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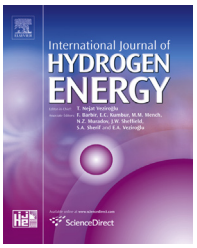

Utilization of bituminous coal in a direct carbon fuel cell

Guoyang Liu [a], *Anning Zhou* [a,*], *Jieshan Qiu* [b], *Yating Zhang* [a], *Jiangtao Cai* [a], *Yongqiang Dang* [a]

[a] *College of Chemistry and Chemical Engineering, Xi'an University of Science and Technology, Xi'an, China*
[b] *State Key Lab of Fine Chemicals, Liaoning Key Laboratory for Energy Materials &Chemical Engineering, Dalian University of Technology, Dalian, China*

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ABSTRACT

Direct carbon fuel cell (DCFC), as a high efficiency and low emissions power generation device, can convert the chemical energy stored in coal directly into electricity without combustion process. In present works, the performance of DCFC with Shenfu bituminous coal as fuel has been investigated in the temperature range 650–850 °C. It has been shown that coal composition, microstructure, chemical characteristics are closely related to the performance of DCFC. The anode solid residues have been analyzed by Fourier transform infrared spectra (FT-IR) and X-ray photoelectron spectroscopy (XPS), and the exhaust gas has been investigated by gas chromatography (GS). The results show that pyrolysis gas such as H_2, CO and short hydrocarbons (e.g. CH_4, C_2–C_4) can be used as fuels to improve the performance of DCFC. The ash of coal plays a vital role in performance of DCFC. The experimental results reveal the higher ash content in coal is; the worse the performance of DCFC is. Anode atmosphere is an important factor on affecting the performance of DCFC, and the maximum power density of DCFC can reach 31.3 mW cm^{-2} when the carrier gas is not used.

Introduction

In order to obtain better suited energy for our daily life, converting fossil fuels to obtain clean energy is usually relied on, and the coal-fired electricity generation is the most straight forward way [1]. In a long-term perspective fossil fuels are limited and if all coal, oil, and natural gas resources are consumed, a huge amount of carbon will be released into the atmosphere. In these cases, we must consider the efficiency and environmental pollution problems in the process of energy conversion. To solve these problems, a direct carbon fuel cell (DCFC) again attracted researchers' interest [2–6]. DCFC, as a power generation device with high energy conversion efficiency, low exhaust emission, high energy density and abundant fuel resources, directly convert the chemical energy into electricity through electrochemical process. In the family of DCFCs, three different concepts of DCFC based on different electrolytes have been put forward: molten hydroxide electrolyte, molten carbonate electrolyte and solid oxide electrolyte, and different electrochemical reactions occur at the anode and cathode due to using different electrolytes in DCFC [7].

* *Corresponding author*. Tel.: +86 29 85583549.
E-mail addresses: liuguoyangxust@126.com (G. Liu), psu564@139.com (A. Zhou).

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In DCFC anode, solid carbon plays an important role [2,8]. One is the solid carbon is directly converted as fuel which is in intimate contact with anode material. The other is the solid carbon is consumed via the reverse Boudouard reaction. Solid carbonaceous material, such as coal, petroleum coke, biomass, organic polymer waste and so on, can be used as DCFC fuel through simple processing, but the characteristics of carbon fuel directly affect the cell performance [8,9]. As the most abundant fuel reserve for DCFC, coal is a physically and chemically complex heterogeneous conglomerate, which contains various organic and inorganic materials [10]. For DCFC with coal as fuel, organic components in coal are the main reactants, and inorganic materials have side-effects on the anodic electrochemical reaction and the lifetime of the DCFC [3,10,11]. The chemical and physical properties, such as chemical composition, crystallinity, surface areas and surface oxygen-containing functional groups and so on, are the key influence factors for electrochemical relativities of coal DCFC. Some inorganic elements such as K, Ca, Fe, Mg, Ni etc. can weakened the carbon–carbon bonds to increase the active sites on the carbon surface, and have a catalytic effect on the electrochemical and chemical reactions. Boudouard reaction is accelerated also, so the product CO can be used as fuel to improve the cell performance. On the contrary, Al, Si have a inhibitive effect for anode reaction [3].

Various coals have been investigated in different DCFC apparatus to analyze the efficacy of coals in the anodic reaction [8]. Ju [12] have investigated the comparable performance of raw and ash-free coal in the operation of DCFC. The volatile organic compounds from raw coal can improve cell performance at low operating temperature, but ash in raw coal reveals a significant inhibition of the anode reaction surface and pore structures for the durability test. Kim et al. [13] using the ash-free coal as DCFC fuel have found that carbon in the ash-free coal is in the liquid-like state at high temperatures, which results in an increase of the cell performance. Jewulski [14] later experimenting with lignite as a fuel for direct carbon fuel cell system, has verified the existence of the ash is the key to the battery durability deterioration reasons. Meanwhile, the inherent catalytic activity of the metal species in the coal ash has been demonstrated by different prototype cells [3,12]. The metal species play the catalytic role for Boudouard gasification. CO, produced via Boudouard reaction, is the availability of reactive species at the DCFC anode, which has a significant contribution to the DCFC performance [15–17].

With coal as the DCFC fuel, pyrolysis gases from coal play an important role in the process of cell anode electrochemical reaction. CO and H_2 as the main pyrolysis gas can actively participate in the anode electrochemical reaction, and improve the cell performance [18,19]. For electrochemical conversion of short hydrocarbons (e.g. CH_4 and C_2–C_4), the catalyst is necessary [20,21].

Each coal sample has its own unique physical and chemical composition, which leads to different electrochemical reaction behaviors. The study reported in this work utilizes a bituminous coal as fuel for DCFC with YSZ as the electrolyte, and focuses on the influences of volatile matters, ash and chemical structure in coal on the cell performance.

Experimental aspects

The raw coal from Northern Shaanxi mining area was ground and sieved to 0.074 mm particle sizes. The ash was obtained by burning raw coal, and the demineralized coal was received by acid treatment. Proximate and ultimate analyses of the coal are shown in Table 1. In order to explore the thermal behavior of the bituminous coal, the weight losses of the coal was investigated by thermogravimetric analysis (STA449F3 NETZSCH) as following procedures:

P1: the pulverized coal was oxidized in air atmosphere. The temperature was heated up to 850 °C at the rate of 10 °C min^{-1} and maintained at this level for 30 min under protection N_2. Then, the sample was oxidized at 850 °C in air flowing at 30 mL min^{-1} and held for 120 min;

P2: the pulverized coal was oxidized in CO_2 atmosphere. The sample was increased to 850 °C at the rate of 10 °C min^{-1} and held at 850 °C for 30 min in the present N_2. Later, additional CO_2 was used a flow rate of 30 mL min^{-1} at 850 °C and kept for 360 min.

Pyrolysis experiments were carried out with an alumina tube reactor closed at one end and having 18 mm ID and 24 mm OD and 500 mm length. About 2.0 g coal sample was heated up from room temperature to 850 °C at a heating rate of 10 °C/min in a static argon atmosphere. The run was continued for another 30 min after the designed temperature was reached. The gaseous products were collected by an air pocket and the carrier gas was argon with a flow rate of 100 mL/min. Distribution of gaseous products was analyzed by Agilent 7890A gas chromatograph equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID).

The surface elemental composition of the raw coal and resulting solid products were measured by XPS (Kratos Axis Ultra DLD). The XPS spectra were obtained using a monochromatic Al Ka X-ray (1486.6 eV) source operated at 150 W (15 kV, 10 ma). Survey spectra were carried out over the binding energy range 0–1200 eV at pass energy (PE) of 50 eV and resolution 1 eV. XPS data analysis contained a background subtraction and peak separation using CasaXPS™. All binding energies were referenced to C(1s) at 284.6 eV. FT-IR was performed on a PerkinElmer Spectrum GX, with spectral range of 400–4000 cm^{-1} at 2 cm^{-1} resolution. Each sample was ground and mixed with KBr up to 0.4 wt.% and then pressed into a sheet.

Yttria-stabilized zirconia (YSZ, from Shanghai JEFU industrial co., LTD, 100 nm) was used as the electrolyte material. The YSZ powder (1.5 g) was uniaxially pressed in a piece at 25 MPa for 30 min. The greenware was then sintered at 1500 °C

Table 1 – Analyses of the raw coal.

Proximate[a]/wt%				Ultimate[b]/wt%				
M	V	A	FC	C	H	O	N	S
3.29	27.42	4.27	65.02	81.78	4.79	11.95	1.1	0.38

[a] As received.
[b] Dry-ash-free basis.

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