



## Full Length Article

## An investigation of mineral distribution in coking and thermal coal chars as fuels for the direct carbon fuel cell

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## ARTICLE INFO

## Keywords:

Carbon anode  
Mineral analysis  
Electrochemistry  
Coal pyrolysis  
Direct carbon fuel cell  
Kaolinite catalyst

## ABSTRACT

For the first time, a combination of coal grain analysis (CGA) and mineral liberation analysis (MLA) has been applied to coal chars prepared at different pyrolysis temperatures. Information collected from these powerful techniques is used here to assess electrochemical activity of coal chars in a solid anode of the direct carbon fuel cell. Mineral distribution and consideration of particle size gives very useful information in terms of showing differences between chars of differing origin, although major differences in mineral distribution between pyrolysis HHT are not observed here. As a result of this analysis, it is proposed that electrochemical performance of coal chars at solid anodes in molten carbonate appear to be dependent on several, interlinked factors. The physical properties of the char including its porosity, resistivity, surface area and crystalline structure have previously been demonstrated to affect electrochemical oxidation of carbons, and these factors are also observed to be important here. Further, however, the prevalence, size and type of mineral matter in the coal char and its contact with char particles also is suggested to play an equally important role. The mechanism of this interaction may include alteration of previously observed sensitivities, such as mineral enhanced gasification of the coal char leading to carbon morphology changes. Additional influences of mineral matter are suggested here to include modification of surface polarity and subsequent contact between carbon and molten carbonate electrolyte (effectively enhancing surface area), or the ability of mineral components to act as a shuttle for active species.

## 1. Introduction

Coal remains a critical commodity globally, and coal fired power stations (CFPS) supply the majority of electrical energy demands to many nations, including Australia, China and the US [1]. The efficiency of CFPSs however are highly limited due to the energy transformations which occur. The most efficient CFPS currently are those using supercritical steam conditions and are able to achieve an efficiency of ~40%. This efficiency limitation is true for all fossil fuels used to extract energy through combustion methods. Fuels cells offer an alternative energy transformation pathway where chemical energy is transformed directly to electrical energy through electrochemical pathways. The direct carbon fuel cell (DCFC) has been developed in order to extend the application of fuel cells beyond gaseous fuels to include solid carbon fuels, such as coal. This technology has a theoretical efficiency of 100%, although more realistic estimates of efficiency specify values in the

range of 60–80%, which is heavily dependent on cell arrangement and fuel used [2,3].

The DCFC has several existing technical challenges to overcome before commercialisation can be realised. Many of these issues are related to practical arrangement and operation of a DCFC cell, including allowance for possible parasitic reactions which may occur for particular arrangements (i.e., reverse Boudouard gasification) [4]. The most critical challenge for progress in the DCFC however is likely to be the slower kinetics observed for the electro-oxidation of carbon fuels (relative to combustion in air). This behaviour limits the overall performance of the DCFC and mechanisms underpinning this behaviour are poorly understood. It has, however, been shown that catalysts can be successfully integrated with a solid fuel to enhance electrochemical performance significantly [5]. In particular, naturally occurring clays in raw coal materials, such as kaolinite, have been shown to activate performance of graphite by up to 50% [5]. Quartz, also often present in

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high concentrations in some coals, has shown the opposite effect, inhibiting electrochemical activity [5–7].

The importance of surface oxygen-functional groups has also been emphasised for coal chars, which has been seen to change as a function of pyrolysis highest heating temperature (HHT) [8,9]. The importance of surface area, porosity, carbon structure and surface functionalisation on the electrochemical performance of carbon materials has further been established in the literature when assessing slurry-type systems [7,9–12]. These studies generally use pure carbon materials which are not fossil fuel or biomass derived and therefore have no mineral component. In a particulate carbon arrangement, ash-free carbons have been shown to have high activity when they have a high mesoporous surface area and a high O/C ratio, these characteristics altered through acid and base washing treatments of activated carbons [10,12]. The importance of bulk lattice disorder and electrical conductivity of carbon fuels was also demonstrated early on by Cherepy et al. [11] and the importance of fuel conductivity has also been investigated in solid carbon anode arrangements subsequently [13,14].

It was found in a previous investigation that the thermal pre-treatment of raw coal effects the resultant coal char electrochemical activity. Assessment of physical properties of chars, including resistivity, BET surface area and chemical activity towards oxidation (reflective of surface functional groups) showed that although these important properties do clearly play a role in the activity of coal char, another variable also appears to impact on the activation of the char [13]. It was suggested that the inorganic minerals present and their distribution within the coal chars was instead causing kinetic activation, which was pyrolysis temperature dependant. Certainly the role of coal mineral constituents has been investigated when using coal chars in the DCFC, for example in the work of Tulloch et al. [5] as well as Li et al. [6]. Further, the role of metallic species present in the coal in the gasification process for a gas-fed DCFC has also been investigated [15]. It is clear that some species have catalytic roles in the electrochemical oxidation reaction while some appear to inhibit or, alternatively, indirectly effect electrochemical performance through impacting on the chemical conversion of the carbon to gaseous fuel carbon monoxide. These studies have generally not considered the link between the different types of char which are formed from different coals and the impact that the proportion of these catalytic species in different minerals, or the size of these minerals in the resultant char, may have on char electrochemistry.

In this work, previously studied coal chars [13] have been further analysed using advanced characterisation techniques including mineral liberation analysis (MLA) and coal grain analysis (CGA) to determine if indeed the mineral content plays a critical electrochemical role on the coal char used. One active and one inactive coal char of each parent coal was investigated and results are presented here. Kaolin doped electrodes have also been investigated to determine interfacial effects on observed kinetics.

CGA is a technique which has been developed by the Commonwealth Scientific and Industrial Research Organisation (CSIRO, Australia) to identify maceral components in coal particles using optical imaging [16,17]. The technique can also be applied to coal chars to determine the ‘type’ of char according to a standard identification system developed by Benfell et al. [18]. Investigation of coal chars as opposed to raw coal macerals is a very new application of CGA analysis under development, having only recently been applied to chars produced using an entrained flow gasifier [19]. This technique is made more powerful through integration of MLA data where the coal char is formed into a solid block and the same block is analysed in both CGA and MLA analysis. MLA uses a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) X-ray analysis to complete an automated scan of a set area and identify mineral components present. The MLA software also identifies particle size and prevalence and gives quantitative information about mineral matter present in coal chars. Through manual analysis, MLA and CGA images

can be matched to give qualitative information about the integration of carbonaceous and inorganic mineral matter [17]. Although this technique is normally applied to raw coals [16], it is also highly relevant in the investigation of coal chars since it has been proposed that the distribution and type of mineral matter present in the coal char is likely to be of high importance in determining electrochemical activity in the direct carbon fuel cell [13].

## 2. Material and methods

### 2.1. Coal preparation and electrochemistry

Detailed information regarding preparation of coal char and testing of char in a half-cell assembly has been presented in previous work [13]. Chars were produced from raw coals by firstly ball milling the raw coal to reduce particle size, then sieving to a size of less than 45  $\mu\text{m}$  in an iterative process until all raw coal was in the correct size range. Chars are produced by slow pyrolysis (heating rate 6–10  $^{\circ}\text{C}/\text{min}$ ) under constant nitrogen flow (100 mL/min). Chars were held at the pyrolysis higher heating temperature (HHT) for 4 h before cooling to room temperature and gently separating particles with a mortar and pestle. Chars are identified here by their raw parent coal char type (Coking – C and thermal – T) as well as the HHT to which they were taken.

Working electrodes were produced by mixing 25 wt% of coal chars with graphite (SFG44, Timrex Switzerland) and compressing to form a pellet which was fixed in an alumina tube. Graphite working and counter electrodes were used within a pre-fused molten carbonate ternary eutectic of  $\text{Li}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  which was also ball milled to ensure homogenisation prior to initial fusing. A carbon dioxide gas environment was used to form a stable and reproducible reference system (see Ref [5] for full details).

Kaolinite catalyst added was procured from Sigma Aldrich and dried under air at 110  $^{\circ}\text{C}$  before sieving to a particle size less than 32  $\mu\text{m}$ . For the coal mixed electrode, the catalyst was firstly mixed with the char (mortar and pestle) and then the homogenous catalyst/char mixture was combined with graphite prior to pressing into an electrode. A distributed kaolinite electrode was made using graphite and sieved kaolinite via mixing with a mortar and pestle. A bulk kaolinite electrode was made by pressing kaolin into a solid disc and then cutting the solid disc into a square. The kaolin chunk was then placed at the bottom of the die press with graphite power loaded over the top before pressing into an electrode where the kaolinite chunk was exposed on one side. Electrode pellets were fixed to an alumina tube and tested as working electrodes.

Electrochemical experiments were carried out after heating the cell assembly containing pre-fused carbonate eutectic to the reaction temperature. Electrodes were held in the assembly under carbon dioxide flow until the eutectic became molten (less than 400  $^{\circ}\text{C}$ ), after which they were inserted into the carbonate fluid. The system was allowed to equilibrate at open circuit for at least 10 min before carrying out linear sweep voltammetry scans from the open circuit potential to 0.5 V versus the reference, conducted at 5 mV/s.

### 2.2. Advanced analysis techniques

Two techniques were used to characterise the carbon and mineral compositions of the char samples on a particle basis. The CSIRO developed coal grain analysis (CGA) technique and the automated SEM-based MLA technique.

The optical reflected light imaging and analysis system, Coal Grain Analysis (CGA) developed in CSIRO provides reflectance and composition information on individual coal particles using a Zeiss Axio Imager reflected light microscope coupled with Coal Characterisation Imaging System (CCIS) software. This software was also developed by the CSIRO. This system was used to collect high resolution (1 pixel = 1  $\mu\text{m}$ ) colour images with the objective to determine the particle composition

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