Journal of Power Sources 281 (2015) 350–361

Contents lists available at ScienceDirect

Journal of Power Sources

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

Investigation of chemical and electrochemical reactions mechanisms in a direct carbon fuel cell using olive wood charcoal as sustainable fuel

Amal Elleuch [a], Kamel Halouani [a, *], Yongdan Li [b]

[a] UR-Micro Electro Thermal Systems, National Engineering School of Sfax, University of Sfax, IPEIS, BP: 1172, 3018 Sfax, Tunisia
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science and Technology, State Key Laboratory of Chemical Engineering (Tianjin University), School of Chemical Engineering, and Technology Tianjin University, Tianjin 300072, China

HIGHLIGHTS

- DCFC fueled by olive wood charcoal was tested and cell performance was proved.
- Thermochemical decomposition mechanisms of carbon–oxygen groups were analyzed.
- Complex chain gasification reactions of ligno-cellulosic fuel were confirmed.
- $CO/H_2/CH_4$ oxidation was proved at the olive wood charcoal/carbonate anode mixture.
- OCV is independent of temperature and Boudouard reaction is ignored until 700 °C.

ARTICLE INFO

Article history:
Received 11 November 2014
Received in revised form
26 January 2015
Accepted 28 January 2015
Available online 3 February 2015

Keywords:
Olive wood
Biochar
Direct carbon fuel cell
Chemical mechanisms
Performance

ABSTRACT

Direct carbon fuel cell (DCFC) is a high temperature fuel cell using solid carbon as fuel. The use of environmentally friendly carbon material constitutes a promising option for the DCFC future. In this context, this paper focuses on the use of biomass-derived charcoal renewable fuel. A practical investigation of Tunisian olive wood charcoal (OW-C) in planar DCFCs is conducted and good power density (105 mW cm^{-2}) and higher current density (550 mA cm^{-2}) are obtained at 700 °C. Analytical and predictive techniques are performed to explore the relationships between fuel properties and DCFC chemical and electrochemical mechanisms. High carbon content, carbon–oxygen groups and disordered structure, are the key parameters allowing the achieved good performance. Relatively complex chain reactions are predicted to explain the gas evolution within the anode. CO, H_2 and CH_4 participation in the anodic reaction is proved.

1. Introduction

The Direct Carbon Fuel Cells (DCFCs) have attracted growing attention nowadays as an efficient generator of electrical power. It has the advantages of a near 100% thermodynamic efficiency and a practical efficiency of about 80% far higher than hydrogen fuel cell technologies and coal fired generator. The overall process of generating electricity by a DCFC system is relatively simple compared to other fuel cell technologies and does not require expensive preparation of any gaseous fuel, as well as accepts a variety of carbon-rich materials (coal, graphite, carbon black, coke, active carbon, etc.) as potential fuels. This cell is an interesting system because it offers the possibility to use, as fuel source, available and abundant raw materials with only minor pretreatment. DCFCs convert directly the chemical energy of carbon without a reforming process. Most fuel materials used in DCFCs are carbon based granular activated carbon (AC) [1–4] or graphite (Gr) powders [1,5–7] because AC has a high degree of micro-porosity surface area and catalytic activity, and Gr are less expensive with higher conductivity, even though the internal surface area is lower. Both are manufactured using two-step process. The cost of AC and Gr is averaged to be between 500 and 2500 US\$ ton^{-1} but is still considered high for large scale applications. Apart from cost, the life-cycle impact of these carbon-rich materials can be significant

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* Corresponding author.
E-mail address: Kamel.Halouani@ipeis.rnu.tn (K. Halouani).

http://dx.doi.org/10.1016/j.jpowsour.2015.01.171
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depending on feedstock choice and manufacturing process. For example, AC is most commonly manufactured from non-renewable coal or petroleum along with a secondary thermal or chemical activation. Gr can be mined from natural deposits or synthetically manufactured through the thermal treatment of carbon based materials. Such feedstock extraction and manufacturing methods for industrial AC and Gr production is energy intensive consumer and result in the release of environmental pollutants, including CO_2 and other greenhouse gases.

In the context of developing cost-effective and environmentally friendly carbon fuel material for DCFCs, biomass-derived charcoals could be a promising option. Charcoal is generally a by-product of one-step thermal decomposition of biomass and has been widely used as an agricultural amendment to improve soil fertility. Lignocellulosic biomass is a mixture of hemicellulose, cellulose, lignin and minor quantities of minerals. Each of these components degrades at different rates and by various mechanisms and pathways. The rate and extent of decomposition of each of these components depends on the process parameters such as reactor design, temperature and biomass heating rate [8]. Slow pyrolysis process (carbonization) is the most common way to generate charcoal from biomass feedstock. Carbonization involves a cracking process on the polymeric structure to convert the biomass into charcoal and volatile matter in inert atmosphere. It is generally assumed that the charcoal yield is expected to increase as the heating rate becomes lower. For this reason, slow pyrolysis processes, in which the fuel material is heated at a rate usually ranged from 5 to 30 K min^{-1}, are preferred over other thermo-chemical processes for producing charcoal [9].

Because charcoal is generally produced from locally available biomass, such as agricultural and forestry residues, costs associated with feedstock purchasing, extraction and transportation are greatly reduced. In return, charcoal is a cost competitive over AC and Gr carbon fuels with prices ranging from 51 to 381 US\$ $ton^{-1,}$ nearly ten times less than AC and Gr [10]. There have been several recent studies demonstrating the potential of AC and Gr in DCFC systems. Different electrolyte concepts including molten hydroxide, solid oxide ceramic, molten carbonate and composite electrolyte have been investigated. Although there are several papers on DCFC, the number of studies about the feasibility of using biomass as feedstock for the production of DCFC's fuels is limited.

Kacprzak et al. [11–13] successfully demonstrated the potential of a DCFC with molten hydroxide electrolyte to be operated with biochar materials issued from apple, energetic willow, sunflower husks and pine. Biochars were characterized by quite good values of power densities between 18.3 mW cm^{-2} and 22.4 mW cm^{-2}. They demonstrated that larger pores (pore size > 0.1 μm) is at the origin of this performance by allowing higher contact surface with the electrolyte.

Dudek et al. [14] performed series of tests for various button DCFCs (2 cm^2 surface area) with the same solid oxide electrolyte (8YSZ) and cathode (LSM-GDC) supplied by commercial charcoals. They showed that charcoals are suitable and attractive fuels for the DCFC providing sufficiently higher power density (50–100 mW cm^{-2}) under load. They also verified the reliability of the obtained data through a scaling-up methodology using a larger DCFC of 13 cm^2 active area.

Alexander et al. [15] tested the conversion of pulverized samples of charred biomass from rice straw, wood (pine bark), almond shell, and corn stover within a solid carbon fuel cell (SCFC) using a YSZ solid oxide electrolyte. Measurements of cell performance indicated peak power densities of 34–39 mW cm^{-2} for the biomass fuels, which compared favorably with a peak power density of 38 mW cm^{-2} for an activated carbon fuel used for benchmarking purposes. Open circuit cell voltages (*OCV*s) against air for all solid fuels tested at 900 °C were in the range 1.00–1.07 V, in good agreement with expected theoretical values. In addition, a kinetic model of the corn stover bed in the SCFC system was developed in order to determine the operational space for a DCFC device. Results showed that the high reactivity of the corn stover char overcomes its low specific surface area compared against activated carbon, allowing the corn stover bed to support current loads exceeding 500 mA cm^{-2} with a high effective char utilization and minimal bed height.

Munnings et al. [16] assessed the viability of using both high grade (coconut char used for the processing of ceramics) and low grade (agricultural waste derived bio-char used for soil enrichment) biomass derived fuels in a novel solid state direct carbon fuel cell. The bio-char gave the highest *OCV* (1.07 V) but the lowest overall peak power density. This high *OCV* is most likely due to the presence of CO which can form in-situ from the decomposition of oxygen-containing ash components (such as Fe_2O_3) or via the Boudouard reaction during the cell operation. Although initial power densities were low, significant improvements to fuel cell materials and designs can lead to practical devices operated with biochars.

Ahn et al. [17] investigated the utilization of wood biomass char in a DCFC system. The delivered power density of the char presents 63%–71% of the power density level of coal under similar experimental conditions. This limitation is found at higher current density and it is related to the low carbon content (21.44 wt%) and to the weak amorphous structure of the char. The low carbon content could be related to the pretreatment process of the wood biomass which is performed at 623 K of nitrogen gas for 20 min in order to remove most of the volatile matters. The char properties do not permit the maintaining of the potential level at the high current density.

Refuse fuels such as refuse derived fuel (RDF) and refuse plastic/paper fuel (RPF), which are pellets made from urban wastes, have been also tested as fuel in DCFC system by Ahn et al. [18]. Despite their significant low carbon content, these renewable fuels exhibited a maximum power density level up to 43–62% compared to that of coals. The surface area and pore size showed an influence on the wetting ability of the molten electrolyte through the porous structure of the RDF/RPF fuels, which affected the maximum power density in the DCFC system.

Many research groups have studied the impact of gases on the electrochemical reactions in direct carbon fuel cell systems using temperature programmed desorption method (TPD). TPD is a commonly used technique to provide the amount, stability, and nature of carbon surface oxygen complex. During the TPD process the surface complexes would release CO_2 and CO at different temperatures. In general, CO_2 evolves from the decomposition of carboxylic acid functionality at low temperatures and/or lactones at high temperatures, while CO arises from the phenols and carbonyls at high temperature. Although it is difficult to directly retrieve information about the exact type of surface functional group, the general information on surface reactive sites can be derived from the TPD profiles [2–3]. Li et al. [3] demonstrated that the electrochemical reactivity of several carbon fuels (coals, AC) was broadly aligned with the concentration of oxygen containing functional groups on the surfaces of the carbon fuels.

Chien et al. [19] studied the effect of Boudouard reaction on the performance of Ni/YSZ anode supported DCFC powered by coconut coke fuels at 800 °C. The obtained high cell performance was attributed to the increasing extent of electrochemical oxidation of CO, a product of Boudouard reaction.

The contribution of CO oxidation to current generation was estimated to 66% with an inert carrier gas flow rate of 50 ml min^{-1}. The pulse transient studies revealed that CO and CO_2 can displace