

Fuel cell as a part of clean coal technologies

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ABSTRACT: Carbon fuel cells directly fueled with coal is a technology for highly efficient conversion of chemical energy, through electrochemical reactions, into electrical energy without combustion. The development of coal technology of fuel cells due to high energy conversion efficiency can help to reduce emissions of pollutants such as NO_x, SO₂ and fly ashes. The article presents the operating characteristics of the carbon fuel cell made of construction materials such as carbon steel, stainless steel or nickel and its alloys. Fuels used to fuel the cell were coal, biomass and graphite. The study also examines the impact of the actual working conditions of fuel cell on changes in cell cathode construction material: Ni-based Inconel[®] alloy 600.

Keywords: direct carbon fuel cells, clean coal technologies, coal, biocarbon.

1 INTRODUCTION

Nowadays, electric power from coal is achieved by coal-fired power plants, however, it is well known that this method is not only a low-efficiency process, but also it emits substantial amounts of greenhouse gases and pollutants, such as NO_x, SO_x and fly ashes. Therefore, it is logical to investigate a new and high-efficiency process for coal to be used for power generation. The direct carbon fuel cell (DCFC) is a power generation device in which the chemical energy of carbon is directly converted into electrical energy by electrochemical oxidation of carbon, without the combustion, gasification process or the moving machinery associated with conventional electric generators. This fuel cell uses solid carbon as fuel, which is different from the molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC) operating on a gaseous fuel.

DCFC has several unique attractive features. Firstly, DCFC offers great thermodynamic advantages over other fuel cell types. Secondly, it has high efficiency alternatively to the traditional coal fired electrical power plants, resulting in reduced carbon dioxide emissions per unit generated electricity. Thirdly, solid carbon fuel can be easily produced from many different resources, including coal, petroleum coke, biomass (e.g. grass, woods, nut shells, corn husks) and even organic garbage. The major motivation for recent work with DCFC has been of higher theoretical energy efficiency (100%) compared to thermal

conversion processes (35-45%). DCFC releases lower emissions than coal-firing power plants. Hence, DCFC may cut carbon emissions from coal by 50% and reduce off-gas volume by 10 times compared to conventional coal-burning power plants (Cao *et al.* 2007).

The present work illustrates the construction and performance of a Direct Carbon Fuel Cell with hydroxide electrolyte. Molten alkaline hydroxides have many long-known advantages e.g. high ionic conductivity, higher electrochemical activity of carbon (higher anodic oxidation rate and lower overpotential), lower operating temperatures (450°C) and consequently allow for the usage of less expensive materials for cell fabrication. Cheaper materials such as carbon steel and stainless steel may be used to fabricate containers, anodes and cathodes, because of the lower corrosiveness at lower temperatures. To date, three generations of DCFC prototypes have been built and tested to demonstrate the technology – all using different fuels (biocarbon, coal and graphite rod) and construction materials.

2 MATERIAL AND METHODS

2.1 Construction materials

A number of construction materials may be used to produce the elements of DCFC (e.g. anode, cathode, container). Metals and alloys most frequently considered for use in carbon fuel cells with molten

Table 1. Alloys used to construction of DCFC with molten hydroxide electrolyte.

Alloy	Composition [wt%]								
	Ni	Cr	Fe	C	Mn	S	Si	P	Other
Carbon Steel	-	-	Bal.	<0.24	<1.1	<0.05	0.10-0.35	<0.05	-
304L	8.0-12.0	18.0-20.0	Bal.	<0.03	<2.0	<0.03	<1.0	<0.045	-
316L	10.0-14.0	16.0-18.0	Bal.	<0.03	<2.0	<0.03	<1.0	<0.045	Mo=2.0-3.0
316Ti	10.0-14.0	16.0-18.0	Bal.	<0.08	<2.0	<0.03	<0.75	<0.045	Mo=2.0-3.0 Ti<0.7
Nickel [®] 201	Min. 99	-	<0.4	<0.02	<0.35	<0.01	<0.2	-	Ti<0.1 Cu <0.25
Inconel [®] 600	Min. 72	14.0-17.0	6.0-10.0	<0.15	<1.0	<0.015	<0.5	-	Cu <0.5

hydroxide electrolyte are carbon steel, stainless steel, nickel and high-nickel alloys. All these alloys have been tested directly in fuel cell to identify which material will be suitable for target device construction. Alloys, with their nominal composition, used to build a fuel cell are given in Table 1.

Carbon steel is the predominant construction material in the first generations of DCFC (Jacques 1896), therefore it was used for building the first generation prototype of fuel cell (Kacprzak *et al.* 2009, 2010).

Austenitic stainless steel (*i.e.* 304, 316) series were chosen to construct the second prototype of DCFC (Kacprzak *et al.* 2011). Type 304L stainless steels are the most widely used of any stainless steel. Although they have a wide range of corrosion resistance they are not the most corrosion resistant of the austenitic stainless steels. The 304 series of stainless steels exhibit high temperature strength, oxidation resistance, ease of fabrication and weldability and good ductility (Schweitzer 2003). Type 316L stainless steel is low carbon version of type 316 and offers the additional feature of preventing excessive intergranular precipitation of chromium chlorides during welding and stress relieving (Schweitzer 2003). In general alloy is more corrosion resistant than type 304 stainless steels.

The third carbon fuel cell was made of nickel and high nickel alloys because of their ability to resist corrosive environments. Nickel is commonly used as the material for the hydroxides service (Paul *et al.* 1993, Davis 2000). However, nickel is rapidly oxidized *in situ* to NiO which is a p-type semiconductor. The good corrosion resistance of Ni-based alloy Inconel[®] 600 in molten NaOH was attributed by Tran *et al.* (Tran *et al.* 1995) to the formation of a protective passive film of Ni–Cr spinel-type oxide which prevents the leaching of Cr as chromite and

chromate from the alloy. The corrosion resistance of the construction materials is listed in Table 2.

Table 2. Corrosion resistance of selected materials in molten NaOH in elevated temperatures.

Materials	Corrosion rate		Reference
	Temp. [°C]	mm/yr	
Carbon Steel	340	≈ 0.5	(Paul <i>et al.</i> 1993)
SS 304L	340	≈ 0.6	(Paul <i>et al.</i> 1993)
Nickel [®] 201	500	0.033	(Davis 2000)
Inconel [®] alloy 600	500	0.06	(Davis 2000)

2.2 Direct carbon fuel cell designs

A photo of the constructed cell is shown in Figure 1. Main part of the cell was a crucible made of carbon steel (depth of 135 mm with a inside diameter of approximately 57 mm) in which molten electrolyte (NaOH) is contained. The steel pot acted also as the cathode. Air from a compressor (necessary for the electrochemical reaction) was distributed to the cathode by sparge pipe (outside diameter of approximately 5.7 mm and wall thickness 1 mm) perforated at the bottom – six holes with a diameter of about 2 mm. A metal basket current collector with particulate carbon fuel, positioned inside the cathode crucible was an anode. In order to maintain the electrolyte in the liquid phase the crucible was heated by an electric heater. Reduce heat loss was achieved by securing a prototype by mineral wool and seal off all in ceramic casing.

Fuel cell prototype called as II is shown in Figure 2. All the cell steel parts were manufactured either from a corrosion-resistant stainless steel or Nickel[®] 201 alloy. The main cell container (inside diameter

of 76 mm and with a height of about 142 mm) was manufactured from the Nickel[®] 201 in order to pro

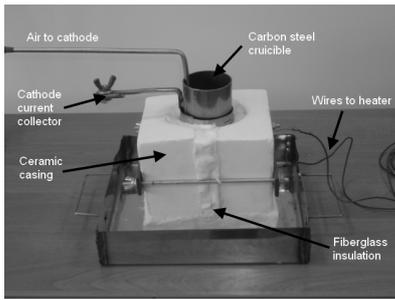


Figure 1. A photograph of experimental prototype I of direct carbon fuel cell made of carbon steel.

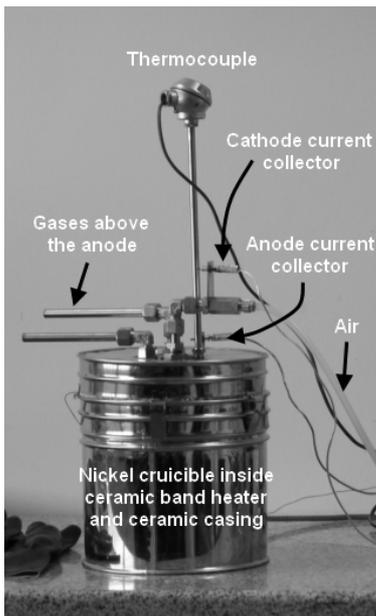


Figure 2. A photograph of experimental prototype II of direct carbon fuel cell made of stainless steels 300 series.

vide sufficient corrosion resistance to liquid sodium hydroxide. Container was covered by ceramic band heaters providing heat for melting the electrolyte and maintaining its temperature at 450°C during the experiments. The cathode was manufactured from sintered stainless steels 316Ti (bottom sparger, average pore size of 20 micrometers) and 316L (main air pipe, outer diameter of 10 mm and wall thickness of 2 mm), while the anode was made of 304L 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. Anode and cathode were mounted in the lid of the cell (the cathode is electrically isolated from the anode with a ceramic plug). Current collectors in the form of copper plates and wires were attached to the anode and cathode for collection of electrons.

A picture of the prototype III fuel cell is shown in Figure 3. That model was built only from nickel and its alloys. In addition, anodic and cathodic chambers

were separated, making gases are not mixed with each other (CO₂ above the anode and excess air above the cathode). As in the case of the second prototype of fuel cell the main cell container (inside diameter of 83 mm and with a height of about 147 mm) was manufactured from the Nickel[®] 201. In that construction of cell anode was made from the Nickel[®] 201 and the cathode was made of Ni-based Inconel[®] alloy 600. The anode and cathode were specially designed constructions made of pipes with the outside diameters of 19.1 mm and 42 mm respectively. The components of the prototype III carbon fuel cell, in particular the anode and cathode materials, were subjected to simultaneous oxidation-lithiation process. Doping cation-defective p-type nickel oxide by lower valence cations (Li⁺) makes them highly conductive, which is a requirement for a high performance cathode material. The lithiated NiO cathodes were made by *in situ* oxidizing and lithium-doping Ni-base cathode material.

Source of Li⁺ was lithium hydroxide monohydrate (LiOH·H₂O, m_p=470°C). Shortly after the salt has been melted air was introduced into the system (0.2 dm³/ min.) in order to accelerate the oxidation of nickel to NiO and lithium ions can incorporate into the surface and inner of NiO film. The process was carried out at 600°C for 24 h. Afterwards anode and cathode materials were slowly cooled to room temperature and then were washed several times in distilled water and HCl solution to remove and neutralize the residue of lithium hydroxide. After washing, the cell components were dried in a convection oven for 2 h. In order to reduce the dissolution of lithium ions in the electrolyte during operation of fuel cell, lithium hydroxide (10 mol%) was melted with NaOH. As in the case of prototype II more details on the electrodes design will be given after the patent is granted.

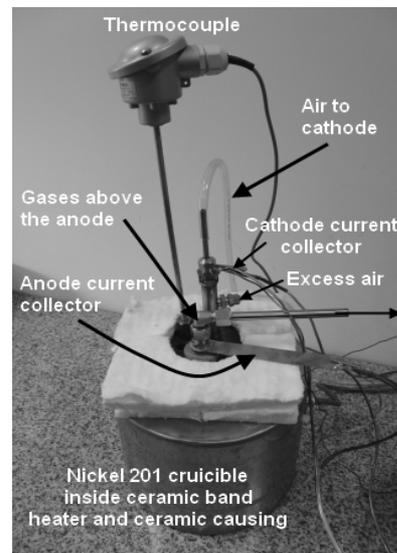


Figure 3. A photograph of experimental prototype III of direct carbon fuel cell made of nickel and high-nickel alloys.

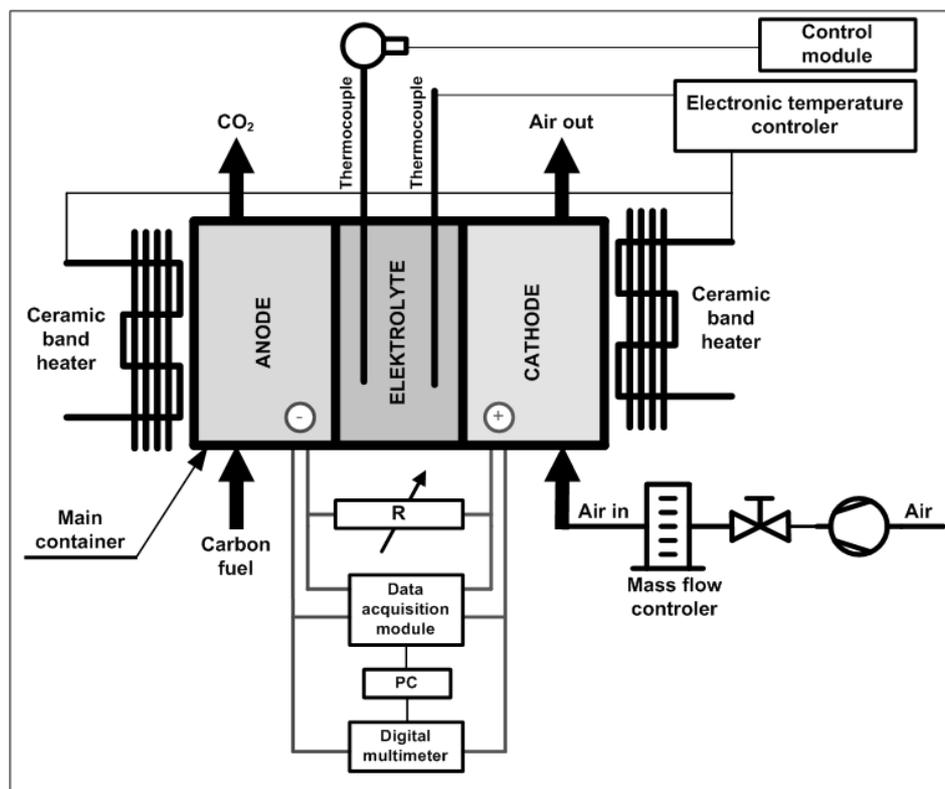


Figure 4. The outline of the experimental setup used for the experiments.

2.3 Characterization of the Inconel[®] alloy 600 after cell tests

The film and the reaction products of cathode material are characterized by using X-ray diffractometry. Phase analysis of the Inconel[®] alloy 600 (after lithiation process, 64, 94 and 115 hours) was carried out by means of XRD Seifert 3003 T-T X-ray diffractometer with the use of $K_{\alpha}Co$ radiation (0.17902 nm).

The corrosion rate was studied with the use of weight loss technique. Measurements on test material were conducted under the same conditions and the results were compared. Weights were determined with a precision of 0.0001 g on a RADWAG AS 220/X digital analytical balance.

2.4 Characterization of apparatus and experimental procedures

The experiments described in the present paper were conducted in a laboratory-scale facility shown schematically in Figure 4.

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 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. The Tektronix DMM 4040 digital

multimeter was used to measure the open circuit voltage of the fuel cell. 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 (in range 0.1-10000 Ω). The amount of air fed into the cell was controlled by a thermal mass flow controller (Brooks 4850) with local operator Interface (LOI) to view, control and configure the control device. It was possible to adjust the gas flow rate from 0.1 dm³/min. to 2 dm³/min. 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.

At the beginning of each test 500 g of sodium hydroxide was put into the main cell container (prototype I and II) or prepared eutectic mixture of NaOH (90 mol%) with LiOH (10 mol%) in case of prototype III 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 25 liters of deionized 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 deionized 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 deionized water. All the elements were then dried for 3 hours in a drier.

2.5 Characterization of Carbon Fuels

Three kinds of carbon fuels with different characteristics were used as anode materials – graphite, biocarbon and coal. The example fuel samples are shown in Figure 5 while the main properties of the fuels are shown in Table 3.

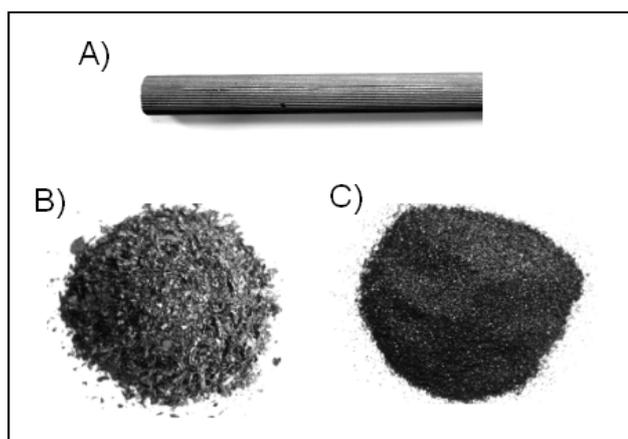


Figure 5. The example fuel samples: A) graphite rod (d=13 mm), B) biocarbon, C) hard coal.

Table 3. 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
Hard coal (granules)	26.7	36.6	11.5	4.5	0.18-0.25
Graphite (rod)	32.3	1.3	1.7	0.1	13 mm outside diameter

These biocarbon and coal samples were ground and sieved on the laboratory vibration shaker to fraction of 0.18-0.25 mm granule size.

3 RESULTS AND DISCUSSION

3.1 Effect of different electrode materials and carbon fuels on the cell performance

Prototype I

Figure 6 shows the voltage and power density versus current density characteristics of prototype I direct carbon fuel cell at 450°C (air flow rate: 0.5 dm³/min).

The voltage-current density characteristics (i-V) show that the limiting current condition is reached nearly 80 A/m² with biocarbon as a fuel and above 40 A/m² for graphite. The figure shows that the maximum peak power densities achieved are 50 W/m² and 24 W/m² for biocarbon and graphite respectively. Biocarbon produced an open circuit voltage (OCV) of up to 1.075 V is compared to graphite rod that produced an OCV of up to 0.85 V.

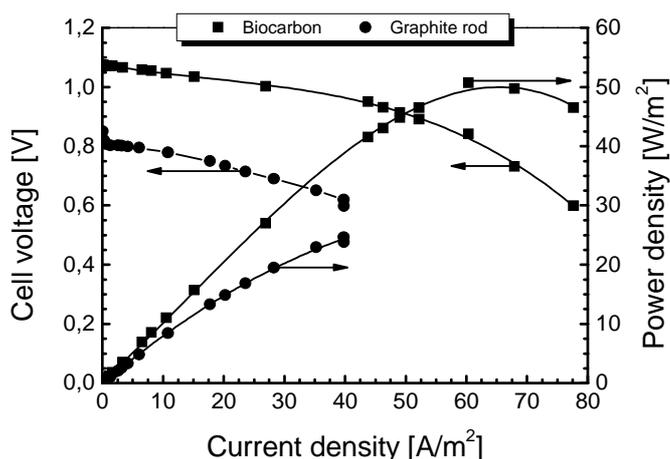


Figure 6. Voltage - current density and power density - current density characteristics of the prototype II fuel cell (electrolyte temperature 450°C, air flow rate 0.5 dm³/min).

The overall simplicity of cell design showed in Figure 6 combined with the cheap construction materials makes it commercially attractive but high corrosion rates of carbon steel used in the cell at the operating temperatures lead to high levels of degradation particularly on the long-term operation.

Prototype II

The materials of construction for this prototype were stainless steels: 304L, 316L and 316Ti. Figure 7 shows the polarization (i-V) curve and power obtained during the experiments on three different carbon materials: biocarbon, coal and graphite at 450°C. As can be seen that the DCFC prototype II produced an increased performance, with maximum power densities of above 65 W/m² with graphite rod

serves as a fuel. For biocarbon the maximum power densities were comparable with the first prototype and equaled to 48 W/m^2 . For coal the cell achieves power density above 40 W/m^2 .

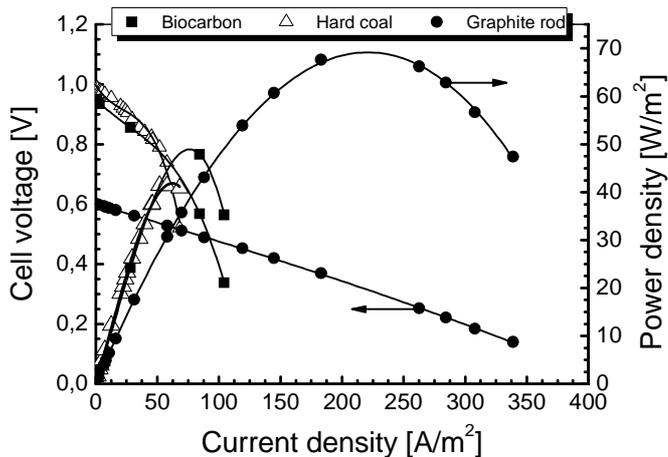


Figure 7. Voltage - current density and power density - current density characteristics of the prototype II fuel cell (electrolyte temperature 450°C , air flow rate $0.5 \text{ dm}^3/\text{min}$).

Figure 7 shows current densities of above 300 A/m^2 achieved with graphite as the fuel and very low for biocarbon (104 A/m^2) and coal (68 A/m^2). The OCV of the prototype II with solid biocarbon and coal is higher than the one with graphite fuel - 0.95 V , 0.99 V and 0.6 V respectively. After fuel cell tests at the temperature of 450°C , stainless steels 300 series were covered with an oxide layers (probably NiO , Fe_2O_3 , Cr_3O_4 , Cr_2O_5 , and CrO). The protective oxide films formation of a dense film of corrosion products that firmly adheres to the steel surface and has a sufficiently high chemical resistance. However, after each test NaOH melt contained loose products of further interaction of oxides with the melt, which poorly adhere to the surface. Therefore, it was decided to build another prototype of the cell made of nickel and its alloys.

Prototype III

In Figure 8 the characteristics of the prototype III, manufactured from the Nickel[®] 201 and Inconel[®] alloy 600, operated with various fuel types are shown. The maximum current density for this cell was very high, more than 700 A/m^2 both for the biocarbon and coal as the fuels.

The observations on three samples of fuels showed a large variation in maximum peak power densities - 335 W/m^2 , 291 W/m^2 and 53 W/m^2 for biocarbon, coal and graphite, respectively. It was suggested that this variation was largely due to a significant differences in structures of those types of fuel samples and in the reactions kinetic on a new construction materials. Alloy 600 with high Ni content shows good catalytic activity to oxygen (cathode side) and new design of cell was employed to

reduce the impact of ohmic losses on DCFC performance. The results presented in Figures 6–8 clearly indicate the effect of fuel type and the

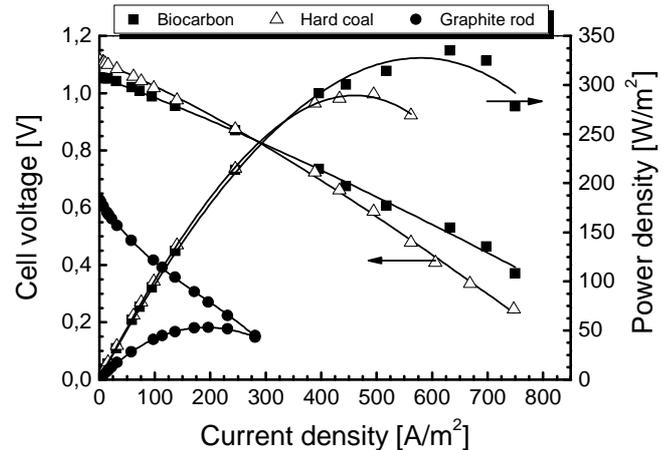


Figure 8. Voltage - current density and power density - current density characteristics of the prototype III fuel cell (electrolyte temperature 450°C , air flow rate $0.5 \text{ dm}^3/\text{min}$).

construction material on the operation performance of the fuel cell, and are quite promising with respect to the 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.

3.2 Inconel[®] alloy 600 (cathode material) characterization.

Figure 9 shows the ring made of Inconel[®] alloy 600 mounted on the cathode cells during each run of the fuel cell. All runs were conducted at 450°C with air flow rate of $0.5 \text{ dm}^3/\text{min}$. Electrolyte composition was NaOH-LiOH (90-10 mol%).



Figure 9. Inconel[®] alloy 600 ring before (left) and after (right) oxidation/lithiation process.

According to the XRD analysis, $\text{Li}_{1-x}\text{Ni}_x\text{O}$ existing in Inconel[®] alloy 600 and coating was in the form of NiO , $\text{Li}_{0.05}\text{Ni}_{0.95}\text{O}$ and $\text{Li}_{0.1}\text{Ni}_{0.9}\text{O}$.

The corrosion rate of Inconel[®] alloy 600 during direct carbon fuel cell operation at 450°C was studied with the use of the weight loss technique. Table 4 shows the weight changes of examined material

during fuel cell operations. Figure 10 shows the XRD patterns of the Inconel[®] alloy 600 ring.

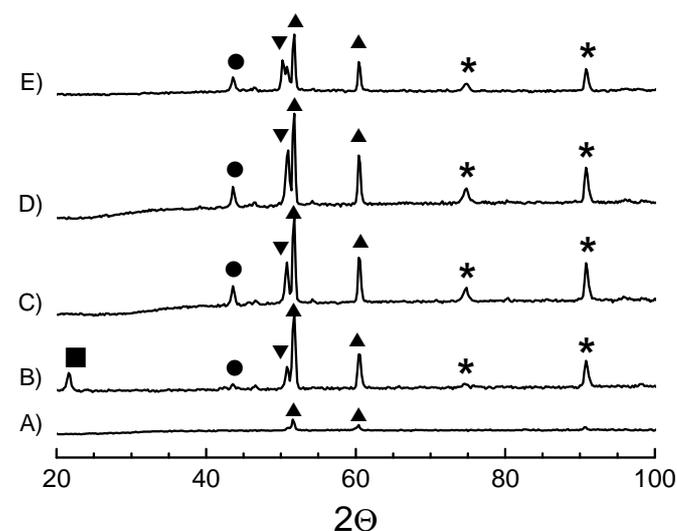


Figure 10. X-ray diffraction patterns for A) pure Inconel[®] alloy 600, B) after lithiation process, C) after 64 hours, D) after 94 hours, E) after 115 hours, (■) $\text{Li}_{0.4}\text{Ni}_{0.6}\text{O}$ peak, (●) $\text{Li}_{0.05}\text{Ni}_{0.95}\text{O}$ peak, (▲) Ni peak, (▼) NiO peak, (*) $\text{Li}_{0.1}\text{Ni}_{0.9}\text{O}$ peak.

Table 4 shows that the weight gain of the Inconel[®] 600 increases during fuel cell operation time. In the first step the weight gain is related with the formation of NiO doped Li^+ ions. During the fuel cell test, firstly it can be observed the weight loss probably related to removal of $\text{Li}_{0.4}\text{Ni}_{0.6}\text{O}$ species (see Figure 10 B). The overall weight gain after 20 and 40 hours of state corrosion test was found to be 0.6 and 7.2 mg, respectively. This result illustrated the corrosion protecting effect of the NiO coating very well (see Figure 10 C-E).

Table 4. Time weight changes measurement of Inconel alloy 600 ring during fuel cell operation.

Exposure period (hours)	Weight change	
	[g]	[%]
24 (after oxidation/lithiation process)	+ 1.95	+ 6.1
10 (first test after lithiation)	- 0.0004	- 0.0008
20	+ 0.0006	+ 0.0038
40	+ 0.0072	+ 0.0723

4 CONCLUSIONS

Three DCFCs with different configurations and construction materials have been successfully tested in the laboratory scale. On the basis of a series of corrosion experiments with a number of different materials, it was decided to use a nickel (Nickel[®] 201) and high-nickel alloy (Inconel[®] alloy 600) to build the cell (anode, cathode, container, *etc.*).

Various carbon fuels have been tested in different DCFC prototypes, a knowledge of the efficacy of carbon fuels is still unclear. Apparently the disordered carbon is more reactive due to a preponderance of edges sites and defects. The physical and chemical properties of carbon fuels can be seen to highly influencing the electrochemical performance. However, the DCFC technology represent a simple way to convert carbon chemical energy to electricity efficiently and without forming by-products associated with conventional combustion (NO_x , SO_x , *etc.*).

Power densities ranging from 24-335 W/m^2 were measured on a variety of carbon materials. The highest power densities were achieved with charred biomass and raw coal for prototype III fuel cell. These power densities are too low for a commercially viable system, however, with research and development in progress there is a potential for further improvements.

Using conventional hard coal without pretreatment fuel cell had achieved power density greater than 290 W/m^2 and current density around 750 A/m^2 at 450°C (prototype III).

The cell performance of direct carbon fuel cell with molten hydroxide electrolyte can be significantly improved by optimizing the cell design and the electrodes material. Inconel[®] alloy 600 was the good catalytic material for the cathode with the good corrosion resistance.

There is also significant work to continue at a cell level on the optimization of operating temperature, air humidity, gas bubbling rate and electrolyte composition (single and mixed hydroxides of alkali metals such as Na, K, Li).

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