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Article (Special Column on Electrocatalysis for Fuel Cells)

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

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ARTICLE INFO

Article history:

Received 12 October 2014

Accepted 8 December 2014

Published 20 April 2015

Keywords:

Direct carbon fuel cell

Internal catalytic gasification

Copper/ceria anode

Copper/ceria catalyst

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/Aglair. 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].

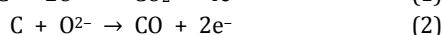
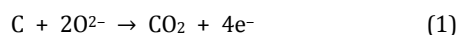
Direct carbon fuel cells (DCFCs) are electrochemical devices that directly exploit the chemical energy of solid carbonaceous materials [7,8]. DCFCs have the following advantages compared with conventional heat engines: (1) higher thermodynamic efficiency [9,10]; (2) direct use of a range of solid carbon 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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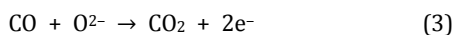
captured and sequestered [12]; and (4) volumetric benefits associated with directly using coal rather than liquid or gaseous carbonaceous fuels [13,14].

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

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