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Highly conductive low nickel content nano-composite dense cermets from nano-powders made via a continuous hydrothermal synthesis route

Xiaole Weng[a], Dan Brett[b,*], Vladimir Yufit[c], Paul Shearing[c], Nigel Brandon[c], Mike Reece[d], Haixue Yan[d], Chris Tighe[a], Jawwad A. Darr[a,*]

[a] Department of Chemistry, University College London, Christopher Ingold Laboratories, 20 Gordon Street, London WC1H 0AJ, UK
[b] The Centre for CO_2 Technology, University College London, Roberts Building, Torrington Place, London, SW1E 7JE, UK
[c] Department of Earth Science and Engineering, Imperial College, Prince Consort Road, South Kensington, London, SW7 2AY, UK
[d] The School of Engineering and Materials Science, Queen Mary University of London, Mile End Road, London, E1 4NS, UK

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ABSTRACT

Homogenously doped and mixed yttria stabilized zirconia, YSZ (with 3 and 10 mol% Y_2O_3 known as 3YSZ and 10YSZ) and NiO/10YSZ co-precipitates (nominally corresponding to 7, 12, 24, 30, 35 and 45 vol.% Ni metal), were synthesized using a continuous hydrothermal flow synthesis (CHFS) system which uses a stream of superheated water at 450 °C and 24.1 MPa as a reaction medium to cause rapid precipitation of metal oxide nanoparticle co-precipitates from a mixed metal salt solution. All products were obtained directly from the outlet of the CHFS reactor as a slurry, which was then cleaned and freeze-dried prior to further processing. The highly crystalline nano-powdered products were characterized using a range of analytical methods, including: powder X-ray diffraction (XRD), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), Raman spectroscopy and BET surface area measurements. Spherical primary particles of 10YSZ and 3YSZ were observed under the TEM and found to be 5.0 ± 0.8 nm (range 3.2–6.3 nm) and 6.2 ± 1.4 nm (range 3.3–8.4 nm) in size, with measured BET surface areas of 160.6 and 241.7 $m^2\ g^{-1}$, respectively. Sintering of the nano-powder co-precipitates was performed via spark plasma sintering (SPS) at 1100 °C for 1 min, leading to densities of ca. 98% for 10YSZ and ca. 96% for Ni/10YSZ cermets (all NiO was converted into Ni due to the reducing atmosphere of the SPS). The 24% Ni/10YSZ cermet was subjected to focused ion beam tomography, which allowed the 3D arrangement of the conducting Ni metallic network of the dense cermet to be elucidated, and showed that a complete 3D network of Ni existed throughout the dense cermet disk. Electrical conductivity tests showed that the samples exhibited higher than expected electrical conductivity (for such low metal content), e.g., the 24 vol.% Ni-containing sample achieved an electrical conductivity of ~200 S cm^{-1} at the fuel cell operating temperature, which corresponds to an effective conductivity of ~117 S cm^{-1} if a porosity of 30% were to be introduced.

1. Introduction

Solid oxide fuel cells (SOFCs) are currently attracting worldwide interest because of their high power generation efficiency and low emissions [1,2]. An SOFC is a ceramic, solid-state energy conversion device that produces electricity by electrochemically combining fuel and oxidant gases across an ionic conducting oxide [3]. It consists of three major components: anode, cathode and electrolyte. All components impose severe demands on the materials used, whilst they need to possess chemical and physical stability in the appropriate oxidizing and/or reducing environments, be chemically compatible with other components and have proper conductivity and fabricability [1,3].

Yttria stabilized zirconia (YSZ) and Ni/YSZ cermets are the most frequently used electrolyte and anode materials, respectively, in SOFCs. In the literature, several different synthetic methods have been used to make YSZ powders, including solid-state reactions [4–6], spray pyrolysis [7,8], sol–gel [9–17], dip coating [18], microwave hydrothermal syntheses [19–21], synthesis in supercritical carbon dioxide [22], co-precipitation routes [23,24], hydrothermal syntheses [25–27] and solution combustion routes [28]. The syntheses of Ni/YSZ cermets are most commonly achieved by physically mixing micron sized powders of NiO and YSZ powders or reacting the respective metal salt solutions into a slurry form or via spray pyrolysis [29], sol–gel [30–35], combustion [28,32,36–41], radio-frequency plasma [42,43] and electroless coating routes [44]. Some of these techniques do not allow the direct (single step) fine control of crystallite size in nanoparticles at relatively low temperatures (<400 °C), rather they require laborious and multi-step processing,

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* Corresponding authors. Darr is to be contacted at Tel.: +44 207 8825191.
E-mail addresses: d.brett@ucl.ac.uk (D. Brett), j.a.darr@ucl.ac.uk (J.A. Darr).

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often with the requirement for special chemical reagents to achieve the desired properties.

Moreover, the doping of yttria into the zirconia lattice via these methods is sometimes inhomogeneous as a result of batch to batch variations. More recently, synthesis techniques such as continuous hydrothermal flow syntheses have gained interest as a direct and rapid method for the synthesis of highly crystalline nano-ceramics in a single step from metal salt solutions [45–48].

Ni/YSZ cermets have found extensive use as SOFC anodes due to their high electrochemical catalytic activity towards hydrogen oxidation, high electrical conductivity and stability of the material. Moreover, Ni–YSZ anodes have good thermo-mechanical and sintering compatibility with many electrolyte materials, which are often YSZ. Ni/YSZ cermets with a nickel volumetric content of 40–70% are commonly used for anodes in SOFCs [49]. However, due to large discrepancy in the coefficient of thermal expansion of Ni (16.9 ppm K^{-1}) and YSZ (10.5 ppm K^{-1}) [50], the Ni content has a crucial effect on microstructural and mechanical stability of Ni/YSZ cermets. For example, the most predominant microstructure change that facilitates the degradation of Ni/YSZ anodes is the agglomeration and coarsening of the Ni phase, which is worse with higher Ni content [51]. Consequently, if one could retain sufficient electrical conductivity at reduced nickel content, this may reduce the deleterious effects of thermal mismatch and coarsening of the Ni phase. However, reducing the Ni content below 35–40 vol.% normally results in an increase in electrical resistance of Ni–YSZ anodes [3]. Recent advances in nanoparticle preparation methods have led to novel fabrication routes for metalloceramic materials that can be used as electrodes for SOFCs. One of the main beneficial characteristics of these materials is that Ni–ceria cermets can exhibit high electronic conductivity with low Ni content [52]. These nickel–ceria cermets were prepared by net-shape technology which combines die pressing of powder and metal oxide polymer impregnation. In the process, a commercially available Sm-doped ceria powder was dry mixed with carbon powder (ratio 90:10 vol.%) and die pressed at 150 MPa. The pellets were sintered at 1300 °C for 2 h, (78% of theoretical density ceria) and a Ni oxide polymer (Ni nitrate and ethylene glycol) was impregnated several times (with a 1000 °C firing step each time) into the ceria skeleton to obtain Ni–ceria cermets with the desired compositions (vol.% of Ni).

Another major cause of SOFC degradation is the change in the microstructural properties of the anode caused by redox cycling of the Ni components [53]. Dimensional changes associated with redox cycling (oxidation of Ni to NiO is accompanied by an increase of ~70% in solid volume) can also compromise the mechanical integrity of the entire cell, manifest by electrode cracking and delamination from the electrolyte. By reducing the amount of Ni in the cermet, the stress induced by redox cycling is minimised and therefore lessens the degradative effect on performance. Consequently, the authors hypothesize that intimately mixed nano-co-precipitates of Ni and YSZ could be generated and then rapidly sintered to produce Ni/YSZ cermets in which the nickel coarsening into 3D networks may be controlled to allow sufficient electrical conductivity at low Ni loadings. Ideally, such a process would be rapid, involve few steps and be reasonably green (avoiding use of organic solvents, or high energy processing steps).

In this paper, we describe our efforts to synthesize highly crystalline YSZ and intimately mixed NiO/YSZ co-precipitates, the latter of which was used to produce dense Ni/YSZ cermets. The powders were rapidly sintered to near theoretical densities in ca. 1 min using the spark plasma sintering (SPS) method in which powdered compacts were pressed whilst being rapidly heated and then cooled to try and reduce grain growth during densification. The electrical conductivities of the formed cermets were measured using a four point DC probe and revealed that the low Ni content cermets possessed high electronic conductivities.

2. Experimental

2.1. General synthesis procedure

The products were manufactured in our laboratory using a three-pump continuous hydrothermal flow synthesis system (Fig. 1) [45–48,54–59]. A brief description is given herein as follows; pump P1 was used to pump water to a pre-heater, whilst pump P2 was used for pumping a mixture of metal salt solution and H_2O_2. Pump P3 was used for pumping the base solution (KOH). In all cases, pump speeds were 10 mL min^{-1}, except for the superheated water (20 mL min^{-1}). Additionally, a small 5 cm 200 W band heater set at 450 °C was placed around the 3/8 inch counter-current mixer [45]. Sample notation used was based on the corresponding nominal Ni vol.% values (i.e. based on the nominal values in the CHFS starting solutions) given in Supplementary Table S1. The syntheses of the nano-sized co-precipitate precursors are described below.

2.1.1. Syntheses of nano-sized 3YSZ and 10YSZ via CHFS

The CHFS method was used herein to produce a range of YSZ co-precipitates in the desired Y_2O_3:ZrO_2 ratios. For the synthesis of 3YSZ (3 mol% Y_2O_3 with respect to ZrO_2), yttrium nitrate hexahydrate (1.15 g, 3.0 mmol) and zirconyl nitrate hexahydrate (14.3 g, 48.5 mmol) were both dissolved in 500 mL of deionised (DI) water to give concentrations of 0.006 M and 0.097 M, respectively. 50 mmol of 35 vol.% H_2O_2 solution was added into the metal salt solution, which was then pumped into the CHFS system (via pump 2). This was mixed with a 1.0 M KOH solution in flow (at point T in Fig. 1) and then brought to meet a superheated water feed at 450 °C at a counter-current mixer (R in Fig. 1). The suspension from the reactor was then collected for approximately 50 min in 50 mL falcon tubes. Each tube was centrifuged (4500 rpm for 3 min). 40 mL of liquid was removed and then replaced with 40 mL of clean DI water with shaking to disperse the solids. Each tube was further centrifuged (4500 rpm for 1 h) and the liquid removed again. The wet solids were freeze-dried. According to the dried mass, the yield from the remaining solids was calculated as ca. 84%.

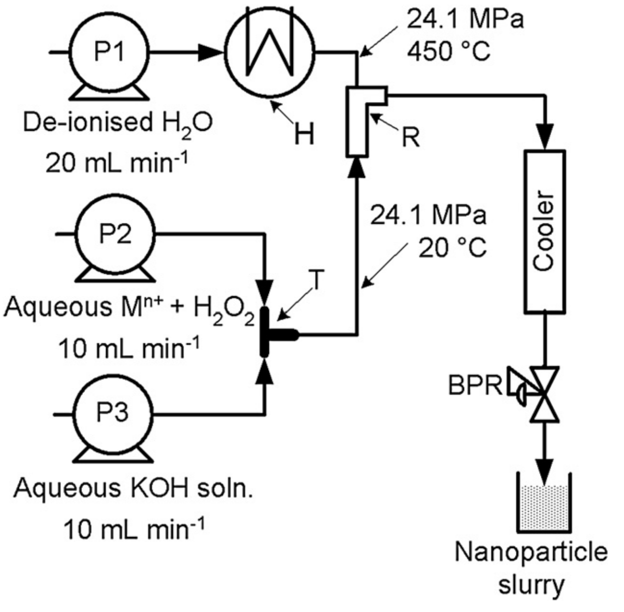

Fig. 1. Schematic representation of the CHFS apparatus that was used to prepare the YSZ and NiO/YSZ co-precipitates. Key: P = Gilson pump, H = heater, R = counter-current mixer, T = tee junction, BPR = back-pressure regulator. Each high pressure line also contains non-return valves, pressure relieving safety devices, electronic pressure transducer and manual pressure gauges which are not shown here for clarity.