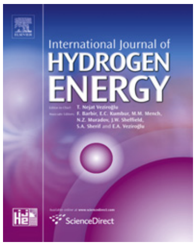
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 38 (2013) 1058–1067

Available online at www.sciencedirect.com

SciVerse ScienceDirect

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



Performance of microtubular SOFCs with infiltrated electrodes under thermal cycling

K.S. Howe [a,*], A.R. Hanifi [b], K. Kendall [a], Mark Zazulak [b], T.H. Etsell [b], P. Sarkar [c]

[a] Centre for Hydrogen and Fuel Cell Research, University of Birmingham, Birmingham B15 2TT, UK
[b] Department of Chemical & Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada
[c] Environment & Carbon Management, Alberta Innovates – Technology Futures, Edmonton, Alberta T6N 1E4, Canada

ARTICLE INFO

Article history:
Received 17 September 2012
Received in revised form
12 October 2012
Accepted 26 October 2012
Available online 26 November 2012

Keywords:
Solid oxide fuel cell
Micro-tubular
mSOFCs
Electrode
Infiltration
Thermal cycling

ABSTRACT

In this research, tubes consisting of a co-extruded dense YSZ electrolyte (~10 μm) and porous NiO–YSZ anode (~200 μm) were modified with different cathodes and anode infiltration to investigate the effects on both power and thermal cycling tolerance. Type of cathode (produced by infiltration of LSM into a porous YSZ matrix or by hand-painting of an LSM–YSZ ink), the type of pore former used in the cathode (graphite or poly (methyl methacrylate), PMMA) and the infiltration of the anode (no infiltration, or with infiltration steps using a co-precipitated SDC (Samaria doped ceria) mixture, or Ni–SDC mixture) were investigated as variables. The overall aim of this work is to produce cells that are more tolerant to thermal cycling, without sacrificing power density.

Testing at 750 °C with 20 mL/min of dry hydrogen shows that anode infiltration has a particularly advantageous effect on performance, raising the peak power and reducing the degradation in peak power seen after aggressive cycling (100 °C/min heating and cooling rates). Cell power can be improved by LSM infiltration into a porous YSZ layer when the thickness of the YSZ layer is optimised and there is sufficient LSM. Infiltrated cells with cathode thicknesses of 20–40 μm functioned better than those 10–15 μm thick despite having a similar LSM/YSZ weight ratio. This may be due to the additional reaction zone available as a result of the higher LSM mass, suggesting that the reaction zone extends beyond 15 μm from the electrolyte. LSM and SDC infiltrated fine particles (50–100 nm) show good distribution and connectivity in the cathode and anode of the cells respectively. When PMMA is used as the pore former in the porous YSZ matrix, a slightly better cell performance is obtained compared with graphite as the pore former. Monitoring the power variation is found to be a more reliable tool than open circuit voltage (OCV) measurements for studying the effect of thermal cycling on cell stability.

1. Introduction

Solid oxide fuel cells (SOFCs) have gained popularity as awareness and concern about environmental and energy issues have increased, due to their high efficiencies [1]. Cell performance depends strongly on electrode microstructure, and has been the subject of a great deal of research [2]. Tubular solid oxide fuel cells were first made in the 1960s [3,4],

---

[*] Corresponding author. Tel.: +44 (0) 121 414 5283; fax: +44 121 414 5324.
E-mail addresses: K.S.Howe.05@cantab.net, kxh984@bham.ac.uk (K.S. Howe).

http://dx.doi.org/10.1016/j.ijhydene.2012.10.098

reducing the problems of brittleness and sealing associated with planar cells. They still required a heat up time of four to 6 h, however, and had power densities of only 0.6 W cm^{-3} (at their operating temperature of around 1000 °C [5]), around half that obtained for planar cells at the time [5]. The power density of tubular cells depends on the inverse of cell diameter (the narrower, the better the performance) and the distance from the anode current collection point [6]. This observation led to the invention of microtubular SOFCs (mSOFCs) by Kendall in the early 1990s [7]. These tubes are on the scale of millimetres, unlike the centimetres of the Westinghouse-type tubular cells. mSOFCs offer shorter start-up times (on the order of a few seconds for a single cell), are more resistant to thermal cycling degradation, have high power densities (around 2.5 W cm^{-3} small stack power reported at 550 °C [8]) and have fewer sealing problems than the planar cells. A comprehensive review comparing mSOFCs to other SOFC designs has been published by Kendall [9].

High electrode porosity is crucial to facilitate gas flow to the triple phase boundary (TPB), where reactions occur, but conductivity and mechanical strength are compromised if the porosity is too high. According to Jin et al. [6], anode porosity should be no greater than 55% to avoid a detrimental increase in resistivity. Pore size was also identified as significant, with large pores reducing mechanical strength. Suzuki et al. [10] found that “a highly porous microstructure” with very small constituent particles (<100 nm for the Ni particles in the anode) optimised the cells’ electrochemical performance. Once a porous electrode or electrode substrate has been formed, additional conductive and/or catalytically active particles can be added by infiltration to improve performance.

Infiltration of the fuel cell electrodes is usually carried out in order to improve the catalytic activity or enhance the ionic and/or electronic conductivity. While fine dispersed infiltrates introduce catalytic activity, connected particles with high surface area form the conduction pathways and can improve the fuel cell performance and lower the required operation temperature, thus reducing degradation [11,12]. Fine particle size and the high surface activity of the infiltrates are achieved by using a lower heat treatment temperature to decompose the nitrates and form the phase compared with the conventional sintering temperatures used in composite electrodes (1200–1500 °C). A new method of electrode production for mSOFCs has been investigated previously with the aim of improving RedOx and thermal cycling resistance [13]. In this method a porous YSZ backbone forming the main skeleton of the tubular fuel cell is coated with a thin layer of dense YSZ electrolyte and cathode. The porous support is infiltrated with nano-size Ni or Ni–SDC mixtures which enables improved redox cycling through reaching the percolation limit of the conducting phase at much lower Ni content compared with conventional cells. Their method has been extended in this work; looking at infiltration into a Ni–YSZ anode supported cell and optimal cathode thicknesses and LSM loadings.

Infiltration of LSM into a porous YSZ structure has been researched by various groups [14–19] and improvement in cell performance due to increased TPB length compared with the composite LSM–YSZ cathode has been reported. Ni infiltration has been found to be an effective technique in reducing the quantity of Ni required for obtaining high anode conductivity and cell performance [20] and also improving the RedOx cycling of nickel containing anodes [21]. Adding a dopant such as ceria has been seen to improve performance on thermal and RedOx cycling of fuel cells [22] (in addition to greatly improving the sulphur tolerance of Ni/YSZ anodes [20,23]). Control of YSZ particle size and porosity also helps to improve the stability under RedOx conditions [10,24]. It has been shown that infiltration of SDC into Ni/YSZ composite anodes inhibits Ni grain growth and improves the electrochemical performance of the anode as the doped ceria is a mixed ionic and electronic conductor and is catalytically active for the oxidation of hydrogen and reduction of oxygen [25,26]. Infiltration of ceria or GDC catalysts is also known to inhibit the grain growth of infiltrated Ni particles significantly [27].

The microstructure of the porous YSZ substrate, including size, connectivity and distribution of the pores and configuration of the YSZ particles, influences the distribution of the infiltrated phase, TPB length and ultimate cell performance [28]. Various materials have been tested for their suitability as pore formers, for example, flour, graphite and magnesium oxide [6,29–31]. Although flour offers a low-cost option, it results in significant shrinkage on sintering, leading to the formation of overly large pores [6]. Graphite and PMMA were tested as cathode pore formers in this work.

Most research on infiltration focuses on planar cells and there is little information available on the influence of anode and cathode infiltration on the performance and cycling of tubular fuel cells. This paper therefore focuses on studying the effects of electrode infiltration and cathode microstructure on electrochemical performance and cycling of micro-tubular fuel cells (mSOFCs). The infiltration processes described in the paper allow facile addition of electro- and catalytically active materials throughout a porous YSZ matrix in the anode and cathode of the tubular fuel cell and improve the performance of the tubular cell.

2. Experiments

Table 1 lists the cells tested: Cells 1–8 were prepared by infiltration and tested alongside two cells (cells A and B) made by traditional techniques (details of preparation methods available elsewhere [32,33]), using the same co-extruded YSZ–NiO anode, YSZ electrolyte tubes. Cells A and B have bi-layer (LSM-YSZ, LSM), hand-painted cathodes, with no infiltration. Cells 1-8 have infiltrated cathodes. To coat a thin porous layer (TPL) for cathode infiltration, YSZ (calcined at 1500 °C, milled for 72 h in water and dried) was mixed with 20 vol.% graphite (Sigma Aldrich <325 mesh) or PMMA (polymethylmethacrylate, CA 6, product of Microbeads Company, Norway), azeotropic solvent (toluene/ethanol), dispersant (100 g Menhaden fish oil dissolved in 1 L of aezotropic solvent), and binder (200 g polyvinyl butyral dissolved in 1 L aezotropic solvent). Table 2 shows the recipes used for preparation of the two types of the coated porous layers using graphite or PMMA as the pore-formers. The components were mixed at 300 rpm for 1 h in a planetary mill prior to coating.

The mixture was applied to the electrolyte surface by dip coating and the tube heated in air at 300 °C and 700 °C for 1 h to burn off the organic components, PMMA or graphite, then