

## Cathode current-collectors for a novel tubular SOFC design

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### Abstract

Two methods of current collection/interconnection are developed for a novel tubular design solid oxide fuel cell (SOFC). Nimonic 90 wires, coated with  $\text{LaCoO}_{3-\delta}$  are used as the cathode current-collectors. When compared with the uncoated Nimonic wires, the  $\text{LaCoO}_{3-\delta}$  perovskite coated Nimonic wires improve the current densities of the cells. The latter is attributed to the fact that the coating improves the electrical contact between the wire and the cathode. The second method of current collection, whereby silver inks are painted on to the surface of the cathodes and then fired in situ, achieves greater cell performances than the Nimonic 90 wire systems. At 900°C and 0.7 V, with 3-cm long cathodes, a current density of  $0.20 \text{ A cm}^{-2}$  is achieved for cells with silver strip current-collectors. © 1998 Elsevier Science S.A.

*Keywords:* Solid oxide fuel cell; Current collection

### 1. Introduction

The tubular solid oxide fuel cell (SOFC) is based upon a single cell of tubular geometry. The advantages of the tubular fuel cell include: the ease of sealing; the ability to cope with higher thermal stresses; rapid response to load variation; tolerance to fuel feed variation; tolerance to load interruption. Power densities of  $0.9 \text{ W cm}^{-2}$  have been achieved with certain tubular SOFCs [1]. Disadvantages of the tubular design include a higher cost of manufacture and longer current paths which result in significant ohmic losses [2].

One of the most prominent tubular SOFC designs is that developed by Westinghouse. It originally consisted of a porous support tube (PST) made from calcia-stabilised zirconia with the cathode, electrolyte and anode layers fabricated over the top, and an interconnect strip joined to the cathode. A later design has dispensed with the performance limiting PST in favour of a thicker walled support tube. Fabrication of the Westinghouse design involves the slurry coating of the manganite cathode on to the support tube, followed by a strip of interconnect material of  $(\text{LaCr}(\text{Mg})\text{O}_3)$  and then yttria stabilised zirconia (YSZ) applied by EVD, and finally the addition of the anode, a

Ni/YSZ cermet, which is coated on top with EVD and slurry coating. To connect the tubular cells electrically, nickel felt is connected to the interconnect of the tubular cell and to the anode of the adjacent cell. Other tubular designs include the bell and spigot configuration and the segmented-cell-in-series design [3]. Recently, a novel tubular SOFC design based on small diameter, thermally shock resistant, zirconia tubes has been developed [4]. A major advantage of this novel tubular design is that it allows for rapid start-up in the order of a few seconds. By contrast, the planar and other tubular designs have typical warm-up times of approximately 6 h and 1 h, respectively. Further advantages of this tubular design include low cost manufacture and ease of sealing.

To enable higher voltage outputs (and, thus, power outputs), the single tubular cells must be stacked into multi-cellular units. Stacking of the single cells is carried out using an electronically conducting interconnect/current-collector for series or parallel connections. Depending on the fuel cell design, the interconnect must be both chemically and physically stable in reducing and oxidizing environments, have good electronic conductivity, have sufficient strength to support other cells (particularly in the planar design), and be easily fabricated into the required configuration. The most common materials used for the interconnect are the alkaline earth-doped lanthanum chromites, used in both the planar and tubular designs, and

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chromia forming alloys (alloys that form a protective and conductive  $\text{Cr}_2\text{O}_3$  coating) used for the planar design [5]. Evaporation of chromium from the surface of the metal interconnect on the cathode side has been shown to be detrimental to cell performance. The chromium evaporation can be suppressed, however, by surface treatment of the alloy separator [6,7]. Furthermore, the coating of the metal interconnect with a perovskite has been shown to decrease the contact resistance and improve the stability of cell performance over time [7–10]. Alternatively, research has revealed that at operating temperatures of around 850–900°C, silver wire wound around the cathode is a simple method of current collection [11]. Due to the low melting point of silver, however, the evaporation rate is very pronounced at present tubular SOFC operating temperatures (850–900°C) [12]. Therefore, either lower operating temperatures have to be achieved or an alternative to silver has to be found. Examples of silver used in a SOFC include  $\text{Ag-La}_{0.7}\text{Sr}_{0.3}\text{CrO}_3$  (Ag–LSC) cathode cermets, covered with a porous LSC cap, that showed no observed silver segregation, evaporation, or change in interfacial resistance over a 200 h period at 750°C [13]. Furthermore, earlier research has demonstrated the value of silver in lowering the cathode interfacial resistance in medium temperature SOFCs run at 750°C [14].

In this study,  $\text{LaCoO}_{3-\delta}$  coated and uncoated Nimonic 90 wire, silver wire and silver strip are studied and compared as potential cathode current-collector/interconnector systems for novel tubular SOFCs.

## 2. Experimental

The ceramic single tubular solid oxide fuel cell consists of an extruded yttria stabilized zirconia (YSZ) electrolyte

Table 1

Weight percentages (wt.%) of dispersant, plasticiser and binder relative to the weight of the  $\text{LaCoO}_{3-\delta}$

Dispersant (wt.%)	Binder (wt.%)	Plasticiser (wt.%)
KD1	PVB6:20Epoxy	PEG4:DOP4:Terp3
3	26	11

DOP: Di-octyl-phthalate.

PEG: Poly(ethylene glycol).

PVB: Polyvinyl butyral.

Terp: Terpeneol.

tube (TZ-8Y, Tosoh), with an outside diameter and thickness of approximately 2.5 mm and 150  $\mu\text{m}$ , respectively. The extrudate was provided by Viking, while the extrusion and subsequent sintering at 1400°C of the electrolyte tubes was performed by SAPCO. A commercial  $\text{La}_{0.82}\text{Sr}_{0.18}\text{MnO}_3$  cathode (LSM82X96019-2, Merck) was applied on the outside of the tube and a Ni/YSZ ceramic metal composite anode on the inside. The cathode current-collectors consisted of a silver ink painted and then fired on to the surface of the cathode, a commercial 0.32-mm Nimonic 90 wire (Ni53, /Cr20/Co18/Fe5/Ti2.5/Al1.5, Alloy Wire Int.) and a 0.25-mm silver wire wound along the length of the cathode. The novel tubular SOFCs are shown in Fig. 1.

The contacting electrochemical layer was applied using a LSM/YSZ ink; 7.5 g LSM, 7.5 g YSZ (Tosoh TZ10Y), 3.1 g 1,1,1-trichloroethane, 2.3 g methanol and 0.2 g glycerol trioleate were milled with zirconia media for 4 h. The LSM outer layer was prepared from 20 g LSM, 24 g acetone and, 0.6 g KD1 (Zeneca). The first cathode layer, consisting of LSM/YSZ, was then painted by hand, using a brush, on to the outside of the zirconia tube and finally dried in an oven at 140°C for 0.5 h. The second layer,

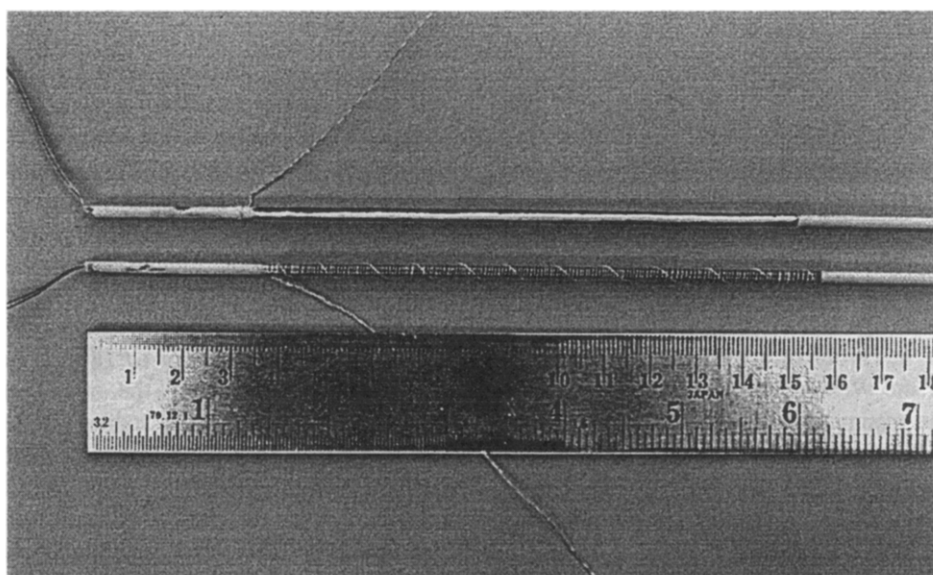
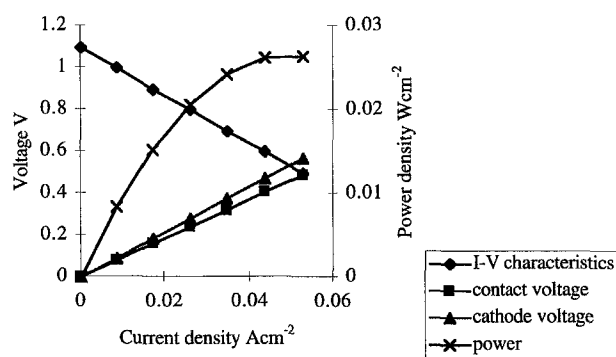


Fig. 1. Photograph of the novel tubular SOFCs with 12-cm cathodes (with silver strip and wire cathode current-collectors, respectively).



I-V characteristics of uncoated Nimonic 90

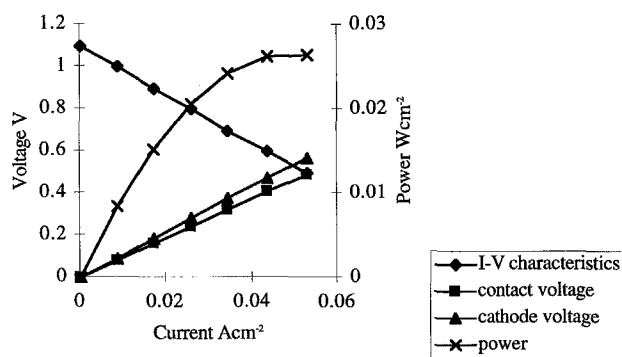


Fig. 2. *I*–*V* characteristics for 3-cm fuel cells measured in air at a constant temperature of 900°C and a constant flow rate of saturated H<sub>2</sub> bubbled through H<sub>2</sub>O at 25 cm<sup>3</sup>/min: (a) uncoated Nimonic 90 wire; (b) Nimonic 90 coated with LaCoO<sub>3-δ</sub>.

consisting of LSM only, was then applied over the top of the first layer and again dried in an oven.

The anode was deposited on the entire inside length of the tubular cells by drawing anode ink up through a cell using a syringe. In order to prepare the anode ink, 5 g of YSZ (Unitec FYT11) was calcined by placing it in a furnace (Carbolite RHF 17/3) and heating at the maximum possible rate to 1500°C, holding for 10 min, and then cooling down to room temperature. The calcined YSZ was then removed from the furnace and sieved through a 212 μm sieve. 10.5 g of NiO (Alfa Chemicals), 0.1 g glycerol trioleate, 2.9 g 1,1,1-trichloroethane and 2.1 g of methanol was added to a plastic container, with zirconia milling media, and milled for 2 h. The previously calcined YSZ was subsequently added to the plastic container and milled for a further 1 h. Finally, 0.1 g PVB (polyvinyl butyral, Aldrich Chemical) was added to the solution and milled for 2 min. The solution was used immediately. A YSZ

tubular cell was attached to a PVC tube that was, in turn, connected to a syringe. The free end of the cell was then placed in the anode ink. The syringe was used to draw the anode ink up through the cell to coat the inside, any excess ink was ejected from the tube using the same syringe. The cell was initially left to drain and then placed in an oven at 140°C to dry. An anode coating of approximately 40 μm was achieved. After the anodes and cathodes were applied, the cells were fired using a ramp rate of 1°C/min to 500°C (no dwell), 5°C/min to 1300°C (dwell 1 h), and then 10°C/min to room temperature.

After firing the electrodes on to the YSZ tube, the current-collectors were added. The cathode current-collector systems used in this work were silver and Nimonic 90 wires wound around the cathodes, and silver ink painted on to the cathodes. The silver wires were wound around the cathodes, and used as a standard to compare the effects on fuel-cell performance of the alternative Nimonic 90 wire and silver strip current collector systems. Before the Nimonic 90 wires were wound around the cathodes, they were coated with LaCoO<sub>3-δ</sub>. The latter compound was chosen because it has exhibited low contact resistance [7]. LaCoO<sub>3-δ</sub> perovskite powders used for the coating of the alloy wires were synthesised using the glycine nitrate process [15]. A slurry system was then developed to coat the cathode wire. The system is shown in Table 1. The appropriate amounts of perovskite powder, solvent (consisting of 31% toluene and 69% 2-propanol) and dispersant were mixed in a beaker for 1 h using a magnetic stirrer. The binder and plasticiser were subsequently added, and mixing continued for a further 1 h. Solvent was evaporated off, until a thick ‘honey-like’ consistency was obtained. A perovskite coating of approximately 20 μm was achieved by drawing Nimonic 90 alloy wire at a constant rate through a syringe containing the slurry. The needle end of the syringe, through which the wire emerged, was covered in plasticine. The plasticine stopped the solution from escaping and aided the coating of the wire. The coating was then dried in air for approximately 6 h, after which the coated and uncoated wires were wound around their respective cathodes on the tubular cells, and fixed at a rate of 5°C/min in air to 1200°C, held for 1 h, and then cooled down to room temperature at a rate of 10°C/min. The effect exerted on cell performance by the coating on the Nimonic 90 wires was then measured.

Unless otherwise stated, the silver strip current-collector was applied by painting two silver ink strips (product C 10503D1, Gwent Electronic Materials, UK), approximately 1 mm in width, on opposite sides along the length of the

Table 2

*I*–*V* characteristics of silver and Nimonic 90 alloy wire current-collection systems at 0.7 V for 3-cm cells

Current collector	Average current density (A cm <sup>-2</sup> at 0.7 V)	Cathode voltage (V)	Contact voltage (V)
Uncoated Nimonic 90	0.034	0.376	0.322
Coated Nimonic 90	0.049	0.356	0.239

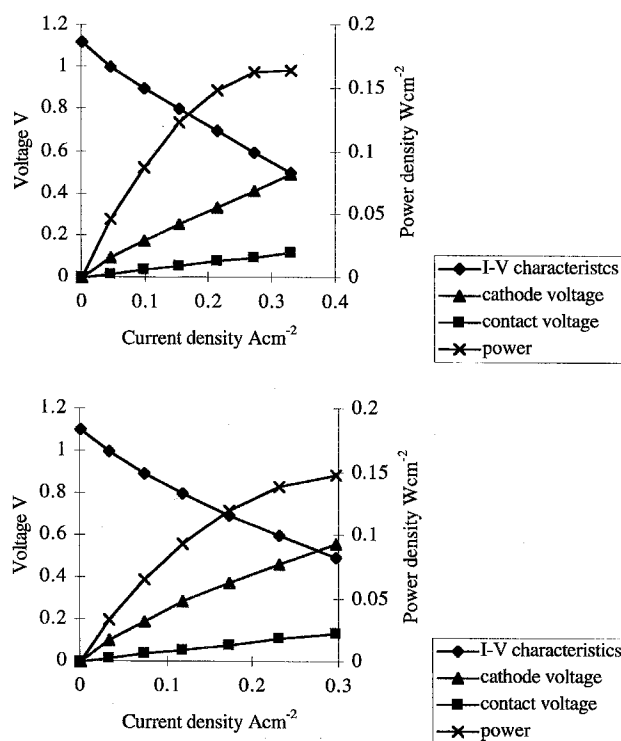


Fig. 3.  $I$ - $V$  characteristics of 3-cm fuel cells measured in air at a constant temperature of 900°C and a constant flow rate of 25 cm<sup>3</sup>/min, saturated H<sub>2</sub>: (a) silver wire; (b) silver strip.

surface of the individual cathodes. The cells were dried in an oven for 15 min at 140°C and then fired. The firing took approximately 40 min, with a dwell period of 6 min, at a maximum temperature of 800°C. Silver wire leads were then attached to the cathode silver strip current-collectors by winding the silver around the tubes to contact the end of the silver strips. To ensure intimate contact between the wire and the strip, silver ink was painted onto the contacting area, dried and then fired as above. The anode current-collector consisted of two 0.5 mm Ni wires (99.98%, Advent Research Materials) placed down the inside of the tube, whereby the two nickel remained in contact with the anode purely by mechanical force exerted by the wires on the inside of the tube.

The cells were placed in a purpose-built furnace. A gas line connected to a dual supply of H<sub>2</sub> and N<sub>2</sub> was then attached to the end of the cell, while the current-collector and associated reference and sensing wires for the electrodes, were brought outside the furnace. Before testing, the cells were heated in a furnace to 900°C, while N<sub>2</sub> was passed through the tube. Upon reaching 900°C, the N<sub>2</sub>

Table 4  
Current densities of 12-cm cathodes at 0.7 V

Length	Average current density (A cm <sup>-2</sup> at 0.7 V)
Silver strip	0.087
Silver wire	0.074

supply was slowly turned off as H<sub>2</sub> was added. The anode was then reduced by passing pure H<sub>2</sub>, at a rate of 25 cm<sup>3</sup>/min, bubbled through water at 25°C, through the cell for 15 min. The current-voltage characteristics ( $I$ - $V$ ) of the cells were then measured using a passive potentiostat [16] in air at a constant temperature of 900°C, and a constant flow rate of 25 cm<sup>3</sup>/min H<sub>2</sub>. The contact resistance was ascertained by measuring the potential difference between the cathode current-collector and a small sensing electrode adjacent to the current-collector on the same cathode. The cathode resistance was determined by the potential difference between the sensing electrode on the cathode and a reference electrode adjacent to the cathode.

### 3. Results and discussion

An issue which proved challenging was the adherence of the coating to the wire before and after firing. A lanthanum cobaltite slurry had to be developed that would adhere to the wire during winding on to the cathode. This was achieved using the formulation detailed in Table 1. A Hitachi S4000 scanning electron microscope (SEM) was used to analyse the surface morphology of the perovskite coating on the wire after testing. The coating did not adhere well to the metal wire. Cobalt-containing perovskite materials previously used as coatings to reduce contact resistance, as well as chromium evaporation on the metal interconnect, have also exhibited poor adherence to the interconnect after testing [7]. It is evident, however, that when a comparison is made between the coated and uncoated Nimonic 90 wires, as shown in Fig. 2a,b, the coating does appear to improve the overall cell performance. For example at 0.7 V, as shown in Table 2, Nimonic 90 coated wires had a contact voltage of 0.322 V and a current density of 0.034 A cm<sup>-2</sup> compared with a contact voltage of 0.356 V and current density of 0.018 A cm<sup>-2</sup> for the uncoated Nimonic 90 wires. Previous research by other authors on planar cells has yielded similar results [7–9].

Table 3  
 $I$ - $V$  characteristics of silver wire and silver strip cathode current-collectors at 0.7 V for 3-cm cells

Current collector	Current density (A cm <sup>-2</sup> at 0.7 V)	Cathode voltage (V)	Contact voltage (V)
Silver wire	0.21	0.34	0.08
Silver strip	0.20	0.38	0.08

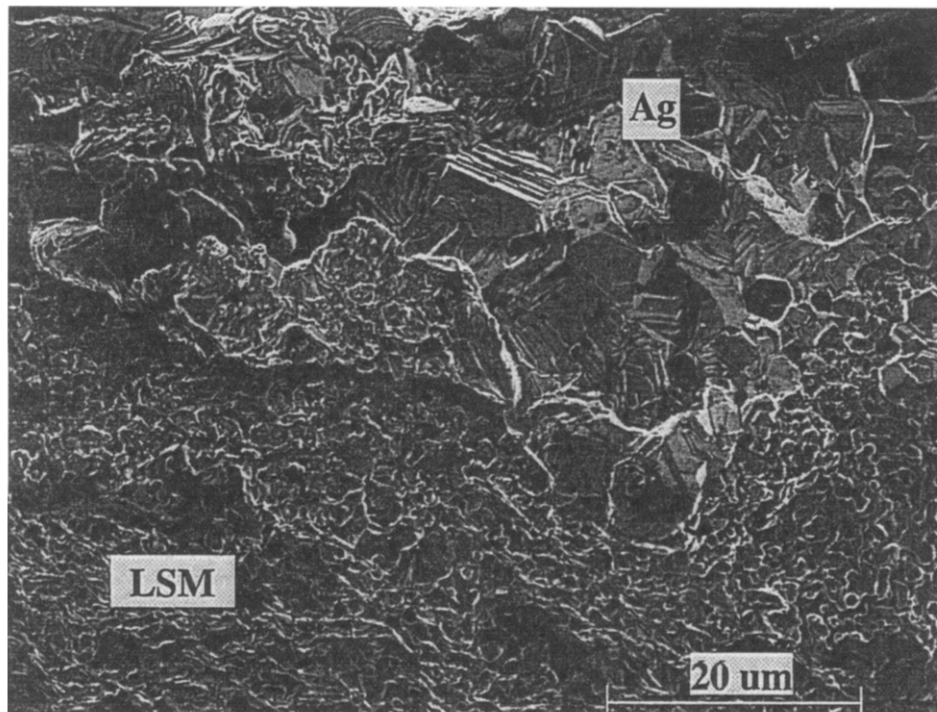


Fig. 4. Electron micrograph of LSM/Ag interface.

The  $I$ - $V$  characteristics, total cathode contribution to resistance and the contact contribution to resistance are presented in Fig. 3a,b for the silver wire and the strip current-collectors, respectively. As shown in Table 3, both the silver wire and the silver strip have similar values of contact voltage and cell current densities. Both methods of current collection exhibit superior performance over the Nimonic 90 coated and uncoated wires. An electron micrograph of the LSM/Ag strip interface is given in Fig. 4.

To ascertain the effect of cell length on performance, cells were fabricated with cathodes of length 3 and 12 cm, the results listed in Tables 3 and 4 reveal that the silver strip performs as well as the silver wire over different cell lengths. The current density for the 3-cm cells is much higher than that of the longer, 12-cm cells. The results are in agreement with similar work carried out previously, whereby current densities decrease with increasing cell length [11].

In order to access the quantity and coverage of silver that is needed to deliver maximum cell performance using

the silver ink, various coverages of ink were applied to the cathodes. Listed in Table 5 are two silver coverages, along with their corresponding current densities, held at a constant potential of 0.7 V. The current density of the two cells is similar. For example, the cell with a cathode covered completely in silver ink gives a similar current density as the cell with two strips of silver along the length of the cell cathode. In addition, the cell with the cathode covered completely in silver performs adequately. This indicates that the presence of silver does not effect cell cathode performance because it is permeable to oxygen. The difference in current density between the cells described in Tables 3 and 5 is ascribed to the fact that the cells are made from different batches of cathode and anode inks.

#### 4. Conclusions

The coating of Nimonic 90 wires with  $\text{LaCoO}_{3-\delta}$  is shown, to a limited extent, to improve cell performance by reducing the contact resistance between the wires and the cathode. The use of Nimonic 90 wires is, however, an unsatisfactory method of cathode current-collection for the novel tubular SOFC used in this work—the overall cell performances are well below that achieved for alternative silver wire or silver strip current-collectors.

From the experimental data, it is found that the silver strips painted on to the surface of the cathodes perform as well as the silver wire, and may prove to be a useful means of current collection in low temperature SOFCs. In addi-

Table 5  
Current densities of 3-cm cells with different coverages of silver current collector ink at 0.7 V

Coverage	Average current density ( $\text{A cm}^{-2}$ at 0.7 V)
Two thin silver strips painted along the cathode	0.11
Silver painted over the entire cathode	0.12

tion, it is observed that the current density is not improved dramatically by an increase in the area of cathode covered by silver. This suggests that the silver does not interfere with the cathode reaction. The current increases with increase in the area of the cathode, but not proportionally.

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