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Thermal decomposition of alkane hydrocarbons inside a porous Ni anode for fuel supply of direct carbon fuel cell: Effects of morphology and crystallinity of carbon



Chengguo Li, Hakgyu Yi, Tahereh Jalalabadi, Donggeun Lee*

School of Mechanical Engineering, Pusan National University, Busan 609-735, South Korea

HIGHLIGHTS

- A first practical method to maximize triple phase boundary at DCFC fuel electrode.
- Carbon spheres, nanotubes, and nanofibers are produced under control.
- Less crystalline nanotubes and nanofibers are more active for longer time period.
- Power density and lifetime are even comparable to H₂-fuel fuel cell.

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ABSTRACT

This study improved the physical contact between anode and fuel in a direct carbon fuel cell (DCFC) by directly generating carbon in a porous Ni anode through thermal decomposition of three kinds of hydrocarbons (CH₄, C₂H₆, C₃H₈). From electron microscope observations of the carbon particles generated from each hydrocarbon, carbon spheres (CS), carbon nanotubes (CNT) and carbon nanofibers (CNF) were identified with increasing carbon number. Raman scattering analysis was performed to determine the crystallinity of the carbon samples. As a result, the carbon samples (CS, CNT, and CNF) produced from CH₄, C₂H₆ and C₃H₈ were found to be less crystalline and more flexible with increasing the carbon number. DCFC performance was measured at 700 °C for the anode fueled with the same mass of the carbon sample. It was found that the 1-dimensional CNT and CNF were more active to produce 148% and 210% times higher power density than the CS. The difference was partly attributed to the finding that the less-crystalline CNT and CNF had much lower charge transfer resistances than the CS. A lifetime test found that the CNT and CNF, which are capable of transporting electrons for much longer periods, maintained the power density much longer, as compared to the CS which can lose their point contacts between the particles shortly at high current density.

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1. Introduction

A direct carbon fuel cell (DCFC) does not require CO₂ separation as it only releases CO₂ [1,2]; such a cell also offers advantages in terms of fuel diversity and efficiency due to its ability to use various carbon solids as fuel [1–7]. DCFCs have thus gained the interest of researchers and users around the world. However, unlike gaseous fuel, which is known for being highly diffusible, solid fuels have essentially very limited contacts with anode and electrolyte. This

would be a possible reason why the power density of DCFCs tends to be far lower than that of hydrogen-used fuel cells. Moreover, long-term operation with continuous or at least piecewise continuous refueling has not been achieved, and research is being actively conducted on the basis of button cells. Instead of utilizing the advantages of solid fuel, researchers have begun to work on modifying solid fuel to CO through various gasification methods such as the reverse Boudouard reaction (C + CO₂ = 2CO) [8–12], a catalytic reaction of C with molten carbonate [13,14] or hydrocarbon decomposition [15–19]. Since such approaches lead to simply other versions of gas-fueled molten carbonate fuel cells (MCFC) or solid oxide fuel cells (SOFC), we have turned our attention back to developing a practical way to solve the technical challenges of

* Corresponding author.

E-mail address: donglee@pusan.ac.kr (D. Lee).

DCFCs: the limited triple phase boundary (TPB) and discontinuous refueling.

As for the issue of limited TPB, there have been a few previous reports proposing new ideas to overcome this problem. For example, some researchers [11,15,20] mixed carbon powder for a fuel, Ni or NiO powder for an anode, and YSZ or SDC powder for a solid electrolyte, and formed a plate-type C-fueled anode in attempts to increase the TPB. Despite the enhanced TPB and high working temperatures (700–900 °C), which might accelerate the electrochemical reaction kinetics, the power density was still less than 110 mW/cm². More recently, we made an attempt to increase the TPB by filling the inside of a porous Ni anode with carbon powders and coating the anode with a ceria to enhance the wettability. As a result, the power density of the new button cell was increased by a factor of 7 as compared to the case of a flat interface between fuel and electrode [21]. It should be noted that the dramatic increase of the performance was obtained even below 700 °C, at which temperatures the reverse Boudouard reaction is thermodynamically minimized. Thus we believe that the promising result was mainly attributable to the enhanced TPB.

As for the issue of discontinuous refueling, which limits long-term operation of DCFC, Lim et al. [9] succeeded in running DCFC for 200 h using CO generated from the reverse Boudouard reaction at 750 °C. However, it is noted that fuel reforming from the Boudouard reaction is only possible at temperatures higher than 700 °C. In addition to the problem of fuel supply, extensive research is being conducted on lowering the operating temperature of SO- or MC-based DCFCs [22]. In summary, there is no practical method that will support the expansion of TPB at lower temperatures and the continuous refueling as well. Among various methods, hydrocarbon decomposition comes close to meeting the aforementioned requirements.

Thermal decomposition or catalytic decomposition of hydrocarbon, together with the typical steam reforming process, has been widely studied to create syngas of H₂ & CO [23,24]. On the other hand, there have been a few interesting attempts to utilize methane gas as a carbon source for DCFCs through the decomposition of the gas in the absence of any oxygen source. For example, Li et al. [19] produced carbon nanofiber (CNF) through thermal decomposition of CH₄ at 500–700 °C for 35–75 h. The CNF fuels were then floated in a pool of molten carbonate in which a rod-shaped Au anode was installed. The power density, when measured at 800 °C, was 45 mW/cm² even for an unrealistically long fueling time. Ihara et al. supplied methane (CH₄) [16,17] and propane (C₃H₈) [18] to a Ni-GDC (gadolinium-doped ceria) porous cermet anode maintaining at 900 °C, to stimulate thermal decomposition. Gaseous residuals such as CH₄ and H₂, generated from the 5–360 min of thermal decomposition, were removed with carrier gas (argon), and only solid carbon formed between the building components of the anode was used as a fuel. A maximum power density of 80 mW/cm² was achieved as a result. Likewise, Li et al. [15] inserted methane (CH₄) gas into a Ni-YSZ cermet anode, maintained at 800 °C, to produce carbon in pores between anode particles. Next, SO-DCFC was activated based on carbon alone after removing gaseous products from the methane decomposition. A maximum power density was again 80 mW/cm². It is noted that the solid fuel tends to be unstable as the reverse Boudouard reaction is dominant at their operating temperature of 800–900 °C, resulting in low fuel utilization. Thus, the operating time ended up shortly; power density decreased 50% within 20 min.

In the present study, we directly produced carbon in a porous Ni anode through thermal decomposition of three different hydrocarbons (CH₄, C₂H₆, C₃H₈) at lower temperatures for 30 min, in an attempt to improve physical contact between the electrode and fuel. The carbon particles, generated from each hydrocarbon, were

characterized in terms of the morphology and crystallinity using electron microscope and Raman spectroscopy. An MC-DCFC system was developed for the three different anodes fueled with the same mass of carbon; the performance was assessed at 700 °C. Longer chains of hydrocarbon are preferred for reducing the decomposition temperatures and producing more active carbon fuels. Possible cause will be discussed.

2. Experimental section

2.1. Sample preparation

Fig. 1 shows an experimental setup used for carbon formation in a porous Ni anode through hydrocarbon decomposition. A 6 cm-long 1.8 cm-thick cylindrical porous Ni foam (with a pore size of 50–75 μm) to be used as an anode was installed inside a quartz tube (80 cm × 1.85 cm). The quartz tube was placed in the middle of a hot-wall tube furnace (w/30 cm-long hot zone) and heated constantly at a certain temperature in a range of 500–900 °C. Methane (CH₄), ethane (C₂H₆) and propane (C₃H₈), with different carbon numbers among alkane hydrocarbons, were chosen as a carbon precursor. A gaseous hydrocarbon among them flowed alone through the hot porous Ni foam, at a rate of 55 ml/min, leading to carbon formation in between metal networks of the Ni foam. Thus, we believe that the carbon fuel makes good physical contact with Ni network. The amount of carbon formed was quite easy to control, simply by varying the furnace temperature or time period of hydrocarbon decomposition. Each hydrocarbon flow lasted constantly for 30 min, unless otherwise noted.

The Ni foam containing carbon samples generated from the hydrocarbons was cut into slices and the carbon morphology in the slice was investigated with a scanning electron microscopy (SEM; S-4800, Hitachi, 10 kV). The carbon particles were brushed from the Ni foam and then dispersed in ethanol with an ultrasonicator. A few drops of the carbon–ethanol suspension were dropped onto a TEM grid by using a micropipette, and then dried at room temperature. Detail microstructure of the carbon particles were observed with a high-resolution transmission electron microscopy (HRTEM; JEOL 2100F, 200 kV). In addition, the crystallinity of the carbon particles was analyzed by Raman spectroscopy (inVia Raman microscope, Renishaw) using a 514 nm Ar laser light, and X-ray diffraction (XRD, D/max 2400, Rigaku). More details of characterization experiments are available elsewhere [25,26].

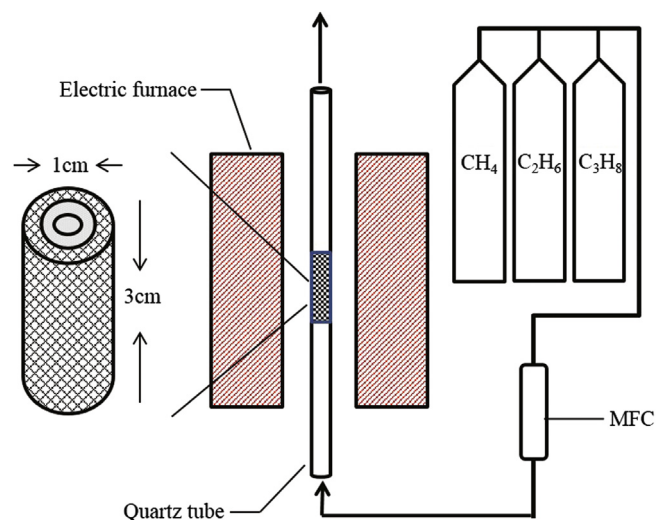


Fig. 1. A schematic diagram for carbon formation in a porous Ni anode through hydrocarbon decomposition.

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