

The effect of coal thermal pretreatment on the electrochemical performance of molten hydroxide direct carbon fuel cell (MH-DCFC)

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Abstract

The direct carbon fuel cell (DCFC) is a power generation device that converts the chemical energy of carbonaceous fuels (e.g. fossil coals, charred biomass, activated carbons, graphite, coke, carbon black, etc.) directly into electricity. However, the use of coal in the DCFC is sometimes problematic particularly if volatile matter evolves from the fuel during fuel cell operation. The recommended course of action to minimize that problem is to pre-treat thermally or even pyrolyze the coal and remove the volatiles before the fuel is used in the fuel cell. In this paper, three raw and thermally-treated coals of various origins have been compared for electrochemical activity in a direct carbon fuel cell with molten hydroxide electrolyte (MH-DCFC). The thermal pre-treatment of selected coals was carried out in an inert gas atmosphere at 1023 K. It was found that—compared to raw coals—the pyrolyzed coals presented lower maximum current and power densities at 723 K but simultaneously provided faster stabilization of the open circuit voltage.

Keywords: Direct carbon fuel cell; molten hydroxide electrolyte; coal; thermal treatment

1. Introduction

Coal is an abundant fuel source that is relatively inexpensive, easy to transport and can be converted into electricity by various energy conversion technologies, such as coal-fired power plants. However, the use of coal for power generation is associated with a number of environmental challenges, primarily emissions to the atmosphere such as SO_2 , NO_x , fly ashes, mercury (Hg) and others. Therefore new technologies are sought, out of a desire to improve the environmental performance of coal-to-energy conversion. One such technology is the direct carbon fuel cell (DCFC)—a power generation device converting the chemical energy of carbon directly into electricity. No combustion or gasification processes are involved, as the energy is converted through direct electrochemical oxidation of the fuel. The basic structure of the DCFC is similar to other cell types, such as the molten carbonate fuel cell (MCFC) or the solid oxide fuel cell (SOFC). However, in DCFC technology solid carbonaceous fuels are used and directly oxidized at the anode surface and no clean gaseous fuels (e.g. H_2 or CO) are required, as is the case with MCFCs or SOFCs. There are four basic types of DCFC under development, which

generally differ as to electrolyte types: molten carbonates (MC-DCFC) [1, 2, 3, 4], solid oxygen ion conducting ceramics (SO-DCFC) [5, 6, 7], aqueous [8] or molten hydroxides (MH-DCFC) [9, 10, 11, 12, 13, 14]. Composite electrolytes (termed 'hybrid electrolytes') are also widely used in DCFC prototypes (H-DCFC) [15, 16, 17]. Compared to other technologies solid carbon fuelled fuel cells have several unique features and advantages, offering higher thermodynamic efficiency, lower emission of carbon dioxide per unit of the generated electricity and no emissions of SO_2 , NO_x , particulate matter, mercury and other trace element pollutants. Furthermore, one of the advantages of DCFC is its fuel flexibility. Moreover, carbon fuel does not require any sophisticated preparation, since the solid carbon (primarily elemental carbon, which is a basic fuel for DCFC) can be easily obtained from various resources such as coal, lignite, petroleum coke and charred biomass (e.g. grass, wood, nut shells, corn husks or even organic wastes) [2, 3, 6, 7, 13]. Coal fuels have various properties that could affect the DCFC working characteristics, such as microstructure, carbon and sulfur content, volatile matter and impurities such as mineral substances (ash). In previous research, testing was carried out on the use of coals directly on the anode surface in the different DCFC prototypes with various electrolytes and configurations. Li et al. [18] investigated the relationship between

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microstructure, surface chemistry, and electrochemical performance of coal as a fuel for the MC-DCFC. They found that the treatment of coal with acid enhanced its electrochemical reactivity, due to the increase of oxygen-containing surface functional groups. By contrast, heat treatment of coal resulted in a sharp and rapid decrease in its electrochemical reactivity in the MC-DCFC due to the decrease in the number of oxygen-containing surface functional groups. A higher surface area of coal may also be helpful, but it is less important than the surface chemistry. Similar results were achieved by Eom et al. [19]. The three raw coals chosen for investigation showed higher open circuit voltage (OCV) and higher maximum power density than those of their chars. It was also noted that the ratio of oxygen to carbon on the surface of the coal chars, which is associated with the amount of surface functional groups containing oxygen, influenced the electrochemical reactions of the solid fuel. Liu et al. [20] focus on the influences of volatile matters, ash and chemical structure in coal on the performance of SO-DCFC. They concluded that the particle size of pulverized bituminous coal and ash content are important factors which affect SO-DCFC performance. The impact of coal on the performance of the DCFC with solid oxide electrolyte was investigated by Kaklidis et al. [21]. It was found that volatile matter content, porosity and coal structure disorder were correlated with the power output. In contrast, high ash and sulfur contents inhibit the electrochemical performance of the cell. Xu et al. [22] tested an electrolyte-supported hybrid direct carbon fuel cell supplied by German Creek coal (among other examined fuels). Their research results show that coal has higher electrocatalytic activity than activated carbon but delivers lower power density due to the sulfur poisoning effect on the Ni catalyst. Coal as a fuel for H-DCFC was also examined by Jiang et al. [23]. The results showed that high volatile matter, high hydrogen content and low moisture are desirable for short-term operation, while in longer-term operations, high carbon content is preferable. This means that coal samples with an ordered crystalline structure, high carbon and low ash content (e.g. anthracite) will be desirable for use in H-DCFCs. The application of coal in molten salt electrolyte DCFC systems might be problematic, mainly because of the volatile components content, which are unstable in fuel cell operating conditions (high temperature and molten electrolyte) and will evolve into gaseous products as the coal is introduced to the hot fuel cell anode chamber. The coal that is intended to be used in high temperature molten electrolyte DCFCs should therefore be pre-treated to remove the volatiles. On the other hand, the removal of volatile matter from coal (by e.g. pyrolysis) may have negative effects on cell performance due to the reduction of surface oxygen-containing functional groups. In authors previous research [13] different fuel samples were investigated, including raw coals, in MH-DCFC. The results showed that the highest current (at 0.5V) and power densities were determined for hard coal. However, coal fuel experienced the longest startup period (time at the beginning of MH-DCFC operation before a stable voltage level is achieved). In the current work, the impact of the thermal

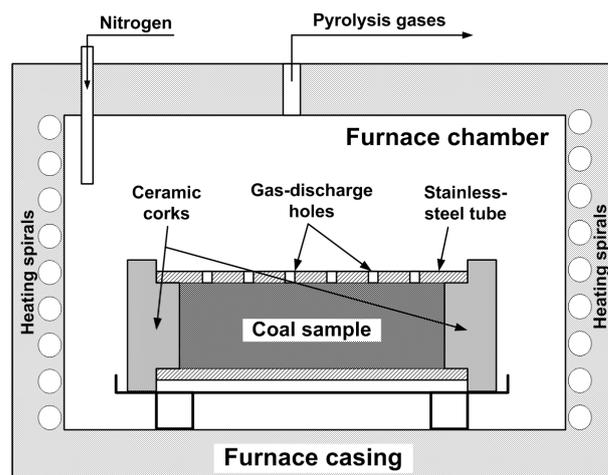


Figure 1: Schematic diagram of the tube reactor for coal pyrolysis

treatment of raw coal on the performance of MH-DCFC was analyzed and reported.

2. Experimental

2.1. Coal samples preparation

The three raw Polish-sourced bituminous coal samples from coal used in thermal power plants were chosen for the investigation. All the samples (air-dry basis) were ground and sieved to 0–200 μm and 180–250 μm size fractions. The raw coal samples were denoted as C1, C2 and C3. Coal char was obtained by pyrolysis of all three raw coal samples. During the experiment, about 15 g of coal (particle size 180–250 μm) was placed in a stainless-steel tube reactor with an internal diameter of 30 mm and length of 120 mm, and both ends were closed by ceramic corks (see fig 1). The reactor was placed in a muffle chamber of an electric heating laboratory furnace at 1023 K and kept for 1 h in a nitrogen atmosphere. After the desired heating time, the reactor was withdrawn from the furnace and cooled to ambient temperature. The resulting char was again sieved to a size range of 180–250 μm . The pyrolyzed coal samples were denoted CP1, CP2 and CP3.

2.2. Coal samples characterization

Proximate analysis was conducted based on the following standards: moisture—ISO 589:2006, ash—ISO 1171:2002, volatile matter—ISO 562:2010. The ultimate analysis of the content of carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) was carried out in an elemental Leco TruSpec CHNS analyzer according to ISO 29541:2010 and ISO 19579:2006 standards. The oxygen content was calculated by difference. An automatic isoperibolic bomb calorimeter (model C2000 Basic, IKA WERKE, Germany) with automatic temperature control module (thermostat) was used to determine the HHV of the samples according to the ISO 1928:2009 standard. A mercury intrusion porosimeter (Poremaster 33, Quantachrome) was used to determine the porosity, specific

surface area and pore volume of the samples. The porosimetry investigations were conducted for the samples of particle sizes 180–250 μm . Moreover, the pore size distributions of all the samples were designated and represented as log differential specific intrusion volume vs. pore diameter. To determine the type of surface oxygen-containing functional groups, a Fourier transform infrared spectroscopy (FTIR) analysis was performed on a JASCO FT/IR-6200 spectrometer equipped with a liquid nitrogen-cooled MCT (Mercury Cadmium Telluride—HgCdTeO) detector. To obtain the IR spectra of coals the nujol mulls (liquid paraffin) were prepared. About 10 mg of dry sample was finely grounded in an agate mortar and 2 small drops of nujol were added and mixed together. The mixture was then placed between two KBr plates. The FTIR spectra were recorded in the range of mid-infrared ($4000\text{--}500\text{ cm}^{-1}$) collecting 60 scans per sample at a resolution of 4 cm^{-1} . Identification of functional groups in the spectrum was performed with the KnowItAll® database search software package from Sadtler.

2.3. MH-DCFC test cell preparation and electrochemical characteristics

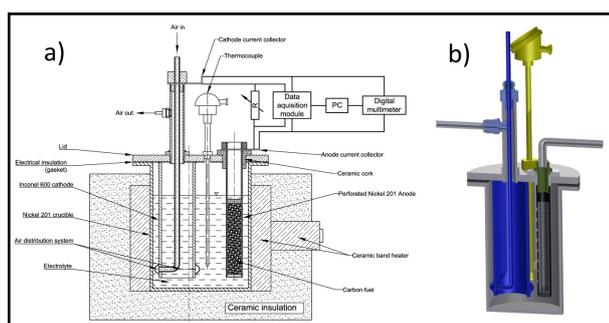


Figure 2: Schematic diagram (a) and view (b) of the MH-DCFC experimental apparatus

The performance of raw and modified coal fuels was evaluated in a self-built laboratory-scale MH-DCFC test cell shown schematically in Fig 2. The cell was manufactured from nickel and nickel alloys. The main molten hydroxide electrolyte container was manufactured from Nickel 201. The anode was also made from Nickel 201, while the cathode was Ni-based Inconel 600. Fuel particles of 180–250 μm in size were used to supply the fuel cell. The details of design, operation procedures and measurement methodology of MH-DCFC have been described elsewhere [13, 14].

3. Results and discussion

3.1. Properties of coals

Three different coals were chosen to investigate the effect of their heat-treatment (pyrolysis) and specific properties on the performance of MH-DCFC. The properties of the raw and pyrolyzed coal fuels used in the present study are summarized in Table 1.

The selected raw coal samples differed significantly in the content of ash, volatile matter, carbon, sulfur and oxygen. Coal C1 had the highest content of carbon (which is a main substrate for electrochemical reactions in DCFCs) and volatile matter. Sample C1 also has the lowest ash content. Sample C2 had the lowest content of elemental carbon, volatile matter and oxygen, and had the highest amount of ash. Sample C3 had a moderate amount of elemental carbon, ash and volatile matter, and the highest content of oxygen. A high quantity of mineral matter will trigger a mass transfer limitation between carbon particles and the anode current collector, and adversely impact fuel cell performance. On the other hand, the composition of the ash may be an important factor in determining the electrochemical performance of a DCFC [24]. Furthermore, volatile matter incorporated into a raw coals structure, can be unstable in fuel cell operating conditions (high temperature molten electrolyte) and will evolve gaseous products as the coal is introduced to the hot fuel cell, which may lead to variable and unpredictable MH-DCFC performance. Heat treatment of the coals results in a sharp decrease in the content of oxygen. Moreover, all pyrolyzed coals had a higher quantity of carbon and ash than raw coals due to the reduction in volatile matter, hydrogen, nitrogen and sulfur elements. It should be pointed that the content of mineral matter in samples CP1 and CP3 was increased compared to coals C1 and C3, but in the case of sample CP2 this trend was the opposite and the coal—after pyrolysis—had a lower amount of ash than the raw coals. The reason for this was probably the decomposition of some of the mineral compounds contained in the ash during pyrolysis. Thermal treatment of coals resulted in an increase in both porosity and pore volume, and also led to a reduction in surface area at the same time. The highest porosimetric data parameters were obtained for sample C3 in a group of raw coals. From the group of pyrolyzed coals sample CP3 the highest recorded porosity and pore volume, whereas coal CP1 had the highest specific surface area. Fig. 3. provides information on pore size distributions for all of the coal samples used in the investigation. An analysis of the log-differential pore size distribution curves showed that macropores (exceeding $0.05\ \mu\text{m}$) made up a majority of the pore diameters in the measured pore volume. Some mesopore bands ($0.002\ \mu\text{m}$ to $0.05\ \mu\text{m}$) were observed, but only in the case of samples C1, CP1 and C3. In addition, heat treatment leads to an increase in the amount of macropores (simultaneously mesopores are reduced) which has a large impact on pore volume formation (the only exception is sample CP1 where we can find a mesopore peak of $0.03\ \mu\text{m}$ after pyrolysis). The increase in pore size causes a decrease in the value of specific surface area. Furthermore, with the gases separated from coal during the thermal treatment, the original pore diameter grew and then the pore volume increased in all pyrolyzed samples.

Fig. 4 shows the FTIR spectra of the raw and pyrolyzed coals. Below 2000 cm^{-1} the FTIR spectrums exhibits absorptions typical of oxygen species. Intense absorption bands at $1650\text{--}1750\text{ cm}^{-1}$ can be attributed to the stretch-

Table 1: Proximate analysis, elemental composition and porosimetric data of the raw and pyrolyzed coals used in the study (all values are in dry basis)

Coal Sample	Proximate analysis			Ultimate analysis					Porosimetry analysis		
	Ash, wt. %	VM, wt. %	HHV, kJ/kg	C, wt. %	H, wt. %	N, wt. %	S, wt. %	O^{diff} , wt. %	Total porosity, %	Surface area, $m^2 g^{-1}$	Pore volume, $cm^3 g^{-1}$
C1	1.74	34.23	30694	78.63	5.01	1.84	0.76	12.03	3.32	2.39	0.0266
CP1	3.14	0	31870	92.97	1.18	1.65	0.65	0.43	7.09	1.52	0.0505
C2	24.98	28.96	22598	57.18	3.95	1.39	1.80	10.71	5.33	0.39	0.0365
CP2	21.06	0	27258	75.21	1.02	1.36	1.19	0.17	7.93	0.24	0.0593
C3	8.50	33.76	26940	68.75	4.52	1.27	1.19	15.77	7.49	3.25	0.0517
CP3	13.11	0	29909	83.28	1.18	1.23	0.74	0.46	10.84	0.34	0.1164

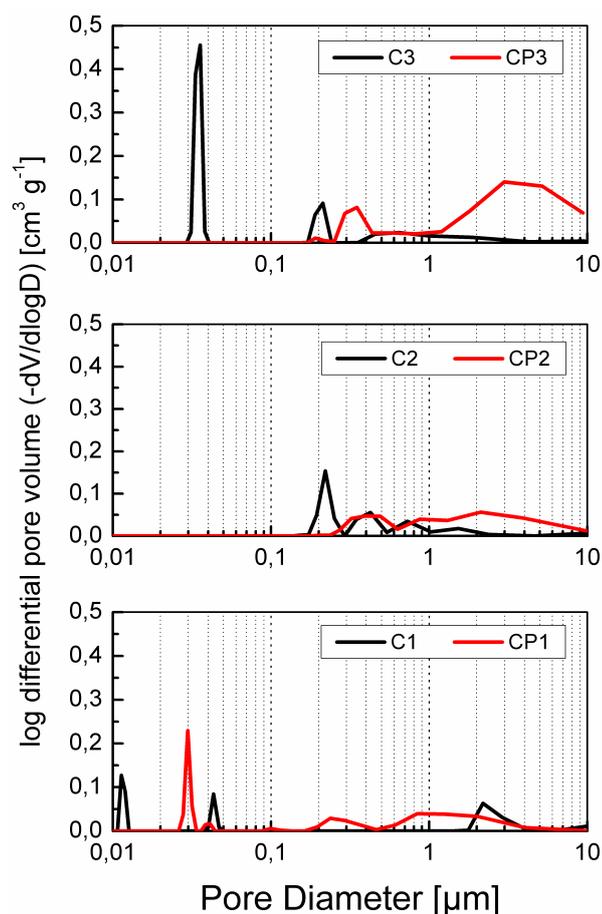


Figure 3: Pore-size distributions measured by mercury intrusion porosimetry in coal fuel samples

ing vibrations of $>C=O$ groups of different origin: esters, ketones, aldehydes and carboxylic acids. A strong peak at about 1580 cm^{-1} (in the range of $1560\text{--}1600\text{ cm}^{-1}$), occurring predominantly in the raw coals spectra, can be attributed to the group $>C=O$ of carbon acids and quinone compounds. Peaks located at the wavenumber of 1410 cm^{-1} are the result of vibrations of the $-C=O$ or $-C-O-H$ bonds of the carboxyl or alcohol groups, respectively. Furthermore, the peaks observed in the range of $1060\text{--}1210\text{ cm}^{-1}$ are derived from stretching vibrations of $-C-O-C-$ (cyclic ethers) or $>C-O-$ groups from alcohols, phenols, esters and carboxylates. Bands at ranges $1100\text{--}1300\text{ cm}^{-1}$ and $1650\text{--}1750\text{ cm}^{-1}$ can also be attributed to the occurrence of the lactone groups ($-C-C(=O)-O-C-$). Taking into account

the results of elemental analysis (Table 1) and recorded FTIR spectra (Fig. 4), the oxygen content in coal samples can be correlated with the presence of surface oxygen-containing functional groups. Raw coals were characterized by high intensity bands assigned to oxygen groups, while the pyrolyzed coals had those bands definitely lower, which means a lower presence of oxidized functional groups on the surface of its particles.

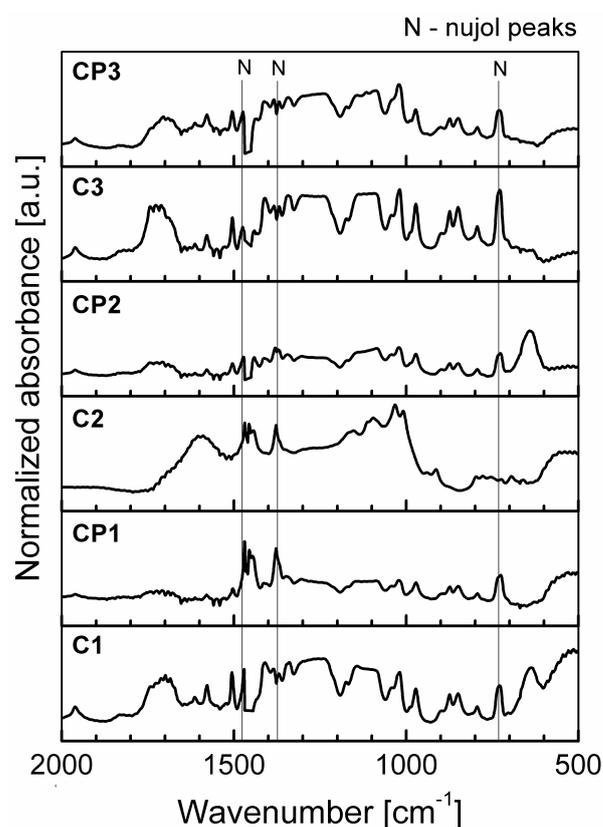


Figure 4: Infrared (FTIR) spectra of coal samples

3.2. Performance of MH-DCFC fuel cell

The variations in cell voltage plotted against time for the open circuit ($I = 0\text{ A}$) and the relationships between cell voltage, power density, and current density are shown in Figures 5–7. The characteristics shown in Figures 5b, 6b and 7b were taken after 3 hours of cell operation in no load (open circuit) conditions (see Figures 5a, 6a and 7a). The main elec-

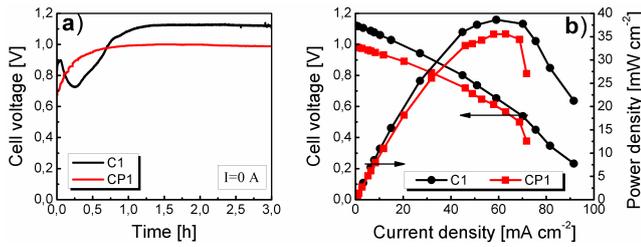


Figure 5: Performance of MH-DCFC with C1 and CP1 coal fuels: a) time-dependent open circuit voltage of the fuel cell, b) current density-voltage (j-V) and current density-power density (j-P) characteristics of the fuel cell

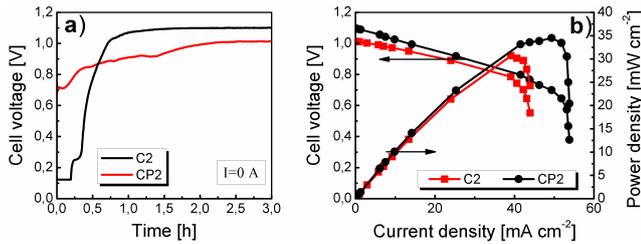


Figure 6: Performance of MH-DCFC with C2 and CP2 coal fuels: a) time-dependent open circuit voltage of the fuel cell, b) current density-voltage (j-V) and current density-power density (j-P) characteristics of the fuel cell

tronic parameters of MH-DCFC performance are compared in Table 2.

The variation in cell voltage vs. time (Figures 5a, 6a and 7a) indicates a notable decrease in voltage measured at the electrode terminals during the first 0.5 hour of cell work in all cases when raw coals were used as a fuel. That was probably caused by the degassing of the coal particles after immersion in the hot molten electrolyte, which was additionally attributed to the observed evolution of gases from the anode chamber. Ignoring the fact that the voltage dropped in the first phase of cell work for raw coal samples for all fuels, the cell voltage increased slowly until it reached a stable plateau after roughly 1 h, and then remained quite stable. The probable reasons for this were the heating of the anode and cathode elements to the desired MH-DCFC working temperature after immersion in the hot electrolyte and/or gradual wetting of the inner surface of the fuel particles by liquid molten electrolyte. That second hypothesis was already discussed by Cooper and Selman [25] who determined that OCV increase was observed during the gradual wetting of

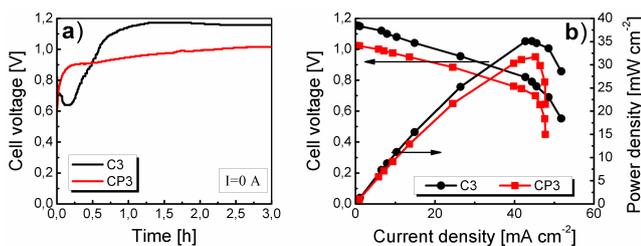


Figure 7: Performance of MH-DCFC with C3 and CP3 coal fuels: a) time-dependent open circuit voltage of the fuel cell, b) current density-voltage (j-V) and current density-power density (j-P) characteristics of the fuel cell

Table 2: Summary of the operation parameters of MH-DCFC

Coal sample	Open circuit voltage (OCV), V	Maximum power density (P_{max}), mWcm^{-2}	Maximum current density (j_{max}), mAcm^{-2}	Internal resistance (R_i), Ω
C1	1.1206	38.61	19.54	0.468
CP1	0.9846	35.56	71.76	0.340
C2	1.1011	34.50	53.82	0.436
CP2	1.0128	30.71	43.94	0.353
C3	1.1572	35.09	51.76	0.470
CP3	1.0156	31.71	47.76	0.353

the entire exterior surface of the graphite rod immersed in molten carbonate mixture. Later on, the OCV in their experiment reached a quasi-steady level value. The authors explained that the phenomenon was associated with the transition of the meniscus between the fuel and the electrolyte from nonwetting to wetting.

The experimental results of the OCV measured with a digital multimeter after 3 h of continuous cell operation showed that the highest values (1.1–1.2 V) were recorded for raw coals, while the OCV values for coal chars were lower and did not exceed 1.0 V. The theoretical OCV (equal to the ideal fuel cell potential—E) calculated from the relationship 1 should be 1.024 V. The OCVs received that were higher than theoretically obtainable can be attributed to the complex anodic reactions with hydrocarbon compounds contained in the coal matrix [26].

$$E = -\Delta G/nF \quad (1)$$

where: ΔG is the Gibbs free energy which represents the MH-DCFC maximum available work potential (in constant temperature and pressure conditions), $\Delta G_{700K} = -395.37 \text{ kJmol}^{-1}$ [27], n is the number of electrons involved in the charge transfer reaction, $n = 4$, F is Faraday's constant, $F = 96485.3 \text{ Cmol}^{-1}$.

The measured maximum power density (P_{max}), maximum current density (j_{max}) and calculated internal resistance (R_i) with the raw coals as the fuel were higher than those measured for pyrolyzed coals (cf. Table 2). The best results was obtained for samples C1 and CP1 from the group of raw and pyrolyzed coals, respectively. Similar results were achieved in the case of C2, C3 and CP2, CP3 group of samples. The calculated internal resistance of the MH-DCFC was in all cases lower when pyrolyzed coals were used as a fuel. The higher values of R_i in respect to the raw coals probably related to the formation of nickel sulfides on the surface of the nickel mesh (anode current collector) which reduced contact with the carbon particulates. Cherepy et al. [28] found that sulfur indicates sulfidation corrosion at the Ni-based anode and degrades cell performance over time. The pyrolysis process caused a decrease in the sulfur content of fuels, therefore very likely inhibiting the sulfidation corrosion of the anode current collector and in turn reducing the internal resistance of MH-DCFC.

Some fuel properties such as carbon and ash content in the ultimate analysis and oxygen functional groups on the

surface had relevance to the maximum power density. The highest electrochemical activity of coals C1 and CP1 is likely due to the highest content of elemental carbon, the relatively high amount of oxygen (which may be correlated with the amount of surface oxygen functional groups [29]) and the lowest amount of mineral matter compared to other tested fuels. Furthermore, samples C3 and CP3 also had the highest comparative amount of oxygen functional groups but the MH-DCFC fuelled by them achieved the second highest power density values. That was probably caused by the higher content of ash and lower content of carbon.

It is interesting that porosimetric data (total porosity, surface area and pore volume) are not as important as might be expected and there is no obvious correlation between these parameters and the performance of MH-DCFC.

4. Conclusions

Three particulate raw coal samples were investigated in this study, and the effects of thermal treatment of those fuels on the performance of the direct carbon fuel cell with molten alkaline electrolyte were analyzed and discussed. The electrochemical oxidation of raw and devolatilized coals in the MH-DCFC is strongly dependent on the carbon, ash and oxygen content in the fuel. For continuous operation of direct carbon fuel cells, in particular the MH-DCFC, a low ash and high carbon content is desirable. Coal chars prepared using pyrolysis had greater porosity, pore volume and carbon content but they are not appropriate fuel because of the lower performance of the MH-DCFC. This is due to the reduction in oxygen-containing compounds on the surface of the pyrolyzed coal particles, which are largely responsible for the electrochemical reactivity of the coals.

Acknowledgements

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