



The anodic reaction zone and performance of different carbonaceous fuels in a batch molten hydroxide direct carbon fuel cell



Liang Guo*, J.M. Calo, Clare Kearney, Pengpeng Grimshaw

School of Engineering, Brown University, Providence, RI 02912, USA

HIGHLIGHTS

- Three phase fuel-anode-electrolyte interface reaction zone in DCFC.
- Linear $V-i$ behavior indicative of ohmic-controlled polarization.
- Significant contribution from fuel-anode contact resistance.

ARTICLE INFO

Article history:

Received 21 October 2013

Received in revised form 20 April 2014

Accepted 4 May 2014

Available online 21 May 2014

Keywords:

Direct carbon fuel cell (DCFC)

Packed-bed anode

Reaction zone

Particulate carbonaceous fuels

Coals

Activated chars

ABSTRACT

Results are presented of an analysis of the nature of the reaction zone in the anode of a direct carbon fuel cell (DCFC). Five different types of particulate carbonaceous fuels were investigated, including nonconductive as-received coals, and more conductive pyrolyzed coal chars and an activated charcoal. All the fuels exhibited linear voltage–current density behavior indicative of ohmic-controlled polarization. The two as-received coals (Pittsburgh No. 8 bituminous coal and Beulah-Zap lignite) exhibited greater open-circuit voltages (OCV) of ~ 1.2 V than their corresponding pyrolyzed forms and the activated charcoal, the latter of which were all *ca.* 1.0 V. It was also found that differences in electrochemical reactivity of the as-received and pyrolyzed coal fuels correlated with their thermal heating values. Even so, maximum power and current densities were comparable for all the particulate fuels investigated, irrespective of the conductivity of the fuel particles. Based on fuel characterization and performance data, it is concluded that the electrochemical reaction zone in packed-bed anodes of the type examined here is limited to the three-phase solid fuel-anode–molten electrolyte contact zone. This intrinsic characteristic represents a limitation on the electrochemical performance of these types of DCFCs, in comparison to other fuel cells with fluid fuels.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The direct carbon fuel cell (DCFC) can be used to generate electricity directly from almost any carbonaceous fuel, including carbonaceous waste materials [1–3], graphite [4,5], charcoals [6,7], carbon blacks [8], carbon fiber [9], and coals [10–13]. Interest in the DCFC is driven primarily by its high theoretical efficiency, concentrated CO₂ product stream, and the high energy density of solid carbonaceous fuels [14–16]. Due to its relatively low cost and abundance, in 2013 coal was used to generate about 43% of the electricity consumed in the United States, with the electric power sector accounting for about 93% of total U.S. coal consumption [17]. Because of well-known characteristics of coal-fired power plants, such as relatively low efficiencies, considerable

contributions to greenhouse gas emissions, acid rain, and particulate and heavy metal pollution, improvement in coal utilization technology remains an important issue. Vutetakis et al. investigated electricity production in DCFCs from coals [13]. Cherepy et al. concluded that electrochemical reactivity of carbons are related to their crystallographic disorder, and that less ordered carbons are more reactive, both chemically and electrochemically [18]. Li and coworkers reported that the electrochemical performance of coals in DCFCs is highly dependent on properties such as chemical composition, surface area, concentrations of oxygen surface functional groups, and the nature of mineral matter [10,11]. It has been shown that the performance of an almond shell biochar as an electrochemical fuel is highly dependent on its intrinsic physico-chemical properties, such as chemical composition, surface area, mineral matter content, and oxygen functional group concentrations [3]. Based on a model of electrochemical oxidation of carbon in a fuel cell anode, Li et al. concluded that carbon fuel reactivity depends strongly on its structure and crystallite size

* Corresponding author. Address: Box D, School of Engineering, Brown University, Providence, RI 02912, USA. Tel.: +1 401 863 5227.

E-mail address: liang_guo@brown.edu (L. Guo).

[19]. Both the form and function of the carbonaceous fuel is also an important consideration for efficient DCFC operation. Solid carbon anodes, such as graphite and coal-derived rods [12,20], serve simultaneously as the fuel and current collector. However, their relatively low surface areas, associated purification and production costs, reduced structural stability in molten electrolytes due to dissolution of binder materials [12,21], and problems associated with continuous refueling, are significant disadvantages. Particulate carbonaceous fuels offer greater interfacial surface area, ease of handling, less costly preparation, and the possibility of continuous dry or hydrodynamic feeding, making them more practical for large-scale fuel cell applications. Different types of particulate carbonaceous fuels (e.g., biomass [22], solid waste [22,23], coals [5,10,11,24], graphite [4,25]) have been used in various DCFC studies.

Maximum power densities of DCFCs typically lie in the range of 17–141 mW/cm² at 500–800 °C [3,10,11,16,18,22,26–28] which is one to several orders of magnitude less than for other types of fuel cells employing gaseous fuels, such as PEMFCs [29,30]. In addition to microstructural properties, chemical composition, and mineral matter, the effectiveness of solid–solid contact in the anode is believed to be primarily responsible for this difference in performance.

There are only a few experimental and modeling studies on the effects of contacting in the anode and the reaction zone in the DCFC [31–33]. Li et al. reported that the fuel–anode contact has a significant effect on electrochemical reactions and performance in a solid oxide DCFC at 800 °C [31]. In this case, the thermally deposited carbon was close enough to the three-phase boundary so that the electrochemical oxidization of the deposited carbon could easily take place, while the other two types of contact anodes used carbon monoxide gas as fuel instead of solid carbon. Using a one dimensional model of the anodic reaction zone, Chen and Selman concluded that the active zone is mostly located in the portion of the anode bed nearest the electrolyte matrix, and that the active zone of a 4-cm high anode bed occupied only ~30% of the total height [32]. Another recent publication focused on the development of a two-dimensional model of a 20 mm diameter, laboratory-scale, planar DCFC, taking into account the electrochemical mechanisms and mass and heat transfer over the entire cell, and it is reported that DCFC output is sensitive to electrolyte porosity and anode specific surface area [33]. Using single cell DCFC experiments, these same workers showed that polarization of the anode dominates the total cell polarization [34]. Li et al. also simulated the performance of DCFC with a mathematical model, and concluded that the reaction surface area and the transport path are among the most important factors [35].

In the current work, an experimental analysis of the anodic reaction zone is presented via comparison of the behavior of selected nonconductive and conductive solid carbonaceous fuels. The electrochemical performance of particulate, as-received coals (bituminous and lignite), pyrolyzed derivatives of the same, and an activated charcoal were compared in a batch, molten hydroxide DCFC in order to explore the nature of the reaction zone in packed-bed anodes. The major conclusion of this work is that the electrochemical oxidation reaction in the packed bed anode is restricted primarily to the local interface between the solid fuel particles and the anode, which is unaffected by the fuel conductivity.

2. Materials and methods

2.1. Fuel characterization

The carbonaceous fuels used in the current work include particulate activated charcoal (AC), Sigma–Aldrich C-3014, C-2889, and

C-2764, with nominal particle sizes of 0.354–0.595 mm (30–45 mesh (USA)), 0.853–2.38 mm (8–20 mesh (USA)), and 1.40–4.75 mm (4–14 mesh (USA)), respectively. As-received Pittsburgh #8 bituminous coal (ARP8) and Beulah-Zap lignite (ARB) (Argonne Premium Coal Sample Bank – APCS [36]) were ground in a ceramic mortar and pestle, and then sieved. Proximate and ultimate analyses of the two coals are presented in Table 1. In addition, samples of these coals were placed in ceramic boats in a tube furnace and pyrolyzed in flowing helium (600 mL/min). Samples were heated for about an hour to 1000 °C and then maintained at this temperature for 90 min. The resultant materials were designated as PP8 and PB, respectively. A graphite sheet (GR) (McMaster) with surface area of 5.4 cm² was also used as a reference fuel in the current work.

The DC electrical resistivity of the particulate fuel samples was determined by measuring the ohmic resistance of packed beds of the materials (~100 mg) in a vertical plastic tube held between two copper rods, 0.32 cm² in cross sectional area, *A*. Constant positive contact of the sample bed with the copper rods was maintained by placing a 250 mg weight on the top rod. The apparent electrical resistivity, ρ (Ω cm), was calculated from $\rho = RA/l$, where *R* is the measured DC resistance, and *l* is the sample thickness.

Fuel wetting was characterized by measurement of the average advancing contact angle of the molten sodium hydroxide electrolyte with fuel particles using a capillary rise method [37,38], based on recording the total bed weight during capillary rise of the molten electrolyte through a packed bed of the particulate fuel as a function of time with a Sartorius microbalance (Sartorius CP|Gem^{plus} Series, GCA2502). The apparatus, experimental procedures, and data analysis are described in another publication [39].

The morphology of fresh and spent particulate fuel samples was examined with SEM (LEO 1530-VP).

The pyrolysis behavior of the coal samples was examined in a downflow thermogravimetric analyzer. ~20 mg of the samples were charged to quartz cone-shaped sample buckets suspended from a microbalance (Cahn D-200 digital recording balance) in a cylindrical quartz hangdown tube.

For ARP8, evolution of volatile material commenced at about 400 °C and ~25% of the original mass was lost by 500 °C. The proximate analysis data in Table 1 indicates that about 40% of ARP8 is volatile (~37.2% VM and 1.65% moisture). Therefore, by 500 °C in the TGA, there was still ~15% of volatile material remaining in the coal. This is close to the 11% mass loss from ARP8 observed from 500 to 800 °C in the TGA measurements. Similar results were obtained for ARB, such that there was about 11% of residual volatiles remaining at 500 °C.

2.2. The batch fuel cell and electrochemical measurements

The batch molten hydroxide direct carbon fuel cell apparatus and experimental procedures are described in detail in a previous publication [26]. A high-form alumina crucible (100 mL, Ceramic Solutions, Inc.) was utilized as the fuel cell container. Two different types of anodes were investigated: a “tea-bag” anode (TBA) made from nickel mesh (100 mesh, 0.1 mm diameter wire; Alfa Aesar) mounted on a Ni–Cr (80–20%) wire frame (1.0 mm diameter wire,

Table 1
Proximate and ultimate analyses of Pittsburgh #8 and Beulah lignite coals [27].

Coals	Ash	Water	Volatile matter	Fixed carbon	Ultimate analysis (MAF)				
					C	H	O	S	N
Pittsburgh #8	9.2	1.65	37.2	52.0	83.2	5.3	8.8	2.2	1.6
Beulah	6.6	32.2	30.5	30.7	72.9	4.8	20.3	0.5	1.2

Download English Version:

<https://daneshyari.com/en/article/242696>

Download Persian Version:

<https://daneshyari.com/article/242696>

[Daneshyari.com](https://daneshyari.com)