



# On the utilization of coal samples in direct carbon solid oxide fuel cell technology



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## ABSTRACT

Coal samples with 3 wt.% ash were chosen as a prospective solid fuel for direct carbon solid oxide fuel cells operating within a temperature range of 600–850 °C. Based upon X-ray and infrared spectroscopy analysis, it was found that the main inorganic impurities in this coal were dolomites. The chemical analysis of ash content in the coal, before and after 3 M HNO<sub>3</sub> treatment, indicated that the applied purification procedure allowed a considerable decrease in the ash down to 0.4 wt.% in the coal samples. The physicochemical properties of raw and modified coal samples were investigated by analytical and physicochemical methods in order to evaluate its potential use as a solid fuel for a direct carbon fuel cell with a solid oxide electrolyte (DC-SOFC). The tests indicated that DC-SOFCs fed with this type of processed fossil coal were characterized by stable operation with reasonable current and power densities.

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## 1. Introduction

Despite strenuous efforts to reduce emissions of CO<sub>2</sub>, carbonaceous fuels remain one of the main energy carriers exploited in the power industry. Statistical and economic analyses show that in the coming decades, in developing countries such as China, India, and Poland, coal-fuelled power plants will maintain their strong position in the power sector due to their reliability, low costs, and large world reserves of coal and lignite. However, even in this scenario, emissions of CO<sub>2</sub> may not necessarily increase, provided that either energy conversion in these plants is handled in a more efficient way or carbon dioxide is sequestered [1,2].

One of the more promising technologies which fulfils these requirements is the direct carbon fuel cell (DCFC), an electrochemical device which directly converts the chemical energy of carbonaceous fuel into electricity without “flame burning.” The electrical efficiency of a DCFC is indeed very high (practically exceeding 80%), and the product of conversion consists of almost pure CO<sub>2</sub>, which eliminates the most expensive step of sequestration: separation of carbon from flue gases [3]. Although the concept of the direct conversion of chemical energy from solid fuels into electricity in fuel cells was discovered in the mid-19th century, it is only in the last decade that there has been a renewed interest in direct carbon fuel cells (DCFCs), supported by record levels of global generation of electricity from coal. This has led to significant progress in the field [4]. Various types of DCFCs have been developed recently. One of the most popular classifications is based on the type of electrolytes used in a cell: alkaline, carbonates, or solid oxide

electrolytes (DC-SOFCs) [5–7]. The latter system, i.e. a direct carbon fuel cell with a solid oxide electrolyte (DC-SOFC), is believed to be the most promising due to its uncomplicated construction and maintenance. However, it suffers from low power density, which must be increased to enable its commercialization [8].

In a DC-SOFC [9,10], carbon can be directly electrochemically oxidized to CO<sub>2</sub> according to Eq. (1):



as well as in a sequence of reactions (2) and (3):



The Boudouard reaction (2), involving CO<sub>2</sub> and C as reactants, is an additional source of the CO consumed in reaction (3).

A DC-SOFC usually operates within a temperature range of 700 and 900 °C. The power density obtained from a DC-SOFC increases along with the temperature; at 850 °C it usually does not exceed 120–180 mW/cm<sup>2</sup>. The physicochemical properties of the applied solid fuel, the construction of the cell, the compositions of electrode and electrolyte materials, the applied catalysts, and the participation of CO produced by the Boudouard reaction (2) in the overall electrooxidation process occurring in the cell – all affect the current and power densities acquired from the DC-SOFC [11–13].

Coal is a complex, chemically and physically heterogeneous conglomerate, containing a variety of organic and inorganic materials.

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The primary inorganic elements found in mineral matters of coals are: silicon (Si), aluminium (Al), potassium (K), iron (Fe), magnesium (Mg), calcium (Ca) and titanium (Ti). These elements are contained primarily in five mineral types: clays, carbonates, sulphides, sulphates, and oxides. The typical representatives of such minerals are: aluminosilicates, such as montmorillonite, illite, kaolinite, muscovite, and chlorite. Note that potassium, magnesium, and iron are contained in some of these clays. Calcium and magnesium are associated mostly with carbonates, calcite and dolomite being principally mineral carbonates. Siderite is also found in coals but iron is primarily associated with pyrite, the dominant mineral of sulphide. Sulphur is also contained in the mineral sulphates: gypsum and jarosite. Most of the oxygen in the mineral matter is associated with  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{TiO}_2$  [14].

Various impurities in coal produce side-effects which impact on the anodic electrochemical reaction and lifetime of a DCFC [15,16]. The effect of the presence of ash in solid fuel was previously investigated in coal using a button-sized DC-SOFC with a Ni-YSZ anode [17]. At a cell operating temperature of 1023 K, the power output of such a cell was doubled compared to cell operation on ash-free coal. This was attributed to the additional release of gaseous fuel from the raw coal in the form of pyrolysis gases. However, when the operating temperature of the DC-SOFC was increased to 1173 K, a similar power output was measured in both cases [18]. Nevertheless, some of the oxides present in the ash apart from degrading the anode materials in a DC-SOFC may also have a positive impact on cell performance. Some of the oxides catalyse the Boudouard reaction [19]. An increase in CO concentration as an additional reagent in the anode chamber could improve the DC-SOFC performance.

In this work, we concentrate on the performance and life-time of the direct carbon fuel cell with solid oxide electrolyte fed with pulverized coal with ash, in which the content is no higher than 3 wt.%. The impact of the purification of raw coal by nitric acid on the performance of such a fuel cell was also analysed and reported.

## 2. Experimental

### 2.1. Coal powder preparation and purification

Coal containing 3% weight ash from the coal mine Wieczorek (Silesia, Poland) was chosen for all the investigations described in this paper. Samples of carbon in the form of pieces ca. 1–2 cm in diameter was obtained from a Polish coal mine. In the first step, coal was dried to an air-dry state, and then crushed in a jaw crusher to the size of a grain – below 3 mm. In the next step, the crushed coal was pre-ground in a ball mill to a grain size of less than 0.02 mm. A portion of this representative coal powder was taken for technical and chemical analysis. The coal powders were additionally milled in an attrition type mill using dry ethyl alcohol. Zirconia grinding media, with a diameter of 2 mm, were applied. The time spent on coal grinding ranged from 15 min to 2 h. By this method coal powders with different surface areas were obtained. The pre-ground coals as well as powders, which were additionally ground in an attrition type mill, were further purified by 3 M nitric acid ( $\text{HNO}_3$ ). The purification process was performed at 100 °C for 24 h, and the coal powders were filtered and washed by distilled water.

### 2.2. Analytical methods of coal evaluation

The phase compositions of the coal powders were evaluated by X-ray diffraction analysis, with reference to the ICDD database. XRD measurements were taken using the Panalytical X'Pert Pro system with monochromatic  $\text{CuK}\alpha$  radiation. Infrared spectroscopic (IR) measurements of the coal samples were taken with a Bio-Rad FTS 60 V spectrometer. The contents of elements such as carbon (C), nitrogen (N), sulphur (S), and hydrogen (H) in all of the investigated samples were determined by the use of a PerkinElmer 2400 CHN Elemental

Analyser. The ash content and volatile matter of the initial coal samples and these after the purification process were determined by gravimetric analysis. The different sulphur forms (especially organic and inorganic in raw coal samples) were also analysed by chemical methods. The sinterability of the original coals, and those after the purification process was also determined by the dilatometry method.

A scanning electron microscope (AEM Philips) coupled with an EDS system was used to characterize the morphology and chemical composition of the carbon particles.

Before and after tests of the surface of the electrode materials and a cross section of the solid fuel cells were examined using a scanning electron microscope.

The thermal effects that occurred while heating the solid carbon fuel within a temperature range of 25–1000 °C in helium gas flow were measured by DTA and TG methods (TA Instruments SDT 2960). The samples (ca. 50 mg) were ramped up to a rate of 10 K · min<sup>-1</sup> in an aluminium crucible.

The following items were determined: the impact of gaseous and liquid products originating from the decomposition of organic and inorganic compounds included in the raw coal samples, and the effect of solid coal on the thermal and chemical stability of the electrolyte and anode materials. Electrolytes composed of 8% mol  $\text{Y}_2\text{O}_3$  in  $\text{ZrO}_2$  (8YSZ) and covered with Ni-8YSZ or Ni-10GDC films were placed in aluminium crucibles and then into a gas-tight quartz reactor heated in a coal bed at 850 °C for 300 h under argon flow as the shielding gas. After cooling the experimental samples to room temperature while shielding the gas flow, they were withdrawn from the reactor and analysed.

### 2.3. Electrochemical performance of the DC-SOFC

The electrochemical oxidation of carbon was studied. The oxidation of the carbon fuel was investigated in the cell:



The ceramic fuel cells were constructed using commercially available SOFC single-cell elements distributed by Fuel Cell Materials. For the purpose of this experiment, 8YSZ denotes an electrolyte of 8-mol%  $\text{Y}_2\text{O}_3$  in  $\text{ZrO}_2$ ; LSM is a  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  cathode material; Ni-8YSZ is a cermet anode, a composite material consisting of 50% vol. nickel particles distributed in an 8YSZ matrix. The geometric area of the active electrolyte surface was ca 1.38 cm<sup>2</sup>. This type of commercial fuel cell was used in our previous investigations, which confirmed the usability of charcoal, as well as of other industrial carbons, such as carbon black N-220 and hyper-coal, for supplying DC-SOFCs [20,21].

The side view of the experimental set-up with a DC-SOFC placed inside is shown in Fig. 1. The cell consisted of two chambers separated by a button solid oxide fuel cell (1) (20 mm in diameter and ca. 0.2 mm thick), which was fixed to  $\text{Al}_2\text{O}_3$  tubes (2) on each side. The cathode (3) was supplied with atmospheric air. The anode current collector (6) was gold mesh welded to gold wire (5) and covered with carbon fuel (4). The cell was located inside an electric furnace (7). During the experiment, argon or  $\text{CO}_2$  was continuously supplied to the anodic chamber as a shield gas.

The experimental setup and procedure of electrochemical investigations were also described previously [22]. Electrochemical measurements were performed within a temperature range of 500–850 °C, using a PGSTAT 300 N potentiostat equipped with GPES (chrono and pulse techniques) and FRA (electrochemical impedance spectroscopy) modules. During the measurements Ar or  $\text{CO}_2$  were used as shielding gases which were introduced to the anode chamber.

In this study the DC-SOFC was supplied by raw coal powders as well as purified coal powders. By this method the destructive impact of some mineral matters on the DC-SOFC performance was determined. The DC-SOFC was also supplied with coal powders with different surface

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