Biomass and Bioenergy 91 (2016) 250–258

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Electricity generation from corn cob char though a direct carbon solid oxide fuel cell

Qian Zhou [a], Weizi Cai [a, b], Yapeng Zhang [a], Jiang Liu [a, b, *], Lili Yuan [a, b], Fangyong Yu [a], Xiangqiang Wang [a], Meilin Liu [a, c]

[a] New Energy Research Institute, School of Environment and Energy, South China University of Technology, Guangzhou, 510006, PR China
[b] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, 510641, PR China
[c] School of Materials Science and Engineering, Georgia Institute of Technology, 771 Ferst Drive, Atlanta, GA 30332-0245, USA

ARTICLE INFO

Article history:
Received 14 February 2016
Received in revised form
26 May 2016
Accepted 30 May 2016

Keywords:
Solid oxide fuel cell
Carbon
Corn cob char
Direct carbon fuel cell

ABSTRACT

Solid oxide fuel cell (SOFC) is a potential technology for utilizing biomass to generate electricity with high conversion efficiency and low pollution. Investigations on biomass integrated gasification SOFC system show that gasifier is one of the high cost factors which impede the practical application of such systems. Direct carbon solid oxide fuel cell (DC-SOFC) may provide a cost effective option for electricity generation from biomass because it can operate directly using biochar as the fuel so that the gasification process can be avoided. In this paper, the feasibility of using corn cob char as the fuel of a DC-SOFC to generate electricity is investigated. Electrolyte-supported SOFCs, with yttrium stabilized zirconia (YSZ) as the electrolyte, cermet of silver and gadolinium-doped ceria (GDC) as the anode and the cathode, are prepared and tested with fixed bed corn cob char as fuel and static ambient air as oxidant. The maximum power output of a DC-SOFC operated on pure corn cob char is 204 mW cm^{-2} at 800 °C and it achieves 270 mW cm^{-2} when Fe of 5% mass fraction, as a catalyst of the Boudouard reaction, is loaded on the corn cob char. The discharging time of the cell with 0.5 g corn cob char operated at a constant current of 0.1 A lasts 17 h, representing a fuel conversion of 38%. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometer (EDS) and Raman spectroscopy have been applied to characterize the char-based fuels.

1. Introduction

Biomass derived from plants is an important carbon-neutral renewable energy resource [1]. It can be converted to more valuable energy forms, i.e., biogas, bio-oil, and biochar, via thermal pyrolysis [2]. Corn cob, as a kind of agricultural byproduct, is available in plentiful amount in China. The yield of corn was up to 215 million tons only in 2013 and corn cob accounts for 16–18% of corn quantity [3]. The HHV (high heating value) for biochar from corn cobs can be as high as 30.0 MJ kg^{-1}, comparable to some coals [4]. Conventionally, the energy stored in corn cob is released through combustion to get heat. As a result, hazardous products, such as SO_2 and NO_x, are formed and emitted, causing air pollution. What's more, the energy conversion efficiency is low, leading to significant waste of fuel [5]. Therefore, it is imperative to search alternative ways to convert the biomass' energy more cleanly and efficiently.

Solid oxide fuel cell (SOFC) is an energy conversion technology that converts chemical energy of fuels directly to electricity via electrochemical reactions, with high efficiency and low pollutant emission [6]. One of its advantages over the conventional electricity generation technologies is that high efficiency can be obtained with small scale [7–9]. This feature is especially important for distributed power generation using local biomass as the energy source, to avoid high cost of transportation and capital investment, caused by low energy density and seasonal availability of biomass, for large scale centralized biomass plant. There have been analyses on the feasibility of generating electricity from biomass by combining the SOFC operation and biomass gasification. Morandin et al. [8] studied a conceptual design of a biomass integrated gasification fuel cell system for small scale applications (40 kg h^{-1} woody biomass input with 50% mass fraction water content). They found that very high system efficiencies (i.e., 65%) could be obtained but

* Corresponding author.
E-mail address: jiangliu@scut.edu.cn (J. Liu).

http://dx.doi.org/10.1016/j.biombioe.2016.05.036
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only at the expense of really high system costs mainly because of the high costs of the fuel cell and of the gasifier. Jia et al. [9] investigated the effect of operating parameters on performance of an integrated biomass gasifier, SOFCs and micro gas turbine system. They pointed out that with a mass flow rate of biomass less than 20 kg h^{-1}, an electrical efficiency above 45% could be obtained. They also concluded that the cost of gasifier, with air, or oxygen, or steam as gasification agent, was the main hurdle for practical application of the biomass integrated gasification fuel cell system.

A direct carbon solid oxide fuel cell (DC-SOFC), which operates directly using biochar obtained from pyrolysis of biomass as fuel, can get rid of the high cost gasifier [10–18]. Theoretically, the electrical efficiency of a fuel cell operated directly on carbon fuel (the reaction Gibbs energy change of $C + O_2 = CO_2$, divided by the enthalpy change, ΔH, i.e., $\Delta G/\Delta H$) slightly exceeds 100% [19–22]. Besides, there is no need of any gas feeding or liquid medium for the operation of a DC-SOFC, as schematically illustrated in Fig. 1. Solid carbon is directly filled in the anode chamber as the fuel and ambient air is used as the oxidant. Actually, it is all-solid-state in configuration.

The reaction mechanism of a DC-SOFC can be described by the following two equations [10,16]:

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (1)$$

$$C + CO_2 \rightarrow 2CO \quad (2)$$

Reaction (1) is the electrochemical oxidation of CO at the anode from which CO_2 is produced. The CO_2 diffuses to the carbon fuel to perform the Bouduard reaction (2) and more CO is produced and provided for reaction (1). Thus the carbon particles don't need to have a physical or chemical contact with the anode/electrolyte interface of the cell and a fluidizing bed for carrying the carbon fuel into the cell can be designed. A peak power density of 465 mW cm^{-2} at 850 °C has been achieved with a tubular cone-shaped Ni-based anode-supported DC-SOFC [15].

Several studies have indicated that operating fuel cells directly using biochar as fuel is a feasible way to reuse agriculture residue [23–25]. Dudek et al. [23] systematically investigated the performances of SOFCs with a variety of anode materials operated on some charcoals and woodchips. In duration of their experiment, argon was continuously supplied to the anode chamber as a shielding gas. C. Munnings et al. [24] used agriculture char and coconut char as the fuel of SOFCs, with an ultra-high purity helium gas as fuel chamber purge gas. They showed that low grade unprocessed char can be used as the fuel of SOFC. However, the ash content is detrimental to the electrochemical performance of cells. As a representative of agriculture byproduct, corn cob has already been used as the raw material of char. Yu et al. [25] obtained the char from pyrolysis of corn cob. Then, they operated a direct carbon molten carbonate (liquid electrolyte) fuel cell with the char and got a peak power density of 185 mW cm^{-2} at 750 °C. During their testing, N_2 was imported into the anode chamber as protective gas. To our knowledge, there has not been any reports on applying biochar as the fuel of an all-solid-state DC-SOFC.

In this paper, we report our work on using corn cob char as the fuel of all-solid-state DC-SOFCs to achieve the goal of efficient reuse of agriculture byproduct. The property and structure of the corn cob char are examined. The performances of the DC-SOFCs are investigated through characterising the electrical power output and the stability of the cells. Thereby, the feasibility of using corn cob char as the fuel of DC-SOFCs is proved.

2. Material and methods

2.1. Preparation of corn cob char

One year old corn cobs were collected as agriculture byproduct from local farmland on 8th of August 2015 in Guangzhou, Guangdong province of China (23°5′N 113°6′E). The corn cobs were left to dry in the sun for three days and then stored in plastic bags before char production. Thermal pyrolysis technique was used to get char from the corn cobs. Some corn cobs were broken into pieces and dried at 140 °C in an oven, resulting in a mass loss of 65%. The dry pieces were put into a quartz tube with ceramic cotton on both ends (Fig. 2). The quartz tube was subsequently heated in a tubular furnace at a temperature increasing rate of 5 °C min^{-1} to 700 °C and then maintained for 2 h. As the temperature increases, pyrolysis occurred and some gaseous products were produced and evaporated. Finally, corn cob char (as a mass fraction of 27% of the dry pieces) was obtained. The corn cob char was pulverized and sieved through a 70 mesh sieve. The pictures of the corn cob and the corn cob char are shown in Fig. 3.

Fe was loaded on the corn cob char with a mass fraction of 5% to catalyze the Boudouard reaction, through an infiltration process [14]. $Fe(NO_3)_3.9H_2O$ was dissolved in deionized water and the char powder was immerged into the ferric nitrate solution with a mass ratio of C:Fe as 95:5. Then the mixture was stirred for 2 h before stewing for 12 h. Then, the mixture was heated to 80 °C to evaporate the water followed by drying at 128 °C for 1 h. Finally, the residue was heated to 500 °C and hold for 1 h under flowing nitrogen to decompose the nitrate.

2.2. Fabrication of SOFCs

The electrolyte material was Al_2O_3-doped-YSZ (the mass ratio of Al_2O_3 to YSZ was 1:99) [26]. 10 g YSZ powder (TZ-8Y, Tosoh Corporation, Tokyo, Japan), 0.1 g Al_2O_3 (Xinfumeng, China), and 6 cm^3

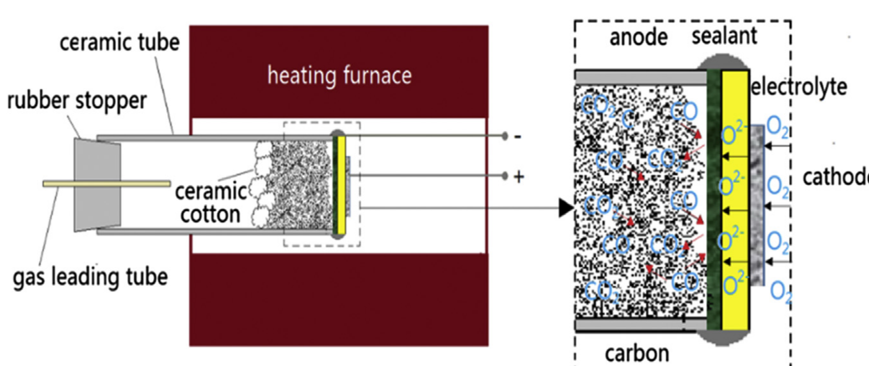

Fig. 1. Schematic illustration of a direct carbon solid oxide fuel cell (DC-SOFC).