DOI: 10.1002/adma.201100194

# High Performance Anode-Supported Micro-Tubular SOFC Prepared from Single-Step Fabricated Dual-Layer Hollow Fibres

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Keywords: Dual-layer hollow fibre, Micro-tubular solid oxide fuel cell, Co-extrusion, Phase inversion, Finger-like voids

Micro-tubular solid oxide fuel cells (SOFCs) have been developed in recent years mainly due to their high specific surface area and fast thermal cycling. Previously, the fabrication of micro-tubular SOFC was achieved through multiple-step processes.[1-3] A support layer, for example anode-support, is first prepared and pre-sintered to provide mechanical strength to the fuel cell. The electrolyte layer is then deposited and sintered prior to the final coating of cathode layer. Each step involves at least one high temperature heat treatment, making the cell fabrication time-consuming and costly, with unstable control over cell quality. For a more economical fabrication of micro-tubular SOFC with reliability and flexibility in quality control, an advanced dry-jet wet extrusion technique, i.e. a phase-inversion-based co-extrusion process, is developed. Using this technique, a dual-layer electrolyte/electrode (either anode or cathode) hollow fibre (HF) can be formed in a single step. Generally, the electrolyte and electrode materials are separately mixed with solvent and polymer binder to form the outer and inner layer spinning suspensions, respectively, before simultaneously co-extruded through a triple-orifice spinneret, passing through an air gap and finally into a non-solvent external coagulation bath. In the mean time, a stream of non-solvent internal coagulant is supplied through the central bore of the spinneret. Thickness of the two layers are largely determined by the design of the spinneret and can be adjusted by the corresponding extrusion rate, while the macrostructure or morphology of the prepared HF precursor can be controlled by adjusting co-extrusion parameters such as suspension viscosity, air gap, flow rate of internal coagulant, etc. The obtained dual-layer HF precursor is finally co-sintered once at high temperature as a procedure to remove polymer binder and form bounding between the ceramic materials. In our previous work,[4-6] a dual-layer HF support for micro-tubular SOFC, which consists of an electrolyte outer layer of approximately 80 μm supported by an asymmetric anode inner layer with 35 % finger-like voids length, was successfully fabricated using the co-extrusion/co-sintering process. A single cell that obtained after deposition of a multi-layer cathode onto the dual-layer HF produced the maximum power density of 0.59 W cm$^{-2}$ at 570 $^{o}$C.[6] Improvement on the structure of the dual-layer HFs was further performed by reducing the electrolyte layer thickness to as thin as 10 μm and the maximum power density of the corresponding cell markedly increased to about 1.11 W cm$^{-2}$ at 600 $^{o}$C.[7] Although this result has proved the potential of the dual-layer HF as a promising support for micro-tubular SOFC, the value of powder density was still slightly lower than the ram-extruded anode-supported cell with similar electrolyte thickness and highly porous anode (about 1.29 W cm$^{-2}$ at 600 $^{o}$C).[8] One of the possible major reasons for the lower power output is the less effective porosity in the anode layer of HFs due to the relatively short finger-like voids structure (only 35% length of the anode thickness), which, we believe, can be further improved by adjusting the co-extrusion parameters.

In this article, we report the development of a high performance micro-tubular SOFC consists of a lanthanum strontium cobalt ferrite (LSCF)-cerium-gadolinium oxide (CGO) multi-layers cathode deposited on a CGO eletrolyte/nickel (Ni)-CGO anode dual-layer HF, which produces power densities of up to 2.32 W cm$^{-2}$ at 600 $^{o}$C, almost doubled than the values previously reported in literatures.[7-8] This result was achieved by improving the anode porosity through the adjustment of co-extrusion parameters, which further shows the advantages of the this technique in producing support for micro-tubular SOFCs. Various asymmetric structures of the anode inner layer are achieved by adding ethanol as a non-solvent into the corresponding spinning suspension. Ethanol was used as a non-solvent additive because it functions as a good dispersant for the mixture of nickel oxide (NiO)-CGO and as a result, the dispersion of NiO and CGO in the prepared hollow fibre would be more uniform and continuous. The detailed compositions of the spinning suspensions for fabricating the HFs are listed in Table 1. As can also be seen in the table, different solvents were used for inner and outer layer spinning suspensions, in which N-methyl-2-pyrrolidone (NMP) was for the inner and dimethyl sulfoxide (DMSO) for the outer one. In addition, in the previous batch of HFs, the co-extrusion rate of outer layer of 0.5 $cm^3$ $min^{-1}$ was employed in producing 10 μm electrolyte. Although the cell with 10 μm electrolyte yielded much higher power output than the thicker electrolyte cell, the open-circuit voltage (OCV) of the cell was relatively low (around 0.77 V at 600 $^oC$), which is probably due to the small gas diffusion across the thin electrolyte layer. Therefore, in this study, the outer layer extrusion rate of 0.8 $cm^3$ $min^{-1}$ has been used in order to prepare HF with a slightly thicker electrolyte layer, as an effort to improve the gas-tightness property of the electrolyte and subsequently, produce cells with better OCV.

Figure 1 shows the scanning electron microscopy (SEM) images of the developed dual-layer HFs co-sintered at 1500 $^oC$ for 12 h and reduced at 550 $^oC$ for 2.5 h. As can be seen, the porous anode inner layer consists of finger-like voids originating from the inner fibre surface of the Ni-CGO layer, and a sponge-like structure occupying the rest volume. As the ethanol content in the spinning suspension affects the anode structure, the HF AS1 with 5 wt.% ethanol shows the longest finger-like voids occupying about 70 % of the anode thickness, the growth of finger-like voids limits to around 60 % of the anode layer thickness with the addition of 10 wt.% ethanol, and further reduces to approximately 50 % with the further increase of the ethanol content to 20 wt.%. Such change in morphology can be explained as; firstly, the addition of ethanol, as a non-solvent, would increase the initial viscosity of a spinning suspension, as shown in Table 1, and secondly, the presence of ethanol would accelerate the precipitation of polymer binder during the phase inversion process because the polymer phase is closer to its precipitation point, which results in the increase of the local viscosity of the nascent fibre. The viscous fingering,[9] which is considered as the main phenomenon for the formation of the finger-like voids in the ceramic hollow fibres, has been limited by these two effects and as a result, confines the growth of finger-like voids in the fibres. As can also be seen in Figure 1, the dense electrolyte outer layer is very well-bounded to the anode inner layer, although different solvents were used for preparing the spinning suspensions of the two layers. Furthermore, the electrolyte of approximately 15 μm in thickness is obtained using the outer layer extrusion rate of 0.8 cm$^3$ min$^{-1}$ and it is believed that the electrolyte of 15 μm would provide better gas tightness than the cell with 10 μm electrolyte.

Prior to the electrochemical test, a multi-layers cathode with 40 μm in thickness was deposited onto the electrolyte of the HFs and the current collectors were applied on the both anode and cathode. The resultant cells consist of 10 mm cathode length with the active electrode area of 0.293, 0.288 and 0.276 cm$^2$ for AS1, AS2 and AS3, respectively. Figure 2 (a) shows the voltage-current (V-I) curves of the cells AS1, AS2 and AS3 at 600 $^{o}$C with a hydrogen stream of 30 cm$^3$ min$^{-1}$ (saturated with water vapour of approximately 0.70 cm$^3$ min$^{-1}$ using a bubbling cylinder at 20 $^{o}$C, 1 atm) fed to the anode and a 40 cm$^3$ min$^{-1}$ (20 $^{o}$C, 1 atm) of air to the cathode. It can be seen that all the cells have almost identical open-circuit voltage (OCV) of about 0.78-0.79 V, which is attributed to the same thickness of the electrolyte layer. However, the OCV values are lower than the Nernst voltage (i.e. 1.1 V) at 600 $^{o}$C that calculated from the equation below:

$$\Delta E_T = \frac{\Delta G_T}{4F} + \frac{RT}{4F} ln\left(\frac{P_{H_2}^2\, P_{O_2}}{P_{H_2O}^2}\right) \qquad (1)$$

This is because of (i) the possible minor diffusion of molecular hydrogen gas from the anode side to the oxidant (i.e. oxygen) region in the cathode side or vice versa through the thin electrolyte thickness of only 15 µm, which then lead to the direct contact of these two gases, (ii) minor electronic conduction of the CGO electrolyte, due to the reduction of $Ce^{4+}$ to $Ce^{3+}$ in reducing atmosphere, which basically creates short circuit pathways for the electrons. However, these OCV values are slightly higher than the previous batch of cell with 10 µm electrolyte as it possessed 0.77 V at lower hydrogen flow rate fed to the anode (15 $cm^3$ $min^{-1}$) and similar air supply to the cathode (40 $cm^3$ $min^{-1}$).[7] Furthermore, the OCV values obtained in this study are in very good agreement with the OCVs of the most of the CGO micro-tubular SOFCs that were previously reported in literatures.[1,8,10-17]

The power density of the cells varies with the anode structure, as can be seen in Figure 2(a). The maximum power density increases from 1.84 W $cm^{-2}$ for the cell AS3 with the shortest finger-like voids to 2.03 W $cm^{-2}$ for cell AS2 with 60 % voids length of the anode thickness and 2.32 W $cm^{-2}$ for the cell AS1 with 70 % voids length. As shown in the previous work, [18] longer finger-like voids normally have bigger finger-like voids entrance pore size, which results to a lower resistance of fuel gas diffusion into the finger-like voids zone. Furthermore, it is believed that the finger-like voids function as a set of hundreds micro-channels in the anode, thus, the presence of longer voids enhances fuel gas mixing and facilitates better fuel gas diffusion to the triple-phase boundary (TPB) in the sponge-like region, the area where the oxidation reaction of hydrogen takes place, and subsequently accelerates the rate of the reaction in the anode. The outstanding cell performances as a result of the optimized cell structure are significantly higher than our previous results, i.e. around 1.11 W $cm^{-2}$ at 600 $^{o}$C for the cell with 35 % finger-like voids length in the anode,[7] and the one reported by Suzuki *et al.*,[8] which further demonstrates the advantages of the co-extrusion/co-sintering process in fabricating high quality dual-layer HFs for better cell performances.

An impedance analysis has been carried out to investigate the effect of anode structure on the cell resistance. Figure 2 (b) shows impedance analysis for the micro-tubular SOFCs at 600 °C and it was used to determine the electrode polarisation resistance of the cells, which is represented by the distance between the high and low frequency intercepts of the curve on the real impedance axis. According to Mogensen and Hendriksen,[19] the electrode polarisation resistance is resulted from the resistance during the gas diffusion and gas conversion (i.e. fuel oxidation and oxygen reduction). As can be seen in the figure, the electrode polarisation resistance of the cells decreases with the increase of the finger-like voids length in the cell, from 0.0478 $\Omega$ cm$^2$ for the cell AS3 to 0.0394 $\Omega$ cm$^2$ for cell AS2 and further drop to 0.0250 $\Omega$ cm$^2$ for AS1. Such result is mainly attributed to the different resistance of gas diffusion in the anode with different asymmetric structures, showing the finger-like voids are really beneficial in promoting the gas diffusion in the anode. In comparison to other cells reported in previous works,[1,3,7,14,20,21] the electrode polarisation resistances in this study are much lower, thus explaining the outstanding power outputs of the fabricated cells.

In conclusion, this work demonstrates the advantages of co-extrusion/co-sintering process in developing high quality dual-layer HF supports for micro-tubular SOFCs. By using ethanol as non-solvent in this study, the viscosity of inner layer spinning suspension successfully varies and results in the different asymmetric structures of the anode layer. The presence of longer finger-like voids structure in the asymmetric anode layer significantly improves the gas diffusion by functioning as a set of hundreds micro-channels in the anode and subsequently increases the cell performance. The results obtained in this study can be used for the development of other functional dual-layer HFs in various applications.

## *Experimental*

In the preparation of the electrolyte/anode dual-layer HFs, two ceramic suspensions were prepared separately. The suspension of the anode inner layer was composed of 60 wt.% of NiO and 40 wt. % of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO), while the one for the electrolyte outer layer contained 100 % CGO powder. Ceramic powders were first mixed with solvent (either NMP or DMSO) and the additive, and stirred for 48 h, after which polyethersulfone (PESf) pellets were slowly added into the mixtures under stirring at ~300 rpm (OST 20 Digital YELLOWLINE IKA). The mixing was further carried out for another 48 h to obtain homogeneous spinning suspension. The prepared suspensions were degassed under stirring at room temperature, loaded into stainless steel containers and extruded simultaneously through a triple-orifice spinneret [5] (the extrusion rates of the inner layer and the outer layer were 6 and 0.8 $cm^3 min^{-1}$ respectively) into a tap water coagulation bath with 20 cm air-gap length. The flow rate of the internal coagulant (de-ionized water) was 14 $cm^3 min^{-1}$. The obtained HF precursors were then co-sintered in static-air at 1500 $^oC$ for 12 h (TSH17/75/450, ELITE). The sintered dual-layer CGO/NiO-CGO HFs were reduced to CGO/Ni-CGO HFs at 550 $^oC$ for 2.5 h using hydrogen.

Viscosity data was collected (Physica UDS-200 rheometer) using concentric cylinder geometry at shear rates between 6-1000 $s^{-1}$ at 20 $^oC$. The morphology of the dual-layer HFs was examined using a JEOL JSM-5610 scanning electron microscope (SEM). Prior to the electrochemical measurements, multi-layers of cathode materials were deposited on the electrolyte of the dual-layer HFs. The cathode multi-layers, which the first and second layers were the mixture of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)-CGO and the third layer was 100 wt.% LSCF, were deposited using brush painting technique and sintered at 1200 $^oC$ for 5 h to form a micro-tubular SOFC with 10 mm length of cathode. The resultant cell was then fixed in a gas-tight alumina tube (Multilab Ceramics, UK) using a ceramic sealing paste (Aremco, USA) after applying current collectors. The current collection was made by wrapping silver wire around the cathode layer and conductive platinum paste was used to reduce potential losses between the wire and the cathode surface. Silver wool was packed inside the fibre lumen for anode current collection, producing excellent electrical contact with the anode wall. The complete cell was inserted in the centre of a tube furnace (MTF 12/25/250, CARBOLITE). The silver wires attached to the anode and the cathode were connected to a potentiostat/galvanostat (Autolab® PGSTAT 30, Netherlands) for measuring the voltage-current performances of the micro-tubular SOFCs at 600 $^{o}$C, with a hydrogen stream of 30 cm$^3$ min$^{-1}$ (saturated with water vapour of 0.35 cm$^3$ min$^{-1}$ using a bubbling cylinder at 20 $^{o}$C, 1 atm) fed to the anode and a 40 cm$^3$ min$^{-1}$ (20 $^{o}$C, 1 atm) of air to the cathode. The AC impedance spectra were measured on the same electrochemical workstation (0.01 Hz-1 MHz) with signal amplitude of 10 mV under open-circuit conditions at 600 $^{o}$C.

*Acknowledgements*

The authors would like to acknowledge to EPSRC (EP/E00136X) in the United Kingdom for the research funding provided. The award of an overseas study bursary to MHDO by the Malaysian Ministry of Higher Education and Universiti Teknologi Malaysia is also gratefully acknowledged.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

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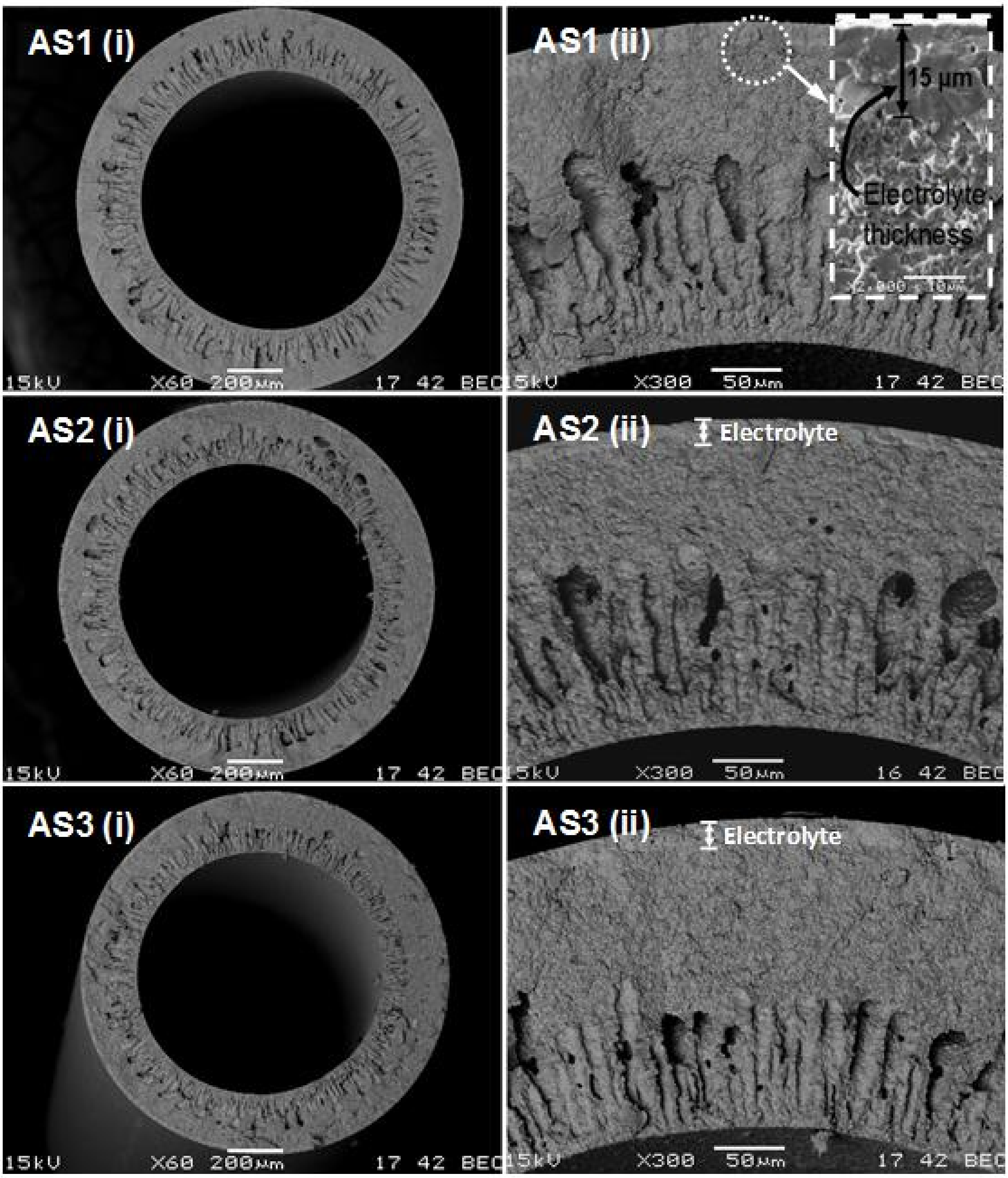

**Figure 1**. SEM images of the (i) overall view, and (ii) cross-section of the dual-layer HFs (co-sintered at 1500 °C for 12 h and reduced at 550 °C for 2.5 h).

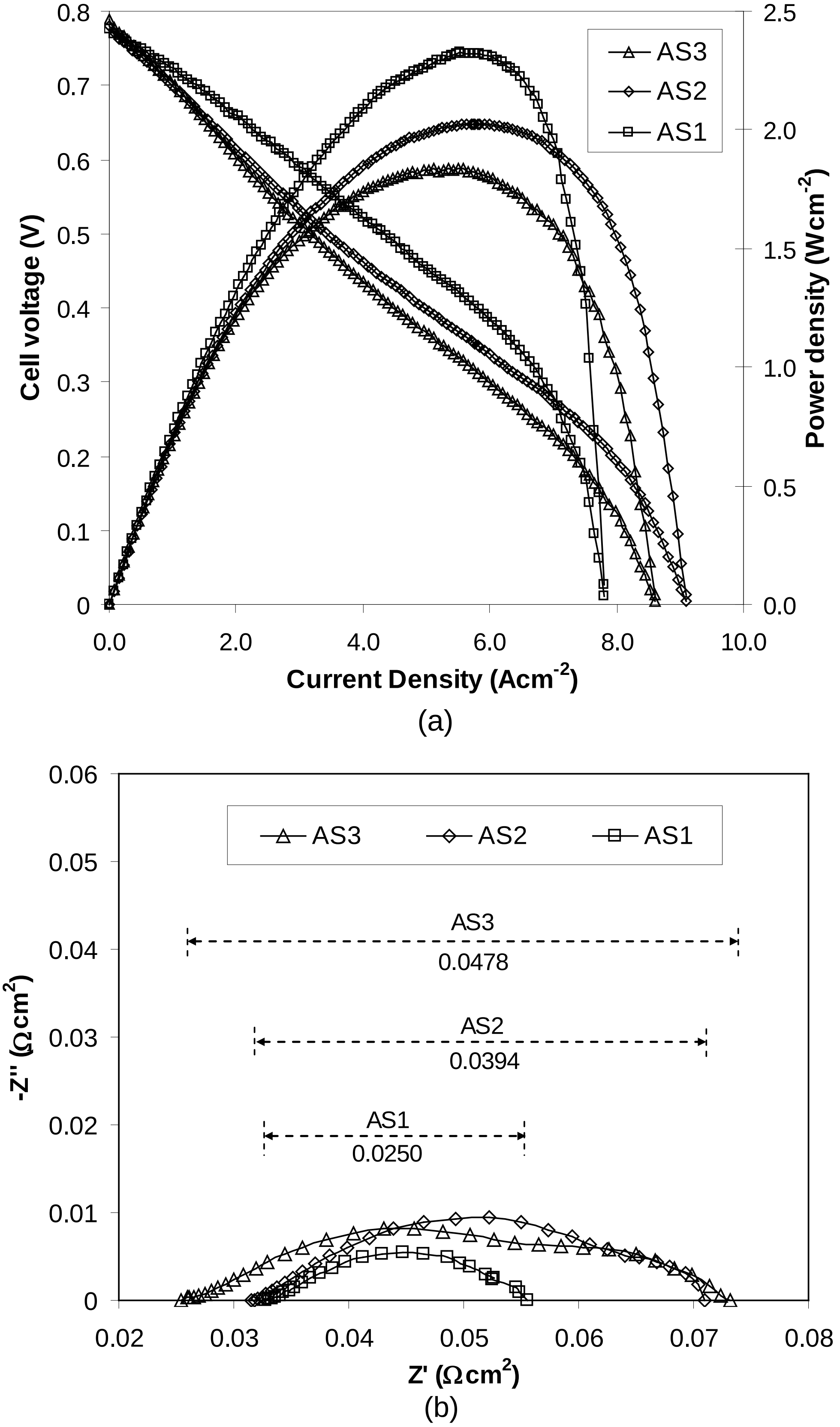

**Figure 2**. (a) Voltage-current (V-I) curves for micro-tubular SOFCs with different anode structures, and (b) Impedance spectra of the cells with different anode structures under open-circuit conditions (operated at 600 $^{o}$C with humidified hydrogen stream fed to the anode and air to the cathode).

**Table 1.** Spinning suspension conditions of dual-layer HFs

| **Experimental Parameters** | **Inner layer** | | | **Outer layer** |
|---|---|---|---|---|
| | **AS1** | **AS2** | **AS3** | **All fibres** |
| Compositions of the suspension (wt.%) | | | | |
| NiO | | 42.00 | | - |
| CGO | | 28.00 | | 60.00 |
| PESf | | 7.00 | | 6.00 |
| Arlacel | | 0.12 | | 0.12 |
| NMP + Ethanol | | 22.88 | | - |
| DMSO | | - | | 33.88 |
| NMP-Ethanol (wt.%) | 5-95 | 10-90 | 20-80 | - |
| Viscosity (cP) | 18,800 | 21,400 | 22,900 | 3930 |

Table of content entry: **A high performance micro-tubular SOFC** was developed using an improved electrolyte/anode dual-layer HF fabricated via a novel co-extrusion/co-sintering technique. This technique allows the control over the porosity of the anode, resulting in the increase of the cell's power output up to 2.32 W $cm^{-2}$ at 600 $^{o}$C, which almost doubled compared to the values previously reported in literatures.

Keyword: Dual-layer hollow fibre, Micro-tubular solid oxide fuel cell, Co-extrusion, Phase inversion, Finger-like voids

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