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Direct carbon fuel cell operation on brown coal

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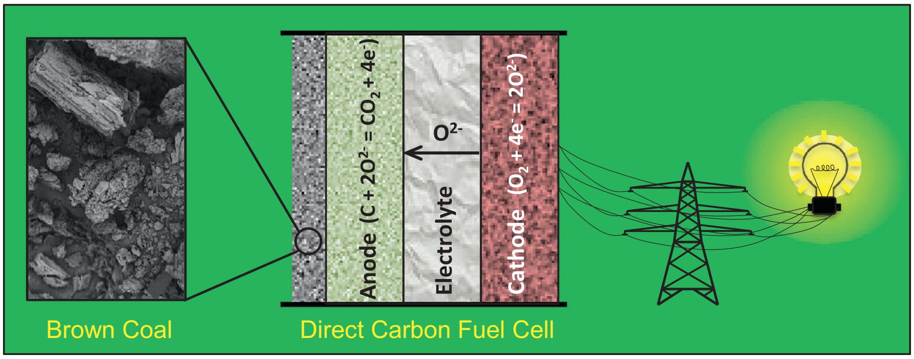
HIGHLIGHTS

- Performance of brown coal has been investigated in a direct carbon fuel cell.
- Fine particle size of the fuel is essential for better performance.
- The raw brown coal char gave superior performance due to a greater availability of CO at the anode.
- Inherent inorganic species in the raw coal catalysed the Boudouard gasification.
- Boudouard gasification kinetics of carbon fuels was compared using TGA.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of a Victorian brown coal with minimal pre-treatment was assessed in a solid oxide electrolyte based direct carbon fuel cell (DCFC) at 700 and 800 °C. In order to evaluate the effect of inherent inorganic species in the coal on the electrochemical performance of DCFCs (voltage – power density – current density), characteristics of button cells fuelled with raw and acid washed (demineralised) coal were compared along with commercially available XC72 carbon black. Peak power densities of 65 and 67 mW cm^{-2} were observed for demineralised coal char and carbon black respectively at 800 °C, whereas the raw coal char achieved a superior power density of 89 mW cm^{-2}. The availability of reactive species at the anode, namely CO, is believed to be the primary differentiator of cell performance, and is related to variations in the physical and chemical makeup of carbon fuels. The reactivity of these fuels in the presence of CO_2 to generate CO (and power) via Boudouard gasification was assessed in the 700–800 °C temperature range via thermogravimetric analysis.

1. Introduction

Fuel cells are able to generate electrical energy from fuels at high efficiency. Direct Carbon Fuel Cells (DCFCs) are the only such fuel cells capable of operating on a solid fuel, such as coal or biomass char, and can produce a product gas stream of concentrated CO_2 ideal for storage with minimal processing.

DCFCs offer the highest efficiency of any fuel cell type at near 100% theoretical efficiency at 600 °C for reaction (1) [1,2].

$$C_{(s)} + O_2 \rightarrow CO_2 \qquad (1)$$

The direct carbon fuel cell efficiency (product of theoretical, voltage and fuel utilisation efficiencies) is around 80%, and overall system efficiencies (inclusive of system auxiliary losses) of above 60–70% have been projected [3]. Not limited by the Carnot cycle, the superior efficiency of DCFCs over conventional stationary coal-fired power generation could realise reductions in CO_2

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emissions in the order of 50%, even without capture and storage. There is also scope for integration of DCFCs within other coal-based power generation technologies [4,5].

Reaction (1) is a familiar reaction in the oxidation or combustion of carbon and is also the overall reaction for a DCFC. However, the oxidation of carbon in a DCFC is electrochemical in nature and involves various intermediate reactions. These reactions may be electrochemical and/or thermochemical and depend on the DCFC type as well as reaction environment which the fuel is exposed to.

There are three main families of DCFC, which are commonly categorised depending on their electrolyte. These are the molten hydroxide, molten carbonate, and solid oxide DCFC. There are also sub-classes of the solid oxide electrolyte DCFCs depending on the physical arrangement of the fuel feed system and the anode. A detailed description of DCFC types can be found in a review by Giddey and co-workers [3].

For the solid oxide DCFC, oxygen is reduced at the cathode as per reaction (2).

$$O_2 + 4e^- \rightarrow 2O^{2-} \tag{2}$$

Oxygen ions migrate across the electrolyte and oxidise carbon at the anode, releasing electrons back into the circuit (reaction (3)).

$$C_{(s)} + 2O^{2-} \rightarrow CO_{2(g)} + 4e^- \tag{3}$$

This is the overall anode reaction (not the complete mechanism of carbon oxidation), with intermediate reaction steps that may occur are given below:

$$C_{(s)} + O^{2-} \rightarrow CO_{(g)} + 2e^- \tag{4}$$

$$CO_{(g)} + O^{2-} \rightarrow CO_{2(g)} + 2e^- \tag{5}$$

The solid oxide DCFC is a high temperature fuel cell and operates between the temperatures of 600 and 900 °C, whereas the molten hydroxide and molten carbonate DCFCs are limited to operation below 800 °C partly due to the corrosive nature of their electrolytes amongst other factors such as the stability of the electrolyte and increasing vapour pressure at higher temperatures [6]. The high temperatures are necessary to ensure sufficiently high ionic conductivity of the ceramic electrolyte, but introduce other considerations, such as different reaction mechanisms and associated efficiency penalties. For example, at temperatures above 700 °C the reverse Boudouard reaction, hereinafter referred to as Boudouard gasification, becomes favourable when carbon dioxide is present (reaction (6)) [7,8].

$$C_{(s)} + CO_{2(g)} \rightarrow 2CO_{(g)} \tag{6}$$

Under these conditions, the fuel may be gasified and the fuel cell will operate off both the electrochemical oxidation of solid carbon (reactions (3) and (4)) and carbon monoxide available from reactions (4) and (6) as per reaction (5).

The mode of operation of the fuel cell is an important consideration for not only the performance, but also the efficiency of the system. Where reaction (6) is allowed to compete with reaction (4) for the consumption of carbon, some fuel may be lost as CO in the product gas, reducing the fuel utilisation and the overall efficiency of the system. For this reason Boudouard gasification is sometimes referred to as 'Boudouard corrosion' of the fuel, in the context of DCFC operation. Understanding what factors promote reaction (6), and its effect on the system, and how the fuel properties contribute, are necessary studies in advancing this technology.

Due to the difficult nature of tracking intermediate reaction products in the gaseous reaction environment, limited work has been done to elucidate the reaction mechanisms for the carbon oxidation in the solid oxide electrolyte based DCFC. A more detailed description of carbon conversion mechanisms in the solid oxide DCFC for carbon deposited by CH_4 is given by Li and co-workers [9]. Their work outlined possible intermediate reaction steps such as the adsorption of oxygen onto the carbon surface, and the importance of carbon reactive sites. However, the interfacial conditions are expected to be quite different in a solid fuel fed DCFC compared to the methane fed solid oxide fuel cell.

Recent advances in DCFC technology as well as a greater understanding of the need for high efficiency and clean sources of power generation, has renewed interest in this area. However, the overwhelming fuel of choice for DCFC research to date is commercially produced carbon black [6,10–16] as it is considered a clean source of carbon with consistent properties. While carbon black has a lot to offer to this field of research, there is a need to explore the possibility of using real world fuels that would be traditionally used as fuels for DCFC to produce power at a commercial scale, such as coals, and expand knowledge on fuel-based performance of these fuel cells [17].

Coal is widely used for electricity generation worldwide, at over 40% of the global share, and its global consumption is expected to increase well into the next century [18]. In Victoria, Australia, brown coal is also the dominant fuel source for electricity generation contributing almost 80% to the total power generation installed capacity [19]. With around 33 billion tonnes [20] of 'potentially economic' reserves representing over 500 years of recoverable lignite at the current consumption rate, it is well positioned to retain this mantle for some time. However, it is widely accepted that the current methods of power generation have substantial negative environmental consequences. For example, the CO_2 emissions per MWh (more than 1.2 tCO_2/MWh [21]) of electricity produced in the Latrobe Valley, Victoria, are among the highest in the world. While the high moisture content of Victorian brown coal at 45–70% [22] is undesirable for thermal power generation, other properties such as its very low ash (<7 wt% db) and sulfur (<1 wt% db) contents make this coal an attractive fuel for use in fuel cells.

Amongst many challenges facing the development of DCFC technology, the delivery of a solid fuel to the effective reaction zones or triple phase boundaries for continuous operation of the fuel cell is the key issue for solid electrolyte based DCFC systems. One approach to overcome this problem is to mix solid fuel with a molten media such as molten carbonates and use traditional SOFC anodes such as Ni–YSZ (yttria-stabilised zirconia) to improve charge and ionic transfer between the anode and the solid fuel particles [15]. Anodes with low melting point metals such as Sn, Sb or Bi have also been trailed instead of molten carbonates in DCFCs with varying degree of success [23]. In short life-time experiments, these DCFCs demonstrate impressive performances, however, these systems present challenging technical issues such as rapid degradation of fuel cell components due to the corrosive nature of the molten media. In comparison, direct contact or fluidized bed type DCFCs potentially have fewer corrosion related issues during long-term operation. In these systems, particulate carbon is directly circulated on the anode surface or pressed onto the anode with external loading. Traditional SOFC anodes such as porous Ni/YSZ and Ni/SDC (samarium-doped ceria) cermets have been trialled in such DCFCs [24,25] with limited success, however, such anodes are unsuitable for continuous operation of a DCFC as discussed in a previous publication [8]. Recently promising power densities have been reported in DCFCs with single phase mixed ionic electronic conductor (MIEC) anodes such as $(LaSr)(CoFe)O_{3-\delta}$ (LSCF) and doped ceria [8,26]. MIEC anodes can carry O^{2-} ions to the anode surface thereby extending effective reaction zone beyond anode/electrolyte interface to anode/fuel interface thus facilitating the solid carbon oxidation on the anode surface itself.

The present work examines the performance of two processed coals from the Morwell mine in the Latrobe Valley, Victoria, in a