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Direct carbon conversion in a helium fluidized bed fuel cell

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Abstract

A solid oxide fuel cell based fluidized bed configuration is employed for the first time to convert solid carbon directly into electricity. Current–voltage characteristics exhibited typical fuel cell behavior with large ohmic losses. Chromatographic analysis of the product gases in the flue stream confirmed conversion of carbon. This is also verified by oxygen mass balance. Peak power densities for carbon compared well with benchmarking tests that employed only gaseous fuels. A possible mechanistic pathway is proposed to explain the observed behavior.

Keywords: Carbon conversion; Fluidized bed; Direct carbon fuel cell; Solid oxide electrolyte; Solid oxide fuel cell

1. Introduction

Fuel cells are inherently efficient electrochemical devices that convert chemical energy into electricity. Due to their high operating temperatures, solid oxide fuel cells (SOFCs) offer the added benefit of fuel flexibility, and in many cases, faster kinetics. There has been growing interest recently for direct conversion (also referred to as direct utilization [1]) of liquid fuels in SOFCs [2–7]. Historically, however, liquid and even gaseous fuels were usually subjected to reforming and water gas shift processes prior to delivering the resulting gaseous fuel products into the fuel cell. The intent has been to maximize the amount of H_2 that can be produced from a given hydrocarbon fuel, and feed the resulting H_2 into a fuel cell.

Although a sought after goal for more than a century, utilization of solid carbon fuels directly inside SOFCs presents serious challenges largely due to the difficulty to make physical contact between the fuel particles and the charge transfer reaction sites at the anode/electrolyte interface. Accordingly, steam gasification has been the preferred way to beneficiate solid carbon fuels for employment in gasified form in SOFCs [8,9]. Currently, there are several large-scale programs, including FutureGen, that utilize steam gasification and deliver the coal derived gaseous fuels into SOFCs after sulfur clean up.

More recently, several groups have reported on direct carbon fuel cells (DCFCs) that employ solid fuels directly inside a fuel cell. All these efforts include dispersing the solid fuel particles in molten carbonate [10], molten hydroxide, or molten metals [11] to enhance contact.

As previously suggested by Gür and Huggins [12], a fluidized bed direct carbon fuel cell (FB-DCFC) approach was adopted here. The goal of this study was placed not on optimized performance, but rather on demonstrating feasibility and confirming direct conversion using commercially available ceramic structures. A bed of synthetic carbon particles were employed in a modified SOFC design that utilized He inert gas as the fluidization medium.

Fluidized beds are commonly used in combustion processes, and are known [13] to provide fuel flexibility, but more importantly, excellent contact between the solid particles and the fluidizing gas. They also help mitigate mass transport limitations. The present study combines these benefits with the known advantages of SOFCs.

The present paper reports the preliminary results of this proof-of-concept study confirming the feasibility of generating electricity directly from solid carbon in a FB-DCFC and verifying conversion by gas chromatographic (GC) analysis of the

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flue stream. Here, "direct conversion" is intended to mean converting chemical energy into electricity in a single process step or chamber, but does not infer or suggest that conversion is achieved in a single elementary reaction step.

2. Experimental aspects

Schematic design of the FB-DCFC is shown in Fig. 1 and consists of a vertically positioned tubular quartz reactor with an expansion chamber at the top for minimizing entrainment of fine carbon particles. The quartz reactor operated under atmospheric pressure. A gas inlet port at the bottom of the tube allowed the fluidizing gas to enter the reactor after it was preheated to the operating temperature of the reactor to prevent the possibility of thermally quenching the reaction system. Helium was used to fluidize the carbon particles in the reactor column, and also to obtain kinetic information through gas analysis of reaction products. Pulverized carbon with particle sizes in the 25–60 micron range was added to the FB-DCFC typically in 30 gram batches at each loading and was restrained in place by a fine metallic gauze. One-end closed ytrria stabilized zirconia (YSZ) electrolyte tube was vertically inserted into the bed of carbon particles inside the quartz reactor such that the open end of the tube was exposed to the ambient air. Supply air was provided to the cathode surface inside the closed-end of the tube. As the fluidizing gas was introduced from the bottom port, the quartz reactor was heated slowly in flowing gas to the operating temperature of 900 °C. By the time the operating temperature was attained, most of the volatile matter had already eluded from the carbon fuel during heating. Hence, for all practical purposes this carbon fuel can be regarded as char. The chemical analysis of the fresh carbon fuel used in these experiments indicated that it contains 0.31% sulfur, 2.45% ash, 3.04% hydrogen, and 80.90% carbon. All experiments were conducted at 900 °C.

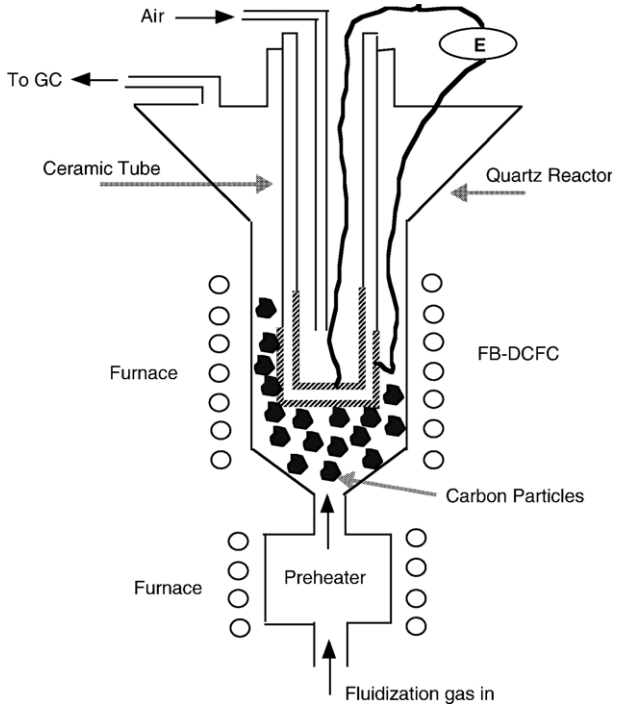

Fig. 1. Schematic design of the fluidized bed direct carbon fuel cell.

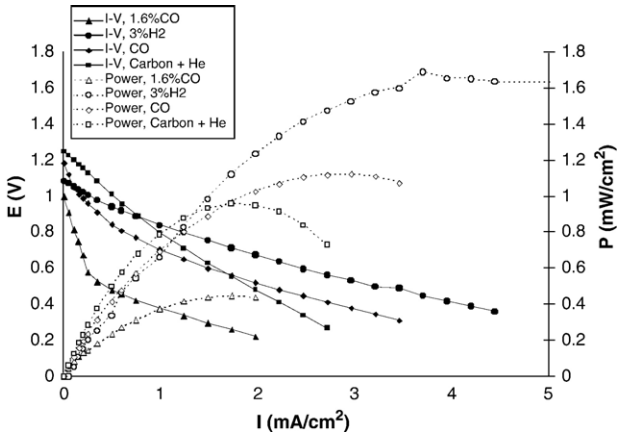

Fig. 2. V–I–P behavior of type I cell with synthetic carbon fluidized by He at 900 °C. For comparison purposes, type I cell performance employing only gaseous fuels are also included. (Solid lines: I–V; dashed lines: I–P).

Two types of commercial tubular structures of stabilized zirconia solid electrolyte were employed in this study. Type I cells were made of one-end closed, 1.3 mm thick, partially stabilized zirconia (PSZ) tubes coated with Pt or Pt/YSZ cermet electrodes. These commercial PSZ tubes, originally manufactured for oxygen sensing applications, contained additives at the expense of higher ohmic resistance. Type II cells were made from 0.2 mm thin 1-inch diameter commercial YSZ discs that were coated by the manufacturer with Ni/ceria cermet anode and ($La_{1-x}Sr_xMnO_3$) (LSM) cathode layers. The YSZ disc was then sealed gas tight to one end of a zirconia support tube such that the anode faced outside the tube. These cells were employed merely to demonstrate the effect of reduced ohmic loss on performance.

3. Results and discussion

Inside the zirconia tube, the cathode surface is in direct contact with the ambient air that furnishes the oxygen needed for the oxidation reaction at the anode, while the outer surface of the tube, the anode, is in direct contact with the bed of carbon particles. The electrochemical potential difference of about 1 V for oxygen between the cathode and the anode drives the fuel cell and facilitates the generation of electricity.

Fig. 2 shows the current–voltage–power (I–V–P) behavior of FB-DCFC utilizing a type I cell in synthetic carbon that was fluidized in He gas. For benchmarking purposes, it also includes the performance of gaseous fuels 3% H_2 (balance N_2) and pure CO in the absence of carbon fuel inside the FB-DCFC. Typical fuel cell behavior was obtained for the carbon fueled FB-DCFC, and the open circuit voltage was above 1 V corresponding to $<10^{-18}$ atm of oxygen activity indicative of a CO/CO_2 ratio of more than 10 at the anode. This was consistent with the behavior of all cells in He fluidizing gas, suggesting that under open circuit conditions small amounts of CO may be formed in the anode compartment possibly by the reaction of oxygen