

Carbon as a fuel for efficient electricity generation in carbon solid oxide fuel cells

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Abstract. In this paper, the impact of the physicochemical properties of carbonaceous solid fuels on the performance of a direct carbon solid oxide fuel cell (DC-SOFC) was investigated. High-purity synthetic carbon powders such as carbon black N-220 and Carbo Medicinalis FP5 were chosen for analytical and electrochemical investigations in a DC-SOFC. The research focussed on choosing an optimised, cost-effective, high-purity carbon powder which could be applied as a solid reference fuel for all tests performed on a single DC-SOFC cell as well as on DC-SOFC stack constructions. Most of the electrochemical investigations described in this paper were performed using square DC-SOFCs with dimensions of 5×5 cm. The relationship between structure, physicochemical properties, and electrochemical reactivity in a DC-SOFC was analysed.

1 Introduction

The economic, cultural, and technological development of present-day societies (particularly rapidly developing countries such as China, India, and the countries of South America and Africa) may be impeded as a result of the growing demand for energy, which cannot be fully satisfied due to the depletion of fossil energy resources. For this reason, many countries have been carrying out intensive research and development work on the use of renewable energy sources (RES), as well as on improving the efficiency of the conversion of fossil fuels in the commercial and distributed power industries, with particular emphasis on protection of the natural environment. In the nearest future, for technological and economic reasons, it will not be possible to replace conventional power plants with new generators on a large scale using renewable energy sources [1, 2].

Therefore, technologies referred to as 'intermediate' are being introduced and developed in many countries, constituting a bridge between conventional and renewable energy technologies. New energy technologies enable more efficient use of fossil resources of energy, often through the co-generation of electricity and heat, which also results in a significant reduction in emissions of greenhouse gas and other harmful substances into the environment. A great deal of hope is placed in fuel cells, which are marked by very high rates of conversion efficiency of the chemical energy of fuels into electricity and by their potential for use in distributed systems. So far, the most commonly used fuel for fuel cells is hydrogen [3, 4].

Currently, the most rapid technological development can be observed in proton exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs). There is a growing interest in utilising different alternative fuels in fuel cell technology. Many authors have presented performance results for different types of fuel cells operated with ethanol, methanol, formic acid, biogas, syngas, or methane ammonia [5, 6].

Carbon-based fuels can also be used to supply fuel cells. This can be done both directly and indirectly. In the first case, coal or carbonaceous-based solid fuels can be gasified, and the resulting gas, usually rich in CO, can be used as a reagent in fuel cells. In some types of fuel cells, the direct conversion of solid carbon-based fuels is also possible. Direct carbon fuel cells (DCFCs) are powered by solid fuel. Powdered carbonaceous-based solid fuels are fed directly to the anode, where gaseous CO₂ is formed during an electrochemical oxidation reaction [7, 8].

DCFCs are of great importance for the global economy, as they require large deposits of hard coal and lignite. In DCFCs, the chemical energy of coals can be directly converted into electricity with very high efficiency (over 70%). The sole product of this conversion is pure CO₂; thus the expensive process of separating CO₂ from flue gases can be avoided [9]. These potentially attractive characteristics of DCFCs make them attractive to a broad spectrum of power sector investors.

Carbon particles can be directly oxidised on the surface of an oxide electrolyte and cermet and oxide-based anode materials in SOFCs according

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to reaction (1). Cells of this type fed directly with solid carbonaceous fuel seem to be a very attractive option in direct carbon fuel cell technology. As early as in 1988, Nakagawa and Ishida [10] described the mechanism of carbon oxidation as a pair of anodic electrochemical half-reactions (2–3).



The additional source of carbon monoxide for reaction (3) is the chemical Boudouard reaction (4):



Direct carbon fuel cells with solid oxide electrolytes (DC-SOFCs) seem to constitute the most promising option in DCFC technology. DC-SOFCs operate at high temperatures of 700–900°C. The increased temperature improves the kinetics of the electrochemical oxidation of carbon particles in the anode process. A variety of SOFC components (electrolyte, anode, cathode and catalysts) can be considered for design and construction of a DC-SOFC stack. Engineers also have a range of construction options: they can use planar and tubular as well as fluidised-bed designs [11, 24].

However, the introduction of DC-SOFC technology into the mass market depends on improvements in carbon conversion rate, electrical efficiency, and fuel utilisation attainable in actual conditions. The DC-SOFCs most frequently investigated in R&D institutions are typically built using planar geometry on the basis of a small button-size cell (diameter: ca. 2 cm) or a larger, square MEA with dimensions of 5 × 5 cm [12, 13]. Performance data for DC-SOFCs with large dimensions (above 10 cm²) are rather scarce. A DC-SOFC stack is generally constructed from MEAs with larger dimensions (5 × 5 or 10 × 10 cm). The problem of scaling up an SOFC system from small cells (active area of electrode materials ~1–2 cm²) to ~16–80 cm² is a difficult one. A single SOFC with larger dimensions enables the acquisition of higher values of current and power than can be obtained from a small button solid oxide fuel cell. Tests of planar DC-SOFCs require more complicated current collectors and electrical connections to avoid electrical losses during measurements. Sealing the electrochemical chamber is also more complicated. Following successful tests of such single MEAs, the construction of a short stack, which usually combines 2–4 single cells, can be planned.

This research focusses on choosing an optimised cost-effective high-purity carbon powder which can be applied as a reference solid fuel for all tests performed on a single SOFC with larger dimensions.

2 Experimental

In order to carry out a comparative interpretation of the performance data, two different types of carbon fuels were investigated in parallel. A commercial carbon black N-220 (Konimpex, Poland), referred to as N-220,

and a charcoal-type activated carbon Carbo Medicinalis FP5 (Gryfskand, Poland), referred to as CM, were analysed. Both carbon-based solid fuels are typical representatives of high-purity synthetic carbon and are readily available and commonly applied in different areas of industry. Raman spectra of carbon particles were collected using a FTS 6000 Bio-Rad Spectrometer with a Raman section (Nd: YAG Spectra Physics T10, 1064-nm laser). The spectra were collected after 10,000 scans at a resolution of 4 cm⁻¹. The specific surface area was determined by multipoint nitrogen adsorption at -196°C (Quantachrome PoreMaster). The contents of elements such as carbon (C), nitrogen (N), sulphur (S), and hydrogen (H) were determined in all of the investigated samples using an elemental analyzer TruSpec Micro CHNS Leco. The proximate analyses were done with a calorimeter AC 500 Leco, laboratory drier and a muffle oven. The chemical reactivity of the carbon-based powders vs CO₂ gas was determined using the thermogravimetric method within a temperature range of 25–850°C. The temperature was increased at a rate of 5°C/min up to 850°C. The mass losses of carbon powders vs CO₂ gas at a constant rate were also analysed at 850°C for 300 min.

2.1 Experimental setup

A planar, electrolyte-supported SOFC cell, 5 × 5 cm, with the structure Ni-YSZ|Ni-GDC|8YSZ|LSM-GDC|LSM and a 150 μm thick YSZ electrolyte layer was provided by Fuel Cell Materials. The cathode and anode surface areas were equal 16 cm². Gold current collectors were applied in a four-probe configuration. Carbon black N-220 and charcoal-type activated carbon CM were introduced into the anode chamber for both single-batch test runs, respectively. The experimental DC-SOFC setup used was similar to the one used in our group's previous paper [11], as schematically presented in Fig. 1.

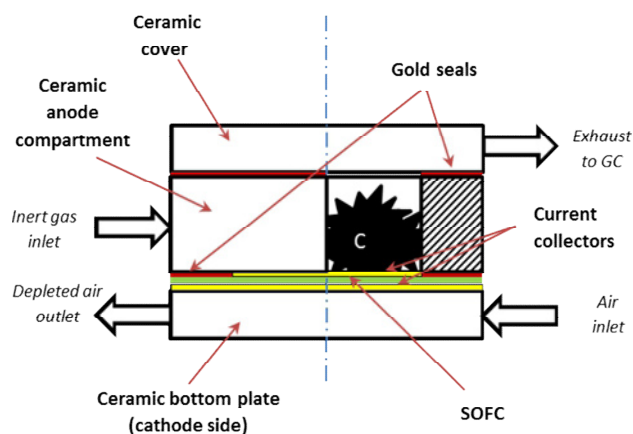


Figure 1. Schematic diagram of the DC-SOFC's housing configuration.

The DC-SOFC current-voltage characteristics were acquired at a temperature of 850°C using a Chroma 6310 electronic load with a Keithley 2000 multimeter. The anodic exhaust gas was analysed with a Varian CP-4900 gas chromatograph (GC) for determining concentrations of CO and CO₂ during the experiment.

2.2 Experimental procedure used for the DC-SOFC test

Before testing each cell with the carbonaceous fuel, both cells' anodes were reduced under hydrogen flow in another test runs in a standard SOFC ceramic setup with gold current collectors. After cooling, each cell was placed in a DC-SOFC housing configuration and filled with carbon. In both experiments, ca. 25 ml of carbon powders was applied. This volume corresponds to 9.25 g of the carbon black N-220 and ca. 5g of charcoal CM. The system was heated to 850°C with a constant flow of 5% H₂ + 95% Ar gas mixture through the carbon bed compartment and air on the cathode side. After the operational temperature had been reached, the flow of hydrogen gas to the anode chamber was stopped and the cell was purged with Ar (190 Nml/min) for 1 hour. Then the argon flow was stopped and the cell operated without any gas supply; however, a minor leak of nitrogen from the inert-gas shield into the cell compartment was detected. The exhaust from the anode compartment remained open at all times and the gas chromatograph was connected to the beginning of the exhaust pipe with a T-junction. After preliminary I-V measurements, the cell was loaded with a current of 0.65 A (40.5 mA/cm²). CO and CO₂ composition in the anode exhaust was measured by GC with 3–10 min intervals.

In the experiment using CM as fuel, no GC measurements were made. Instead, following the initial electrochemical characterisation of the DC-SOFC, the influence of CO₂ flow on electrochemical performance was experimentally verified. For this purpose, the cell was subsequently subjected to a flow of CO₂ of 50, 25, 5, 2, and 0 Nml/min through the anode chamber. The changes in flow were initialised under stable OCV conditions, and a 5-min stabilisation was performed in OCV conditions after each change, allowing the OCV to reach a plateau. Next, an I-V measurement was performed and the subsequent CO₂ flow investigated. This procedure was repeated five times to obtain comparable measurements for all 5 flows of CO₂ through the anode chamber.

3 Results and discussion

3.1 Analyses of solid fuels

Selected physicochemical properties of carbon black N-220 powder and charcoal were the subject of previous investigations. The impact of their physicochemical properties on direct carbon button solid oxide fuel cells were described in papers [14, 15].

Within the scope of the performed research, solid powders of carbon black N-220 and charcoal (CM) were subjected to analytic investigation aimed at identifying the comparative physicochemical properties crucial for application of these solid fuels in a large-scale DC-SOFC. First, the properties of solid carbon-based fuels were determined using proximate and ultimate analysis. The concentrations of major elements in the solid fuels as well as proximate analysis results are listed in Table 1.

Table 1. Proximate and ultimate analysis of applied carbonaceous fuels.

Parameter	Unit	N-220	CM
Water content	%	1.1	5.7
Ash	%	0.4	0.6
Volatile matter	%	1.42	2.54
HHV	kJ/kg	32,408	30,735
LHV	kJ/kg	32,290	30,463
C _t ^a	%	90.6	90.3
H _t ^a	%	0.4	0.6
N _t ^a	%	0.45	0.47
S _t ^a	%	0.96	0.03

The data presented in Table 1 clearly indicates that both chosen solid fuels were characterised by similar amounts of carbon, hydrogen, and nitrogen. A difference occurred in the case of sulphur. The carbon black N-220 exhibited a considerably higher content of sulphur than did Carbo Medicinalis. The chemical composition and content of ash and volatile matter have a considerable impact on DC-SOFC performance; thus, this parameter should be monitored before each electrochemical test of a DC-SOFC.

Raman spectroscopy was used for studies aimed at showing the detail of atomic disorder of carbon in these samples. Raman spectra recorded for N-220 and CM samples are presented in Fig. 2a and b.

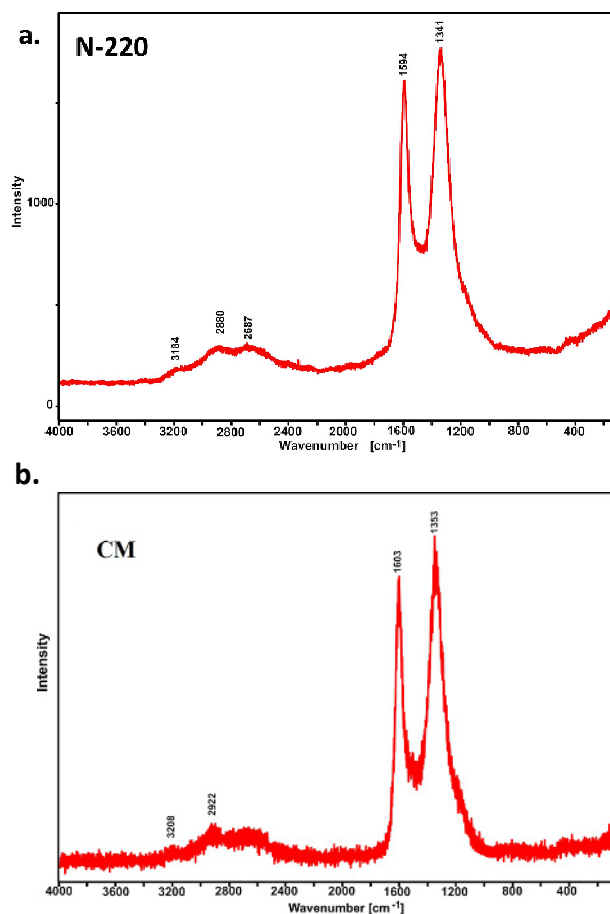


Figure 2. Raman spectra recorded for carbon black N-220 (a) and Carbo Medicinalis (b).

Analysis of the Raman spectra revealed a distinctively visible G band (ca 1594 and 1603 cm^{-1}), which confirms the sp^2 carbon hybrid structure of both samples.

The presence of a D band at ca 1341 and 1353 cm^{-1} indicated the presence of a large number of structural defects in the investigated carbon-based samples. The ratio of the intensities of the G and D bands can be attributed to the degree of disordered carbon structure in both samples.

This kind of Raman spectra for carbon black was previously interpreted by Sadezky et al. [16] as a highly disordered graphite structure. The first-order spectrum of the soot generally exhibited two broad and strongly overlapping peaks with maxima at $\sim 1341\text{--}1353 \text{ cm}^{-1}$ and $\sim 1594\text{--}1603\text{ cm}^{-1}$. Both of these investigated samples represent the short-range graphite or turbostratic structure of the sample [17, 18].

The chemical reactivity of carbon powder with respect to CO_2 may be another crucial factor with a considerable effect on DC-SOFC power output in the temperature range 700–850°C.

One feature preferred for gasification through the Boudouard reaction (4) is high reactivity of carbon with CO_2 , i.e. the ability to reduce CO_2 to CO, according to reaction (4) [19]. The presence of CO as an additional reagent for anodic oxidation of carbonaceous fuel should lead to an increase in the current density as well as in the power acquired from the DC-SOFC [20]. It was found that, in a DC-SOFC, a convection mechanism can occur inside the carbon bed, enabling gaseous CO to be effectively transferred to the triple phase boundary areas inside a porous cermet SOFC anode [21].

The reactivity of carbon black N-220 and activated charcoal CM was evaluated using thermogravimetric analysis. Fig. 3 depicts the variation in carbon mass during a reaction with flowing CO_2 with a temperature increase from 25 to 850°C as well as at a constant temperature of 850°C.

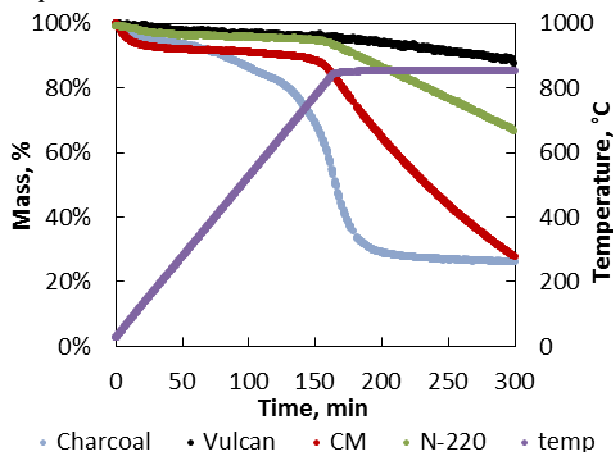


Figure 3. TGA analysis for investigated (N-220, CM) and reference (Vulcan, charcoal) carbon samples in CO_2 . Heating rate: 5°C/min.

As can be seen, the thermogravimetric analysis showed a continuous decrease in total carbon mass weight in the course of heating from 25 to 850°C, as well as at a constant temperature of 850°C. The analysed

dependence of mass losses vs temperature or time indicated a difference in the chemical reactivity of the investigated solid fuels, i.e. both of the analysed carbon black powders, CB-Vulcan and CB-N220, were characterised by rather poor reactivity vs CO_2 .

The charcoal-based samples (charcoal from Sigma Aldrich and Carbo Medicinalis) exhibited greater reactivity vs CO_2 than the carbon black samples. Therefore, application of charcoal as fuel is expected to enable higher performance levels in DC-SOFCs, caused by more intensive gasification processes inside the anodic compartment of the cell.

3.2 Electrochemical performance of a DC-SOFC with a Ni-YSZ anode

The polarisation curves (U-I) measured at 850°C for DC-SOFCs fuelled by charcoal and by carbon black N-220 are presented in Fig. 4. As can be seen, the open circuit voltage for a DC-SOFC supplied by the investigated solid fuels reached values of 1.006 V, close to the theoretical OCV values calculated for reaction (1) ($\text{OCV}_{\text{cal}} = 1.026 \text{ V}$). For the measurements, the following methodology was employed: a 16- cm^2 fuel cell was loaded with a stepwise increasing current, with each step followed by 1 min of voltage stabilisation. The comparative analysis of U-I and P-I curves recorded for an identical DC-SOFC setup supplied with carbon black N-220 or CM indicated different electrochemical outputs.

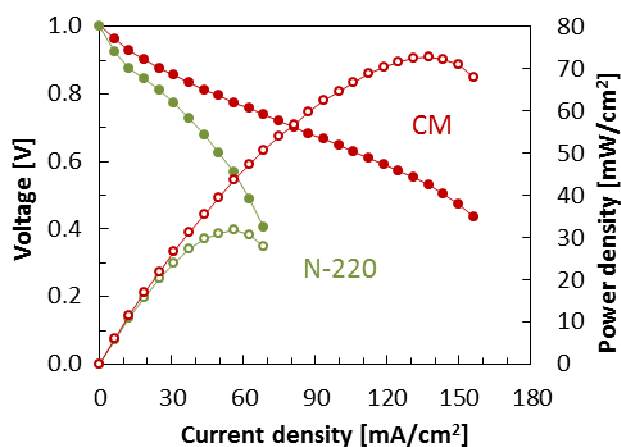


Figure 4. Polarisation and power density curves, cell temperature 850°C, anode flow: none, cathode flow: 200 Nml/min of air.

Analysis of the polarisation curve for the N-220 fuel reveals concentration losses already present in a current density regime of 30–40 mA/cm^2 . This is a consequence of the relationship between reactions 1–4. The concentration losses occur because of the low level of reactivity of the applied carbon to the Boudouard gasification reaction (4). This fact was confirmed by gas chromatography measurements performed under load. The ratio of CO to CO_2 in the outlet stream lied in range 0.89–0.65, being far from the equilibrium state of the $\text{CO-CO}_2\text{-C}$ system, which in 1 atm and 850°C presents CO/CO_2 ratio of 13 [22]. Therefore, under higher current densities, the CO flux from reaction (4) occurring in the carbon bed to the anode surface is significantly

diluted by the CO₂ generated on the anode in reactions 1 and 3. Therefore no higher current densities can be achieved. In the case of a DC-SOFC supplied by Carbo Medicinalis solid fuel, a significantly higher level of performance was observed.

In the case of utilisation of carbon black N-220 as a solid fuel in DC-SOFC, the values of power output and current density were two times lower in comparison to the same cell fed with charcoal CM. The area specific resistance (ASR) calculated according to the linear part of the polarisation curve at ca 0.8 V equalled 5.34 Ωcm² and 2.93 Ωcm² for N-220 and CM, respectively. The various reasons for this behaviour should be analysed.

The electrochemical process of carbon particle oxidation occurred on the YSZ electrolyte according to reaction (1). It had previously been found that electrochemical oxidation of carbon black particles enabled the acquisition of P_{max} ranging from 18 to 25 mW/cm² at 850°C [23], depending on the presence and chemical composition of chemical impurities on the surface of the carbon particles, surface area and ratio of structurally highly-ordered graphite phase to the highly disordered phase of soot. In the case of a DC-SOFC (Ni-YSZ) with dimensions of 1.38 and 16 cm², a similar P_{max} was achieved, ranging from 30 to 50 mW/cm² [15, 23].

This finding clearly indicates that the process of electrochemical oxidation occurred mainly in reaction (1). A different situation was observed in the case of a DC-SOFC supplied with Carbo Medicinalis. It was also found that the electrochemical oxidation of carbon particles on a YSZ surface enabled the acquisition of about 20–25 mW/cm² at 850°C. An increase in the surface area of Carbo Medicinalis powders from 600 to 1200 m²/g had practically no influence on DC-SOFC performance, with values ranging from 23 to 28 mW/cm². In the case of a DC-SOFC with a Ni-YSZ anode, the impact of CO from the Boudouard reaction as an additional reagent was considerable. The previous data recorded for a DC-SOFC with dimensions of 1.38 and 16 cm² were comparable; in that case, P_{max} reached values from 50 to 70 mW/cm² [15]. Fig. 5 presents the variations of a DC-SOFC with Ni-YSZ anode vs the specific surface area of the applied charcoal solid fuels. This measurements were performed for the direct button solid oxide fuel cells (surface active area ~1.38 cm²).

As can be seen, with an increase in the surface area of a charcoal solid fuel applied in a DC-SOFC, the power output increases considerably. Higher values of P_{max} were obtained from a DC-SOFC with the application of CO₂ as a shielding gas. This finding clearly indicated that the presence of CO as a possible product of the reaction between carbon and CO₂ led to an increase in the power output of the DC-SOFC.

In the case of a DC-SOFC supplied with charcoal, the electrochemical oxidation proceeded due to reaction (1) and a combination of possible reactions (2)–(4).

Fig. 6a presents the impact of the volumetric flow of CO₂ to the anode chamber on the power output

of a DC-SOFC with a 16 cm² surface area, supplied with Carbo Medicinalis powder.

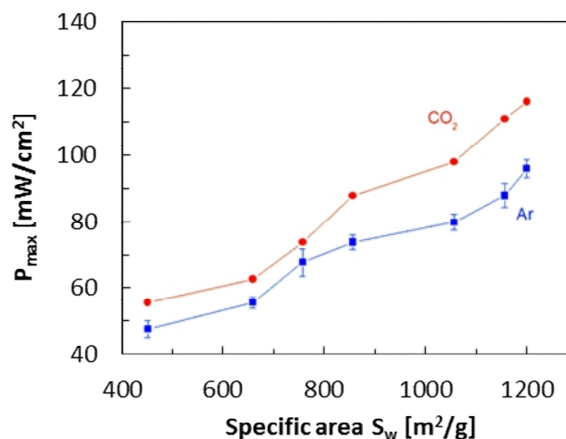


Figure 5. Variation of P_{max} vs specific surface area S_w of applied charcoal as a solid fuel.

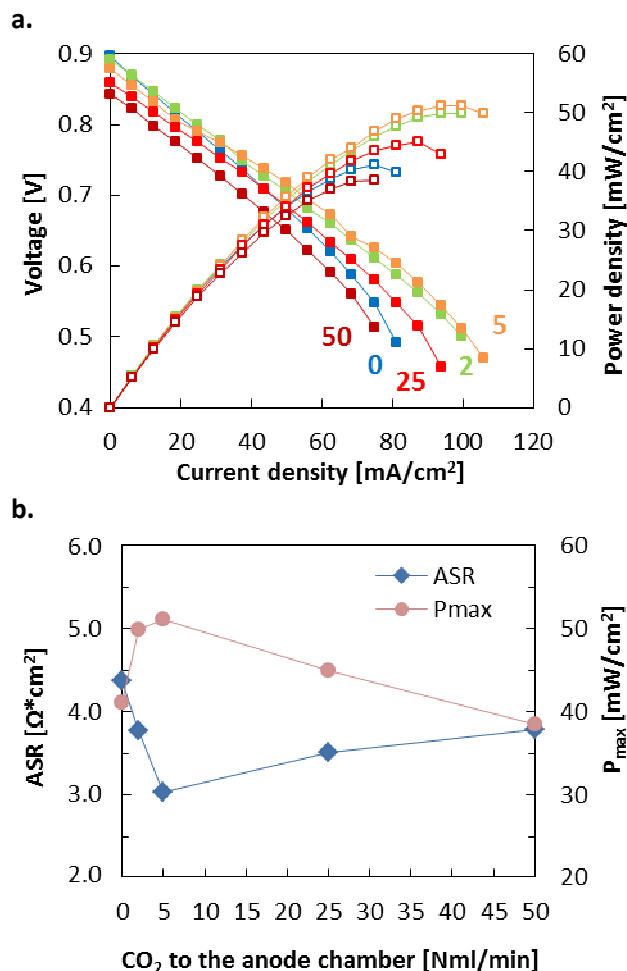


Figure 6. Polarisation and power density curves (a) and ASR and P_{max} (b) for 0, 2, 5, 25 and 50 Nml/min of CO₂ flow through the anode chamber, cell temperature: 850°C, cathode flow: 200 Nml/min of air.

Analysis of the family of voltage (U)-current (I) as well as power (P)-current (I) curves (Fig. 6a) indicated that the power output P_{max} increases slightly with the introduction of CO₂ into the anode chamber up to 25 Nml/min.

An additional increase in the flow of CO₂ to the anode of the DC-SOFC caused a decrease in power output P_{max}. In Fig. 6b, introduction of a minimal flow of CO₂ to the anode chamber enabled significant improvement in the ASR and maximum power of the cell. The optimum (in terms of DC-SOFC performance) CO₂ flow was experimentally determined to be ca. 5 Nml/min. This finding may be directly connected with adsorption of CO₂ on the surface of carbon particles and the establishment of equilibrium between carbon-CO₂ and the rate of CO synthesis as a gaseous product of reaction (4). These results are consistent with Gür's [24] proposed 'CO shuttle mechanism' to explain the mechanism of carbon oxidation under CO₂ or inert gas atmospheres in several types of direct carbon fuel cells. Gür suggested that this reaction involved oxygen on the carbon surface desorbing as CO into the anode and subsequently undergoing electrochemical oxidation to CO₂ at the TPB. Furthermore, at temperatures above 800°C, the Boudouard reaction is thermodynamically favourable. Within this temperature regime, the surface oxygen desorbs CO₂ formed at the anode from the carbon particles on the anode surface.

4 Conclusions

In this paper we analysed physicochemical high-purity synthetic carbonaceous materials which are crucial for application as solid fuels in DC-SOFC technology. Based on this analysis, charcoal-based carbonaceous materials seem to be appropriate reference fuels. The power output of a DC-SOFC supplied by solid fuels of the Carbo Medicinalis type is high compared to the same DC-SOFC supplied by carbon black N-220. One of the main reasons for this was the high chemical reactivity of carbon particles in a CO₂ gas atmosphere, producing CO, which acts as an additional reagent during cell operation.

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