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The effect of fuel type on the performance of a direct carbon fuel cell with molten alkaline electrolyte

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HIGHLIGHTS

- The effect of nine carbonacious fuels on the operation of a DCFC was investigated.
- The tests were performed at 723 K and the air flow rate of 0.5 dm^3 min^{-1}.
- Binary eutectic mixture of Na/Li hydroxides was used as electrolyte.
- The results for a biochar fuel were similar to those obtained for hard coals.

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ABSTRACT

In the paper the behavior of various carbon-rich materials used as fuels for the direct carbon fuel cell (DCFC) with molten hydroxide electrolyte is presented. For the current research various carbonaceous fuels (e.g., different biochars, hard coal, graphite, carbon black) were tested. The electrolyte was the binary eutectic mixture of sodium and lithium hydroxides (90 mol.% NaOH – 10 mol.% LiOH). The fuel cell was operated at 723 K and cathode air flow rate of 0.5 dm^3 min^{-1}. The maximum power densities were achieved for raw coal and commercial biochar and made up 38.6 mW cm^{-2} and 32.8 mW cm^{-2}, respectively.

1. Introduction

The increase of human population, as well as the rapid economic growth and development require safe, trustable, and continuous supply of electricity. Despite the current policy and political situation focused on the promotion of energy conversion from renewable sources [1,2], still the majority of electricity roughly 67% is generated from non-renewables, such as coal (41%), crude oil (4%), or natural gas (22%) [3]. In some countries, e.g., Poland, China, South Africa, or Australia, coal is still the dominant fuel for electricity generation in domestic power plants [3,4].

Since the burning of coal and electricity generation in conventional power plants is often associated with quite low efficiency (30–45%) and brings about significant emissions of pollutants (SO_2, NO_x, particulates, as well as CO_2), numerous attempts have been made to search for new highly-efficient and low emission technologies of electricity generation [5]. One of the promising approaches to improve the efficiency of energy conversion from coal is the use of fuel cells, such as e.g., the Direct Carbon Fuel Cell (DCFC). The schematic of the DCFC operation is shown in Fig. 1. In the DCFC system the electrochemical reaction between the elemental carbon and oxygen is the source of electrons which pass through the external circuit and generate electricity.

This technology may significantly reduce the energy losses by direct conversion of solid carbon chemical energy into electricity [6]. The DCFC technology has been under investigation for several decades but, so far, has received less attention than fuel cell technologies focused on the use of hydrogen or natural gas. However, the DCFCs have two significant advantages over other fuel cells, since 1) their thermodynamic efficiency may theoretically exceed 100% i.e., much higher than that of e.g., hydrogen fuel cells where

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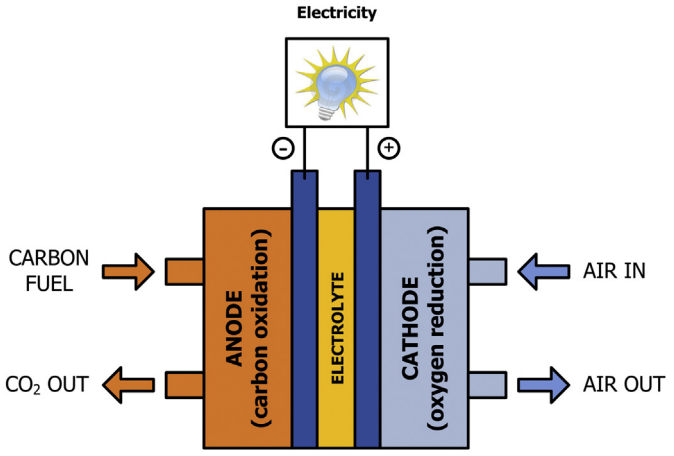

Fig. 1. The schematic of DCFC operation.

the efficiencies of roughly 83% have been reported [7], and 2) the DCFC may be fueled with any carbonaceous and solid (and thus easy to transport and store) fuel, such as e.g., hard coal, lignite, petcoke, biomass, or even carbonized waste [8]. Although the thermodynamic efficiency of the DCFC (η_{th}) calculated by Eq. (1). may theoretically exceed 100% since the oxidation of elemental carbon into gaseous CO_2 is accompanied by almost no entropy change ($\Delta S = 1.6\ J\ K^{-1}\ mol^{-1}$ at 873 K) practical operational efficiencies of the cells are lower and estimated at roughly 80% [6].

$$\eta_{th} = 1 - \frac{T\Delta S}{\Delta H} = \frac{\Delta G_{700K}}{\Delta H_{700K}} = \frac{-395.4\left[kJmol^{-1}\right]}{-394.0\left[kJmol^{-1}\right]} = 1.003 \qquad (1)$$

So far, three different electrolyte concepts (molten hydroxide, molten carbonate or solid oxygen ion conducting ceramic) have been proposed for the DCFC technology [8]. Although, there are several papers on the DCFC issue the number of publications where the authors focus on the investigation of the DCFCs operation with aqueous hydroxide or molten hydroxide electrolytes is quite limited [9–12]. The results reported by Nunoura et al. [12] indicated that aqueous electrolyte provided the conditions for low-temperature operation of the cell (423–523 K) and thus the possibility to use cheaper materials for the cell body. Nunoura et al. [12] used a corncob biochar fueled cell with potassium and lithium hydroxide mixture electrolyte operated at 518 K and 35.8 bar pressure but reported the maximum power density of only 6.5 mW cm^{-2}.

In order to improve the cell performance and electricity yield the molten hydroxides are required. Zecevic et al. [9,10] in cooperation with the West Virginia University [11] reported stable performance of the cell, and the power density of 58 mW cm^{-2} for MARK III-A prototype. Unfortunately, they only focused on the use of some specially prepared carbon rods of graphite and coal origin, and tested no granulates.

Since except for just a few cases [13,14] there has been no information so far, on the experiments where the authors would investigate the possibility to operate the DCFC with minimum fuel preparation (e.g., no rods manufacturing) and with granulate carbonaceous fuels, particularly of biomass origin, the intention of this paper is to provide some experimental data on that issue and report the results of a DCFC operated with various granulate carbonatious fuels, such as biomass-derived biochars, hard coals, carbon black, and graphite.

2. Experimental

2.1. Fuel samples

Nine types of various carbonaceous fuels, i.e., commercial graphite, carbon black (type N220, Konimpex), two types of commercial hard coal and five types of biochar were used for the present investigation. Four of the fuels were produced by the authors from the carbonization of various biomass types (apple tree chips, sunflower husks, pine and energetic willow shavings) while the fifth sample was a commercial biochar. In order to produce the biochars from the 'raw' fuels the biomass samples were crushed, then sieved (particle size <0.5 mm), and finally charred at 873 K for 30 min. The details of the carbonization technology were described elsewhere [15,16].

All fuel samples were analyzed according to Polish standards with respect to their ultimate and proximate analysis. The ultimate analysis was conducted with the use of Leco TruSpec CHNS analyzer, while automatic isoperibol calorimeter (IKA C2000 Basic) was used to determine the higher heating values (HHV) of all the samples. Mercury intrusion porosimeter (Poremaster 33, Quantachrome) was used to determine total surface area and pore volume of the samples, as well as to investigate their pore size distributions. The data provided by the porosimetry is important since those parameters are directly related to the wet-ability, electrochemical reactions of fuels and the performance of the DCFC unit [17]. The information on the pore size distribution is also crucial particularly for the operation of the DCFC with molten electrolyte because the size of the carbon particles affect their surface area and the possibility to be fully wetted by the electrolyte [17].

All the analyses were conducted for samples of particle size less than 0.2 mm except the porosimetry investigations where the samples of particle sizes of 0.18–0.25 mm were used. The results of the analyses are summarized in Table 1. The carbon content in all the fuels exceeds 80%. The surface area differs significantly—the measured values vary from 0.2 $m^2\ g^{-1}$ (graphite rod) to over 31 $m^2\ g^{-1}$ for carbon black.

The pore size distributions of the fuel samples are shown in Fig. 2. The investigations were determined with the use of mercury porosimeter Poremaster 33. The pore size distribution of the sample is represented as dV/dlog D where V corresponds to the cumulative pore volume and D is the pore diameter. The results indicate that in all cases the majority of the pores for biomass-derived biochars (2–6) are characterized by diameters of roughly 0.1–10 μm. In the case of hard coals (7, 8) and carbon black (1) the pore size distributions were quite narrow and, furthermore, the majority of the pore volume peaks corresponded to the pores less than 0.5 μm. The graphite sample (9) showed two separate peaks at 0.07 μm and 1 μm.

2.2. The DCFC

The schematic diagram of the designed fuel cell is shown in Fig. 3. The cell was manufactured from nickel and nickel alloys. The main cell container (83 mm i.d. and roughly 147 mm high) was manufactured from Nickel® 201. The anode was also made from Nickel® 201, while the cathode was Ni-based Inconel® alloy 600. The anode and cathode were designed as pipes with outside diameters of 19.1 mm and 42 mm, respectively. Both electrodes were subjected to simultaneous oxidation–lithiation process before their implementation into the DCFC. The current and power densities were calculated for the measured anode surface area of 17 cm^2. The anode and cathode were separated in order to prevent any mixing at the gases (CO_2 above the anode and excess air above the