Solid State Ionics 180 (2009) 800–804

Contents lists available at ScienceDirect

Solid State Ionics

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

Microstructure and performance of novel Ni anode for hollow fibre solid oxide fuel cells

Francesco Dal Grande [a], Alan Thursfield [a], Krzysztof Kanawka [b], Nicolas Droushiotis [b], Uttam Doraswami [b], Kang Li [b], Geoff Kelsall [b], Ian S. Metcalfe [a,*]

[a] School of Chemical Engineering and Advanced Materials, Newcastle University, Newcastle Upon Tyne NE1 7RU, United Kingdom
[b] Imperial College London, London, United Kingdom

ARTICLE INFO

Article history:
Received 10 September 2008
Received in revised form 4 December 2008
Accepted 31 December 2008

Keywords:
Solid oxide fuel cells
Ni-YSZ anode
Ni electroless plating
YSZ sintering

ABSTRACT

Nickel anodes were deposited on hollow fibre yttria-stabilised zirconia (YSZ) electrolyte substrates for use in solid oxide fuel cells (SOFCs). The hollow fibres are characterised by porous external and internal surfaces supported by a central gas-tight layer (300 μm total wall thickness and 1.6 mm external diameter). The YSZ hollow fibres were prepared by a phase inversion technique followed by high temperature sintering in the range 1200 to 1400 °C. Ni anodes were deposited on the internal surface by electroless plating involving an initial catalyst deposition step with $PdCl_2$ followed by Ni plating (with a $NiSO_4$, NaH_2PO_2 and sodium succinate based solution at 70 °C). Fabrication and nickel deposition parameters (nature of solvents, air gap, temperature, electroless bath composition) and heat treatments in oxidising/reducing environments were investigated in order to improve anode and electrolyte microstructure and fuel cell performance. A parallel study of the effect of YSZ sintering temperature, which influences electrolyte porosity, on electrolyte/anode microstructure was performed on mainly dense discs (2.3 mm thick and 15 mm diameter). Complete cells were tested with both disc and hollow fibre design after a $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) cathode was deposited by slurry coating and co-fired at 1200 °C. Anodes prepared by Ni electroless plating on YSZ electrolytes (discs and hollow fibres) sintered at lower temperature (1000–1200 °C) benefited from a greater Ni penetration compared to electrolytes sintered at 1400 °C. Further increases in anode porosity and performance were achieved by anode oxidation in air at 1200–1400 °C, followed by reduction in H_2 at 800 °C.

1. Introduction

SOFCs are attractive devices for chemical to electrical energy conversion because of their high efficiency, fuel flexibility and low emissions. Three SOFC designs exist: planar, monolithic and tubular. The tubular design exhibits several advantages over planar or monolithic designs such as simple sealing and easy stacking and scale up. The main disadvantages include the long current paths involved and the high electrode/electrolyte thickness; both increase the electrical resistance of the cell [1,2]. A micro-tubular design can offer an improvement over a conventional tubular design by allowing a high volumetric power density to be achieved by reducing the diameter and wall thickness of the tubes whilst also exhibiting a mechanically resilient structure during rapid start-up with enhanced intermediate temperature performance [3].

The state-of-the-art electrolyte-supported micro-tubular SOFC is a YSZ micro-tube coated internally with a Ni anode and externally with a lanthanum strontium manganate (LSM) cathode [4]. The electrolyte is fabricated by extrusion, while the NiO-YSZ slurry is injected inside the micro-tube by a syringe for the anode deposition [5]. Dip-coating is the most commonly employed cathode deposition technique.

Recently YSZ hollow fibres (1.6 mm diameter, 200 μm wall thickness) prepared by phase inversion and sintering have been evaluated for employment as SOFC electrolytes [6]. Phase inversion's main advantage over normal extrusion is the microstructure and porosity control achievable by the optimisation of the fabrication parameters [7,8]. External and internal electrolyte sub layers with connected open pores and a central dense gas tight layer is potentially an ideal initial structure to support the subsequent electrode layers in a micro-tubular SOFC. The overall thickness can be optimised to supply adequate structural support, while the dense thin central layer can be optimised to ensure gas tightness while lowering electrolyte resistance. Moreover, the porous structure of the external and internal sub-layers allows easy impregnation with electrode materials and a high electrode surface area.

Anode deposition is a difficult fabrication step as it must be performed on the internal surface of the tubular electrolyte. Ni electroless plating is a potential anode deposition technique for internal use with such small diameter hollow fibres. Ni electroless plating represents an

* Corresponding author.
E-mail address: i.metcalfe@newcastle.ac.uk (I.S. Metcalfe).

0167-2738/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ssi.2008.12.038

Table 1
Composition of the starting suspension for the YSZ hollow fibre precursor fabrication.

Starting suspension	
Component	Value
YSZ	65.00 wt.%
PESf	6.50 wt.%
Additive	0.12 wt.%
NMP	4.88 wt.%
NCP	23.50 wt.%
Internal coagulant	Water
External coagulant	Water
Spinneret i.d./o.d.	1.2 mm/3.0 mm
Temperature	22 °C
Relative humidity	34%
Air gap	20–100 mm

alternative to NiO-YSZ slurry injection or impregnation techniques recently developed for the fabrication of infiltrated electrodes [9,10]. Electroless plating consists of Ni^{2+} ion reduction to metallic Ni by a reducing agent (sodium hypophosphite) [11] and has been recently tested as a technique for the fabrication of Ni-YSZ cermets [12]. Recent studies [13] revealed that LSCF cathode possesses higher oxygen ion conductivity and catalytic activity with respect to LSM. Moreover, LSCF is considered one of the most promising materials for employment in intermediate temperature SOFC technology [13], intermediate temperature operation being the long-term goal of this work. For these reasons LSCF was chosen as the cathode material.

In this study, electroless Ni plating on YSZ electrolyte disc and hollow fibre (successfully prepared by phase inversion) geometries is investigated as a potential SOFC anode deposition technique. Hollow fibre fabrication parameters, electroless plating conditions and the role of electrolyte sintering temperature on electrode/electrolyte microstructure and fuel cell performance are investigated.

2. Experimental

2.1. Pellet fabrication

YSZ powder (PI-KEM, UK® 8 mol% yttrium, 60 μm mean particle size, 99.9% purity) was die pressed into discs (or pellets) of 20 mm diameter and 3 mm thickness. Samples sintered at 1400 °C for 4 h are denoted *Pellet A* (final dimensions were 15 mm diameter and 2.3 mm thickness) and those sintered at 1200 °C and 1000 °C are denoted *Pellet B* and *Pellet C* respectively.

2.2. Hollow fibre fabrication

YSZ hollow fibres were prepared by phase inversion and sintering. Materials employed in the fabrication were YSZ powder (NexTech Materials® 8 mol% yttrium, mean particle size of 0.3 μm), polyethersulfone (PESf) (Ameco Performance® Radel A-300), 1-methyl-2-pyrrolidone (NMP) (Sigma Aldrich®), 1-cyclohexyl-2-pyrrolidone (NCP) (Sigma Aldrich®, purity 99%).

A fibre precursor was prepared following the parameters and conditions reported in Table 1. The starting suspension was passed through a spinneret and the resultant precursor dipped into the coagulant bath for polymer precipitation. More details about the apparatus and the procedure can be found elsewhere [6,8,14].

Precursors were heated to 600 °C at 3 °C min^{-1} and the temperature kept constant for 2 h allowing for the removal of the polymer binder. The temperature was then raised to 1000 °C at 3 °C min^{-1} to assure complete removal of the polymer binder. The final temperature of sintering was kept constant for 4 h and achieved with a heating rate of 5 °C min^{-1}. Samples denoted *Fibre A* were sintered at a final temperature of 1400 °C while samples denoted *Fibre B* were sintered at 1200 °C.

2.3. Ni anode deposition

Ni was deposited on one side of the pellets and on the internal surface of the hollow fibres. After activation with a catalytic solution the target surface was rinsed with deionised water before Ni was deposited from the plating solution. Solution composition and conditions are summarised in Table 2 [15].

Introduction of the catalyst was achieved by dipping the electrolyte (pellet or hollow fibre) into the catalytic solution. Teflon tape was used to mask the electrolyte area where Ni deposition was not wanted. Ni was deposited on YSZ pellets by dipping the electrolyte into the plating solution, while in the case of hollow fibres the plating solution was pumped through the internal volume (Cole Palmer® Masterflex L/S compact pump). The electrolyte and the deposited anode system (pellet and hollow fibre shape) were co-fired at 1400 °C for 4 h in static air before cathode deposition. This allowed for the formation of a gas-tight electrolyte in the case of the initially not-fully-dense structures (*Pellet B*, *Pellet C* and *Fibre B*) and Ni oxidation to NiO, with subsequent porosity improvement after NiO reduction to Ni in the reducing anode environment of the fuel cell [16]. NiO reduction to Ni was achieved by flowing 30 ml (STP) min^{-1} of 5% H_2 (95% Ar) at 800 °C for 1 h.

Anode and electrolyte microstructure and composition were investigated by SEM (JEOL JSM-5300LV), energy dispersive X-ray spectroscopy (EDS) and inductively coupled plasma mass spectrometry (ICP-MS).

2.4. LSCF cathode deposition

Slurry coating was employed for cathode deposition. The slurry was prepared by mixing 62.50 wt.% $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{3-\delta}$ oxide powder (Praxair Surface Technologies®, 60 nm mean particle size, 99.9% purity) with 6.25 wt.% YSZ powder (PI-KEM® 8 mol% yttrium, 60 μm mean particle size, 99.9% purity) and 31.25 wt.% ethylene glycol (Fluka®, purity ≥ 98.0%). The cathode slurry was painted on the free electrolyte surface of the already co-fired anode/electrolyte. Afterwards the sample was sintered at 1200 °C for 6 h (heating rate 5 °C min^{-1}) in static air allowing cathode co-firing with electrolyte/anode.

2.5. Fuel cell test

Fuel cells based on pellet and hollow fibre geometries were tested at 800 °C, flowing 30 ml (STP) min^{-1} of 5% H_2 (95% Ar) to the anode side and 30 ml (STP) min^{-1} of air to the cathode side. Pellet electrode active surface was 0.64 cm^2 while the fibres' electrode active surface was 0.50–0.70 cm^2. The fuel cell was connected to a potentiostat (AMEL® model 7050) using platinum wire (Sigma Aldrich®, 0.25 mm diameter, 99.9%). The electrical contact between wires and electrodes was achieved with platinum ink (Metalor®) and, only in the case of the disc geometry, an additional platinum mesh (Alfa Aesar® 45 mesh from 0.198 mm diameter wire, 99.9%).

Fuel cell electrodes were characterised by measuring electrode electrical conductivity with a four point DC technique using a potentiostat coupled with a multitester (Meterman® 5XP). The electrode overpotential was measured at 800 °C by DC current interruption using a three electrode symmetrical pellet cell with Pt as a reference electrode. The anode was tested under 5% H_2 (95% Ar) flowing at 30 ml (STP) min^{-1}

Table 2
Electroless Ni plating solutions description [15].

Solution	Compound	Composition [g l^{-1}]	Conditions
Catalytic	$PdCl_2$	0.4	1 min
	HCl	3.3	20 °C
Plating	$NiSO_4$	120.0	1.5–3
	NaH_2PO_2	50.0	hours
	Succinic acid	10.0	70 °C