Achieving high performance in intermediate temperature direct carbon fuel cells with renewable carbon as a fuel source

Wenbin Hao, Xiaojin He, Yongli Mi *

Department of Chemical and Biomolecular Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

HIGHLIGHTS

- Bamboo fiber and waste paper were pyrolyzed to generate bamboo carbon and waste paper carbon as anode fuels of IT-DCFC.
- Superior cell performance was achieved with the waste paper carbon.
- The results suggested the high performance was due to the highest thermal reactivity and the catalytic inherent impurities.
- Calcite and kaolinite as inherent impurities favored the thermal decomposition and the electrooxidation of carbon.

ARTICLE INFO

ABSTRACT

Three kinds of carbon sources obtained from carbon black, bamboo fiber and waste paper were investigated as anode fuels in an intermediate temperature direct carbon fuel cell. The carbon sources were characterized with X-ray photoelectron spectroscopy, thermal gravimetric analysis, etc. The results indicated that the waste paper carbon was more abundant in calcite and kaolinite, and showed higher thermal reactivity in the intermediate temperature range compared with the other two carbon sources. The cell performance was tested at 650 °C in a hybrid single cell, using $Sm_{0.20}Ce_{0.80}O_{2-x}$ as the electrolyte. As a result, the cell fed with waste paper carbon showed the highest performance among the three carbon sources, with a peak power density of 225 mW cm^{-2}. The results indicated that its inherent impurities, such as calcite and kaolinite, might favor the thermal gasification of renewable carbon sources, which resulted in the enhanced performance of the intermediate temperature direct carbon fuel cell.

1. Introduction

Direct carbon fuel cell (DCFC) has been regarded as a desirable power generation technology in the consumption of solid carbon fuels, such as coal [1]. The overall reaction in a DCFC is quite simple, as shown in reaction (1):

$$C_{(s)} + O_{2(g)} = CO_{2(g)} \qquad (1)$$

Due to the negligible entropy change of this reaction, DCFC achieves nearly 100% theoretical efficiency, which is the highest among all fuel cell types [2,3]. Another advantage of DCFC is the diversity of carbon fuels. Various feedstocks can be utilized as the fuel of DCFC, such as fossil fuels, renewable biomass and even rich carbonaceous waste [4]. In addition, DCFC consumes solid carbon to produce CO_2 in relatively high purity, which exempts the expensive gas separation process when it is collected for other applications [5].

Based on the electrolyte types, three main classes of DCFC have been developed, including molten hydroxide, molten carbonate, and solid oxide DCFC [1,6,7]. Three sub-classes of solid oxide DCFC are classified according to the differences in anode configurations. These are carbon fuel in anode chamber, carbon fuel immersed in liquid metal anode, and carbon fuel dispersed in molten carbonate (or hybrid DCFC) [8–11]. The differences in electrolytes and anode configurations of the DCFC lead to differences in the mechanism of anodic reactions, which in turn result in differences in the cell performance.

In a hybrid DCFC, the oxygen is reduced in the cathodic reaction, as shown in reaction (2) [12,13]:

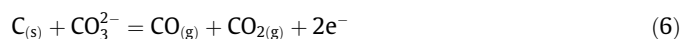$$O_{2(g)} + 4e^- = 2O^{2-} \qquad (2)$$

The mechanism of anodic reaction in a hybrid DCFC is quite complex due to the intermedia of molten carbonate. The possible reaction paths are shown in reactions (3)–(6) [14–16]:

$$C_{(s)} + 2O^{2-} = CO_{2(g)} + 4e^- \qquad (3)$$

* Corresponding author. Tel.: +852 23587127; fax: +852 23580054.
 E-mail address: keymix@ust.hk (Y. Mi).

$$C_{(s)} + O^{2-} = CO_{(g)} + 2e^- \qquad (4)$$

$$C_{(s)} + 2CO_3^{2-} = 3CO_{2(g)} + 4e^- \qquad (5)$$

$$C_{(s)} + CO_3^{2-} = CO_{(g)} + CO_{2(g)} + 2e^- \qquad (6)$$

Here reactions (3) and (4) refer to the reactions that happen at the interface of carbon/solid anode. Reactions (5) and (6) refer to the reactions that occur at the interface of carbon/molten carbonate. The generated CO can be further oxidized via reactions (7) and (8) [17]:

$$CO_{(g)} + O^{2-} = CO_{2(g)} + 2e^- \qquad (7)$$

$$CO_{(g)} + CO_3^{2-} = 2CO_{2(g)} + 2e^- \qquad (8)$$

Meanwhile, the consumed CO_3^{2-} ion can be regenerated via reaction (9), to keep the electric charge of molten carbonate in neutral [18–20]:

$$CO_{2(g)} + O^{2-} = CO_3^{2-} \qquad (9)$$

Oxygen anion produced from the cathodic reaction goes through the electrolyte membrane to sustain the reaction (9) in the anodic site.

The operation temperature also influences the cell performance of hybrid DCFCs. When the temperature is higher than 700 °C, the reverse Boudouard reaction (reaction (10)) will be favorable to consume solid carbon chemically, thus reducing the fuel utilization and overall efficiency in the system [21].

$$C_{(s)} + CO_{2(g)} = 2CO_{(g)} \qquad (10)$$

The mechanism studies concluded that the anode of the DCFC dominantly determines the cell performance, while the anode properties of the DCFC significantly depend on that of the anode fuels, which are carbon sources. In other words, the properties of carbon fuel show significant influence on the cell performance.

Many approaches, including the exploration of new carbon fuels, modification of pure carbon sources, and direct utilization of fossil fuels, have been used to investigate the influence of fuel properties. For example, in Yu's work, the pyrolytic product of corncobs was selected as the carbon fuel and an improvement in cell performance was reported [22]. Choi et al. demonstrated the use of refuse plastic and wood char as carbon fuels in their DCFC system [23,24]. Li et al. investigated the effects of catalytic gasification process on cell performance by mixing metal elements (K, Ca, and Ni) with carbon black fuel [25]. Zhu et al. evaluated the impurity effects on cell performance of raw coal, and found that MgO, CaO, and Fe_2O_3 showed catalytic properties in molten carbonate DCFCs [26]. Rady et al. managed to operate their DCFC device with brown coal (both treated and untreated), and found that the inherent inorganic species in raw coal could catalyze coal Boudouard gasification [27].

In this work, we prepared the carbon fuels by the pyrolysis of bamboo fiber and waste paper. The prepared carbon fuels were investigated using intermediate temperature direct carbon fuel cells (IT-DCFC) with $Sm_{0.20}Ce_{0.80}O_{2-x}$ (SDC) electrolyte, which is an oxygen ion conducting electrolyte used in SOFC in the intermediate temperature range [28]. Carbon black was also tested as carbon fuel for comparison. The study indicated that the inherent impurities of the carbon fuels showed catalytic properties in molten carbonate media. As a result, a great improvement in cell performance was achieved using the renewable carbon fuel generated from waste paper.

2. Experimental

Three carbon sources were studied as the anode fuel, namely carbon black (CB), bamboo carbon (BC) and waste paper carbon (WPC). Carbon black (N330) was chosen as the reference carbon source. The raw material of bamboo carbon was sourced from a kind of bamboo fiber found in Bambusa Pervariabilis. The raw material of waste paper carbon was sourced from shredded printed A4 paper (Fuji Xerox). The carbonates used in this study were bought from Sigma–Aldrich.

2.1. Preparation of the carbon fuels

Two kinds of carbon from bamboo fiber and waste paper were prepared using the pyrolytic process. The bamboo fiber was dried at 100 °C for 3 h, and further decomposed into BC at 550 °C for 10 h in a nitrogen environment [18]. The same pyrolytic procedure was applied to generate WPC. The CB, which was selected as the reference carbon source, did not receive pyrolytic pretreatment. The prepared carbons were mixed with binary carbonates (38 mol% of potassium carbonate and 62 mol% lithium carbonate) in a mass ratio of 1:1, and then ball milled in ethanol at 400 rpm for 10 h in a planet type machine (QM-3SP04, Nanjing University), respectively [29]. Finally, the acquired fine powders were dried at 75 °C in an oven for 24 h, and used as the carbon fuels directly.

2.2. Characterization of the carbon fuels

In order to determine the properties of the prepared carbon sources, a variety of techniques were applied to characterize the carbon sources, including X-ray diffraction spectra (XRD), scanning electron microscope (SEM), Brunauer–Emmett–Teller test (BET), thermal gravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). The crystallinity of the carbon was examined via Philips PW1830 powder X-ray diffraction spectrometer equipped with a Cu Kα radiation source (wavelength of 1.540562 Å) and graphite monochromator. The applied voltage and current were 40 kV and 40 mA, respectively. The scan range was from 10° to 80°. The step size and scan step time were 0.033° and 10 s, respectively. The acquired data were analyzed using MDI Jade 6.0. The SEM images were acquired to investigate the morphology information of the carbon via JEOL 7100F. The applied accelerating potential was 20 kV, and the applied working distance was 15–16 mm. The specific surface areas of the carbon were measured via Quanta chrome Autosorb-1 surface area analyzer by applying the multiple points BET equation at 77.35 K. The pore volumes of the carbon were obtained from the measured data as well. TGA was applied to investigate the thermal properties of the carbon. The weight losses of the carbon were determined using TA Instrument TGA Q5000. The experiments were carried out from room temperature to 800 °C at a ramping rate of 10 °C min^{-1} in pure N_2 environment. The surface elemental compositions of the carbon were measured by Kratos Axis Ultra DLD multi-technique surface analysis system with an Al anode source, operating at an applied power of 150 W. The XPS survey scans were acquired by passing energy of 160 eV, and then high resolution scans of the detected elements were analyzed with passing energy of 40 eV.

2.3. Cell fabrication

An anode-supported button cell was used for cell fabrication. The anode powder was obtained by ball milling nickel (II) oxide (NiO, Sigma–Aldrich) and samaria doped ceria (SDC, Fuel Cell