On-demand supply of slurry fuels to a porous anode of a direct carbon fuel cell: Attempts to increase fuel-anode contact and realize long-term operation

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HIGHLIGHTS

- A potentially continuous fuel supply with increasing fuel-anode contacts in a DCFC.
- Of importance was the size match between the anode pores and fuel particles.
- Maximal power density under the optimal size-matching reached 645 mW cm^{-2}.
- More than 20-h steady operation was achieved at a current density of 700 mA cm^{-2}.

ABSTRACT

In this paper, we propose a novel idea that might allow resolution of the two biggest challenges that hinder practical use of direct carbon fuel cells (DCFC). This work involved 1) the use of three types of porous Ni anode with different pore sizes, 2) size matching between the anode pores and solid fuel particles in a molten-carbonate (MC) slurry, and 3) provision of a continuous supply of fuel-MC slurry through the porous Ni anode. As a result, larger numbers of smaller pores in the anode were preferred for extending the triple phase boundary (TPB), as long as the fuel particles were sufficiently small to have full access to the inner pore spaces of the anode. For example, the maximal power density achieved in the case of optimal size matching, reached 645 mW cm^{-2}, which is 14-times greater than that for the case of poorest size-matching and 64-times larger than that for a non-porous anode, and lasted for more than 20 h. After 20 h of steady operation at a fixed current density (700 mA cm^{-2}), the electric potential slightly decreased due to partial consumption of the fuel. The cell performance readily recovered after restarting the supply of MC-fuel slurry.

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1. Introduction

Recently, a large number of studies have been performed on direct carbon-fuel-cells (DCFC) because of their great potential for use in applications affecting energy and environment. The highest theoretical efficiency (near 100%) [1–7], does not require CO$_2$ separation from flue gas in a conventional power plant [1,2], and the usable fuels are diverse: any carbon-containing fuel, including coal, biomass, and even organic waste [7–11]. These potential advantages have undoubtedly led to the recent attention attracted by DCFC.

Because DCFC systems use solid rather than gaseous fuels (e.g., H$_2$, CO, and CH$_4$), two big issues are raised. One relates to the unacceptably low activity of the fuel electrode, caused mainly by very limited formation of triple phase boundaries[1] (TPBs) between solid

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[1] The concept of triple phase boundary could be drawn from an anodic reaction in Eq (1) (will be shown). To produce electrons, the fuel (C) should have a chance to encounter the carbonate ions (CO$_3^{2-}$). As the ions transported from a cathode could be available only in the liquid-phase MC, the fuel particles should be in contact with the MC. In addition, as-produced electrons need to be drawn from the anode and then delivered to the cathode in order to continue the cathodic reaction (Eq (2)). This requires additional contact between the electrode and the site of anodic reaction. Thus, effective electrochemical reaction presumably occurs only at coincident contacting sites between three different phases: solid fuel particles, a liquid electrolyte, and a solid electrode. This is why TPB formation is limited when using solid fuels that are hard to handle, compared to gaseous fuels.

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fuel, anode, and electrolyte [12–14]. The second relates to their too short operation time owing to discontinuous refueling [1,15–17]. As for the issue of the limited TPBs, there are a few previous reports proposing new ideas to overcome this problem. In some of the studies on DCFC systems based on SOFC, for example, metal/metal oxide powders were mixed with solid electrolyte powder to form cermet-type anodes (e.g., Ni-YSZ and Ni SDC). The pores in the anode could be used as extended surfaces when being filled with carbon, leading to an increase in the TPBs [12,14]. Li et al. [13] used thermal decomposition of methane at temperatures above 800 °C to produce carbon inside a porous cermet. Despite large increases in the TPBs (expected) and its high working temperature (700−900 °C), both of which could accelerate the electrochemical reaction kinetics, the power density was barely 110 mW cm^{-2}, still far from the levels required.

More recently, we attempted to maximize the TPB by filling the pores of porous Ni foam with carbon powder, together with a ceria coating of Ni foam to enhance the electrolyte (molten carbonate, MC) wettability of the Ni. A button cell of MC-based DCFC having a C-filled Ni anode was tested, and the result showed that the power density of the button cell was increased by a factor of seven, as compared to a flat interface between fuel and electrode [18]. However, the button cell structure of the DCFC limits long-term cell operation due to the impracticality of refueling the porous anode. Most recently, we changed our direction by producing the carbon fuels inside the porous anode, rather than supplying solid fuels from outside. Thermal decomposition of gaseous hydrocarbons was quite successful for this purpose, and this approach allowed for control of the morphology and amount of fuel along with great enhancement of the TPBs [19]. We found that a material with a 1-D structure (carbon nanofibers) was preferred for filling the pore space of the anode, and was successful at raising the power density to ~500 mW cm^{-2}. Thus, we believe that the idea of using porous Ni foam was quite successful.

As for the issue of discontinuous refueling, Cooper et al. [16] presented another design allowing for continuous fuel supply in the form of a MC-C slurry into the cell. This resulted in a peak power density of 55 mW cm^{-2} at 800 °C, and the longest operation of the cell was for 30 h. LLNL [17] designed a self-feeding cell with an inclined electrode that could be refueled pneumatically. The design concept was extended for a 75–150 W, 5-cell self-feeding bipolar stack (120–160 mW cm^{-2} per cell). Heydron et al. [20] proposed another DCFC-concept based on a supply of carbon powder through a fluidized-bed-type assembly. Their fuel supply system offers advantages such as continuous fueling with easy scale up, and simple separation of heavier ash components from carbon. Though they successfully demonstrated continuous fuel feeding, the physical contact between carbon particles floating in the gas and the anode was very limited. Overall, there has been no success in resolving both of the issues simultaneously: maximizing TPBs with continuous fuel feeding.

Here, we propose a novel solution to both challenges. This involves four types of Ni anode with different pore sizes, and the continuous feeding of graphite powder-MC slurry into the Ni anode. We attempted to maximize the TPBs by optimizing the size match between the fuel particles and the anode pores. As a result, the size of the anode pores needed to be as small as possible, as long as the fuel powder was small enough to get inside them. Measurements of I–V, at the optimal size combination, demonstrated that the current fuel-feeding anode has produced a power density of ~645 mW cm^{-2} for 20 h. After partial consumption of the fuel powder, the power generation readily recovered after restarting the supply of fuel-MC slurry through the anode.

2. Experimental

Fig. 1 shows a schematic of the three-electrode electrochemical cell that was developed in this study, based on the design of Vutetakis [4]. A 6-cm long, 1.8-cm thick, cylindrical piece of porous Ni foam was used as an anode (WE), after being spot-welded to a flat-plate-type silver current collector (6 cm high × 0.4 cm thick). Four types of Ni foam with different pore sizes (20, 40, 60, 80 ppi) were considered. The counter electrode (CE) and reference electrode (RE) were made from a silver sheet (surface area 3.2 cm^2) spot-welded to a silver wire. The silver parts were each sheathed in a 12-mm diameter closed-bottom alumina tube. A 1.0-mm hole at the bottom of the alumina sheath allowed carbonate ions to conduct between the electrodes through the MC electrolyte.

We considered two types of graphite powder with two different particle sizes (average diameter 0.15 and 1.3 mm). The specific surface area, pore size, and volume of the fuel particles were measured by a gas sorptometer (Autosorb-1, Quantachrome) using nitrogen adsorption at 77 K and Brunauer−Emmett−Teller (BET) analysis. The results are summarized in Table 1. Both of the fuel particles have similar BET properties and their specific surface areas both remain in the non-porous levels. Thus, we did not pay attention to the surface area of the fuels.

Scanning electron microscopy (SEM; S-4800, Hitach, 15 kV) equipped with energy dispersive spectrometer (EDS) was used to explore the microstructure of the porous Ni anode. Fig. 2 shows SEM images of three-dimensional (3D) porous structures of the four types of Ni anodes used in this study. EDS measurement for the anodes confirmed that there are no foreign species (but Ni) beyond detectable lower limit. X-ray Diffraction (XRD, D/MAX-2400, Rigaku) was also conducted to analyze the purity of the Ni anodes by scanning the angle of 2θ in the range of 10−90° at a rate of 6° min^{-1} while irradiating Cu Kα X-ray (30 kV, 40 mA, 0.15218 nm). In Fig. S1, the 2θ positions of the three major peaks are 44.4, 51.7, and 76.3°, all of which are very close to the JCPDS data (44.5, 51.8, and 76.4°, respectively) for pure metallic Ni. This suggests that the Ni anode was very likely metallic Ni without any further crystalline contaminants. A similar result was also shown in our previous publication [18].

To make the MC-carbon slurry, 350 g of dry carbonate powder (consisting of 32-wt% Li$_2$CO$_3$ and 68-wt% K$_2$CO$_3$) was mixed with 50 g of graphite powder of two different particle sizes in an alumina container, and then heated at 700 °C to melt the carbonates. As shown in Fig. 1, an alumina stirring-rod was placed in the center of the container and rotated to stir the slurry. This served to trap some of the fuel particles inside the porous WE. The amount of fuel powder trapped inside was gradually increased with stirring time. If the internal pore space of the WE were completely filled with fuel powder, further rotation of the slurry would not cause any difference in electricity production. We tested several stirring periods and confirmed that 10 min of stirring was long enough for complete fueling of the WE. Thus, the stirring continued for only 10 min, and then was stopped to perform electrochemical measurements. Though this intermittent stirring was employed to measure the timing and duration of fuel consumption, steady fuel feeding is possible, in principle, by stirring continuously.

Prior to measurement of electrochemical performance, any residual oxygen in the system was removed by flowing CO$_2$ gas at a rate of 50 ml min^{-1} to the CE and RE, during the warm-up process of the system. When the operating temperature of 700 °C was attained, a mixture of CO$_2$ and O$_2$ (mole ratio of 2:1) was injected into the CE and the RE at a total flow rate of 100 ml min^{-1}. During the electrochemical reaction of carbon, Ar gas was continually supplied to the WE at 200 ml min^{-1} in order to purge the CO$_2$ gas produced.