



Influence of selected coal contaminants on graphitic carbon electro-oxidation for application to the direct carbon fuel cell



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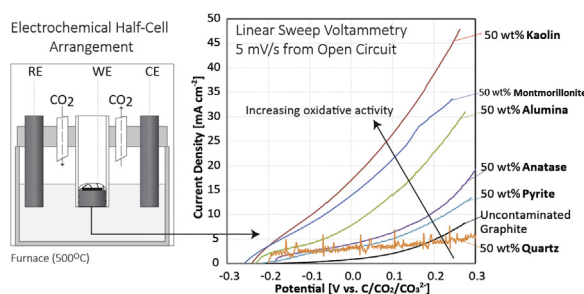
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HIGHLIGHTS

- Anodic carbon electrochemistry in a molten carbonate electrolyte has been examined.
- Anodic oxidation of graphite is enhanced/catalyzed in the presence of mineral clays.
- The mechanism involves a solid phase interaction between the minerals and graphite.
- Clays such as kaolin and montmorillonite modify the carbon oxidation mechanism.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method examining the fundamental electrochemical behaviour of carbon is outlined here involving the use of a half cell set-up and solid sacrificial anode. Using this method, electrochemical oxidation of graphite is assessed using selective contamination of a graphite electrode with major coal contaminants identified in selected Australian black coals using X-ray diffraction. Contaminants identified include anatase, alumina, pyrite, quartz, kaolin and montmorillonite. From the systematic introduction of these contaminants it is shown that clay materials, such as kaolin and montmorillonite, act catalytically to increase the rate of graphite oxidation. Metal oxides and sulfides such as anatase, alumina and pyrite give a limited increase in the normalised current, whereas quartz gives a significant decrease in performance. This demonstrates a clear effect of the solid phase interaction of these contaminants on the electrochemical oxidation of graphite since the same effect is not observed when the contaminants are added instead to the molten carbonate electrolyte.

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1. Introduction

Fossil fuel-based energy production is neither sustainable nor in good favour with current climatic concerns. Modern energy

production is heavily reliant on fossil fuels such as coal, gas and oil, all of which produce emissions such as carbon dioxide (CO₂), nitrogen oxides (NO_x) and sulfur dioxide (SO₂), which interrupt natural cycles and processes. Furthermore, demand for electricity production is globally increasing and many current research interests focus on the design and development of new power generation technologies which also act to reduce emissions intensity. One such technology is the Direct Carbon Fuel Cell (DCFC).

The DCFC produces electrical energy through the reduction of oxygen within the cathode of the cell, with oxidation of the carbon

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fuel source occurring within the anodic side. Half and full-cell reactions are shown in Eqs. (1)–(3);



Direct carbon fuel cells are a unique type of fuel cell as they have the ability to utilise solid carbon fuel. They are similar in many regards to the molten carbonate fuel cell (MCFC), differing only by fuel type and minor cell design characteristics [1]. Coal, a well-known source of amorphous carbon, is widely used in energy production around the world and has been identified as a candidate for use in the DCFC [1–5]. Carbonaceous material in coal can be transformed directly to electrical energy within the DCFC with high efficiency assuming non-Boudouard conditions; i.e., chemical conversion of carbon through reaction with carbon dioxide at elevated temperatures [2,6]. This direct conversion has the potential to increase electrical conversion efficiency of the energy contained in coal to over 80% (it is theoretically 100% efficient) compared to conventional coal fired power stations operating below 40% [1] since only one energy transformation takes place. In reality, the conversion of the calorific value of the coal into electrical energy may be somewhat lower than 80% efficient as a result of the need to pre-process the coal to remove volatile components.

Kinetics and limitations of the oxidation reaction of carbon to carbon dioxide under different cell conditions and arrangements have been highlighted recently as important avenues for research pertaining to the DCFC [1,7]. There exist a number of cell designs used in recently published literature that give information on the overall electrochemical performance of different carbon materials and cell components under DCFC conditions [8–15]. A relatively smaller number of research groups have focused on the anodic oxidation reaction specifically, including analysis of electrochemical processes at the anodic electrode [3,16,17].

The electrochemical oxidation reaction was studied in this work using graphite as a base through the use of a specifically designed electrochemical test cell. The cell was designed in order to enable testing of a solid anode arrangement rather than suspended carbon, which has been used in previous investigations [3,13,17]. There are a number of drawbacks in investigations using suspended carbon as a basis, primarily the mass transfer limitations of a cell masking other kinetic behaviour of a particular fuel. Further, if a carbon source artificially contaminated with mineral matter is suspended and stirred within a molten salt (electrolyte) for any period, it is likely that the contaminant phase will interact with the molten salt. However, it has been assumed previously that mineral matter remains a part of the carbon material and affects the reactions on the surface of the particle [3].

Graphitic carbon was chosen for the basis of the study as it represents significantly less variability in carbon type, surface functionalities, ash content and chemistry, and general physical and chemical behaviour compared to other carbon materials tested for use in the DCFC [8,16,18]. Basic oxidative behaviour of graphite was established in order to compare the effect of different contaminants on the oxidation of graphitic carbon.

Contaminants for investigation were chosen based on those present in coal samples. Coal contains a significant amount of mineral matter, commonly in the form of clays, mixed metal and non-metal oxides and pyrite, some of which have been shown to affect the electrochemical oxidation of carbon within test DCFC cells in the form of coal ash [19]. In this work, four Australian

bituminous coals (sourced from the Hunter Valley region) and an American coking coal were analysed using XRD to identify mineral phases which exist in significant concentration within the coals studied. Particular care was made to identify contaminants present in the coal as it will be introduced to a DCFC system rather those identified following high temperature ashing—which is known to affect chemical structure of contaminants and coals [20–22].

2. Experimental

2.1. Coal characterisation and treatment

2.1.1. Proximate analysis of coals investigated

Proximate analysis on the coal materials used the method ATSM D3175-11. Ash analysis was also performed on the coals using ASTM D4326-11.

2.1.2. Low temperature ashing

Low temperature ashing was performed in an oxygen plasma low-temperature asher (PE-100, Plasma Etch, Carson City, NV) with an RF power supply providing 200–240 W at frequencies necessary to provide a sustained oxygen plasma (~13.65 MHz). Selected, pre-dried (at 368 K), 20–30 g samples were evenly distributed on 150 mm Pyrex dishes and loaded into the ashing chamber, which was then evacuated to 0.15 Torr. Maintenance of the low-pressure oxygen (BOC industrial grade) atmosphere was through a bleed line (5–30 mL min⁻¹) and a scavenging vacuum pump. Samples were reweighed and gently overturned every 48 h period. Ashing was assumed complete when the mass loss was no greater than 5 mg after a 48 h cycle, complete ashing was observed after 3 weeks. After completion, samples were sealed in airtight containers until further analysis.

2.1.3. Structural analysis

X-ray diffraction (XRD) patterns for selected samples were recorded using a diffractometer (PW-170, Philips). Cu K α radiation (1.5418 Å) was used to analyse the sample at room temperature using settings of 40 mA and 40 kV, 2 θ range of 10°–90°, step size of 0.05° 2 θ , scan step time of 2 s, divergence slit–receiving slit–scatter slit widths of 1°–0.2°–1°, respectively.

2.1.4. Morphological analysis

Scanning electron microscopy (SEM) of manufactured electrode surfaces was carried out. To enable microscopic examination of the pelleted carbon samples, a polished specimen was prepared. This was achieved by initially mounting the carbon pellets under pressure in a two-part, cold setting, epoxy resin. The sample was then ground using various grades of silicon carbide paper on a rotating turn-table and finally polished using diamond and silica compounds. This resulted in a relatively flat, representative cross-section, making microscopic examination possible. For SEM examination the sample was mounted on an aluminium stub and carbon evaporation was carried out with a 20 nm conductive layer of carbon suitable for imaging and elemental X-ray analysis. SEM images were taken on a Zeiss MA15 instrument with a silicon drift X-ray detector (SDD) and a back-scattered electron (BSE) detector.

2.2. Working electrode fabrication and selective contamination

2.2.1. Graphite pellet preparation

Graphite (SFG15; Timcal Timrex®, Switzerland) pellets were manufactured in a 13 mm diameter pellet press and compressed at 740 MPa for 5 min. To ensure stability under test conditions, the graphite pellets were then sintered for 4 h under a nitrogen atmosphere at 773 K with no observable changes in appearance or

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