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Carbon to electricity in a solid oxide fuel cell combined with an internal catalytic gasification process

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ABSTRACT

This study explores strategies to develop highly efficient direct carbon fuel cells (DCFCs) by combining a solid-oxide fuel cell (SOFC) with a catalyst-aided carbon-gasification process. This system employs Cu/CeO₂ composites as both anodic electrodes and carbon additives in a cell of the type: carbon|Cu-CeO₂/YSZ/Ag|air. The study investigates the impact on *in situ* carbon-gasification and DCFC performance characteristics of catalyst addition and variation in the carrier gas used (inert He versus reactive CO₂). The results indicate that cell performance is significantly improved by infusing the catalyst into the carbon feedstock and by employing CO₂ as the carrier gas. At 800 °C, the maximum power output is enhanced by approximately 40% and 230% for carbon/CO₂ and carbon/catalyst/CO₂ systems, respectively, compared with that of the carbon/He configuration. The increase observed when employing the catalyst and CO₂ as the carrier gas can be primarily attributed to the pronounced effect of the catalyst on carbon-gasification through the reverse-Boudouard reaction, and the subsequent *in situ* electro-oxidation of CO at the anode three-phase boundary.

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1. Introduction

Coal is generally viewed as an abundant and widely distributed fossil resource that is relatively inexpensive to extract. Currently, coal accounts for more than 30% of global energy consumption, and is the fastest-growing form of energy other than renewables [1,2]. However, coal use in conventional coal-fired electricity plants is constrained by Carnot's theorem on thermodynamic efficiency. In plants operating at subcritical pressures, the efficiency of converting thermal energy to electrical energy is typically less than 40%. By contrast, fuel cells

directly convert a fuel's chemical energy into electricity, which yields higher efficiencies and a smaller environmental footprint [3–6].

Direct carbon fuel cells (DCFCs) are electrochemical devices that directly exploit the chemical energy of solid carbonaceous materials [7,8]. DCFCs have the following advantages compared with conventional heat engines: (1) higher thermodynamic efficiency [9,10]; (2) direct use of a range of solid carbon reserves, such as biomass, coal, petroleum coke, pyrolytic carbon, and municipal organic wastes [9,11]; (3) lower CO₂ emissions per unit of produced power, with these emissions more easily

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captured and sequestered [12]; and (4) volumetric benefits associated with directly using coal rather than liquid or gaseous carbonaceous fuels [13,14].

DCFCs can be categorized according to the electrolyte employed as either molten carbonate, molten hydroxide or solid oxide fuel cells (SOFCs). Carbon-fed SOFCs offer the established advantages of oxygen anion conducting solid oxide fuel cells. However, the limited interaction between the solid fuel and the solid electrolyte/electrode interface is the main factor hindering higher carbon electro-oxidation rates and higher associated DCFC performance. Molten carbonate/hydroxide electrolyte DCFCs have been proposed as an alternative approach; however, the corrosive nature of the electrolyte limits the durability of these systems [15–17].

Power generation in DCFCs follows a more complex pathway than in gas-fueled SOFCs with a combination of direct and indirect carbon electro-oxidation reactions potentially occurring simultaneously in DCFCs. Carbon particles in contact with the solid electrolyte/electrode interface at the anode are completely or partially electro-oxidized by oxygen anions (O^{2-}), transported through the electrolyte membrane from the air-exposed cathode, to form CO_2 or CO via the following reactions:

CO can be further electro-oxidized to CO_2 through the following charge transfer reaction:

An alternative process has been recently established, which initially involves carbon-gasification to CO via the following reaction and its subsequent electro-oxidation to CO_2 via reaction (3) [7,8]:

Reaction (4) is a non-electrochemical step, known as the reverse-Boudouard reaction, which is favored at temperatures higher than approximately 700 °C. The chemical formation of CO via the reverse-Boudouard reaction does not itself contribute to cell power. However, the subsequent electrochemical oxidation of CO at the anode's three phase boundary (TPB) via reaction (3) significantly contributes to power generation. Tang et al. [18] reported that cell performance was notably improved by catalyzing the reverse-Boudouard reaction.

Based on the above reaction scheme, one approach to enhance DCFC performance is to combine a carbon-fueled SOFC with the internal catalytic CO_2 -gasification of carbon [19–22]. Here, gaseous CO and CO_2 significantly contribute to power generation because CO can be electrochemically oxidized at the TPB, while CO_2 can undergo the reverse-Boudouard reaction to generate additional CO [23,24].

The present study aims to overcome the inherent limitations of DCFCs, associated with electrode kinetics and mass-transport phenomena, by introducing an *in situ*, catalyst-aided, carbon-gasification process. Instead of using highly corrosive molten electrolytes, this process aims to internally produce CO , which can be diffused and electro-oxidized at TPB. To this end, Cu/CeO_2 catalysts were chosen on account of their established electronic conductivity, electro-oxidation activity

for CO and hydrocarbons, and resistivity to poisoning by coke [25–29]. The catalysts were used both as carbon additives and anodic electrodes in a SOFC of the type: carbon| $Cu-CeO_2$ /yttria-stabilized zirconia (YSZ)/ Ag |air.

To promote improvements in DCFC performance, this work investigates and discusses the impact on CO production and overall DCFC performance characteristics of the operating temperature, the catalyst infusion to carbon feedstock and the carrier gas (He or CO_2). The obtained results are further discussed on the basis of AC impedance spectroscopy studies.

2. Experimental

2.1. Materials synthesis

2.1.1. Catalyst preparation

Cu/CeO_2 catalysts with a nominal Cu content of 20 wt% were prepared using the wet-impregnation method. The $Ce(NO_3)_3 \cdot 6H_2O$ (99%, Sigma-Aldrich) precursor was dissolved in distilled water, and the solution was heated under stirring to 125 °C until the water evaporated. The resulting sample was dried at 110 °C for 16 h. The temperature was then increased at a heating rate of 5 °C/min, and the sample was then calcined at 600 °C for 2 h. The appropriate amount of $Cu(NO_3)_2 \cdot 3H_2O$ (99%, Sigma-Aldrich) precursor was dissolved in distilled water and then impregnated into the calcined CeO_2 support to yield a Cu content of 20 wt%. The as-prepared composites were dried at 110 °C overnight, and then calcined at 600 °C for 2 h.

2.1.2. Feedstock preparation

A commercial carbon-black (VXC72R, Cabot Corp.), either pure or mixed with Cu/CeO_2 catalyst at a 2:1 weight ratio (800 mg carbon:400 mg catalyst), was employed as feedstock. This specific carbon/catalyst proportion was determined in preliminary studies on the effect of catalyst loading on DCFC performance. For carbon/catalyst feedstock preparation, 800 mg of carbon was initially diluted in 250 cm^3 *n*-hexane. The solution was agitated in an ultrasonic device for 15 min, and then 400 mg of catalyst was added. The resulting solution was heated at 70 °C for 4 h after which the *n*-hexane had totally evaporated.

2.2. Materials characterization

The surface area of the carbon sample and the carbon/catalyst mixture was determined by N_2 adsorption-desorption at –196 °C using multipoint Brunauer-Emmett-Teller (BET) analysis in an Autosorb-1 Quantachrome flow system. The BET surface area (S_{BET}) was determined at relative pressures in the range of 0.005–0.99. The total pore volume was calculated based on nitrogen volume at the highest relative pressure. The average pore diameter was determined using the Barrett-Joyner-Halenda (BJH) method. Samples were degassed at 250 °C overnight before analysis.

Crystallographic information on the synthesized materials was obtained by performing powder X-ray diffraction (XRD). The diffraction intensity– 2θ spectra were acquired using a

Siemens D 500/501 with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) at a scanning rate of $0.04^\circ/2 \text{ s}$.

The morphology of the synthesized materials was examined by performing scanning electron microscopy (SEM) using a JEOL 6300 microscope coupled with energy-dispersive X-ray analysis (EDX; Oxford Link ISIS-2000) to determine local elemental composition.

2.3. DCFC fabrication

The fuel cell experiments were performed in an oxygen-anion (O^{2-}) conducting cell (Fig. 1). The cell consists of an 8 mol% YSZ tube (15 cm long, 16 mm inside diameter, and 1.2 mm wall thickness) as the electrolyte, closed flat at the bottom end. The open end of the YSZ tube was clamped to a stainless-steel, gas-tight cap. The cap has provisions for inlet and outlet gas lines, as well as a hollow cooling ring where a flow of cooling water protects the sealing o-rings. The cathode electrode (Ag) was prepared from silver paste (05X metallo-organic Ag resinate), calcined in static air at 850°C for 2 h, and deposited onto the outside bottom wall of the YSZ tube. The anodic (working) electrode was prepared from Cu/CeO₂ powder (see Section 2.1) mixed with ethylene glycol. This viscous suspension was deposited by painting it on the inside bottom of the YSZ tube to form an electrode with a superficial surface area of 1.7 cm^2 . The calcination procedure involved heating in air at 250°C for 1 h and at 850°C for 2 h, and then cooling in a reducing atmosphere (10% v/v H₂ in He). Heating and cooling rates were $4^\circ\text{C}/\text{min}$. Two Au wires anchored on the electrodes surface were employed to establish the necessary electrical connections. To improve electrical contact at the cathode electrode, a thin Au film was applied to the attached Au wire on the Ag electrode surface.

2.4. DCFC testing

Pure He and CO₂ (both 99.99% purity, Air Liquide) were employed as purging gases. The gas flow was controlled by mass-flow meters (Tylan FM 360), and introduced into the

reactor cell at a rate of $30 \text{ cm}^3/\text{min}$ (STP conditions). In each experiment the cell was loaded either with 800 mg of carbon or a carbon/catalyst mixture (800 mg carbon:400 mg catalyst). Experiments were performed at 750 and 800°C under atmospheric conditions. Cell voltage and electrical current were monitored with digital multimeters (Uni-T UT 55), and the external resistive load was controlled by a resistance box (Time Electronics 1065). 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. The Versa Stat 4 electrochemical workstation (Princeton Applied Research) and its corresponding software (Versa Studio) were used for data processing. Gas chromatography (GC) analysis of the effluent stream was performed using a Shimadzu GC-14B gas chromatograph equipped with a 13X molecular sieve and a Porapak N columns. The CO and CO₂ concentrations were also continuously monitored using a Rosemount Binos 100 infrared CO-CO₂ analyzer.

3. Results and discussion

3.1. Characterization studies

3.1.1. Textural characterization

To elucidate the catalyst's effect on the carbon feedstock's textural characteristics, the BET surface area, total pore volume, and average pore size diameter of the carbon, catalyst, and carbon/catalyst mixtures were determined using multipoint BET analysis (Table 1).

The catalyst had a low BET surface area of $45 \text{ m}^2/\text{g}$ and a total pore volume of $0.15 \text{ cm}^3/\text{g}$. By contrast, the carbon feedstock had a BET surface area of $231 \text{ m}^2/\text{g}$ and a total pore volume of $0.56 \text{ cm}^3/\text{g}$. The carbon/catalyst mixture (800 mg carbon + 400 mg catalyst) exhibited a reduced BET area of $162 \text{ m}^2/\text{g}$, which is approximately equivalent to the theoretical value expected for a physical mixture ($169 \text{ m}^2/\text{g}$). This result suggests that the wet impregnation method for feedstock preparation does not significantly modify the carbon feedstock's specific surface area. However, the observed catalyst-induced increase in total pore volume and mean pore diameter (Table 1) indicates that the catalyst strongly affects the porosity of the carbon. This may be due to the incorporation of catalyst particles into the carbon structure. Here, depending on the individual size of the carbon and catalyst particles and their weight ratio, the incorporation of catalyst into the carbon structure could increase its pore volume. Furthermore, the textural characteristics of the carbon/catalyst mixtures may have been affected by the synthesis procedure of *n*-hexane dilution and ultrasonic pretreatment. Previous work in this area has shown

Fig. 1. Schematic illustration of the direct carbon fuel cell (DCFC).

Table 1

Textural characteristics of catalyst (Cu/CeO₂), carbon, and carbon/catalyst mixture.

Sample	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Mean pore diameter (nm)
Catalyst	45	0.15	13
Carbon	231	0.56	10
Carbon/catalyst	162	0.65	16

Fig. 2. XRD patterns of the carbon feedstock, the catalyst (Cu/CeO₂), and the carbon/catalyst mixture.

that carbon supports with high surface area and adequate porosity can facilitate both reactant-diffusion and electron-transfer [30].

3.1.2. Structural and morphological analyses

Figure 2 presents XRD patterns of the carbon feedstock, the Cu/CeO₂ catalyst, and the carbon/catalyst mixture. The carbon feedstock's pattern has a distinctively asymmetrical wide peak centered at approximately $2\theta = 25^\circ$, which is attributed to the (002) reflection of graphite, although it is extremely diffuse compared with that of ideal graphite [31]. In addition, the weak, sharp peak at $2\theta = 44^\circ$ corresponds to the (100) graphite crystal phase reflection [32]. These peaks are characteristic of short-range graphite-like structures [33]. A weaker peak signal at $2\theta = 25^\circ$ is observed for graphitic carbon in the carbon/catalyst mixture, though the peak is dominated by the CeO₂ and CuO phases observed for the catalyst sample. Therefore, no new phases evolve during carbon/catalyst sample preparation, implying a behavior that is typical for physical mixtures.

The SEM/EDX study of the carbon/catalyst sample (Fig. 3) revealed agglomerated materials containing particles ranging in size from submicron to a few micrometers. EDX detected a uniform elemental distribution in the samples that showed no distinct spatial distributions of carbon or metal oxides.

The effect of physicochemical characteristics of the carbonaceous feedstock and the impact of catalyst incorporation into the carbon framework have been extensively reviewed by Lahijani *et al.* [34]. It was reported that the reactivity of carbon in the gasification process was strongly influenced by the pore structure of the carbon and its morphology, as well as by the availability of active carbon sites [34]. Furthermore, several operational parameters, including temperature, pressure, gasification agent, size of carbon particles and use of catalysts, were found to have a complex influence on the reactivity of the carbon feedstock in the CO₂-gasification process [34]. Regarding the impact of the catalyst employed, in most cases the pronounced effect of catalyst was attributed to the increase of reaction centers which play a critical role in the gasification progress. In this regard, the catalytic activity of several materials is

Fig. 3. Representative SEM images (magnification $\times 10000$) of the carbon/catalyst mixture and the corresponding elemental maps.

remarkable only when they are well dispersed within the carbon matrix. It has also been reported that incorporating the catalyst into the carbon framework modified the surface chemistry of the carbon and enhanced its physicochemical properties, which eventually contributed to higher gasification reactivities [34].

3.2. DCFC performance

3.2.1. Effect of Cu/CeO₂ catalyst as a carbon additive

Figure 4 presents the effect of the Cu/CeO₂ catalyst on DCFC performance characteristics, including cell voltage, current density, and power density, at 750 and 800 °C under a flowing He atmosphere, and with a constant carbon/catalyst weight ratio of 2. The increase in cell temperature and the addition of catalyst to the carbon feedstock both clearly improve cell performance. Catalyst addition results in a maximum power of 5.0 and 7.3 mW/cm² at 750 and 800 °C, respectively, compared with that for the bare carbon feedstock (3.0 and 4.6 mW/cm² at 750 and 800 °C, respectively). These catalyst-mediated improvements may be due to the pronounced effect of catalyst on carbon electro-oxidation kinetics [21], which is further discussed in subsequent sections. Kulkarni *et al.* [35] studied the performance of La_{0.3}Sr_{0.7}Ti_{0.93}Co_{0.07}O₃ (LSCT) as the anode material in a DCFC of the type LSCT/YSZ/LSCF that was fed with carbon black (Vulcan XC-72, Cabot Corp.) at 800 °C and employed pure N₂ as the carrier gas. They reported a maximum power density of 7.5 mW/cm², which is similar to that obtained in the present work.

Figure 4(b) presents the corresponding open circuit (OC) AC impedance spectra obtained at the same conditions as those employed to generate the data in Fig. 4(a). It is clearly shown that both the ohmic (intercept of the high frequency arc with the real axis) and electrode resistances are substantially decreased upon increasing cell temperature and adding the Cu/CeO₂ catalyst into carbon feedstock. These results are in agreement with the observed changes to DCFC performance characteristics (Fig. 4(a)). Specifically, the ohmic resistance decreased from 11.4 to 8.1 Ω cm² upon increasing temperature from 750 to 800 °C. A further decrease of the ohmic resistance to 5.5 Ω cm² at 800 °C was obtained by catalyst incorporation

Fig. 4. (a) Effect of catalyst addition on direct carbon fuel cell performance at 750 and 800 °C employing He as the carrier gas and (b) the corresponding AC impedance spectra. Carbon loading = 800 mg; catalyst (Cu/CeO₂) loading = 400 mg; He flow = 30 cm³/min.

into the carbon feedstock. A similar trend was obtained for the electrode resistances, as reflected by the size of the two overlapping arcs. The dominant feature in the impedance spectra is the overlap of the small high-frequency arc with the large low-frequency arc. The size of both arcs decreases significantly by increasing the cell temperature and by infusing catalyst in the carbon feedstock.

Through ensuring that the cathodic atmosphere and the material for the anode, the cathode and the electrolyte were identical in the examined cases, the alterations in the AC impedance spectra at a constant temperature can be attributed to the catalyst infusion into the carbon feedstock. More specifically, as shown in Fig. 6, even under a He atmosphere the CO formation rate increased in the presence of the catalyst. This surplus CO can improve DCFC performance (Fig. 4(a)) due to its faster diffusion and electro-oxidation rates compared to solid carbon. Furthermore, the differences observed in the ohmic resistance at the same cell temperature can plausibly be ascribed to the increased electrical conductivity of the anode due to its partial reduction by the excess CO. In addition, even in the inert (He) atmosphere, CO₂ could be formed through the direct

electro-oxidation of carbon or CO *via* reactions (1) and (3), respectively. Any produced CO₂ can therefore undergo the reverse-Boudouard reaction (4) to generate additional CO, which then can be electro-oxidized at the anode TPB sites.

3.2.2. Combined effect of catalyst and gasification agent

To understand the importance of *in situ* carbon gasification *via* the catalyst-aided reverse-Boudouard reaction, the effect of the carrier gas on DCFC performance characteristics at 800 °C was examined with and without the catalyst (Fig. 5). In both cases switching from He to CO₂ enhances the cell power output by approximately 45%.

The absolute open circuit voltage (OCV) values were higher for the He atmosphere; however, they didn't change upon catalyst addition (Fig. 5). It should be pointed out that the complex network of chemical and electrochemical reactions taking place in the anodic chamber and at the anode/electrolyte and the anode/fuel interfaces, makes it difficult to predict the equilibrium oxygen concentration and thus the theoretical OCV. Furthermore, OCV can be notably affected by the fuel's physicochemical properties (*i.e.*, reactivity, conductivity, morphology,

Fig. 5. (a) Effect of two carrier gases (He, CO₂) on direct carbon fuel cell performance with and without a catalyst infused into the carbon feedstock and (b) the corresponding AC impedance spectra. Carbon loading = 800 mg; catalyst (Cu/CeO₂) loading = 400 mg; total carrier gas flow rate = 30 cm³/min.

crystal structure, and fluidity), carrier gas type (inactive He or reactive CO₂) and operating conditions (*i.e.*, temperature, carrier gas flow rate and carbon loading) [36]. It can therefore be assumed that the equilibrium oxygen concentration and the OCV are dependent on a number of factors including the fuel characteristics, the chemical reactions taking place at the anode surface and the charge transfer reactions occurring at the TPB as well as the gas phase environment surrounding the anode.

The inferior power output under He flow can be mainly attributed to mass transfer limitations at the anode due to the limited interaction between solid carbon and the solid electrolyte/electrode interface. However, a notable improvement in DCFC performance was obtained under CO₂ flow, which can be ascribed to *in situ* CO formation via the reverse-Boudouard reaction [23,24] and its subsequent diffusion and electro-oxidation at the anodic TPB. Furthermore, this additional CO was thought to modify the electrical conductivity of the Cu/CeO₂ anode electrode, as shown by the overall cell resistances.

The aforementioned arguments are clearly reflected on the corresponding AC impedance spectra shown in Fig. 5(b). From a value of 8.1 Ω cm² for the bare carbon feedstock, the ohmic resistance substantially decreased to 4.8 and 6.8 Ω cm² for carbon/catalyst/CO₂ and carbon/CO₂ configurations, respectively. In addition, the electrode resistance decreased when both CO₂ and catalyst were used as carrier gas and carbon additive, respectively. Particularly for the results derived without using the catalyst, the high frequency arc is lower when the anode is exposed to He while the opposite trend is observed for the low frequency arc. However, catalyst infusion into the carbon feedstock with CO₂ as the carrier gas results in a larger high frequency arc followed by a decreased low frequency arc. Taking into account the above aspects and the reaction steps proposed in Ref. [35], two suggestions are made to describe this behavior. First, the high frequency arc, which is enlarged by both CO₂ as the carrier gas and especially when the catalyst is infused into the carbon feedstock, can be mainly ascribed to the electro-oxidation of carbon and the associated physical processes (adsorption/desorption and diffusion of reactive species). Second, the low frequency arc, which is notably reduced with CO₂ as the carrier gas, could be ascribed to the electro-oxidation of CO and the corresponding physicochemical processes.

To verify the catalyst's role in CO formation and the effect on cell performance of CO generated *in situ*, the transient response of the CO formation rate to step changes in carrier gas (He to CO₂) was investigated at 800 °C for the carbon feedstock and carbon/catalyst mixture under OC and closed circuit (CC) conditions (Fig. 6). During the first stage ($t = 0$ –30 min), He flowed into the anode chamber under OC operation until the OCV stabilized. In the second stage ($t = 30$ –75 min), the circuit was closed and a constant cell voltage that corresponds to maximum power conditions was applied. In the last stage ($t = 75$ –120 min), the circuit was opened again until a steady state OCV was obtained. CO₂ was then introduced to the cell ($t = 120$ min), and the previous stages carried out under a He atmosphere were repeated. Under a He atmosphere and OC condi-

Fig. 6. Transient changes in CO formation rate in response to step changes in carrier gas at 800 °C under open circuit (OC) and closed circuit (CC) conditions. Carbon loading = 800 mg; catalyst (Cu/CeO₂) loading = 0 or 400 mg; carrier gas flow rate = 30 cm³/min.

tions, the CO formation rates were approximately 3.3×10^{-8} and 7.4×10^{-8} mol/s for the bare carbon feedstock and the carbon/catalyst mixture, respectively. This difference can be ascribed to the presence of CO₂ in the anode compartment ($\sim 5.0 \times 10^{-8}$ and 10×10^{-8} mol/s without and with the catalyst, respectively), which undergoes the un-catalyzed (carbon/CO₂) or catalyzed (carbon/catalyst/CO₂) reverse-Boudouard reaction, forming CO. The CO formation rate is higher in the latter case due to the beneficial effect of the catalyst on the reverse-Boudouard reaction. The formation of a small amount of CO₂, even under a He atmosphere and OC conditions, can be explained by taking into account the oxidation of carbon by different oxygen species. These oxygen species could be derived from the oxygen functional groups of carbon feedstock, the lattice oxygen of solid electrolyte (YSZ) or anodic electrode (Cu/CeO₂), the carrier gas impurities, or other sources.

Under closed circuit conditions ($t = 30$ –75 min, Fig. 6), the CO and CO₂ formation rates slightly increased both with and without the catalyst. However with the catalyst, where the increases were more obvious, the CO formation rate increased from 7.4×10^{-8} to 8.6×10^{-8} mol/s. The rate of CO₂ formation increased by the same amount (1.2×10^{-8} mol/s) from 1.03×10^{-7} to 1.15×10^{-7} mol/s. The increase in CO formation rate under these specific conditions indicates that the rate at which CO is formed through the partial electro-oxidation of carbon and the reverse Boudouard reaction is higher than the rate at which CO undergoes electro-oxidation to CO₂. Conversely, the increment in CO₂ formation rate implies that the reaction rates for the complete electro-oxidation of carbon and the *in situ* formation of CO₂ from CO electro-oxidation are together greater than the consumption rate of CO₂ by the reverse-Boudouard reaction.

With CO₂ as the carrier gas and under OC conditions, the rate of CO production was significantly higher for the carbon/catalyst mixture than for the bare carbon feedstock (Fig. 6). These results reveal the beneficial effect of the catalyst on the CO formation rate through the catalyzed re-

verse-Boudouard reaction. Under CC with the same carrier gas the CO formation rate decreased from 2.5×10^{-7} to 2.0×10^{-7} mol/s for the carbon feedstock and decreased from 6.0×10^{-7} to 4.4×10^{-7} mol/s for the carbon/catalyst mixture. This decrease, observed in both cases, is explained by the electro-oxidation of the CO that was formed *in situ* during DCFC operation.

Other work in this field has reported that the addition of Sn to carbon-black in a SOFC with a Ni/YSZ anode enhanced the power density compared with the Sn-free fuel by 4-fold, which was attributed to Sn-facilitation of carbon-oxidation kinetics [37]. Similar conclusions for the effect of He or CO₂ as the carrier gas on DCFC performance have been reported for a LSF/GCO/LSF-Ag cell that was fueled with carbon; DCFC performance was enhanced under a CO₂ atmosphere at temperatures higher than 700 °C due to the higher amount of CO formation and its electro-oxidation at the TPB [14]. The increased performance of a Ni/YSZ anode-supported SOFC with coke fuel and CO₂ as the carrier gas was attributed to the increased electrochemical oxidation of CO [16]. Recent work has also established a close correlation between the CO formation rate under OC conditions and cell performance [36].

The results obtained in the current work are consistent with these previous studies and confirm that the enhanced DCFC performance in terms of power output in the presence of CO₂ is due to the faster rates of diffusion and electro-oxidation of the CO produced by the catalyzed reverse-Boudouard reaction at the anodic TPB. A schematic diagram of the process is shown in Fig. 7.

3.2.3. DCFC optimization

Considering the results presented in this study, the following four aspects should be accounted for during DCFC optimization.

- (1) Catalyst incorporation into the carbon feedstock can result in improved DCFC performance independently of the carrier gas used. This emphasizes the key role of the catalyst in the overall cell efficiency.
- (2) The presence of CO₂ in the anode compartment can lead to superior DCFC performance compared with that when He is present.
- (3) The CO formation rate is substantially accelerated in the

presence of both CO₂ and the catalyst, as the catalyst promotes carbon gasification *via* the reverse-Boudouard reaction.

(4) An increase in the amount of CO formed *in situ* improves DCFC performance as CO bypasses mass-transfer limitations and displays higher rates of electro-oxidation than solid carbon.

It is important to note the limited power densities obtained in the present study, even for the best-performing DCFC configuration. These power outputs were considered to have been limited primarily by the ohmic resistances attributed to the YSZ solid electrolyte membrane (thickness of approximately 1.2 mm), the anodic and cathodic electrodes, and poor contact and adherence of electrodes on the YSZ surface. Therefore, work is in progress to develop state-of-the-art cells with thin solid electrolyte membranes and employing more sophisticated electrode deposition techniques which could considerably enhance DCFC performance. Other work that increases CO production by recirculating off-gases or optimizes SOFC geometries for continuous operation at maximum current output is also needed prior to widespread deployment of DCFCs.

4. Conclusions

This study explores strategies to enhance the performance of carbon-fueled SOFCs of the type carbon|Cu-CeO₂/YSZ/Ag|air. Through fuel cell experiments accompanied by AC impedance spectroscopy studies, a novel approach was tested that involved the simultaneous use of Cu-based catalysts as carbon additives and CO₂ as a gasifying agent. Promising results were obtained in terms of DCFC output characteristics at 800 °C; the maximum power output was enhanced by approximately 40% and 230% for carbon/CO₂ and carbon/catalyst/CO₂ configurations, respectively, compared with that of the carbon/He system. These results clearly demonstrate the benefits of catalyst infusion into the carbon feedstock. The beneficial impact on performance can be attributed to the catalyst's pronounced effect on the reverse-Boudouard reaction rate and the subsequent diffusion and electro-oxidation at the anodic TPB of CO formed *in situ*. A number of contributions to improving DCFCs' performance characteristics were provided through a catalyst-aided gasification process that offers the potential of development of carbon fuel cells without the need for highly corrosive carbonates.

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Fig. 7. Schematic illustration of the proposed concept. CO formed through the catalyst-aided reverse-Boudouard reaction is diffused and electro-oxidized at the anode TPB sites leading to an improvement in power output.

Graphical Abstract

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Carbon to electricity in a solid oxide fuel cell combined with an internal catalytic gasification process

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Catalyst-aided Direct Carbon Fuel Cell (DCFC) concept

The feasibility of enhancing the performance of direct carbon fuel cells by an internal, catalyst-aided carbon gasification process is explored. The maximum power is 3-fold enhanced in comparison to bare carbon (He) configuration.

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