Applied Energy 165 (2016) 983–989

Contents lists available at ScienceDirect

Applied Energy

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

Biomass carbon fueled tubular solid oxide fuel cells with molten antimony anode

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HIGHLIGHTS

- Two biomass charcoals were studied as fuel for DC-SOFC.
- Sb anode DC-SOFCs achieved reasonable running performance with biomass fuels.
- Fuels properties had an obvious influence on the cell running and efficiency.
- Fuel utilization and electrical efficiency was calculated and discussed.

ARTICLE INFO

Article history:
Received 13 September 2015
Received in revised form 22 October 2015
Accepted 29 November 2015

Keywords:
Solid oxide fuel cells
Biomass carbon fuel
Molten antimony anode
Fuel utilization
Electrical efficiency

ABSTRACT

Cell performance and efficiency of tubular molten antimony (Sb) anode direct carbon solid oxide fuel cells (DC-SOFCs) was investigated with two different biomass carbon fuels. The 8 mol.% Y_2O_3 stabilized ZrO_2 (YSZ) supported cells with $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$-10 mol.% Gd_2O_3 doped CeO_2 (LSCF-10GDC) as the cathode were fabricated by slurry-casting, slurry-dipping and sintering processes. A relatively high power density of 196 and 304 mW cm^{-2} was achieved at 750 and 800 °C, respectively. Two biomass carbon, cocoanut active charcoal (CAC) and pyrolysed corn starch (PCS), were used as the fuels for cell running at 750 and 800 °C and the exhausted gas consist was recorded. The proceedings of anode reactions were closely related to the fuel properties and working temperature and had an obvious influence on the cell running in turn. The fuel utilization and electrical efficiency of the special molten Sb anode cell was defined and calculated by the experimental data. The fuel utilization was above 50% but the electrical efficiency was below 34%, limited by the low Nernst voltage of the reaction of Sb oxidation, thick YSZ electrolyte used and significant heat generated by Sb_2O_3 reduction.

1. Introduction

In order to alleviate the climate change, effort has to be made to substantially reduce the fossil energy consumption through the development of high-efficiency energy conversion technologies [1]. The solid oxide fuel cell (SOFC) technology is one of such technologies that provide the highest efficiency for direct conversion of the chemical energy stored in fuels into electricity [2–4]. The fuels usually used in SOFCs can be hydrogen, natural gas, biomass, fossil fuel derivatives and any other types of hydrocarbons; and direct carbon SOFC (DC-SOFC), utilizing solid carbonaceous fuels, has been receiving increasingly attention [5–7].

In direct carbon fuel cells with a solid oxide electrolyte component, the cathode reaction usually is the reduction of oxygen via the following reaction [8,9].

$$O_{2(g)} + 4e^- \rightarrow 2O^{2-} \quad (1)$$

With a Ni cermet anode, the oxygen ions transported across the electrolyte from the cathode can only enter the anode within an effective thickness of 10 more microns for fuel oxidation reaction [10], depending on anode microstructure and operating conditions [11]. Thus the access of oxygen ions to the solid carbon fuel is critical for cell performance. To increase the accessibility, eutectic carbonate salts (e.g. K_2CO_3–Li_2CO_3) have been introduced into the anode as a media [12,13]. Alternatively solid carbon fuels are gasified firstly by the reverse Boudouard reaction [14–16] to

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http://dx.doi.org/10.1016/j.apenergy.2015.11.050
0306-2619/

produce CO, which then reaches the anode for oxidation. In a different approach from those mentioned above, Jayakumar et al. [17,18], McPhee et al. [19] and Abernathy, Harry et al. [20] investigated the feasibility of using low melting point metals as anode materials, especially antimony (Sb) [21,22] with a melting point of 903 K and a density of 6.78 g cm^{-3}. The antimony oxide, Sb_2O_3, has a melting point of 928 K, which is higher than that of Sb, and a density of 5.58 g cm^{-3}, which is lower than that of Sb. As the solubility of oxygen ion is limited in the Sb/Sb_2O_3 liquids [23], its transportation in the liquid anode is severely restricted, which in turn hampers its direct contact with carbon fuels. In a vertically positioned tubular DC-SOFC with molten Sb as an anode, the electrochemical reaction is as follow [17].

$$4/3Sb_{(l)} + 2O^{2-} \rightarrow 2/3Sb_2O_{3(l)} + 4e^- \quad (2)$$

Sb_2O_3 is electrochemically formed by the reaction between Sb and O^{2-} at the Sb/electrolyte interface. It then immigrates away from the interface to the top of the molten Sb, and finally is reduced to molten Sb by the solid carbon fuel via the following reactions:

$$C_{(s)} + 2/3Sb_2O_{3(l)} \rightarrow 4/3Sb_{(l)} + CO_{2(g)} \quad (3)$$

$$2C_{(s)} + 2/3Sb_2O_{3(l)} \rightarrow 4/3Sb_{(l)} + 2CO_{(g)} \quad (4)$$

At temperatures above 973 K, the reverse Boudouard reaction is inevitable.

$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)} \quad (5)$$

The running performance of this liquid anode DC-SOFC is dependent on these reactions. Consequently, the characteristics of carbon fuels may have a great influence on the fuel utilization and cell performance stability.

As a the supplement to fossil fuels, biomass fuels, derived from crops and plants, are an intuitive choice as they are produced by naturally-occurring photosynthesis without greenhouse gas CO_2 emission in their life cycle [24,25]. If they can be used as a direct fuel for SOFCs, a new path to high-efficient and environment-friendly utilization of vastly available biomass energy is developed [26,27]. Won et al. [28] and Su et al. [29] are among the first ones who explored bio-derived glycol and acetic acid as the fuels for SOFCs and encouraging cell performance was achieved. In the present study, two different solid biomass carbonaceous fuels, porous cocoanut active charcoal (CAC) and flaky pyrolysed corn starch (PCS), were comparatively investigated in tubular DC-SOFCs with molten Sb as the anode; the tubular cell design was selected because it has structural advantages in cell sealing, interconnecting and refueling [30,31]. In this paper, the cell performance at different temperatures was reported; the influence of fuel properties on anode reaction was discussed; and fuel utilization and cell efficiency for SOFCs with a molten Sb anode were defined.

2. Experimental

2.1. Cell fabrication

The 8 mol.% Y_2O_3 stabilized ZrO_2 (YSZ) substrate tube of the tubular cell was prepared by a slurry-casting method [32] using a ball-milled slurry containing YSZ powder (Tosoh) with mixed xylene and ethanol (Sinopharm) as the solvent and polyvinyl butyral (Sinopharm) as the binder. The prepared slurry was poured into a tubular plastic mold and degassed centrifugally at a speed of 2000 rpm for 2 min. The mold was rotated vertically on a rotating plate at a constant angular speed, while the slurry hanging on the wall was gradually dried. The YSZ green tube was detached from the mold automatically due to shrinkage, and then heated slowly to and sintered at 1500 °C for 5 h in air in a box furnace. Porous 10 mol.% Gd_2O_3 doped CeO_2 (10GDC) and LSCF-10GDC (1:1 weight ratio) layers were applied on the outer surface of the sintered YSZ tube in sequence as the baffle and composite cathode by slurry dipping and sintering in air for 2 h at 1250 and 1000 °C, respectively. Both the LSCF and 10GDC powders used in the slurries were synthesized by a wet chemical method [33,34] with metal nitrates (Sinopharm) as the precursors and ethylene diamine tetraacetic acid (Sinopharm) as the chelating agent. A scanning electron microscope (SEM, Sirion 200 and Quanta 200, FEI) was employed to examine the microstructure of the prepared cell.

2.2. Fuel characterizations

Two types of biomass carbon, CAC and PCS, were used for this study. The CAC (Sinopharm) was fabricated by pyrolyzing cocoanut shells, and the PCS was prepared by pyrolyzing fresh corn starch in-house at 500 °C in pure N_2 atmosphere for 30 min. Their crystal structure, degree of graphitization and specific surface area and microstructure were examined by X-ray diffraction (XRD) (X'Pert PRO, PANalytical B.V.), Raman spectroscopy (LabRAM HR800, Horiba JobinYvon), nitrogen adsorption analysis (Micromeritics ASAP 2020) and scanning electron microscopy (SEM, Sirion 200 and Quanta 200, FEI), respectively. The mass changes of the fuels with temperature were recorded by a thermogravimetric analyzer (TGA) (Perkin Elmer Instruments, Pyris1 TGA) in pure argon stream at 100 ml min^{-1}.

2.3. Cell testing

The CAC and PCS biomass carbon fuels for DC-SOFCs were evaluated using the prepared tubular cells in an in-house developed setup, as shown in Fig. 1. The cells, loaded with 5 g Sb powder (Sinopharm) and 2 g biomass carbon, were lap sealed to an alumina tube by using a ceramic 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) wires were used as the cathode current collector. Pure nitrogen gas was flowed at 100 ml min^{-1} into the tubular cell to prevent Re, Sb and carbon fuel from oxidation during heating from 100 to 800 °C and cell testing at temperatures between 800 and 700 °C. Pure argon at a flowing rate of 50 ml min^{-1} was used as the carrier gas for the composition analysis of the anode exhaust gas by a gas chromatography mass spectrometer (GC–MS) (Prisma-Plus, Pfeiffer Vacuum). A Solartron 1260 frequency response analyzer (Solartron Analytical) was utilized to measure the cell impedance in a frequency range between 100 kHz and 0.1 Hz with signal amplitude of 10 mV at open circuit. The current–voltage (*I–V*), current–power (*I–P*) and voltage–time (*V–t*) curves were obtained by using a Solartron 1287 electrochemical interface (Solartron Analytical) and a DC power source (IT-6720, iTech).

3. Results

3.1. Fuel properties and cell microstructure

CAC and PCS carbon powders were examined by X-ray diffraction and Raman spectroscopy, the results are shown in Fig. 2. Both CAC and PCS demonstrated characteristics of amorphous structure featured by broadened X-ray diffraction peaks (Fig. 2a). The Raman spectra showed two bands, the G (graphite) and D (defect or disorder). The G band originates from the in-plane E_{2g} phonon vibration of the sp^2-bonded carbon atoms in graphite lattice, and the D band from the vibrations of carbon atoms with dangling bonds at the plane terminations of disordered graphite [15,35]. The intensity ratio of band D and G (I_D/I_G) for CAC and PCS (Fig. 2b) was 0.98