

Clean energy from a carbon fuel cell

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Abstract The direct carbon fuel cell technology provides excellent conditions for conversion of chemical energy of carbon-containing solid fuels directly into electricity. The technology is very promising since it is relatively simple compared to other fuel cell technologies and accepts all carbon-rich substances as possible fuels. Furthermore, it makes possible to use atmospheric oxygen as the oxidizer. In this paper the results of authors' recent investigations focused on analysis of the performance of a direct carbon fuel cell supplied with graphite, granulated carbonized biomass (biocarbon), and granulated hard coal are presented. The comparison of the voltage-current characteristics indicated that the results obtained for the case when the cell was operated with carbonized biomass and hard coal were much more promising than those obtained for graphite. The effects of fuel type and the surface area of the cathode on operation performance of the fuel cell were also discussed.

Keywords: Fuel cell; Coal; Biomass; Carbonization; Torrefaction; Biocarbon

1 Introduction

So far, the world needs for electricity and heat are still satisfied by fossil fuels. However, that 'historical' situation is about to change and it is believed that the current crude oil resources will almost be depleted by the mid of the 21st century, while the access to the natural gas reservoirs will be quite

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considerably limited [5]. As a result, significant increase of the fuel costs is predicted [5]. Since modern electricity generation technologies (such as e.g. solar or photovoltaic) are still far away from large-scale applications, either due to the economical or political situation, the above mentioned quite pessimistic prognoses associated with the future of the crude oil or natural gas bring about again an increased interest towards the use of coal/carbon as an energy source. Accordingly, more research is recently focused on the development of clean and efficient carbon/coal-based energy conversion technologies [5,13].

The driving factors favoring the development of any particular technology are usually, among others, its availability, simplicity, high efficiency, and low price. Nowadays, an additional requirement associated with the demand to convert energy in a sustainable and environmental-friendly way must also be taken into consideration. Accordingly, recent development trends in coal/carbon-to-electricity processing technologies are focused, on one hand, on the increase of the process efficiency, and, on the other hand, on maintaining the emission of unwanted byproducts (e.g. SO₂, NO_x, particulate matter (PM), CO₂, etc.) below the allowable limits [13].

Since, so far, Poland's own known crude oil and gas resources are quite poor and insufficient to cover the country's energy needs and the development of nuclear or renewable technologies is hedged either about the plant operation safety and fuel disposal problems (nuclear), or economics and resources (renewable sources), the current power production technologies have to use the available hard coal and lignite reserves in order to meet Polish energy needs and ensure the, so called, 'energy safety' for Poland's economy. However, regardless of the fact that Polish Government policy is currently focused on rational and economical management of the own coal deposits, the development of modern coal/carbon based technologies must also take into consideration the environment protection issues and provide the conditions for low emission of pollutants.

All the above aspects and requirements associated with power production are met by the direct carbon fuel cell (DCFC) technology. The experimental results obtained so far by several authors, e.g. [6–9], are quite promising and thus further investigations are led with increased interest [1,3,4,10,11]. The DCFC provides excellent conditions for direct conversion of fuel's chemical energy into electricity without the combustion process and with no use of any 'intermediate' technologies or machinery (e.g. steam turbines, thermal engines, etc.). Accordingly, during its operation the DCFC

emits also no pollutants, such as SO_x , NO_x , or PM, since the only product of the electrochemical oxidation of carbon is the carbon dioxide, CO_2 . Apart from the ‘environmental advantages’ the DCFC technology may also become a perspective one due to its high efficiency and generation of a concentrated CO_2 product (theoretically pure carbon dioxide) that may be easily stored, reused or further processed, e.g. by the chemical industry.

The maximum theoretical efficiency of a DCFC may reach 100% [1], however in practical cases the efficiencies of energy conversion of up to 80% may be reached; calculated on a higher heating value (HHV) basis. Such efficiency seems to be sufficient for numerous practical applications and furthermore is still higher than the efficiency of hydrogen-fuelled fuel cells [2]. In case of a DCFC technology three types of electrolytes are commonly known and used, i.e.: 1) molten sodium, potassium or lithium carbonates, 2) molten sodium, potassium or lithium hydroxides, or 3) solid body (mostly ZrO_2 stabilized by yttrium Y_2O_3 , YSZ).

Despite the existence of numerous papers dealing with the DCFC technology [1,2,6–11] there are not many publications, e.g.[8,11], where the operation of a DCFC with hydroxide-based electrolyte is reported. Accordingly, the intention of this paper is to present and discuss some chosen experimental results from authors’ own DCFC facility. Particular attention is put to investigate the effect of fuel type on the cell operation, as well as the possibility to supply the fuel cell with an ‘unpressed’ and ‘unprepared’ loose granular solids, i.e. the type of fuel that is more easily achievable in a bulk and may be directly used for large-scale electricity generation without any preprocessing.

In order to meet the above goals the results obtained for graphite, hard coal, and carbonized biomass (biocarbon) are presented and discussed.

2 Experimental

The experiments described in the present paper were conducted in a laboratory-scale facility shown schematically in Fig. 1. All the cell steel parts were manufactured either from a corrosion-resistant stainless steel or Nickel[®] 201 alloy. The main cell container was manufactured from the Nickel[®] 201 alloy in order to provide sufficient corrosion resistance to liquid sodium hydroxide (NaOH 98.8%, produced by POCH S.A.) that was used as electrolyte. The main container was covered by ceramic band heaters providing heat for melting the electrolyte and maintaining its temperature at 450 °C

during the experiments. The electrolyte temperature was determined by a K-type thermocouple (NiCr-NiAl) and was maintained at the desired value by an electronic temperature controller. The cathode was manufactured from stainless steels 316Ti (X10CrNiMoTi1812) and 316L (X2CrNiMo17-12-2), while the anode was made of 304L (X2CrNi18-9) steel and formed as a specially-designed tube of 25 mm diameter. Since the design of some parts of the electrodes is subjected to be patented more details on the electrode design will be given after the patent is granted.

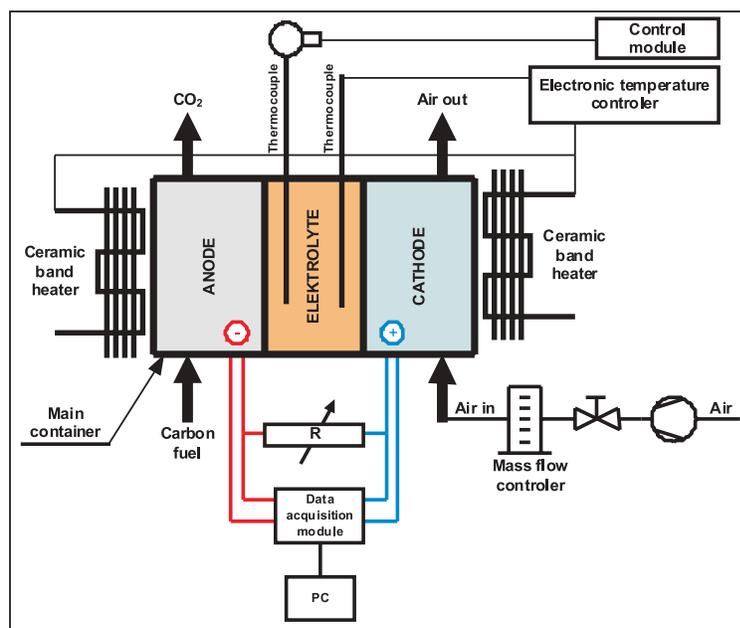


Figure 1. The outline of the experimental setup used for the experiments.

The data acquisition module Advantech USB-4711A was used for the measurement of the cell voltage and the decrease of the voltage on an external resistor. The module was connected to a personal computer (PC) where the data was displayed and stored. In order to determine the cell current intensity at various loads an external resistance setup MDR-93/2-52 was used and connected to the cell circuit thus providing the possibility to adjust the electrical resistance of the external circuit. The amount of air fed into the cell was controlled by a rotameter. It was possible to adjust the gas flow rate up to 30 dm³/h. In order to attenuate short-term surge suppression and eliminate the effects of power grid interferences on the recorded data

the emergency standby backup power device PowerCom UPS BNT-1500AP with a noise filter EMI/RFI was also used during the experiments. The tool also acted as an 'emergency power supply device' for the data recording system in case of power failure.

During the experiments the DCFC was supplied with three types of fuels, i.e. the biocarbon (carbonized biomass) [12], hard coal and graphite. The main properties of the fuels are shown in Tab. 1, while example fuel samples are shown in Fig. 2.



Figure 2. The example fuel samples: a) biocarbon, b) hard coal, c) graphite rod (d=13 mm).

As shown in Tab. 1 the high heating value (HHV) of the fuels was quite high, roughly 27–32 MJ/kg. The biocarbon and the hard coal samples were in the form of 'loose' solids (cf. Fig. 2), and the particle fraction of 0.18–0.25 mm was chosen for the experiments. The graphite fuel was a 13 mm diameter rod. The biocarbon and the hard coal samples were characterized by quite significant volatile matter contents (18.4% and 36.6%, respectively), while the graphite rod contained relatively low amount of the volatiles (1.3%). The amount of ash varied quite significantly for the fuels chosen – the corresponding values for the biocarbon, graphite and hard coal were 2.6%, 1.7%, and 11.5%, respectively.

At the beginning of each test 500 g of sodium hydroxide was put into the main cell container (cf. Fig. 1) and then heated up to the desired temperature. After the temperature level of 450 °C was reached and the electrolyte was completely molten both the cathode and the anode were slowly immersed into the electrolyte and the cell data (current intensity, voltage, temperature, etc.) were recorded.

After each test was finished the heating was turned off and the cell was 'shutdown'. The setup was then cooled down to room temperature and then all its parts were placed in special plastic container filled with roughly

Table 1. The main parameters of the fuels used during the experiments (air-dry state).

Fuel type	HHV [MJ/kg]	Volatile matter [%]	Ash [%]	Moisture [%]	Particle size [mm]
Biocarbon (granules)	29.9	18.4	2.6	4.5	0.18–0.25
Coal (granules)	26.7	36.6	11.5	4.5	0.18–0.25
Graphite (rod)	32.3	1.3	1.7	0.1	–

25 liters of ionized water. All the elements were kept there for three hours in order to get the solidified electrolyte removed. A mechanical stirrer was used to improve the dissolution of the electrolyte. The water-electrolyte mixture was then removed and new 25 liters of ionized water were put into the container. The whole procedure was then repeated. Afterwards, the cell elements were removed from the container, cleaned with a soft sponge, and finally again rinsed with ionized water. All the elements were then dried for 3 hours in a drier.

3 Results and discussion

The changes of the cell voltage versus time are shown in Fig. 3 for various fuel types. Analysis of the results indicates that the highest voltage, roughly 1 V, was achieved for the cases when the cell was supplied with ‘loose’ granular fuels, such as the biocarbon and the hard coal. The maximum stable voltage achieved for graphite rod was much lower (roughly 0.55 V).

Similar to the results reported and discussed in [3,4], regardless of fuel type the DCFC requires some time at the beginning of its operation before a stable voltage level is achieved. As shown in Fig. 3 the longest startup period was ascertained for hard coal while the best results (i.e. the shortest startup period) was determined for graphite electrode.

In Figs. 4–5 the characteristics of the cell operated with various fuel types are shown. The results indicate that the current intensities for the cases when the cell was supplied with ‘loose’ granulated fuels are much higher than the values obtained for graphite. Such results were probably the effect of lower surface area of the graphite electrode. As it is shown in Fig. 4 for an assumed reference cell voltage of 0.5 V, the highest current intensity (roughly 0.22 A) was achieved when the cell was supplied with the biocarbon. The results obtained for the hard coal are, however, very

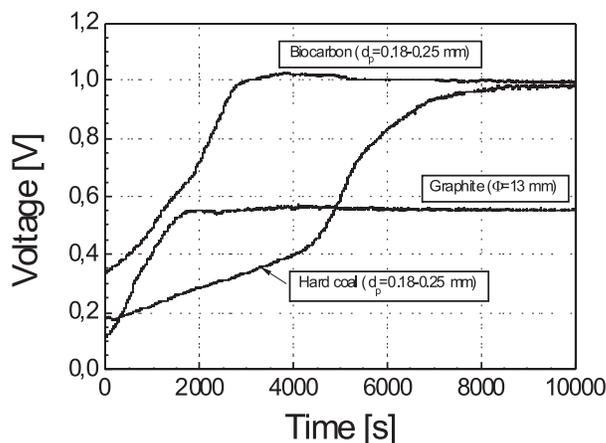


Figure 3. The DCFC open circuit voltage vs. time for various fuels. Electrolyte temperature 450 °C, air flow rate 0.5 dm³/min.

similar. The lowest current intensity, roughly 0.07 A at 0.5 V, was obtained for graphite rod.

Similar conclusions to those shown in Fig. 4 may be drawn from Fig. 5 where the relationship between the current intensity and cell power is shown. The data indicate that the maximum power generated from the DCFC supplied with biocarbon was over two times higher than in the case of the DCFC operated with graphite. The corresponding values of the cell power were roughly 0.14 W and 0.06 W, respectively.

The results presented in Figs. 4–5 clearly indicate the effect of fuel type on the operation performance of the fuel cell, and are quite promising with respect to potential application of the DCFC technology for large-scale power generation since the data indicate that the DCFC may be easily supplied with granulated hard coal or carbonized and granulated biomass. Furthermore, the results obtained for those two fuels are much better compared to the values recorded when the cell was supplied with the graphite rod.

The differences in cell operation, associated with a particular fuel, are probably the effect of the fuel specific surface area (and thus the reaction kinetics), or are brought about by the, so called, crystallographic disorders and the presence of some microelements that may support or catalyze the electrochemical reactions in the DCFC [1]. The above assumption needs, however, some further investigation.

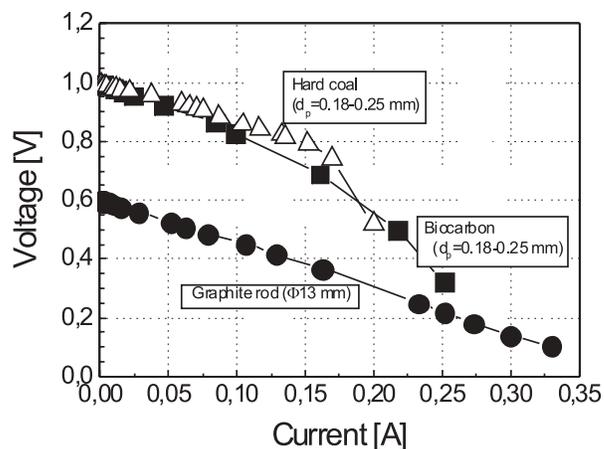


Figure 4. Fuel cell voltage vs. current intensity for various fuel types. Air flow rate $0.5 \text{ dm}^3/\text{min}$, electrolyte temperature $450 \text{ }^\circ\text{C}$.

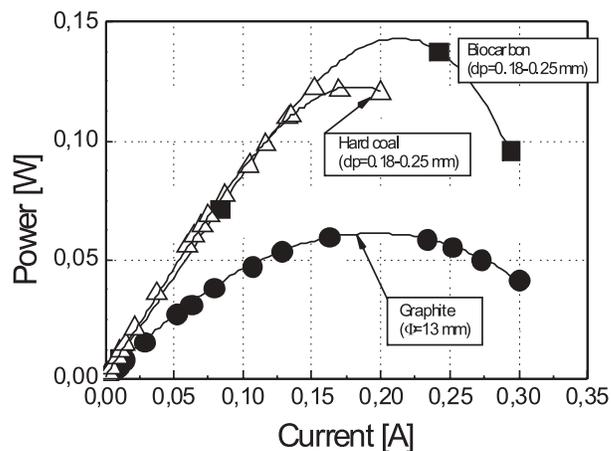


Figure 5. The power generated by the DCFC vs. current intensity for various fuel types. Air flow rate $0.5 \text{ dm}^3/\text{min}$, electrolyte temperature $450 \text{ }^\circ\text{C}$.

The effect of the cathode surface area on the cell performance is shown in Fig. 6. In order to compare the results the same anode, manufactured from graphite rod, was used for both cases, i.e. the ‘standard’ and the ‘en-

hanced' one. As it is shown in Fig. 6, for a given voltage the increase of the cathode surface area brings about increase of the cell current intensity, while for a given current intensity the cell power increased when the 'enhanced' cathode was used. The results indicate that the cell performance is quite sensitive to the size of the cathode since the latter one is responsible for providing the space for the reduction of oxygen molecules.

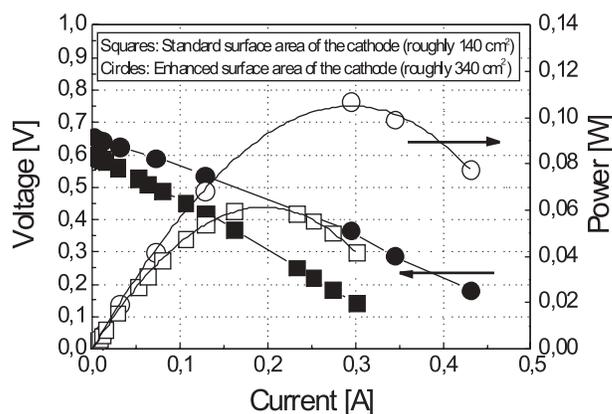


Figure 6. Effect of the surface area of the cathode on cell performance. Fuel: graphite rod ($d=13$ mm), electrolyte temperature 450 °C, air flow rate 0.5 dm³/min.

4 Conclusions

The results of the investigations reported and discussed in the present paper may be briefly summarized as follows:

1. Acid-resistant steels, such as 304L, 316L, or 316Ti, as well as the Nickel[®] 201 alloy, may be used to manufacture the elements of molten hydroxide electrolyte DCFC. The application of those materials brought about much better performance of the cell compared to the results obtained previously [3,4].
2. It was demonstrated that the DCFC may be directly supplied with granulated carbonized biomass (the biocarbon), as well as granulated hard coal. However, particularly in the case of the hard coal, more and detailed long-term investigations are required in order to determine

precisely the effect of coal ash and some microelements on the cell operation.

3. By supplying the DCFC with 'loose' granulated fuels the cell performance was improved and higher values of the current intensity and cell power were obtained compared to the case when the cell was supplied with graphite rod. The promising results obtained for granulated fuels were probably the effect of higher specific surface area of those fuels or their crystallographic disorder and presence of some microelements that may support or catalyze the electrochemical reactions.
4. In order to improve the cell performance and its current intensity the contact area between the air and the cathode body should be maximized.

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