Contents lists available at ScienceDirect

Electrochimica Acta

Degradation Mechanism in a Direct Carbon Fuel Cell Operated with Demineralised Brown Coal

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ARTICLE INFO

ABSTRACT

The performance of a demineralised and devolatilised coal from the Morwell mine in the Latrobe Valley, Victoria, has been investigated in a direct carbon fuel cell (DCFC) operated at 850 °C. The focus of the investigation has been on understanding degradation issues as a function of time involving a sequence of electrochemical impedance spectroscopy and voltage-current characteristic. Diffusion limited processes dominate the electrode polarisation losses in pure N_2 atmosphere, however, these decrease substantially in the presence of CO_2 as the anode chamber purge gas, due to in situ generation of fuel species by the reaction of CO_2 with carbon. Post-mortem analysis of anode by SEM and XRD revealed only a minor degradation due to its reduction, particle agglomeration as well as the formation of small quantity of new phases. However, major fuel cell performance degradation (increase of ohmic resistive and electrode polarisation losses) occurred due to loss of carbon/anode contacts and a reduction in the electron-conducting pathways as the fuel was consumed. The investigations revealed that the demineralised coal char can be used as a viable fuel for DCFC, however, further developments on anode materials and fuel feed mechanism would be required to achieve long-term sustained performance.

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1. Introduction

With increasing global consumption of fossil fuels for electricity generation resulting in growing levels of CO_2 in the atmosphere, the search for low CO_2 emission technologies is paramount. Fuel cells offer a high efficiency means of generating electricity and typically operate on a gaseous fuel [1–8]. Direct carbon fuel cell (DCFC) is the only such fuel cell which can operate on a solid carbonaceous fuel, potentially negating the need for a costly transition to an alternative fuel-based economy [1].

DCFCs operate at high temperatures, typically in the range of 600–900 °C with the overall cell reaction being:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{1}$$

The entropy change associated with this reaction is small and this allows for a theoretical efficiency close to 100% for DCFCs across a broad range of operating temperatures [1]. The high temperatures are necessary for high ionic conductivity of the electrolyte, as

well as assisting with the reaction kinetics at the electrodes. The operation of the DCFC has been described in previous publications [1,9,10]. In summary, the oxygen in air supplied to the cathode (reaction 2) is reduced to oxygen ions at the cathode or air electrode.

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

Electrons are supplied via the electrical circuit and the produced oxygen ions migrate across the electrolyte to the anode, where they are consumed by either solid carbon or gaseous carbon monoxide via reactions (3), (4) or (5).

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

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

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

Reactions (3) and (4) require the solid carbon to be in direct contact with the anode. Under this arrangement, given the proximity of the product CO_2 and the carbon fuel, the CO_2 may react with the carbon in the form of Boudouard gasification (reaction 6).

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

The kinetics of this reaction depends strongly on temperature and the reactivity of the carbonaceous fuel towards Boudouard gasification. This can be an important factor in fuel cell performance as the CO generated via Boudouard gasification can contribute to current generation via reaction (5). The relative concentration of these gaseous species can also influence cell performance in other more subtle ways. The equilibrium between CO, CO_2 and O_2 (reaction (7)) can have a considerable impact on cell open circuit voltage (OCV) which is highly sensitive to the partial pressure of oxygen at the anode/electrolyte interface.

$$2CO_{(g)}+O_{2(g)}\rightleftharpoons 2CO_{2(g)} \tag{7}$$

With DCFC research efforts entering the phase of laboratory scale-up, engineering issues such as fuel feed mechanism and anodic gaseous environment control will present a challenge in system and cell design. It is therefore necessary to understand the fundamentals of how the solid fuel is consumed within the cell, both in the direct solid form and/or via gas phase reaction through its gasification. Further to this, knowledge of factors contributing to the degradation of critical cell components is essential for the development of a DCFC which can operate reliably during long-term power generation applications.

There is very little data reported in the literature on the degradation behaviour in direct carbon fuel cells although there is considerable information available in the literature on anode (Ni/O^{2-} conducting ceramic cermets) degradation [11,12]. In the case of DCFC, the performance degradation has been broadly attributed to carbon consumption [13,14]. There have been no detailed reaction mechanism studies on real world fuels using a combination of electrochemical and material characterisation techniques to investigate the causes of cell performance degradation.

This study investigates the sources of performance degradation of the fuel cell operating on Morwell coal (Victoria, Australia) following demineralisation and devolatilisation to understand the effect of residual impurities in the demineralised coal. The fuel cell operation included loading the cell at various current densities for both short and extended times in different anode chamber gas atmospheres and performing electrochemical impedance spectroscopy diagnostics to deconvolute contributions of different factors to increasing cell resistance. In addition, the post-mortem of the cell anodes has been carried out to investigate the extent of degradation during fuel cell testing.

2. Experimental

2.1. Fuel Processing and Characterisation

The fuel used in this study was a Victorian brown coal from the Morwell mine, which has been demineralised and devolatilised, and will be referred to hereafter as 'DM char'. Details of the fuel preparation and analysis can be found in a previous study [10]. In summary, air-dried raw coal from the Morwell mine was acid washed with 4 mol/L HNO_3, followed by rinsing with distilled water and devolatilising charring at 600 °C in N_2. Electrical conductivity measurements of the DM char were made in an in-house designed and constructed 4-probe test fixture at temperatures in the 600 and 850 °C temperature range. The fixture was comprised of a high density alumina tube (ID: 6.0 mm; OD: 9.7 mm; and length: 25 mm) with two voltage probe wires (0.5 mm dia. Pt-Rh) passing through the middle of the tube cross section and separated from each other by 10 mm. The carbon powder was ground and held packed in the ceramic tube (as per loading in the fuel cell) to about 20 mm depth under spring loading. The current was passed through the cylindrical carbon bed in the tube by employing Pt foils (diameter same as the tube ID) placed on both sides of the carbon bed. The sample

was taken up to 850 °C and held under N_2 where current was passed and voltage recorded, followed by measurements at 800, 700 and 600 °C.

2.2. Fuel Cell Construction and Evaluation

The electrolyte supported button cells were fabricated for this investigation. The electrolyte powder (8 mol% yttria stabilised zirconia from Tosoh Corporation, Japan) was pressed isostatically (at 205 MPa) into disks and subsequently the discs were sintered at 1500 °C (heating and cooling rate of 300 °C hr^{-1}) in air for 2 hrs. The sintered discs were approximately 1 mm in thickness and 17 mm in diameter and had a density >99% of the theoretical. The discs were then ground to ~0.5 mm thickness on a stone wheel prior to application of electrodes. Lanthanum strontium cobalt ferrite powder (LSCF, Fuel Cell Materials Inc., OH, USA) of composition $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\pm\delta}$, was ball milled in a 1:1 weight fraction with a terpinol-based ink vehicle (Fuel Cell Materials Inc., OH, USA) for 4 hrs to produce an electrode ink. This ink was screen printed as 8 mm diameter air electrode on one side and applied via brush to the entire opposite face as the fuel electrode. The coated electrolyte discs were heated in air at 800 °C with a holding time of 2 hrs and a heating rate of 180 °C hr^{-1}. The cathode side of the cell was further coated with Pt paste to improve current collection. Three cells (cell # 1, 2 and 3) were fabricated by employing the above procedure. The cell test fixture including the fuel supply arrangement to the anode has been described in detail in a previous publication [10]. The current collection from the anode was achieved by pressing (spring loaded arrangement) Pt mesh on the anode and the carbon fuel was then embedded in the perforations of the mesh. For cell #1, a Pt mesh with a wire diameter of 0.25 mm and sieve openings of 0.80 mm × 0.80 mm was used. In order to improve the current collection, in the case of cell # 2, the Pt mesh was attached to the anode by using Pt ink at few places on the electrode. The mesh was also finer, with a wire diameter of 0.12 mm and sieve openings of 0.30 mm × 0.30 mm.

Cells #1 and #2 were used to study the detailed cell anode side degradation behaviour with and without the cell under different current loads and also to study the effect of anode chamber gas atmosphere on the reaction mechanism. Cell #3 was not subjected to any fuel cell testing and was used to perform XRD (phase identification) and obtain SEM images of the electrode material fabricated in an identical fashion to the cells used in DCFC testing for comparison.

The anode and cathode chambers were isolated via a Borosilicate glass seal. The seal was formed by heating the cell at 300 °C hr^{-1} to ~910 °C under 99.999% N_2 and holding for 5 min before cooling slowly to the operating temperature (850 °C), after which air could be introduced into the cathode chamber. A N_2 flow rate of 40 mL min^{-1} was used during heating, normal operation, and cooling. In the operation of cell #2, for the final few experiments the anode chamber purge gas was switched from N_2 to a CO_2/N_2 mixture (Cellamix, 40 vol% CO_2).

Cells #1 and #2 were subjected at 850 °C to a series of loadings via potentiodynamic voltage-current (V-I) scans at a sweeping scan rate of 5 mV s^{-1} using a Versastat 4 Potentiostat-Galvanostat (Princeton Applied Research, USA). These cells were also loaded during electrochemical impedance spectroscopy (EIS) scans at various constant current loads over the frequency range of 1 MHz–50 mHz at an excitation amplitude of 20 mV with an IM6 Impedance Analyser (Zahner, Germany). Prior to each EIS data acquisition under a constant current load, the cell was held at the appropriate loading for two minutes to allow for the voltage to stabilise before commencing the EIS scan. EIS spectra were also collected at open circuit voltages across the same frequency range. A chronological summary of fuel cell experiments is given