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# A performance study of hybrid direct carbon fuel cells: Impact of anode microstructure

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## ABSTRACT

Direct carbon fuel cells (DCFCs) have recently attracted great interest because they could provide a considerably more efficient means of power generation in comparison with conventional coal-fired power plants. Among various types of DCFCs under development, a hybrid system offers the combined advantages of solid oxide and molten carbonate electrolytes; however, there is a significant technical challenge in terms of power capability. Here, we report an experimental study demonstrating how anode microstructure influences the power-generating characteristics of hybrid DCFCs. The anode microstructure (pore volume and surface area) is modified by using poly(methyl methacrylate) (PMMA) pore-formers. Polarization studies indicate that cell performance is strongly dependent on the anode surface area rather than on the pore volume. The incorporation of PMMA-derived pores into the anode leads to improved power capability at typical operating temperatures, which is attributed to an enlarged active zone for electrochemical CO oxidation.

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## Introduction

Direct carbon fuel cells (DCFCs), which directly convert the chemical energy of carbon into electricity, have received significant attention in recent years owing to an increasing need for efficient and clean power generation from coals and other carbon-containing fuels (coke, biomass, waste materials, etc.) [1–3]. The theoretical thermodynamic efficiency of a DCFC is close to 100% because there is almost no change of the entropy in the electrochemical oxidation reaction of carbon to CO<sub>2</sub>

[1,2]. DCFC systems could therefore offer great benefits in conversion efficiency compared to conventional coal-fired power plants that typically operate at 30–35% efficiency [3]. Moreover, they would not produce undesirable emissions, such as particulates, NO<sub>x</sub>, and SO<sub>x</sub>, which are the common by-products of carbon combustion.

There are several types of DCFCs that can be classified according to the electrolyte used, including systems based on an aqueous or molten hydroxide electrolyte, a molten carbonate (MC) electrolyte, and a solid oxide (SO) electrolyte [1–3]. Among these, much of focus has been on SO electrolyte

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systems with oxygen ion ( $O^{2-}$ ) conducting ceramics (e.g., yttria-stabilized zirconia, YSZ) due to their high-temperature stability [1–6]. These systems adopt cell architectures similar to traditional solid oxide fuel cells. In a DCFC with an SO electrolyte (YSZ) and a Ni–YSZ anode, carbon oxidation should occur over three-phase boundaries (TPBs) among YSZ (electrolyte), Ni (electrode catalyst and electronic conductor), and carbon (fuel). However, there would be very little physical contact between the solid carbon and the anode, resulting in poor power capability.

To overcome this drawback, Irvine and others [7] proposed a modified design – a “hybrid” DCFC that makes use of both SO and MC electrolytes. The SO electrolyte separates the cathode and anode compartments, preventing direct contact of the cathode (e.g.,  $(La,Sr)MnO_3$ ,  $(La,Sr)(Co,Fe)O_3$ , etc.) with the corrosive MC electrolyte, while the MC electrolyte holds carbon particles and thus facilitates the kinetics of carbon oxidation by enlarging the reaction zone. The authors demonstrated that YSZ-based hybrid DCFCs could successfully operate at 700–900 °C on carbon fuels suspended in a eutectic  $Li_2CO_3$ – $K_2CO_3$  mixture (MC electrolyte). Since then, various attempts have been made to understand the mechanism of carbon oxidation in hybrid DCFCs and to improve their electrochemical performance through the optimization of carbon fuels, carbon–MC compositions, electrode and electrolyte materials, as well as cell architectures [8–21]. Little attention has been given to the microstructural aspects of anodes that can substantially affect the reaction kinetics, and there may be still room for improvement by microstructural engineering of anodes.

The purposes of this paper are to investigate the impact of anode microstructure on hybrid DCFC performance as well as to propose an effective approach to improving power capability. Poly(methyl methacrylate) (PMMA) particles were employed as a pore-former to produce pores of various sizes in a Ni–YSZ anode and thus to modify the anode microstructure (i.e., pore volume and surface area). The polarization behaviors of the hybrid DCFCs were examined using the anodes with three different microstructures, and they were analyzed to establish a relationship between the anode microstructure and electrochemical performance. The results demonstrate that the incorporation of PMMA-derived pores in the anode leads to an increased power density under typical DCFC operating conditions. A series of electrochemical experiments with various cell configurations were also conducted to provide insight into the relationship between the anode microstructure and the observed cell behavior.

## Experimental

### Fabrication and characterization of a unit cell

An 8 mol%  $Y_2O_3$ -stabilized  $ZrO_2$  (YSZ) pellet (ca. 250  $\mu m$  in thickness and 25 mm in diameter, NexTech Materials Ltd.) was used as an SO electrolyte support. An anode (ca. 50  $\mu m$  in thickness) of NiO (J.T. Baker) and YSZ (Tosoh Co.) was coated on one side of the electrolyte support using a screen-printing process, followed by sintering at 1400 °C. The microstructure of the anode was controlled by varying the size ( $d_{PMMA}$ ) of the

PMMA beads used as the pore-former. The amount of the PMMA beads was 10 wt.% of the NiO–YSZ powder mixture. A cathode (ca. 30  $\mu m$  in thickness) composed of  $(La_{0.85}Sr_{0.15})_{0.9}MnO_3$  (LSM) (NexTech Materials Ltd.) and YSZ (NexTech Materials Ltd.) was screen-printed onto the other side of the electrolyte support, and then it was sintered at 1150 °C. The geometric area of the anode and cathode is 1  $cm^2$ . The NiO–YSZ anode was heat-treated in 30 vol.%  $H_2$  in  $N_2$  at 700 °C to reduce NiO to Ni. The microstructures of the Ni–YSZ anodes were characterized by scanning electron microscopy (SEM, Hitach X-4900) and mercury porosimetry (AutoPore 9500, Micromeritics). To avoid experimental errors in calculating the specific pore volume ( $cm^3 g^{-1}$ ) and surface area ( $m^2 g^{-1}$ ), 200  $\mu m$ -thick anodes prepared by repeated screen-printing were used for the porosimetry study.

### Electrochemical measurements

A unit cell was attached to an alumina tube using a ceramic adhesive (Ceramic bond 668, Aremco Products Inc.). The alumina tube serves as a chamber that accommodates a carbon fuel and an MC electrolyte. Current was collected using Pt meshes and wires. Carbon (Super P<sup>®</sup> Li, Timcal Ltd.) was mixed with a binary eutectic mixture of 62 mol%  $Li_2CO_3$  (99.0%, Sigma–Aldrich Co.) and 38 mol%  $K_2CO_3$  (99.0%, Sigma–Aldrich Co.) [7]. The molar ratio of carbon and MC was 1:1.5 g of the carbon–MC mixture was placed in the alumina chamber. Prior to heating up, the anode compartment was thoroughly purged with high-purity Ar gas to remove any remaining oxygen species. The open circuit voltage (OCV) of the DCFC was monitored upon heating, and then the polarization curves were measured at various temperatures. During the electrochemical measurements, the cathode was left open to air, and Ar gas was allowed to flow over the anode. An on-line gas chromatograph (GC) (Perkin Elmer, Clarus 580) was employed to determine the composition of the effluent gas, such as CO and  $CO_2$ , leaving the anode side.

## Results and discussion

### Performance study of hybrid DCFCs with various anode microstructures

To study the effect of anode microstructure on hybrid DCFC performance, in this work, the following three types of Ni–YSZ anodes were fabricated: (i) a conventional anode prepared without any pore-former (designated as A), (ii) an anode prepared using the PMMA pore-former with  $d_{PMMA} = 5 \mu m$  (B), and (iii) an anode prepared using the PMMA pore-former with  $d_{PMMA} = 10 \mu m$  (C). When the anode was coated onto the electrolyte support, the paste composition was carefully tailored to obtain a porous layer with the desired thickness (~50  $\mu m$ ). Fig. 1 presents SEM images of the surfaces and cross-sections of the Ni–YSZ anodes A, B, and C reduced in  $H_2/N_2$ . Anode A (Fig. 1(a) and (b)) has sub-micron-sized pores that are irregular in shape and size, while anodes B (Fig. 1(c) and (d)) and C (Fig. 1(e) and (f)) have relatively large pores that resulted from the burning off of PMMA beads. The PMMA-derived pores have different sizes,

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