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Electrode design for direct-methane micro-tubular solid oxide fuel cell (MT-SOFC)

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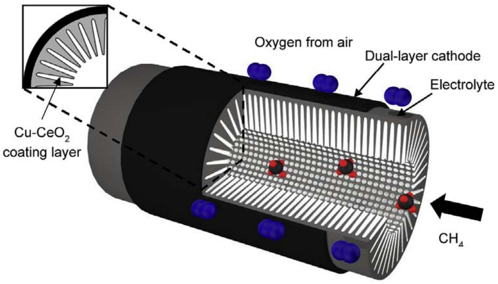
HIGHLIGHTS

- A hierarchical structured YSZ micro-tube is fabricated.
- It is composed of self-organised micro-channels and a thin electrolyte layer.
- The self-organised micro-channels are useful for incorporation of anode components.
- Micro-channels contribute to a lower transport resistance.
- Excellent stability during long-term test with negligible coking is observed.

GRAPHICAL ABSTRACT



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ABSTRACT

Herein, a micro-structured electrode design has been developed via a modified phase-inversion method. A thin electrolyte integrated with a highly porous anode scaffold has been fabricated in a single-step process and developed into a complete fuel cell for direct methane (CH_4) utilisation. A continuous and well-dispersed layer of copper-ceria (Cu-CeO$_2$) was incorporated inside the micro-channels of the anode scaffold. A complete cell was investigated for direct CH_4 utilisation. The well-organised micro-channels and nano-structured Cu-CeO$_2$ anode contributed to an increase in electrochemical reaction sites that promoted charge-transfer as well as facilitating gaseous fuel distribution, resulting in outstanding performances. Excellent electrochemical performances have been achieved in both hydrogen (H_2) and CH_4 operation. The power density of 0.16 Wcm^{-2} at 750 °C with dry CH_4 as fuel is one of the highest ever reported values for similar anode materials.

1. Introduction

Solid oxide fuel cells (SOFCs) are types of fuel cells generally known for their high operating temperatures ranging from 600 to 1000 °C [1–3]. In addition to the typical attractive features of fuel cell technology, such as high efficiency and environmentally friendly operation, SOFCs provide some unique features, such as full solid-state operation and flexibility in fuel sources [4,5]. Hydrogen (H_2) is the most commonly used fuel for SOFCs, with excellent electrochemical performances frequently reported [6,7]. However, the vast majority of H_2 is produced from hydrocarbons through the steam reforming process, during which 20–30% of fuel value is lost [8]. As a result of this, the concept of direct hydrocarbon utilisation in SOFC has attracted research interest worldwide [9–12]. By using hydrocarbons, alternative cell materials need to be utilised in order to suppress carbon formation, which is an inherent problem associated with conventional nickel (Ni)-cermet anodes [13,14]. In a qualitative index of various SOFC anode materials by Ge et al., Ni-based anodes show superior electrocatalytic activity over Cu-based anodes, however the latter has the advantage of better fuel flexibility and a lower tendency towards coke formation [2]. Gorte and co-workers reported the development of planar SOFCs with Cu-based anodes operated with several types of hydrocarbons in which

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good cell performances with no or trivial coke formation have been demonstrated [8,14–16].

Fabrication is a primary challenge associated with the copper-based anodes. Copper and its oxides have relatively low melting points, viz. 1085 °C, 1326 °C and 1232 °C for Cu, CuO, and Cu_2O, respectively [17,18]. This makes the preparation of a cell with Cu-based anode through standard high-temperature ceramic processing techniques (i.e. tape casting and sintering) impracticable. Instead, impregnation has been almost exclusively applied to incorporate Cu in an additional step [14,16,19]. Geometrically, a micro-tubular design offers additional benefits compared to flat and tubular designs, including improved thermal shock resistance, quick start-up and shut-down, and enhanced volumetric power density [20,21].

Anode design is a critical aspect of the direct utilisation of hydrocarbons in SOFC operation. In this study, a micro-structured yttria-stabilised zirconia (YSZ) micro-tube has been fabricated via a phase inversion-assisted process to develop micro-tubular (MT)-SOFC with a Cu-based anode which is operated using CH_4 as a fuel source. One major benefit of the phase inversion-assisted process is the flexibility in control and tailoring of the micro-structure. The microstructured YSZ scaffold is composed of self-organised micro-channels and a skin layer. The thin skin layer functions as the electrolyte, whereas the micro-channels perform as a substrate for the anode materials ($Cu\text{-}CeO_2$). These anodic materials are firmly positioned into the micro-channels, thus, deterring their thermal movement. Furthermore, this unique micro-tubular feature helps avoid delamination and defect formation, contributing towards improved structural integrity. After a complete cell was constructed, a performance test was conducted with direct CH_4 utilisation.

2. Experimental

2.1. Materials

YSZ and lanthanum strontium manganite (LSM) powders were obtained from Inframat Advance Materials (USA). Polyethersulfone (PESf) (Radel A300, $M_w = 42500\ g\ mol^{-1}$, Ameco Performance, USA), N-Methyl-2-pyrrolidone (NMP) ($M_w = 99.13\ g\ mol^{-1}$ from VWR, UK), and Arlacel P135 (polyethyleneglycol 30-dipolyhydroxystearate, Uniquema) were applied as binder, solvent, and dispersant, respectively. NMP was also applied as bore fluid (internal coagulant) after mixing with ethanol (VWR, UK, NMP/Ethanol = 60/40 in weight). Deionised water was adopted as external coagulant. Anode components: 99% copper (III) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$) and 99.5% cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$) were purchased from Fisher Scientific (UK). Ethylene glycol (99+ %) from Acros Organic (UK) was used as cathode ink vehicle.

2.2. Preparation of micro-structured YSZ micro-tubes

The ceramic suspension was prepared by mixing the YSZ powder with the solvent (NMP) and dispersant. The resultant mixture was milled for 60 h (MTI Corporation model SFM-1 Desktop Planetary Ball Miller). PESf was subsequently added to the suspensions and milled for another 60 h to attain a homogeneous mixture. Before spinning, the suspension was degassed by stirring under vacuum for 2 h to eliminate air bubbles. The suspension was transferred to a stainless steel syringe and extruded through a custom-designed spinneret into an external coagulation bath of DI water. The spinneret was immersed in the coagulant bath to eliminate any air gap. The extrusion rates of the suspension and the bore fluid were precisely controlled using two Harvard PHD 22/2000 Hpsi syringe pumps. The micro-tube precursors were left in water overnight to complete the phase inversion before sintering. Table 1 presents the fabrication parameters for the preparation of YSZ micro-tube.

Table 1
Parameter for YSZ micro-tubes fabrication.

Suspension composition	
Ceramic – YSZ (wt.%)	56.5
Solvent - NMP (wt.%)	34.2
PESf (wt.%)	8.6
Dispersant (wt.%)	0.7
Fabrication conditions	
Extrusion rate (ml min^{-1})	8
Bore fluid rate (ml min^{-1})	10
Air gap (cm)	0
Sintering conditions	
Temperature (°C)	1450
Dwelling period (h)	6

2.3. Preparation of a complete fuel cell

Fig. 1 shows the schematic diagram of the phase-inversion based extrusion process. The inset (Fig. 1a) shows the picture of the dual-orifice spinneret used in this work. Fig. 1b illustrates the procedure for preparing a complete single cell. After completetion of the YSZ micro-tubes (Fig. 1b(i)), a dual-layer cathode consisting of an inner LSM-YSZ layer (LSM/YSZ = 50/50 by weight) and an outer LSM layer was brush-painted onto the YSZ micro-tube and sintered at 1000 °C for 2 h (Fig. 1b (ii)). Subsequently, the anode materials ($Cu\text{-}CeO_2$), were incorporated into micro-channels of YSZ micro-tubes via vacuum-assisted co-impregnation process. A mixed aqueous solution of copper nitrate and cerium nitrate was prepared prior to impregnation, with a concentration of 4 M and 1 M, respectively. The set-up for the impregnation process is shown in Fig S1 with additional description of the impregnation process. The co-impregnated micro-tube underwent heat treatment at 450 °C for an hour to decompose the nitrates. This impregnation was repeated until a target loading of 25 wt % was achieved.

2.4. Reactor assembly and sealing

The MT-SOFC was placed into two alumina supporting tubes (Almath Crucibles Ltd., UK) and sealed with a ceramic sealant (Ceramabond 552-VFG, Aremco, USA). The sealant became gas-tight following successive heat treatments at 95 °C and 260 °C for 2 h at each temperature with a heating rate of 5 °C min^{-1}. This assembly was placed inside a 300 mm long quartz tube with 20 mm outer diameter (OD) (Almath Crucibles Ltd., UK) with stainless steel end-caps made in-house, and sealed to the quartz tube by Viton O-rings (Polymax, UK). The whole set up is shown in Fig. S2.

2.5. Characterisation

The morphology of the micro-tube was examined using scanning electron microscopy (SEM) (JEOL JSM-5610 and LEO Gemini 1525 FEGSEM). Samples were gold-coated under vacuum at 20 mA for 60 s (EMITECH Model K550), and the SEM images with various magnifications were acquired. Energy dispersive spectrometry (EDS, JEOL JSM-6400 electron microscope) analysis was undertaken to evaluate the elemental distribution of anodic materials. The gas-tightness of the sintered micro-tubes was assessed using N_2 permeation method. The N_2 permeance was calculated from the pressure drop over 8 h using the following equation:

$$P= \frac{V}{RT\times A_m t}\ln\left(\frac{p_0 - p_a}{p_t - p_a}\right) \tag{1}$$

where

$$A_m = [2\pi(R_0 - R_{in})L]/\ln(R_0/R_{in}) \tag{2}$$

where P denotes the N_2 permeance of the tested membrane (mol $m^{-2} s^{-2} Pa^{-1}$); V is the volume of the test vessel (m^3); R is the gas