Microporous and Mesoporous Materials 145 (2011) 26–31

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Engineering of porosity, microstructure and electrical properties of Ni–$BaCe_{0.9}Y_{0.1}O_{2.95}$ cermet fuel cell electrodes by gelled starch porogen processing

Gilles Taillades *, Pierre Batocchi, Abdel Essoumhi, Mélanie Taillades, Deborah J. Jones, Jacques Rozière

ICGM, Agrégats, Interfaces et Matériaux pour l'Energie, UMR CNRS 5253, Université Montpellier II, 34095 Montpellier, France

ARTICLE INFO

Article history:
Received 12 May 2010
Received in revised form 18 January 2011
Accepted 16 April 2011
Available online 23 April 2011

Keywords:
Ni-cermet
Starch
Mercury porosimetry
Proton ceramic fuel cell

ABSTRACT

The synthesis of electrode materials with controlled microstructural characteristics and high conductivity over 1000 S cm^{-1} is a key factor in improving the performance of fuel cells. In this work, we propose an alternative route to the partial sintering of a powder mixture to control the porosity of a ceramic–metal composite currently used as an anode material in Protonic Ceramic Fuel Cells working at 400–600 °C. This new method is based on the use of nanopowdered cermet materials and starch in gelling form for the elaboration of Ni–$BaCe_{0.9}Y_{0.1}O_3$ (Ni–BCY) cermets. The microstructure and the electrical properties have been investigated with respect to the initial starch content. A porous microstructure consisting of homogenously distributed Ni and BCY phases is observed. It is shown that the degree of open porosity and the electrical conductivity of the cermets are sensitive to the starch content. Anodes elaborated from initial compositions comprising 10 and 20 wt.% of starch offer sufficient mechanical strength and an open porosity >30 vol.%. The measured conductivities vary with the composition, from 1000 to 3000 S cm^{-1} at 600 °C. The use of starch in gelled form as porogen allows the engineering of the porosity and the control of pore shape and distribution.

1. Introduction

Protonic Ceramic Fuel Cells (PCFC) are especially attractive for operation at intermediate temperatures of 600 °C and below. In comparison to their oxygen ion conducting counterparts (SOFC), in PCFCs the water is produced at the cathode preventing fuel dilution and so, high conversion efficiency may thus be reached [1–3].

Nevertheless, the current status of PCFC is far beyond expectations and one of the key to the development of efficient cells is the optimisation of electrode materials, in terms of microstructures and electrical properties. The electrodes, in contrast to the electrolyte, are often heterogeneous materials and their properties depend largely on the microstructure. Currently, porous Ni-electrolyte cermet materials are the most commonly used for anode-supported fuel cells. In such a cermet, a ceramic porous network is required to create an extended reaction zone and to adapt the thermal and mechanical properties of the anodes to the electrolyte. In addition, the nickel acts as a catalyst for the electrochemical oxidation of hydrogen and as current collector, and the electrical properties of the cermet are mainly controlled by the nickel content. The percolation threshold for the conductivity is close to 30 vol.% [4], however it depends on the porosity and on the pore sizes as well as on the distribution and size of the nickel oxide and electrolyte ceramic powder particles. As gas permeability and electrical conductivity are strongly dependent on the anode microstructure, control of porosity, pore shape and distribution are crucial for the optimisation of performance [5]. The required porosity of supporting anode, enabling good gas diffusion through the cermet to the active three phase boundary region of the anode, is about 35 vol.% [6,7]. Different methods can be used to obtain this porosity: the simplest method involves a partial sintering of the anode material that develops the expected pore structure. Alternatively, a common processing method involves pressing a powder mixture of ceramic particles and a pore-forming agent which usually comprises an organic component such as carbon, polymers or polysaccharides having low decomposition temperature [8]. Starch is a low cost pore former, which, due to its high decomposition temperature, can act simultaneously as a porogen and as a binder. Starch $(C_6H_{10}O_5)_n$ is a mixture of two polysaccharide types, one that is linear, amylose, and one that is highly branched, amylopectin. At temperatures around 80 °C, aqueous dispersions of starch become gel-like as a result of swelling and disruption of the starch granules, which absorb water and irreversibly swell to several times their initial size. The swollen granules then begin to rupture and collapse. Thus, a viscous dispersion of granule fragments and dissolved starch molecules may finally become a starch gel, which may be considered as a composite of swollen gelatinized granules of mainly amylopectin, dispersed in an amylose gel matrix [9,10].

---

* Corresponding author.
E-mail address: gilles.taillades@univ-montp2.fr (G. Taillades).

1387-1811/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2011.04.020

Gelled starch has been used to prepare many complex bodies of alumina [11] by the starch consolidation method. In this method based on gel casting of ceramic powders, water and starch are mixed together and heated for gelling. After drying, the sample is subjected to calcination and sintering.

The starch consolidation method has been also used to obtain porous [12] or dense [13] ceramics but in spite of this, no work on the processing of porous cermet fuel cell anode using gelled starch has been found in the open literature and only few articles describe the use of powdered starch. Recently several authors have studied the influence of the volume fraction of powdered starch and sintering temperature on the microstructure of porous yttria stabilised zirconia (YSZ) substrates [14], and $La_{0.995}Sr_{0.005}NbO_4$/NiO anodes [15] obtained by tape-casting. It has been shown that the morphology and the size of pores depend on the type of starch used to create the porosity. Haslam et al. [16] have prepared anode materials by mixing the desired quantities of nickel oxide, YSZ and rice starch as pore forming agent and demonstrated a significant improvement in the power density of single cells.

In the present work, $BaCe_{0.9}Y_{0.1}O_3$ has been chosen as the electrolyte due to its well-known high protonic conductivity (10^{-2} S cm^{-1}) and porous Ni–$BaCe_{0.9}Y_{0.1}O_3$ cermets were prepared using gelled and powdered starch as pore forming agents. As porosity formation with gelled starch is different from that obtained using starch granules, the aim of this work was to study the influence of the pore former content on the amount and shape of the porosity, in order to obtain a microstructure suitable for proton ceramic fuel cell applications.

2. Material synthesis and characterisation

The NiO–$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ powder with 40 wt.% of NiO was prepared by the flash combustion method as previously reported [1,3,17]. An aqueous solution containing the appropriate molar ratios of $Ni(NO_3)_2{\cdot}6H_2O$, $Ba(NO_3)_2$, $Y(NO_3)_3{\cdot}6H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$ and glycine (Aldrich) was concentrated and placed into an oven at 600 °C to start the combustion reaction. The powder obtained was annealed at 600 °C for 10 h and heat treated at 900 °C for 2 h. This material has been denoted NiO–BCY in this work.

For the synthesis of the various porous Ni–$BaCe_{0.9}Y_{0.1}O_{3-\delta}$ anodes, corn starch was used as a pore forming agent. Its decomposition temperature was studied by thermogravimetric analysis (Netzch TG 439), and its morphology and grain size observed by scanning electron microscopy (SEM, FEI Quanta 200). Different anode material powders have been prepared using starch in powder or in gelled form and in different proportions. A first material, denoted NiO–BCY–30P, was prepared by mixing the prepared NiO–BCY and 30 wt.% of starch powder. Three other materials were prepared with different amounts of gelled starch: in a first step, desired quantity of starch powder was added to water, heated to 80 °C and stirred until pre-gellification occurred then the prepared NiO–BCY was mixed with gelled starch and the mixture was dried for 12 h at 110 °C. The three materials were prepared with 10, 20 and 30 wt.% of starch and the powders obtained after drying are denoted NiO–BCY–G10, NiO–BCY–G20, NiO–BCY–G30.

Quantities of each of the five powders, to produce a desired anode thickness of 1 mm were pressed in a 13 mm die under vacuum at 220 MPa and then sintered at 1350 °C for 4 h The five Ni–BCY anodes (Ni–BCY, Ni–BCY–P30, Ni–BCY–G10, Ni–BCY–G20, Ni–BCY–G30) were obtained by reduction under 10% H_2/N_2 flow in a quartz tube at 700 °C. Reduced pellets were used for mercury porosity and conductivity measurements.

Phase analyses of the anodes before and after nickel oxide reduction were carried out by X-ray diffraction (Seifert θ–θ diffractometer with Cu Kα radiation). Microstructures of the Ni cermets were observed by scanning electron microscopy (SEM, FEI Quanta 200). The pore size distribution of each anode was measured by mercury intrusion using a Micromeretics Autopore II instrument. Previous to analysis, the samples were out-gazed for 1 h under 6.67 Pa. Low pressure operation enables the determination of pore diameters in the range of 360–3.6 μm whereas high pressure operation enables the determination of pore diameters in the range of 10–0.003 μm. The pressure range used in the current measurements extended from 0.0014 MPa to 420 MPa. The electrical conductivity of the pellets was determined using the four-probe method. Four tungsten wires ($\phi = 0.1$ mm) were connected to the sample. The applied current density was ca. 100 mA cm^{-2}. The electrical conductivity of the electrodes was measured under reduced pressure in the temperature range 50–800 °C.

3. Results and discussion

The X-ray diffraction patterns given in Fig. 1 show that the phases present in NiO–BCY material (b) are orthorhombic BCY perovskite (a) and nickel oxide. Also, NiO is completely reduced to Ni metal in 10% H_2 in N_2 at 700 °C for 10 h (c).

Corn starch was used to obtain different porous anode materials. The grain size of this starch, observed by SEM, is 10–20 μm (Fig. 2a). The advantage of corn starch is its high decomposition temperature. Corn starch is fully decomposed at 550 °C in air as observed by TGA analysis (Fig. 3) so when the decomposition occurs, it acts as a pore forming agent but has also acted as a binder and so consolidated the framework.

Scanning electron microscopy observations and mercury porosimetry studies have been performed on the different cermets and have shown the benefit of the pore forming agent in gelling form on the anode porosity.

The observations by SEM have been performed on the anodes elaborated without porogen and on Ni cermets prepared using 30 wt.% of starch in powder and 10, 20 and 30 wt.% of starch in gelling forms. Significant interdistribution of the BCY10 perovskite phase (lighter in colour) and Ni nanoparticles (darker) is observed in backscattered mode for the Ni–BCY anode (Fig. 2b) with a low porosity due to the reduction of NiO to Ni. When powdered starch is used, two types of porosity are observed (Fig. 2c), smaller pores, due to the reduction of NiO, and a macroporosity distributed throughout the composite matrix, with pore shape and size consistent with those of the starch grains. This macroporosity decreases both the mechanical strength of the electrode, and the extent of the three phase boundary. Observation of the images obtained in secondary electron mode (Fig. 2d–f) corresponding to Ni–BCY–G10,

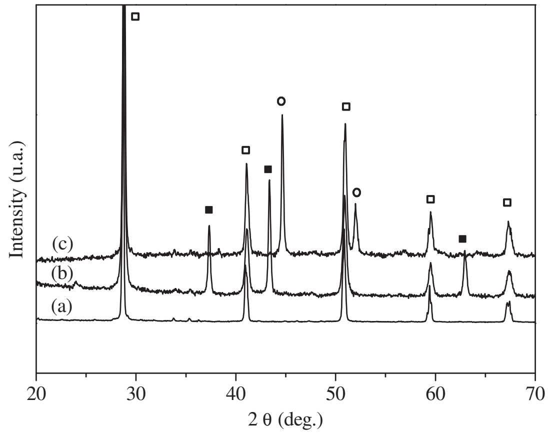

Fig. 1. X-ray diffraction patterns of: (a) BCY10 powder, (b) NiO–BCY sintered at 1350 °C, (c) Ni–BCY after sintering and reduction. □: BCY, ■: NiO, ○: Ni.