



## The combined impact of carbon type and catalyst-aided gasification process on the performance of a Direct Carbon Solid Oxide Fuel Cell



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### ABSTRACT

The combined impact of carbon type (anthracite coal, bituminous coal and pine charcoal) and *in situ*, catalyst-aided, carbon gasification process on the electrochemical performance of a Direct Carbon Fuel Cell (DCFC) is explored. The effect of operation temperature (700–800 °C) and catalyst (Co/CeO<sub>2</sub>) infusion to carbon feedstock under CO<sub>2</sub> atmosphere at the anode chamber is systematically investigated in a cell of the type: Carbon + CO<sub>2</sub>|Cu-CeO<sub>2</sub>/YSZ/Ag|Air. All fuel samples were characterized, in terms of chemical composition, crystallite structure (XRD), pore structure (BET), surface morphology (SEM), particle size distribution (PSD) and thermogravimetric analysis (TGA), in order to obtain a close relationship between the carbon characteristics and the DCFC performance. The results reveal that in the absence of catalyst, the optimum performance is obtained for the charcoal sample ( $P_{\max} \sim 12 \text{ mW/cm}^2$ ), due to its high volatile matter, oxygen content, porosity and carbon disorder as well as its low amount of impurities. Catalyst infusion to carbon feedstock results in a considerable increase in the achieved cell power density up to 225%, which is more pronounced for the less reactive coals and low temperatures. The enhanced performance obtained by infusing Co/CeO<sub>2</sub> catalyst into carbon is ascribed to the positive effect of catalyst on the *in situ* carbon gasification, through the reverse Boudouard reaction ( $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ ), and the subsequent faster diffusion and electro-oxidation of formed CO at the anodic three-phase boundary.

### 1. Introduction

Coal is by far the most abundant, economic and widely distributed fossil resource, presently accounting for > 30% of the global energy consumption [1]. Nowadays, carbon conversion to energy mainly takes place in conventional coal-fired plants, in which, however, several issues related to the thermodynamic limitations of conventional thermal cycles and the increased emissions per unit of produced power, render this process insufficient for a sustainable future. Direct Carbon Fuel Cells (DCFCs) can effectively exploit the chemical energy of solid carbonaceous fuels in an efficient and environmental friendly manner, where contrary to conventional power plants the chemical energy of the carbonaceous feedstock can be directly converted to electricity, with a lower CO<sub>2</sub> footprint [2–4]. Moreover, DCFCs have several advantages, compared to conventional power plants and gaseous fuelled Solid Oxide

Fuels Cells (SOFCs), such as the high theoretical energy efficiency [2,5–7], the high energy density of carbon compared to liquid or gaseous fuels [8], the abundance and low price of coal [4,9], the almost zero NO<sub>x</sub> effluents and the ease of handling the associated CO<sub>2</sub> emissions [10], facilitating the coupling of a DCFC unit with CO<sub>2</sub> capture and sequestration.

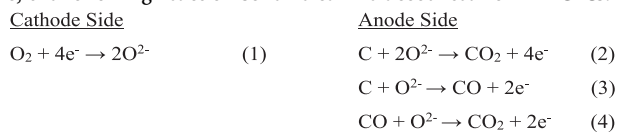
Up to date, various electrolytes, such as molten hydroxides, molten carbonates and solid oxides have been employed in DCFC applications. Among them, the solid oxide (e.g., YSZ as the solid electrolyte) DCFCs offer the well established advantages of SOFC technology. However, the limited interaction between solid carbon and solid electrode/electrolyte interphase hinders the delivery of carbon and its direct electro-oxidation at three-phase-boundary (TPB). Hence, research efforts have mainly been focused on molten hydroxide [8,11] or molten carbonate electrolytes [12,13], to overcome the mass transfer restrictions.

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However, durability problems relating to the corrosive nature of these electrolytes have restricted the development of molten electrolyte fuel cells [12–14].

Lately several strategies have been explored to increase the electrochemical performance in DCFCs, including among others: the integration of a DCFC with an internal or external gasification process [15–19], and the modification [5,20,21] or activation [22–24] of the employed carbon fuels. For instance, Gür et al. [16] and C. Li et al. [17] have independently reported high power densities in a SOFC fueled with CO generated in a decoupled Boudouard gasifier. Y. Wu et al. [18] have reported improved power output in a carbon-fueled SOFC involving internal catalytic gasification of carbon by a  $\text{Fe}_m\text{O}_n$ -alkali metal (Li, K, Ca) catalyst. In a similar manner, the DCFC performance was notably enhanced by catalyst (Fe, Ni, Ag) incorporation in the carbon fuel [15,19,25,26]. In this context, it has been suggested that gaseous CO and  $\text{CO}_2$ , formed during the internal gasification of carbon, can significantly contribute to power generation, since CO can be better diffused and electro-oxidized at the anodic Active Electrochemical Zone (AEZ), while the generated  $\text{CO}_2$  can undergo the reverse Boudouard reaction ( $\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$ ) resulting in further CO formation [4,27,28]. In specific, the following reaction scheme can be accounted for in DCFCs:



The  $\text{CO}_2$  formed at anode AEZ [Eqs. (2) and (4)] or directly employed as carrier gas in anode can react with carbon toward CO, through the reverse Boudouard reaction:



which although a non-electrochemical reaction, it has a key role in the DCFC performance, since its gaseous product, CO, can easily diffuse at the active electrochemical zone much more rapidly than the solid carbon, contributing to power generation via reaction (4). Hence, it has been proposed that the overall carbon fuel cell efficiency can be ascribed mainly to gas-AEZ interactions, rather than to the limited carbon-AEZ contact [16,17]. In this perspective, a linear correlation between the maximum power output and the CO formation rate was recently established [29].

Various types of carbonaceous materials have been tested as fuels under DCFC operation and it has been demonstrated that the electrochemical performance is strongly affected by their composition and physicochemical properties [12,29–34]. In view of this fact we recently investigated the impact of various carbons [29] and biochars [35] on the DCFC performance. The results revealed that fuel physicochemical characteristics, such as volatile matter, structure disorder and sulfur content, notably affect the DCFC performance [29,35].

In light of the above aspects, the present work aims at investigating the combined impact of carbon type and catalyst-aided gasification process on the DCFC performance. Three different carbon samples, i.e., anthracite coal, bituminous coal and pine charcoal, were employed as fuels in a DCFC. The impact of internal catalytic gasification was assessed by utilizing a Co/CeO<sub>2</sub> catalyst as carbon additive and  $\text{CO}_2$  as carrier gas, toward promoting the rate of reverse Boudouard reaction. The results are interpreted based on the combined effect of catalyst addition and fuel properties on cell's electrochemical performance.

## 2. Experimental

### 2.1. Materials preparation

#### 2.1.1. Carbon fuels

Three types of carbons with different composition and properties were employed as fuels. Specifically, two different coals were

evaluated: a bituminous coal (BC) and an anthracite coal (AC), both from Spanish basins. These coals were selected in order to examine the influence of the coal maturation on carbon characteristics and consequently on DCFC performance. The third carbon was a pine charcoal (PCC), also from Spain.

#### 2.1.2. Catalysts

The wet impregnation method was used to prepare the 20 wt% Co/CeO<sub>2</sub> and 20 wt% Cu/CeO<sub>2</sub> samples, employed as feedstock additive and anode, respectively.  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  precursor (99%, Sigma-Aldrich) was dissolved in distilled water and heated to 125 °C, under stirring, until all the water evaporated. The resulting sample was dried for 16 h at 110 °C, and then calcined for 2 h at 600 °C. Then, following identical steps, stoichiometric amounts of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (99%, Sigma-Aldrich) were dissolved in distilled water and impregnated onto the calcined CeO<sub>2</sub> in order to yield a metal loading of 20 wt% in both mixed oxide samples.

#### 2.1.3. Carbon-catalyst feedstock

The impact of Co/CeO<sub>2</sub> catalyst on DCFC performance was examined by mixing 800 mg of carbon (< 75 μm) with 400 mg of catalyst. The carbon fuels were initially dissolved in 250 cm<sup>3</sup> of *n*-hexane, with sonication for 15 min. Then the catalyst was added and the resulting solution was stirred on a heating plate at 70 °C for 4 h until *n*-hexane was evaporated. SEM/EDS analysis (see below) reveals a uniform distribution of both counterparts, implying the effectiveness of the proposed procedure toward the formation of a homogeneous carbon-catalyst feedstock.

### 2.2. Materials characterization

Carbons were characterized, in terms of chemical composition, crystallite structure (XRD), pore structure (BET), surface morphology (SEM), particle size distribution (PSD) and thermogravimetric analysis (TGA). Prior to each characterization all samples were dry-milled in a bench mortar mill and sieved to under 75 μm.

#### 2.2.1. Textural and morphological analysis

The textural characteristics of the samples were determined by N<sub>2</sub> adsorption-desorption isotherms at –196 °C in the pressure range of 0–1 bar in a Micromeritics Tristar 3020 apparatus. The morphology of the carbon fuels as well as of the carbon/catalyst mixtures was examined by scanning electron microscopy (SEM) using a Quanta FEG 650 microscope, equipped with an Apollo X detector for EDX measurements. The particle size distribution of the samples was determined by coulter analysis in Beckman Coulter LS 13 320 Laser Diffraction Particle Size Analyzer with Aqueous Liquid Module (ALM).

#### 2.2.2. Structural analysis

Diffraction patterns were recorded in a Bruker D8 powder diffractometer. It is equipped with a monochromatic  $\text{CuK}\alpha$  X-ray source and an internal standard of Silicon powder, while the scanning rate used was 0.02° per 2 s, in the range of 5–90°.

#### 2.2.3. Chemical analysis

All fuel samples were chemically characterized by means of elemental analysis (C, H, N, S and O wt% content) in a LECO CHNS-932 (C, H, N, S) and LECO VTF-9000 (O) analyzers. Proximate analysis (volatile matter, ash and moisture content) was carried out using the LECO TGA-601 equipment. Ash composition was determined by X-ray fluorescence in a Bruker SRS 3000 device.

#### 2.2.4. Thermogravimetric analysis

The reactivity of the samples was determined by means of thermogravimetric analysis in a Q5000 IR (TA Instruments) thermobalance. The weight loss profile was determined by increasing the temperature

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