.5}CoO_3$ [6], $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$ [8,9], $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [8,9].

When fabricating electrodes for fuel cell testing, three approaches are used for producing templated structures. In the first approach the template is deposited onto the electrolyte directly and infiltrated with the electrode precursor solution [17] and sintered at high temperature to produce the electrode as a thin film. The second approach is to pre-fabricate the templated electrode as loose powder by infiltration, and then press and sinter the electrode onto the substrate or into a pellet for testing. The infiltration method produces better ordering and more precise replication of the templated matrix, however additional handling of the powder in the pre-fabrication stage tends to damage the templated powder.

The third approach is to use nano- or submicron powder mixed with the template and sinter it into a pellet or directly onto the electrolyte. In this non-infiltration method, the ordering is diminished, and large degree of randomisation of pores is present.

All of the groups that synthesised testable quantities of powder did so at the expense of microstructure. For example, Ruiz-Morales et al. [8,9], used a mixture of YSZ powder, monodisperse 500 nm PMMA microspheres and polyvinyl alcohol to prepare well ordered YSZ pores, and subsequently electrodes at fabrication temperatures up to 1200 °C. Although they found superior fuel cell performance compared to non-optimised structures, as the microspheres were not infiltrated with a solution prior to sintering a certain degree of randomness remained in the ordering of the pores. This may account for the structural collapse at 1200 °C and by 1400 °C no regular structure was observed. In contrast, Lashtabeg et al. [17] found that the infiltration method produced highly ordered structures which remained stable to 1400 °C during sintering, yet no one to date has addressed an issue of scaling up the procedure for large scale powder production, which remains a challenge.

In our previous study [17] we demonstrated that a well studied templating technique can be used to synthesise well ordered highly porous structures for YSZ that are stable to 1400 °C, however the major challenge is to use this method to produce electrodes that can be sintered onto the electrolyte and tested in fuel cell conditions, i.e. bulk powder production for processing. In the previous study the electrode films showed cracking and domain formation, the occurrence of which was attributed to large shrinkage during the template and metal nitrate decomposition at 400–650 °C.

In this study we are looking at different approaches to produce a continuous and well structured electrode using both infiltration and mixing techniques and examining the effect on the microstructure. This study also aims to examine the effect on microstructure of the addition of NiO to form a NiO/YSZ cermet. In addition we are looking to control the drying and decomposition conditions in order to use the infiltration technique to produce an electrode that can be directly sintered onto the electrolyte. The success would have wide reaching implications for SOFC technology if achieved in that the hard templating method would be a viable route to mass scale electrode manufacture.

2. Experimental

Three approaches to electrode production were examined:

1. A one step direct infiltration of commercially available polystyrene (PS) spheres deposited directly onto the electrolyte surface, followed by decomposition and sintering steps.
2. A two step process, involving the production of templated electrodes followed by screen printing of the modified powder onto the electrolyte.
3. A two step non-infiltration approach, involving the production of inks consisting of nano-powder, PS, solvents and binding agents, followed by screen printing onto an electrolyte and sintering.

2.1. Hard templating by infiltration directly onto the electrolyte

A 2.5% solution of monodisperse (1 ± 0.05 μm) PS spheres (Fluka) in water was used as received to create the template. The PS spheres were added drop wise to an 8 mol% Yttria Stabilised Zirconia (8YSZ) solid electrolyte plate, density >99%. The spheres were left to self-assemble into a close packed structure by drying in air at ambient temperature, before the addition of a subsequent droplet of PS spheres, thus eventually producing a self-organised PS template to serve as three-dimensional scaffolding.

Due to the small size of PS spheres high permeation of the voids was achieved by a drop wise addition of reagent quality $ZrO(NO_3)_2{\cdot}xH_2O$ (Sigma–Aldrich) and $Y(NO_3)_3{\cdot}6H_2O$ (Sigma–Aldrich) dissolved in methanol, in the correct stoichiometric ratios to form the 4 mol% Yttria Stabilised Zirconia (4YSZ) backbone. It was found that methanol allows a better surface wetting than water or ethanol, and causes the least disruption to the polystyrene template during infiltration.

The ratio of PS spheres volume and 4YSZ volume was kept at 76:24, corresponding to the free volume between the spheres in the fcc packing arrangement. An exact amount of 4YSZ precursor solution was added drop wise to the PS template and after 1–2 drops the solvent was allowed to evaporate in air at room temperature before further addition of the solution. After the final addition of the solution the 'wet' samples were subjected to a series of thermal and humidity treatments in order to dry the coatings. A tube furnace with flowing humidified air was used to control the temperature and the humidity. The ramp rate to the drying temperature was kept at <1 °C/min by the fine control of the furnace controller PID parameters.

The final decomposition and sintering were carried out at 650–1000 °C with heating and cooling ramp rates of 5 °C/min and dwell times of 1 h.