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Effect of fuel thermal pretreament on the electrochemical performance of a direct lignite coal fuel cell

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ABSTRACT

The impact of fuel heat pretreatment on the performance of a direct carbon fuel cell (DCFC) is investigated by utilizing lignite (LG) coal as feedstock in a solid oxide fuel cell of the type: lignite|Co–CeO_2/YSZ/Ag|air. Four LG samples are employed as feedstock: (i) pristine lignite (LG), and differently heat treated LG samples under inert (He) atmosphere at (ii) 200 °C overnight (LG200), (iii) 500 °C for 1 h (LG500) and (iv) 800 °C for 1 h (LG800). The impact of several process parameters, related to cell temperature (700–800 °C), carrier gas type (He or CO_2), and molten carbonate infusion into the feedstock on the DCFC performance is additionally explored. The proximate and ultimate analysis of the original and pretreated lignite samples show that upon increasing the heat treatment temperature the carbon content is monotonically increased, whereas the volatile matter, moisture, sulfur and oxygen contents are decreased. In addition, although volatiles are eliminated upon increasing the treatment temperature and as a consequence more ordered carbonaceous structure remained, the heat treatment increases the reactivity of lignite with CO_2 due mainly to the increased carbon content. These modifications are reflected on the achieved DCFC performance, which is clearly improved upon increasing the treatment temperature. An inferior cell performance is demonstrated by utilizing inert He instead of reactive CO_2 atmosphere, as purging gas in the anode compartment, while carbonate infusion always results in ca. 70–100% increase in power output (15.1 mW cm^{-2} at 800 °C). The obtained findings are discussed based also on AC impedance spectroscopy measurements, which revealed the impact of LG physicochemical characteristics and DCFC operating parameters on both ohmic and electrode resistances.

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1. Introduction

Nowadays, coal is by far the most abundant natural resource, accounting for more than 30% of the global energy consumption [1]. However, the energy conversion of carbon is principally carried out in coal-fired plants, resulting in low conversion efficiencies and high emissions of environmentally harmful gases. Hence, the elaboration of novel technologies for efficient and clean coal energy production is of vital importance toward a sustainable energy economy [2–9].

A direct carbon fuel cell (DCFC) is the only electrochemical device in which the chemical energy of solid carbonaceous feedstock can be directly converted to electricity at efficiencies much higher than those thermodynamically predicted in common heat cycles [4]. More specifically, DCFCs have several advantages, as compared to conventional power plants and gas-fuelled solid oxide fuel cells (SOFCs) [6–8], involving the extremely high theoretical efficiency (~100%), the easy capture and sequestration of CO_2 emissions as well as the abundance and variety of carbon-based fuels [6–9].

In DCFCs based on SOFC configuration, the electrochemical oxidation of carbon is taking place *via* the reactions (1) and (2), which are standing for carbon complete and partial electro-oxidation by oxygen anions (O^{2-}) transported through the dense solid electrolyte. The non-electrochemical Boudouard reaction (3) can also contribute to the *in situ* formation of CO, which then can be subsequently diffused and electro-oxidized at the anode three phase boundary (TPB) *via* reaction (4) [10].

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \quad (1)$$

$$C + O^{2-} \rightarrow CO + 2e^- \quad (2)$$

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$$CO_2 + C \rightarrow 2CO \quad (3)$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \quad (4)$$

The carbon delivery to the anode TBP can be significantly improved by the infusion of a molten carbonate eutectic mixture into the carbon feedstock (hybrid carbon fuel cell, HCFC), enhancing the fluidity of solid fuel. In the presence of carbonates, the following stoichiometries, along with reactions (1)–(4), can be simultaneously carried out at the anode [11–14]:

$$C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^- \quad (5)$$

$$C + CO_3^{2-} \rightarrow CO + CO_2 + 2e^- \quad (6)$$

$$2C + CO_3^{2-} \rightarrow 3CO + 2e^- \quad (7)$$

Various carbonaceous feedstock have been examined as fuels in DCFCs to investigate their electrochemical reactivity. It has been revealed that their physicochemical characteristics notably affect the achieved DCFC performance [10,15–20]. For instance, the carbon and volatile matter contents as well as the structure disorder greatly enhanced the power output, whereas ash and sulfur contents have a detrimental effect on cell characteristics [15–20]. In this regard, acid and heat treatment are usually applied to modify the fuel characteristics and consequently the DCFC performance.

In the present communication, the effect of heat pretreatment on feedstock physicochemical characteristics and DCFC performance is investigated. Several parameters related to cell temperature (700–800 °C), purging gas type (He or CO_2) and molten carbonate infusion into the carbon feedstock were also examined. Lignite, a coal of significant importance for many countries', is employed as fuel.

2. Materials and methods

2.1. Materials synthesis

The wet impregnation method was used in order to prepare the anode electrode, 20 wt.% Co/CeO_2 [19]. The $Ce(NO_3)_3 \cdot 6H_2O$ precursor (99%, Sigma-Aldrich) was initially dissolved in distilled water and heated to 125 °C, under stirring, till all the water evaporated. The resulting sample was dried for 16 h at 110 °C, and then calcined for 2 h at 600 °C. A stoichiometric quantity of $Co(NO_3)_2 \cdot 6H_2O$ (99%, Sigma-Aldrich) precursor was then impregnated onto the calcined CeO_2. The drying and calcination procedures in this step were identical to that described for the ceria support.

2.2. Fuel characterization

In the present study lignite coal was employed as the main feedstock. To investigate the impact of pretreatment on DCFC characteristics, the pristine lignite (LG) was subjected to three different thermal treatment procedures under pure He atmosphere (30 cm^3/min): a) at 200 °C overnight (LG200), b) at 500 °C (LG500) and c) at 800 °C (LG800) for 1 h. The obtained samples were chemically analyzed by means of elemental analysis in LECO CHNS-932 and LECO VTF-9000 analyzers. Proximate analysis was carried out using the LECO TGA-601 equipment. Surface functionalities were also characterized by Fourier transform infrared spectroscopy (FTIR) in a Nicolet FTIR 8700 with the diffuse reflectance module Smart Collector. A high-sensitivity detector MCT-A of mercury cadmium telluride was used. The data were recorded between 4000 and 650 cm^{-1}, using 100 scans and a resolution of 4 cm^{-1}. The carbonaceous structure of the samples was characterized by means of XRD and Raman spectroscopy. X-ray diffractograms were acquired in a Bruker D8 powder diffractometer equipped with a monochromatic Cu-K_α X-ray source and an internal standard of silicon powder. Diffraction data were collected by step scanning with a step size of 0.02° in the range of 5–90°, with an interval of 2 s between steps. The Raman spectroscopy analyses were carried out in a LabRam HRUV 800 using JYV-Jobin Yvon equipment and an argon laser CDPS532M 532 nm at 24.3 mW. Finally, the reactivity of the samples was determined by thermogravimetric (TG) analysis. Samples were heated up to 1000 °C with a rate of 10 °C/min in a thermobalance (Q5000 IR, TA Instruments). The weight loss profile was recorded with increasing temperature, under both inert (N_2) and reactive (CO_2) atmosphere at a constant flow rate of 20 cm^3/min.

2.3. DCFC fabrication and cell testing

The fuel cell experiments were performed in a reactor cell consisting of a YSZ tube (CERECO) with 1.2 mm thickness, closed flat at its bottom end [18,19]. The cathode was deposited on the outside wall of YSZ tube, prepared from a silver paste (05X Metallo-organic AG RESINATE) after calcination for 2 h at 850 °C in stagnant air, with a heating rate of 4 °C/min. The anode was prepared from a Co/CeO_2 powder, mixed with ethylene glycol at a 1:2 weight ratio [19]. The resulted solution was heated at about 200 °C and stirred at 400 rpm until half of its volume was evaporated. Then the viscous suspension was deposited, by applying consecutive thin films with a paintbrush, on the inside bottom wall of the YSZ tube. The calcination procedure involved heating, under atmospheric air, to 850 °C for 2 h. After calcination, the cell was cooled down to 200 °C, where the anode was reduced in a flow of 30 cm^3/min of H_2 (100 vol.%) for 2 h. In all cases, the amount of the deposited film was equal to 115 mg, resulting in an apparent electrode area of 1.7 cm^2.

The electrochemical measurements were carried out in the temperature range of 700–800 °C, at atmospheric pressure. In each experiment the cell is loaded either with bare carbon (800 mg) or a carbon/carbonate mixture at a 4:1 weight ratio [18]. Pure He or CO_2 (99.999% purity, Air Liquide) was employed as purging gas, whereas the cathode was always exposed to atmospheric air. The flow rate of carrier gas was controlled by mass flow meters (Tylan FM 360) and equaled to 30 cm^3/min. The cell voltage and developed electrical current were monitored by means of digital multi-meters (RE69) and the external resistive load was controlled by a resistance box (Time Electronics 1051). The electrochemical impedance spectra were obtained under open circuit conditions in the frequency range between 0.1 Hz and 1 MHz with an amplitude of 30 mV RMS, using the Versa Stat 4 electrochemical workstation by Princeton Applied Research and the corresponding software (Versa Studio) for data processing. Analysis of the effluents was performed by an on-line Gas Chromatograph (SRI 8610B) equipped with a Molecular Sieve 5A and Porapak Q columns.

3. Results and discussion

3.1. Characterization of lignite fuel samples

In Table 1 the proximate and ultimate analysis of the different heat treated lignite samples is depicted. It is obvious that upon increasing the temperature of heat treatment the carbon content and fixed carbon are monotonically increased, whereas the volatile matter, moisture, sulfur and oxygen contents are decreased due to the loss of volatiles.

The heat treatment removed most of the labile compounds in the pristine coal, notably affecting the carbonaceous structure. XRD spectra (data not shown) revealed very similar structures for all examined samples, showing a similar characteristic peak of the carbonaceous structure at ca 25°, plane (002), although not very well defined as it is expected for lignite samples. To gain further insight into the impact of heat treatment on the crystallite structure, the Raman spectra of original and thermally-treated lignite samples were acquired (Fig. 1).

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