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Operating Characteristics of a Tubular Direct Carbon Fuel Cell Based on a General Anode Support Solid Oxide Fuel Cell

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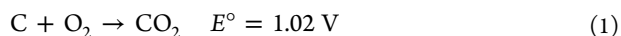
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ABSTRACT: A tubular direct carbon fuel cell (DCFC) based on a general anode support solid oxide fuel cell was fabricated and studied. For this purpose, we fabricated tubular anode support tubes through an extrusion process, and the essential fuel cell components, the electrolyte and the electrode, were coated on the surface of the anode support consecutively using a vacuum slurry and dip-coating method. Carbon black and molten carbonate as the fuel and the electrochemical mediator were filled in the inner part of the tubular DCFC. The performance of the tubular DCFC in carbon + carbonate (1:1 wt %) and air at 900 °C had a maximum power density of 122 mW/cm². It was operated at variable operating conditions: operating temperature, anode and cathode gas supply, and so on. These results indicate that the fabricated tubular DCFC is a promising candidate for many other practical applications, such as residential power generation and auxiliary power unit systems.

INTRODUCTION

Coal is the most extensive fossil fuel in the world. In 2013, the coal production output was near 6940 million metric tons, and it accounted for 68% of the total primary energy output in the world.^{1–3} Nowadays, electric power from coal is achieved by coal-fired power plants, but not only is this method a low-efficiency process but it also emits substantial amounts of greenhouse gases and pollutants, such as NO_x, SO_x, etc. On the other hand, the dependence upon coal as a fuel source continues to be widespread, as other natural resources remain in short supply. Therefore, it is important to find an innovative and high-efficiency technology to process coal to be used for power production.^{4–6}

In an attempt to solve these problems, direct carbon fuel cells (DCFCs) are an attractive electrochemical power source for central power plants and even portable applications.^{7,8} DCFCs can convert chemical energy directly into electric energy from various types of carbon sources; this method can convert coal, coke, natural gas, petroleum, refining byproducts, and even biomass. The overall cell reaction in DCFCs is the electrochemical oxidation of carbon to carbon dioxide (CO₂):



Recently, three different concepts of a DCFC based on different electrolytes have been investigated: molten carbonate, molten hydroxide, and solid ceramic material yttria-stabilized zirconia (YSZ). It should be mentioned that performance data on the different concepts presented in this paper cannot be compared directly because they strongly depend on such factors as the carbon fuel material, the operating temperature, and the concept.^{5–7}

The most developed DCFC systems are those based on a molten carbonate electrolyte. Cooper and co-workers⁴ from the Lawrence Livermore National Laboratory achieved power densities in the range of 40–100 mW/cm² (0.8 V/cell, 800 °C) for different carbon materials. They operated a cell for 30 h

at a power output of 27 mW/cm² (1 V/cell, 800 °C). Nevertheless, carbonate-based cells suffer from corrosion problems, which have limited the choice of materials.

Zecevic et al. at Scientific Applications and Research Associates⁶ developed a DCFC using a molten hydroxide electrolyte. Peak power densities up to 120–180 mW/cm² have been observed, and an average power output of 40 mW/cm² (0.3 V/cell, 630 °C) over 540 h has been achieved. The most important problems with hydroxide cells have been corrosion of materials and degradation of the electrolyte due to the formation of carbonates during carbon electrooxidation.

Another new concept of a DCFC is based on the combination of solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) technology. A solid oxide electrolyte is employed to separate the cathode and anode compartments, while a molten carbonate electrolyte is utilized in the anode compartment. Oxygen is reduced to O^{2–} at the cathode and transported across the solid electrolyte membrane to the carbon/carbonate slurry, where carbon is oxidized (Figure 1). Carbon is oxidized to CO and CO₂ in the anode compartment, with the selectivity dependent on the temperature.^{8–12} Balachov and co-workers¹⁰ at Stanford Research Institute demonstrated peak power densities of 10–110 mW/cm² (0.7 V/cell) in a temperature range of 700–950 °C using different carbon-containing materials, e.g., plastic. Irvine and co-workers¹¹ kept a cell running for over 10 h at a power output of 10 mW/cm² (0.5 V/cell, 700 °C).

In this work, we present an easy and simple fabrication procedure for the tubular DCFC based on the general anode support SOFC and design basic operating variables for the

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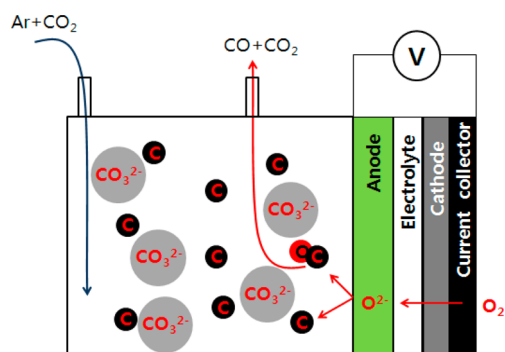


Figure 1. Electrochemical reaction mechanism of the DCFC with carbon/carbonate as a fuel and air as an oxidant.

tubular DCFC. On the basis of these experimental results, we fabricated and analyzed the basic properties and operation characteristics of a tubular DCFC.

EXPERIMENTAL SECTION

The extruded porous tubular tube served as a one-end-closed anode support for the tubular DCFC and as an anode compartment filled with a carbon fuel and an electrochemical mediator. The other cell components were fabricated in thin layers and attached on the surface of the tubular support.

The powder of the tubular anode support and activated carbon as a pore former were weighed and mixed in ethanol by ball milling and then dried. An organic binder and distilled water were added to the dried powder, and then the well-dispersed paste was extruded in the form of a tubular anode support.¹³ The extruded tubes were dried in a rolling dryer at room temperature and then presintered at 1100 °C. After that, an anode functional layer (AFL) was deposited onto the presintered anode support using the dip-coating method to form a homogeneous surface for coating the electrolyte film. The YSZ electrolyte layer was coated onto the surface of the presintered tubular anode support using a vacuum-slurry dip-coating method to form a thin and crack-free layer, which was then cofired¹⁴ at 1400 °C. The cathode materials ($\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF)) were synthesized by a solid-state powder reaction, for which the materials were weighed in the required proportions and mixed in ethanol by ball milling.¹⁵ The multilayered cathode, composed of a LSM/YSZ composite, LSM, and LSCF, respectively, was coated onto the surface of a YSZ electrolyte by a slurry dip-coating method and cosintered¹⁶ at 1150 °C. The active area of the single DCFC was 10 cm².

A high-surface-area carbon black (Super-S, Timcal; 45 m²/g) was used as the carbon fuel. Lithium carbonate (Li_2CO_3 ; Fluka) and potassium carbonate (K_2CO_3 ; Aldrich) were mixed at a ratio of 62:38 (mol %) to prepare the eutectic mixture that was

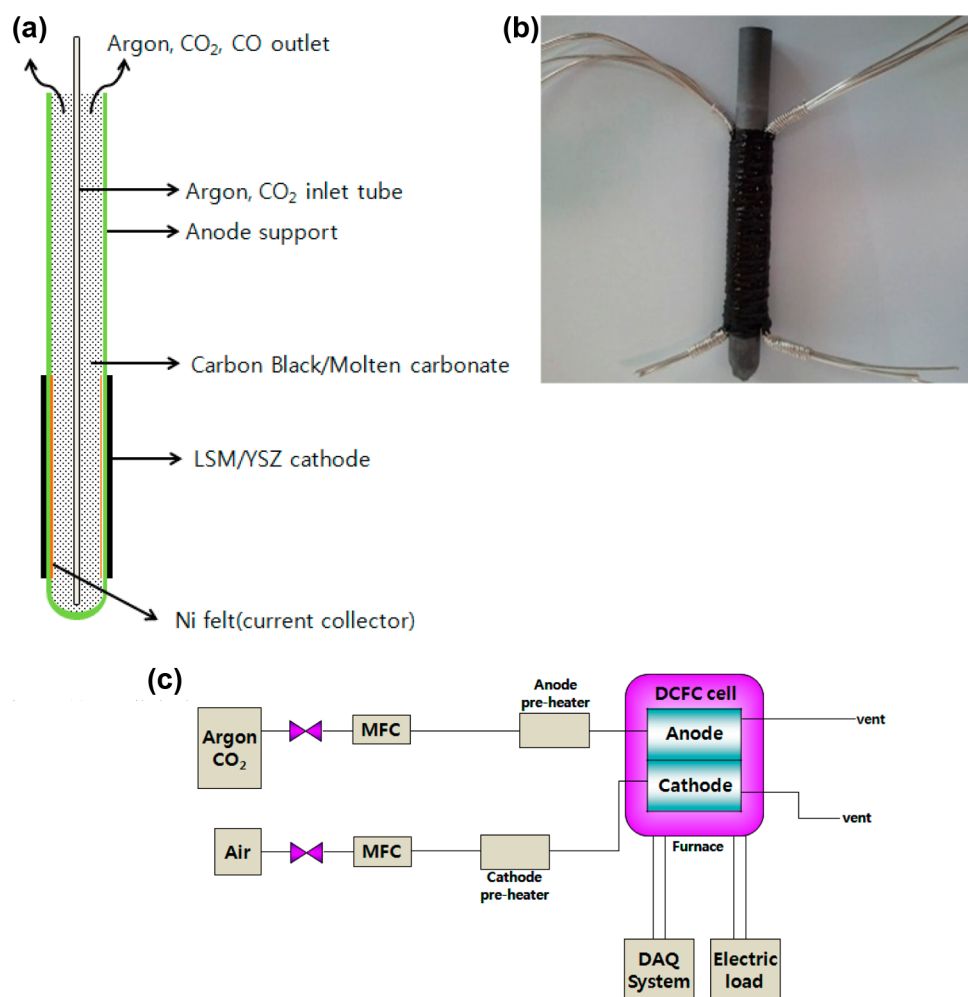


Figure 2. Schematic of the performance evaluation equipment for the DCFC.

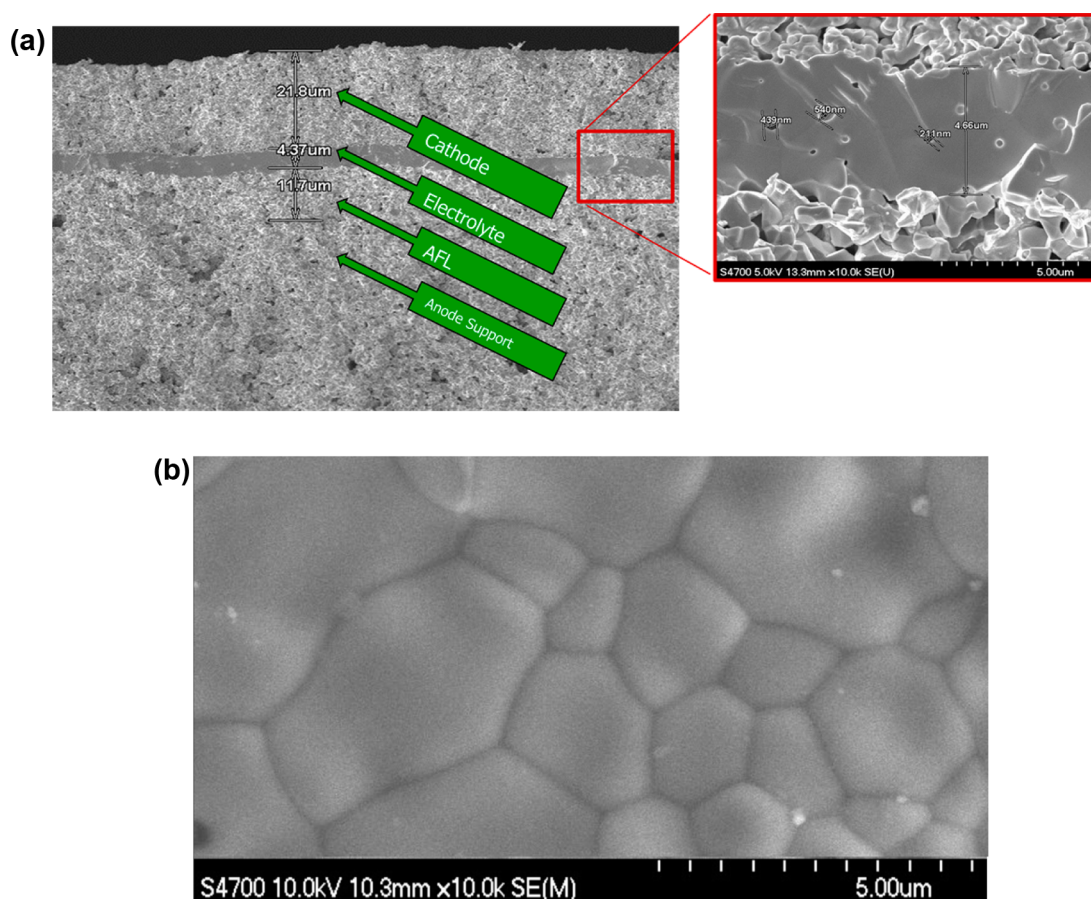


Figure 3. Microstructures of the whole DCFC and electrolyte before testing: cross-sectional image (Figure 3a) of regions showing anode, electrolyte, cathode, and anode support.

used as the electrochemical mediator in the anode side compartment. The electrochemical mediator as a eutectic mixture was mixed with carbon fuel in a weight ratio of 1:1. Then the mixture was dried at 100 °C for 24 h in a drying oven. The dried fuel mixture was filled into the anode side compartment. Nickel wire and felt were used as a current collector in the anode, while LSCo ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}$, PRAXAIR) paste and silver wire and mesh were used as the electrical contact on the cathode side.

A metal cap was installed at the upper part of a single tubular DCFC using ceramic glue as a sealing and joining material (Ceramabond, Aremco, New York, NY); argon gas was used as an inert gas at the anode side with a flow rate of 60 sccm, and ambient air was used as an oxidant at the cathode side. The cell was tested in a temperature range of 700–900 °C. The voltages of the tubular DCFC were measured by means of silver wires attached at the middle point of the electrode of the DCFC. To measure the operating temperature of the DCFC, we used a thermocouple at the middle position of the air chamber. All of the data, the temperature, voltage, mass flow, etc., were continuously monitored, acquired, stored, and controlled on a laptop computer for experimental data analysis through the Agilent DAQ system. The equipment for the performance test for the tubular DCFC was composed of a control system, a heating furnace, and an electronic load (Figure 2c). The DCFC performance was evaluated by adjusting the electric load (1000 K, DawGil, Korea).

RESULTS AND DISCUSSION

Figure 3 shows the microstructure of the DCFC and the surface of the YSZ film. Figure 3a is a representative fracture cross-sectional scanning electron microscopy image of the single DCFC and confirms that a 4.4- μm -thick YSZ film was successfully coated on the AFL. As can be seen in Figure 3a, the electrode (AFL and cathode) layers possess the expected porosity, while the YSZ electrolyte film is quite dense and with no cracks or delaminations. All of the layers are reasonably flat and uniform, with intimate contact at the interfaces. The thickness of the AFL is about 11.7 μm . The AFL is relatively denser⁵ than the porous anode support, and it can be considered as the transition from the anode to the electrolyte. Two roles are expected to be performed by the AFL. First, a fine thinner¹⁶ YSZ electrolyte film can be formed on the less porous AFL so that the ohmic resistance of the DCFC can be decreased. Second, the adaptation of the AFL increases the triple-phase boundary (TPB) area, which decreases polarization of the anode of the DCFC. Both functions are critical to improving the performance of the DCFC.¹⁶ Figure 3b is a surface view of the sintered YSZ electrolyte film. It can be seen that the YSZ electrolyte is composed of irregular grains without cracks.

In order to investigate the effect of the operating temperature on the voltage of the DCFC, the voltages of the DCFC were measured at operating temperatures in the range from 200 to 900 °C. As can be seen in Figure 4, an increase in the operating temperature generally led to an increase in the voltage in the

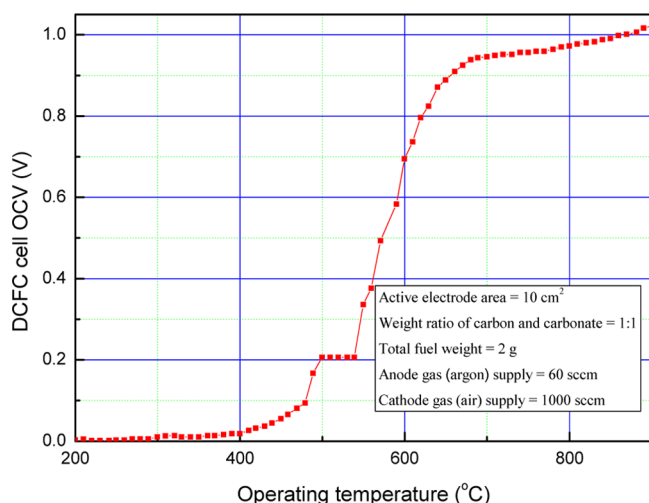


Figure 4. Voltage profile of the tubular DCFC with the operating temperature.

DCFC. In particular, the voltage of the DCFC increased gradually with the operating temperature until it was near 500 °C, exhibited a constant value (approximately 0.2 V) during some period, then increased showing an increment degree, and reached a constant high value of more than 1.0 V at a high temperature of around 800 °C. These behaviors imply that melting of carbonate as the general eutectic characteristic of carbonate^{8,12} may induce and enhance the conductivity and fluidity of carbon fuel within the molten carbonate at higher operating temperatures. Further, these results may be comparable to others⁸ and exhibit relatively similar trends.¹²

The electrochemical oxidation of carbon in the presence or absence of carbonate was studied to compare it to the performance of the DCFC with the weight ratio of carbon and carbonate. At a higher carbon ratio, such as in pure carbon, there was a relatively lower performance (Figure 5). The sluggish electrochemical reaction rate might be due to the limitation in contact between the solid carbon fuel and the solid YSZ electrolyte.¹⁷ In the presence of 25 and 50 wt % carbonate, the electrochemical oxidation of carbon in the DCFC increased significantly. No further improvement was found when the

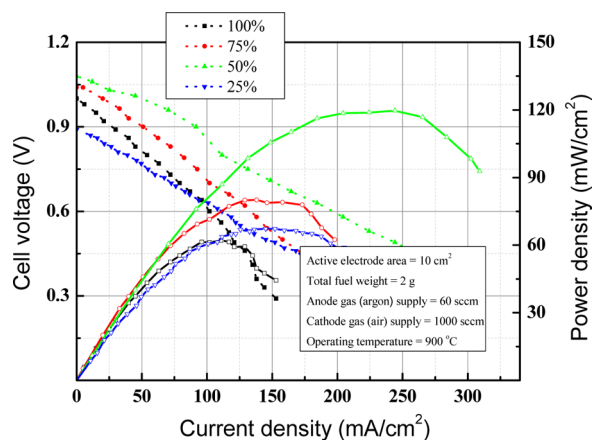


Figure 5. Effect of the weight ratio between the carbon fuel and carbonate on the electrochemical performance of the tubular DCFC (weight ratio between the carbon fuel and carbonate: black ■, 1:0; red ●, 3:1; yellow-green ▲, 1:1; blue ▼, 1:3).

carbonate amount was increased to 75 wt %; on the contrary, a much larger performance degradation was observed. On the basis of the performance comparison of a DCFC, these results revealed that the optimum weight ratio of carbon and carbonate for maximum performance of a DCFC is approximately 1:1. In the case of catalysis and oxidation of carbon in a hybrid DCFC⁷ combining MCFC and SOFC technology, the behavior of a carbon/carbonate slurry exhibited trends similar to those of our experimental results. These results indicate that good fluidity of the carbon fuel within carbonate is essential to enhancing the electrochemical performance of a DCFC, and the weight ratio of carbon and carbonate is an important factor to obtain good fluidity of the carbon fuel within carbonate.

Furthermore, another problem resulting from the higher weight percent carbonate was corrosion of the DCFC material and sealing issues.¹⁸ Therefore, a suitable amount of carbonate, 50 wt % (i.e., 50 wt % carbon), was used in the following DCFC experiments in order to obtain the maximum performance but minimize any corrosion problems in the DCFC.

Argon may be introduced as an inert carrier gas to help with transport of the carbon fuel and carbonate and stabilization of the atmosphere inside the anode compartment and to push away product gases such as CO₂ or CO from the reacting surface, as mentioned by another researcher.¹⁸ The effect of the flow rate of an inert carrier gas in the anode on the DCFC at 800 °C with an air constant flow rate at 1000 sccm is shown in Figure 6. The maximum power density of the DCFC increased

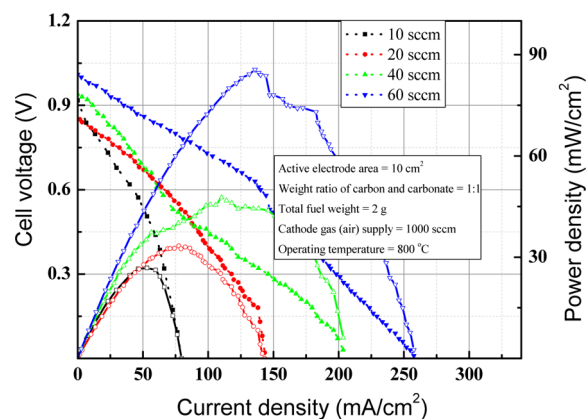


Figure 6. Effect of the anode gas supply on the electrochemical performance of the tubular DCFC (argon gas flow rate: black ■, 10 sccm; red ●, 20 sccm; yellow-green ▲, 40 sccm; blue ▼, 60 sccm).

by approximately 3.2 times from 26.8 to 85.6 mW/cm² as the inert carrier gas flow rate increased 6 times from 10 to 60 sccm. These results suggest that the introduction of large amounts of fresh argon enhances the transport of carbon fuel around the anode compartment, favoring better contact between the carbon fuel and anode layer and improves the DCFC performance by reducing the concentrations of product gases that suppress anode reactions on the anodic surface.^{18–20}

Figure 7 shows the *I–V–P* characteristics of the tubular DCFC. The results are shown at various temperatures (700–900 °C) with 50 wt % carbon fuel/carbonate filled with the anode support with a total weight of 2 g; argon flowed at the anode side at a flow rate of 60 sccm, and air flowed outside the DCFC at a flow rate of 1000 sccm. The DCFC exhibited open-circuit voltages of somewhat different values with different operating temperatures. In addition, in comparison with the

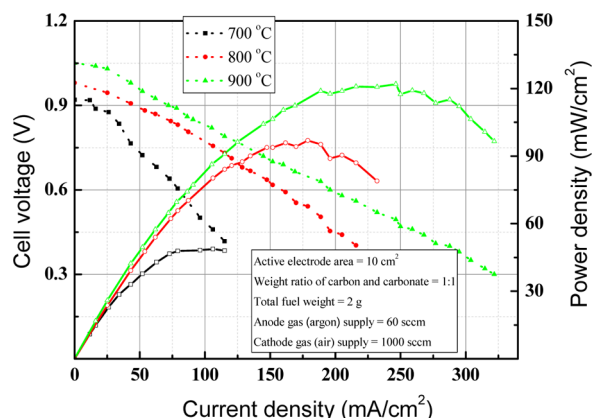


Figure 7. Performance curves of tubular DCFCs with temperatures based on the obtained variable operating conditions (operating temperature: black ■, 700 °C; red ●, 800 °C; yellow-green ▲, 900 °C).

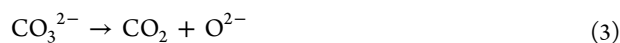
experimental results between Figures 6 and 7, some experimental results exhibited somewhat different trends although the same experimental condition. The reasons for this phenomenon may be complicated and not well understood. Therefore, further study will be needed.

Further, the maximum power output of the tubular DCFC was 0.49 W (49 mW/cm² calculated using the active cell area) at 700 °C, 0.97 W (97 mW/cm²) at 800 °C, and 1.22 W (122 mW/cm²) at 900 °C, respectively. The liquid-like state of the carbon fuel at higher temperatures over the melting point of carbonate might affect the electrochemical performance of the DCFC, although the reasons for this phenomenon may be complicated and not well understood. Activation polarization can be decreased because the electrochemical reactions of liquid-like carbon and carbonate at the TPBs on the anode can be extended.^{17,19,21} Thus, the electrochemical performance of the DCFC can be enhanced.

Instead of argon as an anode supplying gas, CO₂ was chosen and adjusted to a suitable amount at approximately 60 sccm. The carbon oxides have a major influence on the electrochemical performance of the DCFC.^{7,19} First, the cell potential is dependent upon CO₂ partial pressure (eq 2)

$$E_{\text{cell}} = E_0 + \frac{RT}{nF} \ln \frac{a_{\text{CO}_2}}{a_{\text{C}}a_{\text{O}_2}} \quad (2)$$

where $E_0 = -(\Delta G_0/nF)$ and a_{CO_2} , a_{C} , and a_{O_2} are the activity of each component in the entire reaction. Consequently, first, CO₂ stabilizes the gas condition inside the anode compartment. Second, the gas flow of CO₂ enhances the mass transport of the carbon fuel and carbonate around the anode compartment. Third, the flux of CO₂ into the anode compartment inhibits decomposition of the carbonate salts, as shown in eq 3.



As can be seen in Figure 8, the maximum power density of the DCFC increased by approximately 127% from 122 to 154.7 mW/cm² when argon and CO₂ are compared as an anode supplying gas at the same operating conditions. This result confirms that a suitable addition of CO₂ gas into the anode side of the DCFC can improve the power of the DCFC because it enhances the mass transport of carbon fuel around the anode compartment, creating better contact between the carbon fuel⁷

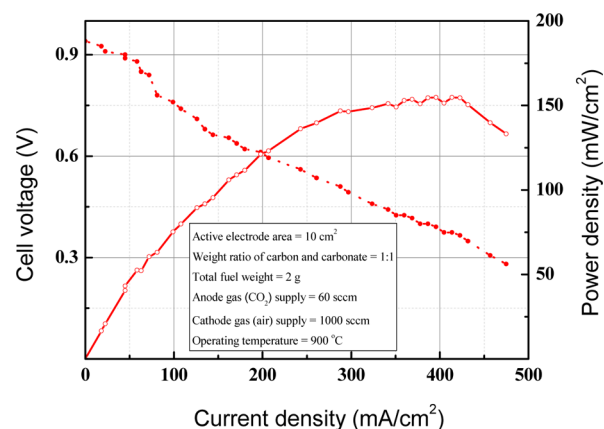


Figure 8. Effect of the addition of CO₂ gas in the anode side on the electrochemical performance of the tubular DCFC.

and the anode layer and inhibiting decomposition of the carbonate salts by maintaining its concentration constant.¹⁹

CONCLUSION

A tubular DCFC based on a general anode support SOFC was fabricated and characterized by optimizing the weight ratio between the carbon fuel and carbonate and the anode gas supply. In addition, basic operation characteristics were analyzed. The tubular DCFC showed a maximum power density of 0.155 W/cm² at 900 °C using carbon/molten carbonate and air/CO₂ as the fuel and oxidant/anode supplying gas, respectively. This shows that the developed tubular DCFC can be a potential candidate for many other practical applications, such as RPG and APU systems.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Ahn, S. Y.; Eom, S. Y.; Rhie, Y. H.; Sung, Y. M.; Moon, C. E.; Choi, G. M.; Kim, D. J. Utilization of wood biomass char in a direct carbon fuel cell (DCFC) system. *Appl. Energy* **2013**, *105*, 207.
- (2) Ahn, S. Y.; Eom, S. Y.; Rhie, Y. H.; Sung, Y. M.; Moon, C. E.; Choi, G. M.; Kim, D. J. Application of refuse fuels in a direct carbon fuel cell system. *Energy* **2013**, *51* (1), 447.
- (3) Yuta, N.; Kevin, D. P.; John, T. S. I. Ni/C Slurries Based on Molten Carbonates as a Fuel for Hybrid Direct Carbon Fuel Cells. *J. Electrochem. Soc.* **2009**, *156* (6), B716.
- (4) N urnberger, S.; Bu ar, R.; Desclaux, P.; Franke, B.; Rzepka, M.; Stimming, U. Direct carbon conversion in a SOFC system with a non-porous anode. *Energy Environ. Sci.* **2010**, *3*, 150.
- (5) Turgut, M. G.; Michael, H.; Anil, V. V. High performance solid oxide fuel cell operating on dry gasified coal. *J. Power Sources* **2010**, *195*, 1085.

- (6) Yaohui, B.; Yan, L.; Yubao, T.; Yongmin, X.; Jiang, L. Direct carbon solid oxide Fuel Cell: a potential high performance battery. *Int. J. Hydrogen Energy* **2011**, *36*, 9189.
- (7) Cairong, J.; John, T. S. I. Catalysis and oxidation of carbon in a hybrid direct carbon fuel cell. *J. Power Sources* **2011**, *196*, 7318.
- (8) Xiang, L.; Zhong, H. Z.; Roland, D. M.; Andrew, D.; John, B.; Shaomin, L.; Gao, Q. L. Factors That Determine the Performance of Carbon Fuels in the Direct Carbon Fuel Cell. *Ind. Eng. Chem. Res.* **2008**, *47*, 9670.
- (9) Jayakumar, A.; Vohs, J. M.; Gorte, R. J. Molten-Metal Electrodes for Solid Oxide Fuel Cells. *Ind. Eng. Chem. Res.* **2010**, *49*, 10237.
- (10) Sneh, L. J.; Lakeman, J. B.; Kevin, D. P.; Marshall, R.; John, T. S. I. Electrochemical performance of a hybrid direct carbon fuel cell powered by pyrolysed MDF. *Energy Environ. Sci.* **2009**, *2*, 687.
- (11) Yuta, N.; Kevin, D. P.; John, T. S. I. Electrochemical oxidation of solid carbon in hybrid DCFC with solid oxide and molten carbonate binary electrolyte. *Energy Environ. Sci.* **2008**, *1*, 148.
- (12) Cairong, J.; Jianjun, M.; Alfredo, D. B.; John, T. S. I. Demonstration of high power, direct conversion of waste-derived carbon in a hybrid direct carbon fuel cell. *Energy Environ. Sci.* **2012**, *5*, 6973.
- (13) Park, B. K.; Lee, J. W.; Lee, S. B.; Lim, T. H.; Park, S. J.; Song, R. H.; Shin, D. R. A flat-tubular solid oxide fuel cell with a dense interconnect film coated on the porous anode support. *J. Power Sources* **2012**, *213* (1), 218.
- (14) Lim, T. H.; Park, J. L.; Lee, S. B.; Park, S. J.; Song, R. H.; Shin, D. R. Fabrication and operation of a 1 kW class anode-supported flat tubular SOFC stack. *Int. J. Hydrogen Energy* **2010**, *35*, 9687.
- (15) Lim, T. H.; Song, R. H.; Shin, D. R.; Yang, J. I.; Jung, H.; Vinke, I. C.; Yang, S. S. Operating characteristics of a 5 kW class anode-supported planar SOFC stack for a fuel cell/gas turbine hybrid system. *Int. J. Hydrogen Energy* **2008**, *33*, 1076.
- (16) Yun, U. J.; Lee, J. W.; Lee, S. B.; Lim, T. H.; Park, S. J.; Song, R. H.; Shin, D. R. Fabrication and Operation of Tubular Segmented-In-Series (SIS) Solid Oxide Fuel Cells (SOFC). *Fuel Cells* **2012**, *12* (6), 1099.
- (17) Sneh, L. J.; Yuta, N.; Barry, J. L.; Kevin, D. P.; John, T. S. I. Solid state electrochemistry of direct carbon/air fuel cells. *Solid State Ionics* **2008**, *179*, 1417.
- (18) Bonaccorso, A. D.; John, T. S. I. Development of tubular hybrid direct carbon fuel cell. *Int. J. Hydrogen Energy* **2012**, *37*, 19337.
- (19) Liu, R.; Zhao, C.; Li, J.; Zeng, F.; Wang, S.; Wen, T.; Wen, Z. A novel direct carbon fuel cell by approach of tubular solid oxide fuel cells. *J. Power Sources* **2010**, *195*, 480.
- (20) Kim, J. P.; Lim, H.; Jeon, C. H.; Chang, Y. J.; Koh, K. N.; Choi, S. M.; Song, J. H. Performance evaluation of tubular fuel cells fuelled by pulverized graphite. *J. Power Sources* **2010**, *195*, 7568.
- (21) Kim, J. P.; Choi, H. K.; Chang, Y. J.; Jeon, C. H.; Jeon, H. J. Feasibility of using ash-free coal in a solid-oxide-electrolyte direct carbon fuel cell. *Int. J. Hydrogen Energy* **2012**, *37*, 11401.