

# Tubular direct carbon solid oxide fuel cells with molten antimony anode and refueling feasibility



Nan-Qi Duan <sup>a</sup>, Yong Cao <sup>a</sup>, Bin Hua <sup>b</sup>, Bo Chi <sup>a</sup>, Jian Pu <sup>a</sup>, Jingli Luo <sup>b</sup>, Li Jian <sup>a, c, \*</sup>

<sup>a</sup> Center for Fuel Cell Innovation, State Key Laboratory of Coal Combustion, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

<sup>b</sup> Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 2G6, Canada

<sup>c</sup> Research Institute of Huazhong University of Science and Technology in Shenzhen, Shenzhen, Guangdong 518000, China

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## ABSTRACT

Tubular direct carbon SOFCs (solid oxide fuel cells) supported by YSZ (Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub>) electrolyte are fabricated by slurry-casting, slurry-dipping and sintering processes with La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3–10 mol.% Gd<sub>2</sub>O<sub>3</sub> doped CeO<sub>2</sub> (LSCF-10GDC) as the cathode. Their electrochemical performance is examined at temperatures from 700 to 800 °C using molten antimony (Sb) anode and activated carbon fuel. The ohmic resistance of the cell is between 1.01 and 0.37 Ω cm<sup>2</sup> mainly originated from the thick YSZ electrolyte (150 μm); the polarization resistance ranges from 0.22 to 0.06 Ω cm<sup>2</sup>. The maximum power density at 800 °C is 304 mW cm<sup>–2</sup> and can be greatly increased by using a thinner and/or more conductive electrolyte. With 1 g activated carbon as the fuel, the cell performance is stable at 200 mW cm<sup>–2</sup> at 800 °C for more than 6 h by chemical consumption (oxidization) of the carbon, which reduces the electrochemically formed Sb<sub>2</sub>O<sub>3</sub> to Sb. The cell performance decreases as the fuel is used up and is recovered by refueling.</sub>

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## 1. Introduction

Coal, composed primarily of carbon, is the largest energy source for the generation of electricity and one of the largest anthropogenic sources for carbon dioxide emission. Thus the clean and efficient utilization of carbonaceous fuel is a vital challenge for humankind. SOFC (Solid oxide fuel cells) electrochemically convert the chemical energy of carbon (C) into electricity and heat without involving combustions and mechanical motions. In this way the energy conversion is highly efficient with limited emission and easy capture of CO<sub>2</sub> [1,2].

In the DC-SOFC (direct carbon solid oxide fuel cell), C is oxidized in the anode compartment by oxygen ions transported from the cathode through the electrolyte [3]. A key issue of this technology is the lack of contact between the solid carbonaceous fuel and the oxygen ion [4,5]. Some approaches have been reported to increase

the contact area for the anode reaction, such as using molten carbonates (K<sub>2</sub>CO<sub>3</sub>–Li<sub>2</sub>CO<sub>3</sub>) in the anode to generate 3-dimensional contact between solid carbonaceous fuel and oxygen ions [6,7] and gasifying the solid carbonaceous fuel to produce CO via the Boudouard Reaction [8,9]. However, the carbonate ions in the molten salts are consumed gradually by side reactions with carbon [10,11]; and the catalyzed gasification reaction of C lowers the efficiency of energy conversion [12,13].

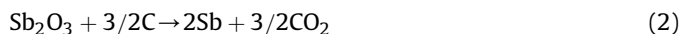
Recently, low melting point metals, such as tin (Sn) (505 K) [14,15], indium (In) (430 K), bismuth (Bi) (544 K), lead (Pb) (601 K) [16] and antimony (Sb) (903 K) [17], were reported as the anode of DC-SOFCs. At the operating temperature, the molten metal forms an intimate contact with the electrolyte. Oxygen ions transported through the electrolyte electrochemically oxidize the metal to form metal oxide, which is then chemically reduced by the solid carbonaceous fuel added into the anode. Among these low melting point metals, Sb is often selected as the anode material, since its oxide Sb<sub>2</sub>O<sub>3</sub> also has a low melting point of 928 K. In this case, the anode reactions are



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\* Corresponding author. Center for Fuel Cell Innovation, State Key Laboratory of Coal Combustion, School of Materials Science and Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China. Tel.: +86 27 87557694; fax: +86 27 87558142.

E-mail address: [lijian@hust.edu.cn](mailto:lijian@hust.edu.cn) (L. Jian).



The low density and insulating liquid  $\text{Sb}_2\text{O}_3$  formed during cell operation migrates away from the anode/electrolyte interface, which ensures a good contact between unreacted molten Sb and electrolyte for further reaction without increasing interfacial resistance. This kind of novel liquid anodes can be used with various types of carbonaceous fuel with easy capture of emitted  $\text{CO}_2$  and are expected to be more sulfur resistant than Ni-based anodes, as the addition of Sb and Sn in a Ni-based anode can enhance its resistance to sulfur poisoning [18].

So far, the feasibility of using molten Sb anode in DC-SOFCs was only demonstrated by planar button-size cells supported by ScSZ ( $\text{Sc}_2\text{O}_3$  stabilized  $\text{ZrO}_2$ ) [17], YSZ ( $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$ ) [19,20] or SDC ( $\text{Sm}_2\text{O}_3$  doped  $\text{CeO}_2$ ) [21] electrolytes. High power density of  $350 \text{ mW cm}^{-2}$  was achieved at  $700^\circ\text{C}$  by Jayakumar et al. [17] using a thin ( $100 \mu\text{m}$ ) ScSZ supported cell; however, ScSZ was found chemically unstable and dissolved in molten Sb/ $\text{Sb}_2\text{O}_3$  [19]. Compared with ScSZ and SDC electrolytes, YSZ is more reliable due to its high stability in molten Sb/ $\text{Sb}_2\text{O}_3$  [19] and reduced atmosphere and high mechanical strength [22].

With molten Sb anode, the planar cell design may not be suitable for stacking and scale-up due to the difficulties in cell sealing, interconnecting and refueling; and its possibility of practical applications is limited. In contrast, the tubular cell design possesses advantages in the aspects of cell sealing, cell-to-cell connection, thermal cycling and rapid start-up [23,24], and is promising for refueling for continuous power generation. In the present study, tubular cells, with YSZ electrolyte, molten Sb anode and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-10 \text{ mol.}\% \text{ Gd}_2\text{O}_3}$  doped  $\text{CeO}_2$  (LSCF-10GDC) composite cathode, were employed for the first time to demonstrate electrical power generation at intermediate temperatures from  $700$  to  $800^\circ\text{C}$  by using solid carbon fuel. During the test, fuel refilling was also conducted to prove the capability of continuous power generation.

## 2. Experimental

The YSZ substrate tube of the tubular cell was prepared by a slurry-casting method [25] using a ball-milled slurry containing 8% mol  $\text{Y}_2\text{O}_3$  stabilized  $\text{ZrO}_2$  powder (Tosoh) with xylene/ethanol (Sinopharm) as the solvent and polyvinyl butyral (Sinopharm) as the binder. The homogeneous slurry was poured into a tubular plastic mold and degassed centrifugally at a speed of 2000 rpm for 2 min. The viscosity of the slurry was carefully adjusted to between 14,000 and 16,000 mPa s, allowing the slurry to perfectly wet the inner wall of the plastic mold. The slurry hanging on the wall was gradually dried, while the mold was rotated vertically on a rotating plate at a constant angular speed, and detached from the mold due to shrinkage. The green body of the YSZ tube obtained was debound in air at a slow heating rate in a box furnace and then sintered at  $1500^\circ\text{C}$  for 5 h.

To prevent the reaction between LSCF and YSZ, porous baffle layer of 10GDC and LSCF-10GDC composite cathode (1:1 weight ratio) were built in sequence on the outer surface of the sintered YSZ substrate tube by slurry dipping and sintering in air for 2 h at  $1250^\circ\text{C}$  and  $1000^\circ\text{C}$  respectively. Both the LSCF and 10GDC powders used in the slurries were synthesized by a wet chemical method, using metal nitrates (Sinopharm) as the precursors and ethylene diamine tetraacetic acid (Sinopharm) as the chelating agent. The dried gels were calcined in air at  $850^\circ\text{C}$  for 2 h.

The electrochemical evaluation of the tubular cells was carried out using an in-house developed setup shown in Fig. 1. The tubular cell was loaded with 5 g of Sb powder (Sinopharm) and 1 g of activated carbon powder (Sinopharm) as the anode and fuel, respectively, and lap-sealed to an alumina tube using a ceramic

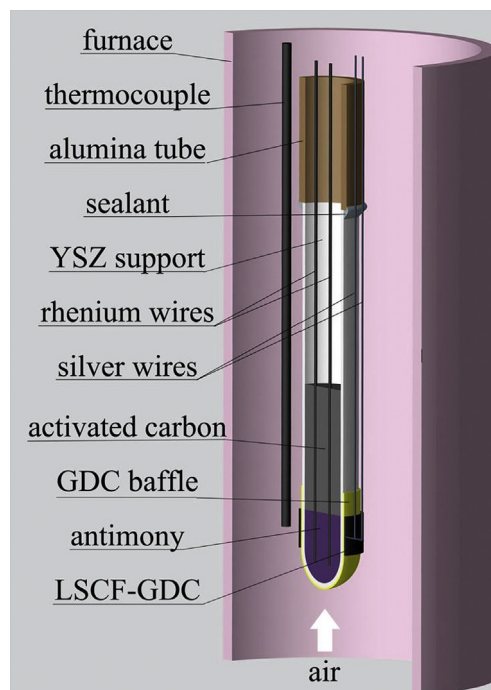


Fig. 1. Schematic drawing of the in-house developed setup for tubular DC-SOFC evaluation.

sealant (Ceramabond 668, Aremco Products). Rhenium (Re) wires of 0.5 mm in diameter were used as the anode current collector; and platinum (Pt) paste and twined silver (Ag) wire were used as the cathode current collector. Pure  $\text{N}_2$  was flowed into the tube to prevent the oxidation of Re, Sb and C at testing temperatures from  $700$  to  $800^\circ\text{C}$ . A Solartron 1260 frequency response analyzer (Solartron Analytical) was employed to measure the impedance of the cell in a frequency range between 100 kHz and 0.1 Hz with signal amplitude of 10 mV at open circuit. The current–voltage–power (I–V–P) and voltage–time (V–t) curves were obtained using a Solartron 1287 electrochemical interface (Solartron Analytical) and a DC power source (IT-6720, iTech). The cell microstructure was examined by means of scanning electron microscopy (SEM, Sirion 200 and Quanta 200, FEI).

## 3. Results and discussion

### 3.1. Cell structure and initial electrochemical performance

Fig. 2 shows the YSZ-supported tubular cell and its cross-sectional microstructure. The substrate was 10 mm in outside diameter and 60 mm in length; and the thickness of the YSZ substrate, 10GDC baffle and LSCF-10GDC cathode was 150, 2.5 and  $30 \mu\text{m}$ , respectively. The cathode was 6 mm in height with an active area of  $2 \text{ cm}^2$ . The level of the molten Sb was slightly higher than that of the cathode to maximize the reaction area.

Four cells were evaluated with molten Sb anode and activated carbon fuel, and similar performance was obtained within a fluctuation of 5%. This slight inconsistency was possibly caused by the unrealized condition variations in the preparation and testing of each cell. Fig. 3 shows the representative results of electrochemical impedance spectra (EIS) at open circuit voltage and I–V–P curves. The ohmic resistance was 1.01, 0.54 and  $0.37 \Omega \text{ cm}^2$  at  $700$ ,  $750$  and  $800^\circ\text{C}$ , respectively, which mainly arises from the thick ( $150 \mu\text{m}$ ) YSZ electrolyte [26], while the corresponding polarization resistance was 0.22, 0.11 and  $0.06 \Omega \text{ cm}^2$ , which includes the

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