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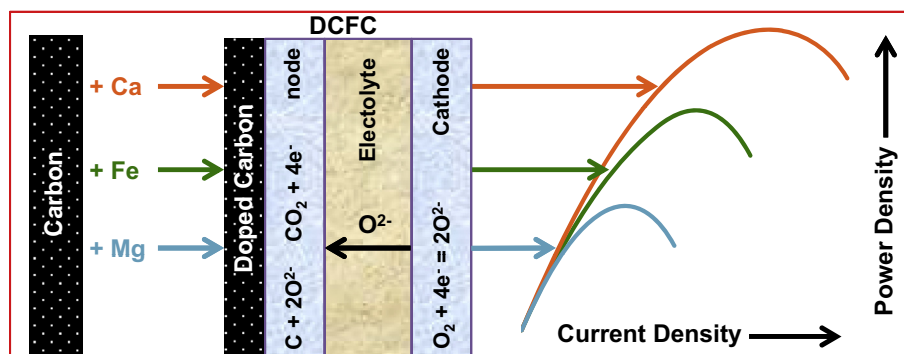
Catalytic gasification of carbon in a direct carbon fuel cell

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HIGHLIGHTS

- Carbon black impregnated with Ca, Fe, and Mg species have been evaluated in DCFCs.
- Ca and Fe species catalyse Boudouard gasification of carbon as confirmed with TGA.
- Doped and pure carbon tested in DCFC under N_2 and N_2/CO_2 anodic atmospheres.
- Fuel performance in DCFC correlated well with reactivity ranking from TGA analysis.

GRAPHICAL ABSTRACT

ABSTRACT

The present study investigates the catalytic properties of metallic species commonly present in brown coal (Ca, Fe, and Mg), towards Boudouard (CO_2) gasification, by individually doping pure carbon black with these species, and examining their electrochemical performance in a direct carbon fuel cell (DCFC). Thermogravimetric analysis was used to study the effect of added catalysts on carbon oxidation at 850 °C and compared to those of chars produced from a Victorian brown coal. The relative catalytic activities of dopants were found to increase from Mg < Fe < Ca, in the presence of CO_2. The carbon black fuels doped with the catalytic species, when tested in a direct carbon fuel cell, were also found to influence the fuel cell performance under both N_2 and N_2/CO_2 anode purge gases in line with relative catalytic activities of dopants. Electrochemical impedance spectroscopy measurements, under open circuit conditions, were used to assess the nature of performance variations in fuel cell environments. Availability of gaseous CO via in-situ Boudouard gasification of the fuel is believed to be the primary differentiating factor for various carbon fuels in cell operation. Finally, it was established that the catalytic dopants added to the carbon fuel had an effect on the equilibrium oxygen partial pressure in the $C/CO/CO_2$ system and hence the open circuit voltage.

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1. Introduction

Direct carbon fuel cells (DCFCs) provide an exceedingly efficient means of converting the chemical energy in a carbonaceous fuel into high-grade electrical energy. With a thermodynamic efficiency of around 100% for carbon oxidation at fuel cell operating temperatures in the 600–900 °C range [1,2], they are the most efficient amongst various fuel cell systems. However, the modes of utilisation of the solid fuel within the fuel cell, among other factors, can impact on fuel cell efficiency as well as performance [1,3]. The direct electrochemical oxidation of solid carbon would lead to maximum efficiency, however, in practical operations, the

mechanism of reaction would be a combination of direct electrochemical oxidation as well electrochemical oxidation of CO produced *via* Boudouard gasification (C + CO$_2$ = 2 CO). In the case of pure CO as the fuel, the theoretical efficiency at the DCFC operating temperature in the 800–850 °C range is around 70% [1]. Detailed description on DCFC reaction mechanism and modes of fuel utilisation are given in detail in reviews [1–3]. Further insight into internal fuel reaction mechanisms and fuel-based performance is necessary for the continued development of this technology. Another factor that contributes to fuel cell efficiency is the fuel utilisation factor. In the case of a solid fuel, the fuel utilisation is expected to be near 100% as opposed to 85–90% for gaseous fuels.

DCFCs operate on solid carbonaceous fuels. In a direct-contact solid electrolyte DCFC system, this fuel is oxidised electrochemically by delivery of oxygen ions to the carbon in direct contact with the anode *via* Eq. (1) and/or (2):

$$C_{(s)} + O^{2-} \rightarrow CO_{(ads/g)} + 2e^- \tag{1}$$

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

The fuel cell can also operate on gaseous species, such as CO as in Eq. (3):

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

Apart from CO formed by the electrochemical oxidation of carbon as per reaction in Eq. (1), it may also be available to the anode during cell operation as a result of *in-situ* Boudouard gasification of the fuel as per reaction below (Eq. (4)) leading to a significant influence on the cell performance [4,5].

$$C_{(s)} + CO_{2(g)} \rightleftharpoons 2CO_{(g)} \tag{4}$$

The high temperature (600–900 °C) environment of a DCFC anode chamber is conducive to Boudouard gasification of carbon, since CO$_2$ is a product of cell operation and is generated in close proximity to the carbon fuel. However, a fuel with low reactivity towards Boudouard gasification will not contribute significantly to cell performance *via* gasification reactions.

The inorganic content inherent in coals and biomass is known to influence Boudouard gasification kinetics through catalysis and in some cases inhibition [6]. Of these inorganic species, Fe is particularly well known for its catalytic properties in coal gasification [7]. In addition, alkaline earth metal carbonates exhibit catalytic activity at temperatures around 900 °C [8,9].

Iron in all of its oxide states as well as its metallic state is catalytically active through redox reactions with carbon and CO$_2$ [10,11]. However, as with most transition metal catalysts, its activity increases as it is reduced [12]. Furimsky et al. [11] proposed an Fe-catalysed Boudouard gasification mechanism which involves a redox cycle of Fe *via* various intermediate oxide states, summarised by Tang and Liu [12] as shown in Eqs. (5) and (6):

$$Fe_mO_n + CO_2 \rightarrow Fe_mO_{n+1} + CO \tag{5}$$

$$Fe_mO_{n+1} + C \rightarrow Fe_mO_n + CO \tag{6}$$
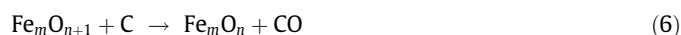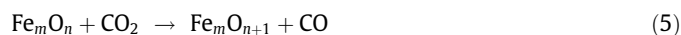
The mechanism also extends to metallic Fe, i.e. $n = 0$, [11]. The reduction of CO$_2$ *via* chemisorption onto Fe$_m$O$_n$ (Eq. (5)) is a fast process, whereas the reduction of the formed Fe$_m$O$_{n+1}$ by carbon (Eq. (6)) is a solid–solid interaction and is identified as the rate-determining step in this redox catalysis process [11]. Tang and Liu [12] observed an Open Circuit Voltage (OCV) increase for their Fe-doped activated carbon over that of pure carbon fuel and attributed this to the greater CO concentration in product gas of the Fe-catalysed system. The authors used an Fe(NO$_3$)$_3$ precursor to achieve a C:Fe mixture (4:1 weight ratio), and heat treated the mixture at 800 °C in Ar for 30 min.

For alkaline earth metal carbonates such as CaCO$_3$ and MgCO$_3$, McKee [13] proposed the following mechanism, where "M" is the metal cation:

$$MCO_{3(s)} + C_{(s)} \rightarrow MO_{(s)} + 2CO_{(g)} \tag{7}$$

$$MO_{(s)} + CO_{2(g)} \rightarrow MCO_{3(s)} \tag{8}$$
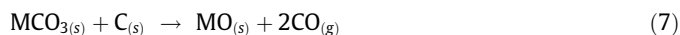
Eq. (7) may also be written as a combination of Eqs. (9) and (4):

$$MCO_{3(s)} \rightarrow MO_{(s)} + CO_{2(g)} \tag{9}$$

The authors observed that the decomposition of CaCO$_3$ *via* either Eq. (7) or (9) occurs between temperatures of 700–900 °C under an inert atmosphere, and commences between 850 and 900 °C under CO$_2$, completing at 1000 °C. MgCO$_3$ is not stable under either inert or CO$_2$ atmospheres at fuel cell operating temperatures [13] and decomposes to MgO through the evolution of gaseous CO$_2$. The inability of the stable MgO to readily form MgCO$_3$ may be the reason for its poor catalytic properties in terms of Boudouard gasification. The catalytic activity of carbonates of group IIA metals, in terms of gasification, has been reported to increase with increasing atomic radii for the temperature range of 700–1100 °C [13].

While there is substantial information in the literature on gasification reaction mechanisms, investigations into specific and targeted fuel-based catalysis in DCFC systems and the effect on fuel cell performance is very limited [12,14,15]. In a previous publication, the performances of raw and demineralised coals in a solid electrolyte DCFC were compared and were related to Boudouard gasification reactivity studies using thermogravimetric analysis (TGA) [16]. The superior performance of the raw coal sample in DCFC and TGA testing was attributed to the catalytic influence of inherent inorganic constituents on Boudouard gasification. However, it was not clear which particular species promoted Boudouard gasification and enhanced DCFC performance. In the present work, the role of three major species has been investigated, using a similar inorganic content to what was observed in the raw coal char [16]. The performance of carbon black impregnated with these gasification catalysts has been studied in direct contact solid electrolyte based DCFCs. The relative activities of these catalysts under CO$_2$ atmosphere were also investigated *via* TGA analysis and have been related to their performance in DCFCs. For fuel cell studies, a batch type fuel arrangement has been used where carbon fuel is pre-loaded into the anode chamber. In some literature reports, such cells are also referred to as fuel cell battery [17,18]. A continuous fuel feed arrangement of solid carbon to DCFC anode is frequently identified as an engineering challenge for the scale-up of DCFC technology. However, for practical applications, the fuel feed systems such as fluidised bed, mechanical solid fuel feed, carbon in molten media (carbonate or molten metal) circulation are being explored as well as integrated DCFC gasification systems [1,3]. The batch process used in this work is for convenience and for understanding reaction mechanism while the fuel is in contact with the anode.

2. Experimental

2.1. Fuel preparation and analysis

Four types of carbon fuels were used in this study: pure carbon and carbon with the addition of Mg, Fe and Ca salts. Nitrates of Magnesium (as Mg(NO$_3$)$_2$·6H$_2$O, Univar, WA, USA), Iron (as Fe(NO$_3$)$_3$·9H$_2$O, Merck Millipore, Germany), and Calcium (as Ca(NO$_3$)$_2$·4H$_2$O, Sigma-Aldrich, MO, USA), were mixed separately with carbon black (CB – Vulcan XC-72, surface area 254 m^2 g^{-1}, Cabot Corporation, USA) in a 97.5:2.5 wt% carbon to respective