



Utilization of corn cob biochar in a direct carbon fuel cell



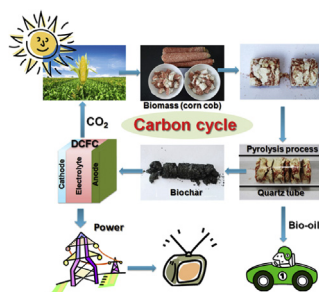
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HIGHLIGHTS

- Corn cob biochar is prepared with a pyrolysis process.
- Electrochemical performance of the biochar is examined in DCFC.
- Boudouard reaction takes part in the anode mechanism.
- Biochar is suitable for DCFC.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 27 May 2014

Accepted 19 July 2014

Available online 24 July 2014

Keywords:

Direct carbon fuel cell

Biomass

Carbon cycle

Composite electrolyte

ABSTRACT

Biochar obtained from the pyrolysis of corn cob is used as the fuel of a direct carbon fuel cell (DCFC) employing a composite electrolyte composed of a samarium doped ceria (SDC) and a eutectic carbonate phase. An anode layer made of NiO and SDC is utilized to suppress the cathode corrosion by the molten carbonate and improves the whole cell stability. The anode off-gas of the fuel cell is analyzed with a gas chromatograph. The effect of working temperature on the cell resistance and power output is examined. The maximum power output achieves 185 mW cm^{-2} at a current density of 340 mA cm^{-2} and $750 \text{ }^\circ\text{C}$. An anode reaction scheme including the Boudouard reaction is proposed.

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1. Introduction

A huge amount of biomass is produced every year by nature through photosynthesis with solar energy from CO_2 and H_2O . Biomass and its fossil deposits actually provide the basic necessities in people's daily life including food, clothe, house and medication [1]. Biomass utilization as an energy source generates significantly less CO_2 than that of fossil fuels since its formation is a part of the carbon cycle in nature [2–6]. Biomass has been converted in a number of ways to produce biofuels [7,8]. Among them, pyrolysis

has a very long history and has been improved and widely used to produce coke and charcoal [9]. In recent years, pyrolysis of biomass, a thermal decomposition process in nature, is employed to obtain bio-oil and biochar [7–9]. The bio-oil is further modified to transportation fuel and the biochar can be burned to produce electricity and heat [6]. However, the efficiency of energy utilization of biochar is low if direct combustion and thermal transformation processes are applied.

Direct carbon fuel cell (DCFC) converts the chemical energy stored in solid carbon into electricity directly without the reforming and thermal cycle processes [10–12]. The overall cell reaction of a DCFC can be considered as the electrochemical oxidation of carbon in the anode with releasing CO_2 ($\text{C} + \text{O}_2 = \text{CO}_2$). Due to a near zero entropy change ($\Delta S = 1.6 \text{ J K}^{-1} \text{ mol}^{-1}$ at $600 \text{ }^\circ\text{C}$), DCFC has a theoretical thermal efficiency approaching 100% and a practical

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efficiency of around 80% [11]. Solid carbon fuels have a wide diversity and can be derived from either fossil or bio sources. Many kinds of carbon fuels have been tested in DCFC with various configurations [13]. Cherepy et al. [10] studied the electrochemical oxidation performance of carbon fuels in a molten carbonate fuel cell (MCFC) and reported that three important factors of carbon, including crystallographic disorder, electrical conductivity and adequate reactive surface sites, influence the cell power output. Direct conversion of carbon in a solid oxide fuel cell (SOFC) has also been explored and the effect of contact between anode and carbonaceous fuels was discussed [14].

Both solid oxide and molten carbonate materials have been used as the electrolyte of DCFC. Zhu et al. [15] demonstrated the high ionic conductivity of the composite electrolytes, composed of an oxide ion conducting semiconductor and a molten salt phase, in intermediate temperature range, *i.e.* 400–700 °C. Xia et al. [16,17] utilized the composite electrolyte to compose a very efficient fuel cell with hydrogen as the fuel. Jia et al. [18] utilized further the conductivity and reactivity of the molten carbonate with nano-carbon and constructed a DCFC with an anode composed of carbon in molten carbonate suspension, which was elaborated with a kinetic model by Li et al. [19]. More recently, Jiang et al. [20] extended the concept and proposed a hybrid fuel cell utilizing a solid oxide phase as the electrolyte and a carbon in molten carbonate anode. With their configuration, the thickness of the electrolyte can be effectively reduced. In our recent works, the DCFCs with different carbon fuels have been investigated and effort was made to improve the output with modifying the configuration [21–26].

To achieve the goal of clean and efficient utilization of biomass to generate electricity, in this work, corn cob biochar is used as the fuel of the DCFC based on a composite electrolyte. The cell exhibits promising performance in a temperature range of 650–750 °C.

2. Experimental

2.1. Preparation of the fuel and the fuel cell materials

Corn cobs were broken into small pieces and pressed into pellets. The pellets were subsequently heated in a quartz tube at 700 °C in N₂ with a flow rate of 50 ml min⁻¹ (STP) for 2 h. Bio-oil and biochar were obtained during the pyrolysis process. The yield of biochar is 25 wt. % on dry base.

Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) powder was prepared with an oxalate coprecipitation method as described in previous work [16]. Li₂CO₃ and Na₂CO₃ powders with a mol ratio of 2:1 were ball milled for 4 h and then heated at 700 °C in air for 1 h to obtain a binary carbonate eutectic. SDC powder and the eutectic salt were mixed with a weight ratio of 7:3 and calcined at 700 °C in air for 1 h to form a composite material. A mixture of LiOH and NiO with a mol ratio of 1:1 was sintered at 700 °C in air for 2 h to prepare the lithiated NiO. A mixture of lithiated NiO and the composite electrolyte with a weight ratio of 7:3 was heated at 700 °C in air for 2 h to obtain the cathode material. A mixture of SDC and NiO with a weight ratio of 4:6 was sintered at 700 °C in air for 2 h to prepare the anode material.

The pellet containing an electrolyte layer and a cathode layer was fabricated with a co-pressing method followed by sintering as described in previous work [18,22]. The anode material was made into a slurry with a binder (10% ethyl cellulose + 90% terpeneol), and then screen-printed on the electrolyte layer followed by sintering at 700 °C in air for 1 h to form the three-layer cell pellet. Ag paste was coated on both sides of the pellet as the current collector. The fuel was a mixture of biochar and the eutectic salt with a weight

ratio of 1:9, which was put in the anode cavity on top of the pellet before the performance test.

2.2. Characterization

The surface morphologies of biochar and the single cell were characterized with a Hitachi S-4800 scanning electron microscope (SEM). The X-ray diffraction (XRD) pattern of the biochar was recorded with Bruker AXS, D8-S4 equipment using Cu K α radiation. Thermogravimetric analysis (TGA) of the biochar was conducted in air with a flow rate of 50 ml min⁻¹ (STP) and a heating rate of 10 °C min⁻¹ from room temperature to 1000 °C in a NETZSCH STA, 449F3 instrument.

2.3. Fuel cell test

The anode off-gas was analyzed using an online gas chromatograph (Clarus 500, Perkin Elmer) with a thermal conductivity detector. The electrochemical impedance spectroscopy (EIS) of the fuel cell was measured at open circuit voltage (OCV) in a temperature range of 600–750 °C using an electrochemical workstation (Versastat 3, Princeton Applied Research) in a frequency range of 100 KHz to 0.1 Hz. The performance of the single cell was tested in a temperature range of 600–750 °C under atmospheric pressure with a similar configuration as in the published work [18]. Nitrogen was used as the anode protective gas with a flow rate of 100 ml min⁻¹ (STP) and the cathode gas was a mixture of CO₂ (120 ml min⁻¹, STP) and O₂ (60 ml min⁻¹, STP). The heating rate of the fuel cell was 5 °C min⁻¹. The *I*–*V* characteristics of the single cell were measured with the electrochemical workstation with a scan rate of 10 mV s⁻¹.

3. Results and discussion

3.1. Properties of the biochar

Fig. 1(a) is a photo of the corn cob pieces used in this work. After pyrolysis, the biochar was obtained as shown in Fig. 1(b). The surface morphology of the biochar illustrated in Fig. 1(c) is very similar to the activated carbon from coconut used in our previous work [18]. Pores can be found on its surface, which enlarge the surface area and provide more electrochemical reaction sites.

Two weak broaden peaks are observed in the XRD pattern of biochar at around $2\theta = 24^\circ$ and $2\theta = 44^\circ$ (Fig. 2). The first peak is attribute to the (0 0 2) reflection and the other is the (1 0 0) reflection of graphite crystal. The average stacking height (L_c) and the average diameter (L_a) of biochar can be calculated according to the Scherrer equation [$L_c = 0.89\lambda / (B_{(002)} \cos\theta)$, $L_a = 1.84\lambda / (B_{(100)} \cos\theta)$], where λ is the wavelength of the X-ray beam, B is the peak width at half-maximum intensity, and θ is the Bragg angle [27]. Unlike carbons with high crystallinity such as graphite and carbon fiber, the self-made biochar has a more disordered structure (L_c is 1.1 nm and L_a is 3.8 nm). With high concentration of edge atoms, biochar is easy to be oxidized in the chemical reaction. Meanwhile, less graphitized carbon is also favorable in the electrochemical reaction for getting high performance [10,19].

A slight weight loss of the biochar below 150 °C is observed in the TGA curve (Fig. 3), which is due to the vaporization of water and other volatile substance absorbed in the sample. The oxidation of the biochar started at about 290 °C. The oxidizing rate increases with the increase of the operating temperature, and reached the maximum at 516 °C, as shown in the differential thermogravimetry (DTG) curve. Above 590 °C, the carbon in the sample was completely oxidized to CO₂, and the residual, about 3.98 wt. % of the biochar, was the ash component. Compared to the carbon materials

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