Preparation of Ordered Macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ as Cathode for Solid Oxide Fuel Cells

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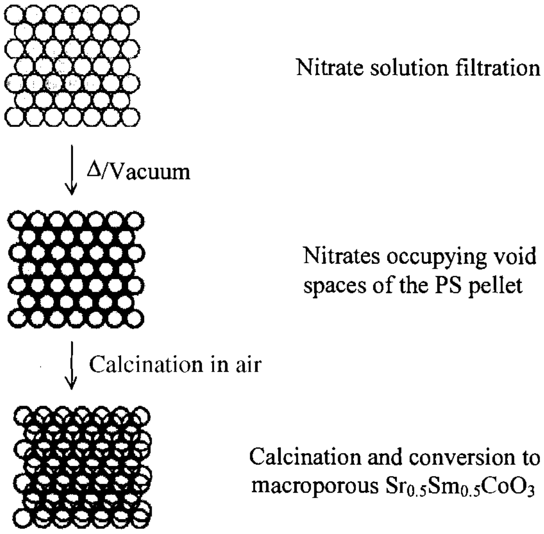
Ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ structrures with an average pore size of 140 nm have been prepared using close-packed arrangement of monodispersed polystyrene spheres as templates. A fuel cell using ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ as the cathode, gadolinia-doped ceria (GDC) film as the electrolyte, and GDC–NiO as the anode generated maximum power densities of 150, 196 and 267 mW/cm^2 at 500, 550 and 600 °C, respectively.

Templates are widely used in the preparation of porous materials.[1,2] Microporous silicates and aluminosilicates are usually crystallized around small molecular templates.[3] Mesoporous molecular sieves are generally templated by supramolecular aggregates of surfactant molecules.[4] The pore size can be adjusted using the surfactant aggregates with different length; however, the obtained pores are limited to about 30 nm in size.[5] In order to achieve pores of up to a few hundreds nanometers, colloidal crystals assembled from monodisperse submicrometer spheres are used as templates.[6,7] Recent reports illustrate that techniques using polystyrene (PS) spheres can be effectively used to create ordered macroporous oxides,[8] carbon,[9] and polymers[10] with monodisperse, periodic voids in the 100–1000 nm size range. These syntheses rely on filling the void spaces between close-packed spheres with liquid metal alkoxides, resins, or gas phase precursors. Macroporous materials hold promise for use as photonic crystals, advanced catalysis, porous electrodes, sensors, and in a variety of other applications.[8] The advantage of ordered macroporous electrode structures in solid oxide fuel cells (SOFCs) is its ability to facilitate gas diffusion and transport to the electrolyte–electrode interface. In particular, macroporous electrodes with mesoporous walls will significantly improve not only mass transport but also catalytic property of the porous electrode.

It is quite a challenge, however, to apply the synthesis schemes for macroporous materials based on PS sphere templating to the synthesis of macroporous complex transition metal oxides such as ABO_3. One difficulty is to obtain a macroporous phase with desired stoichiometry from a solution containing more than one types of metal ions, each having very different properties. Another difficulty is to retain the macroporous structure of the inorganic framework during PS removal.

Mixed ionic–electronic conductors (MIECs) are usually complex transition metal oxides such as ABO_3 and are attractive materials due to their wide range of electrical and catalytic properties.[11] Among them, $Sr_{0.5}Sm_{0.5}CoO_3$ has been widely used as cathode material for SOFCs because of its high catalytic activity for oxygen reduction and its chemical and thermal compatibility with ceria electrolye.[12] Here, we report a general procedure for preparation of ordered macroporous complex metal oxides with about 140 nm monodisperse voids surrounded by nanocrystalline complex metal oxide walls. Ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ structrures are templated using close-packed arrangement of monodispersed PS spheres. Further, the electrochemical performance of the macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ has been evaluated in a fuel cell.



Scheme 1. Schematic showing the formation of ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$.

Scheme 1 illustrates how ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ can be prepared by a PS templating–solution filtration–chemical conversion process. The template for the inorganic macroporous skeletons consists of close-packed PS spheres of uniform size (200 nm). To create the PS template, dried PS powder from the monodisperse PS particles was compressed into pellets (10 mm in diameter, 1–2 mm in thickness) at a pressure of 20 MPa. Scanning electron microscope (SEM) images reveal that the PS particles formed close-packed polycrystalline aggregates (Figure 1). A stoichiometric metal nitrate solution yielding the

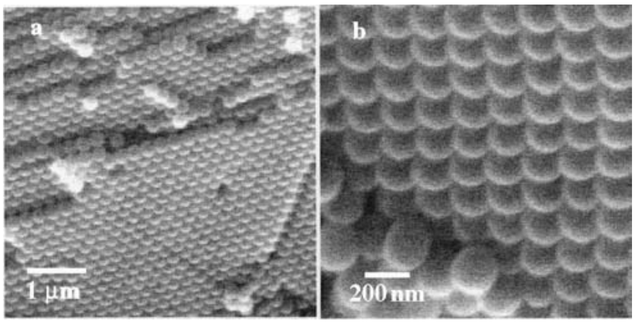


Figure 1. Representative SEM images of the pressed PS pellets: (a) low magnification and (b) high magnification.

formula of $Sr_{0.5}Sm_{0.5}CoO_3$ was filled into the voids of the PS pellets. The metal nitrate solution penetrates into the void spaces between the PS spheres by capillary forces facilitated by vacuum, depositing metal nitrates inside the array upon solvent removal. The dried metal nitrates form the pre-arranged precursor skeleton for the macroporous complex metal oxide. Ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ is obtained by calcination of the precursor skeleton at 800 °C for 2 h in air.

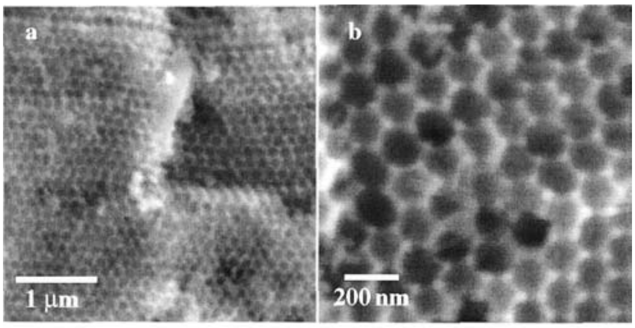


Figure 2. Representative SEM images of $Sr_{0.5}Sm_{0.5}CoO_3$ calcinated at 800 °C: (a) low magnification and (b) high magnification.

Simultaneous thermal analysis, thermogravimetry (TG) and differential scanning calorimetry (DSC), shows that the decomposition of the metal nitrates, the decomposition of PS, and the formation of $Sr_{0.5}Sm_{0.5}CoO_3$ phase occured below 600 °C. There are no detectable thermal events above 600 °C. Figure 2 displays a representative SEM image of the ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ structure. The size of the pores is about 140 nm, revealing a shrinkage of about 30% compared with the size of the PS template (200 nm in diameter). Thickness of the walls between adjacent pores is about 50 nm. Pure perovskite $Sr_{0.5}Sm_{0.5}CoO_3$ phase was confirmed by powder X-ray diffraction (PXRD). Brunauer–Emmett–Teller (BET) surface area of the ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ is 14 m^2/g, measured using a Coulter SA 3100 surface analyzer.

The macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ was then used as the cathode for a fuel cell with gadolinia-doped ceria (GDC) film electrolyte and GDC-NiO anode. GDC electrolyte film was fabricated onto porous NiO-GDC anode as described elsewhere.[13] A cathode slurry of ordered macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ powder and a Heraeus binder (V006) was applied to the GDC electrolyte film by screen printing. The cathode was fired at 950 °C in air for 4 h to establish a good contact between the cathode and the GDC electrolyte film. Analysis of the SEM images of the $Sr_{0.5}Sm_{0.5}CoO_3$ fired at 950 °C in air for 4 h indicates that the pore size is about 130 nm, but the macroporous structure was still maintained. The single cell was sealed on an alumina tube support with silver paste (Heraeus, C8710). The cell was horizontally mounted into an electric furnace. Electrochemical characterizations were performed at ambient pressure at temperatures from 400 to 600 °C. Fuel cell performances were measured with an EG&G potentiostat/galvanostat (model 273A). Humidified (3% H_2O) hydrogen was used as fuel and stationary air as oxidant.

Shown in Figure 3 are the I–V curves and the corresponding power densities for an SOFC tested at temperature from 400 to 600 °C. Each datum point was recorded about 30 min after the cell reached the steady state. SEM image of the cross-sectional view of the cell reveals that the thickness of the GDC electrolyte film is about 30 μm. The cell generated maximum power densities of 150, 196 and 267 mW/cm^2 at 500, 550 and 600 °C, respectively. The observed current and power densities of the fuel cells at low temperatures (400–600 °C) are encouraging.

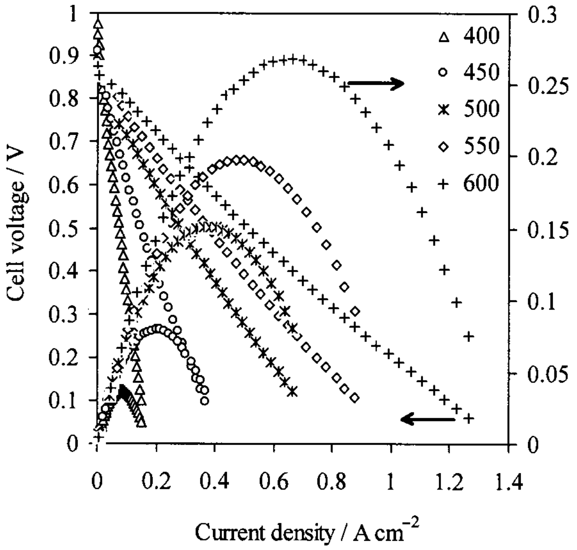


Figure 3. Cell voltages and power densities as a function of current densities for an SOFC with a macroporous $Sr_{0.5}Sm_{0.5}CoO_3$ cathode.

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