



# The effect of coal type and pyrolysis temperature on the electrochemical activity of coal at a solid carbon anode in molten carbonate media



J.A. Allen, M. Glenn, S.W. Donne\*

University of Newcastle, Discipline of Chemistry, Callaghan 2308, Australia

## HIGHLIGHTS

- Two main pathways for carbon electro-oxidation are observed.
- A catalytic oxidation pathway is observed for specific coal chars.
- Catalytic activation is suggested to be dependent on coal ash component.
- Pyrolysis HHT greatly effects electrochemical performance of coals.

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## ABSTRACT

A systematic assessment of the electrochemical activity of two different parent coal types, pyrolysed at temperatures between 500 and 900 °C higher heating temperature (HHT), is presented in this work. Analysis shows that certain coal chars are catalytically activated in molten carbonate media at 600 °C, however activity does not appear to follow trends established for ashless carbon sources. It is seen here that it is not possible to predict activity based solely on electrical resistance, surface functionalization, or the BET surface area of pyrolysed coals. Instead, it is suggested that coal ash type, abundance and distribution plays a pivotal role in activating the coal char to allow fast electrochemical oxidation through a catalytically enhanced pathway. Activation from ash influence is discussed to result from wetting of the molten carbonate media with the carbon surface (change in polarity of electrode surface), through ash mediated oxide adsorption and transfer to carbon particles, or possibly through another catalytic pathway not yet able to be predicted from current results.

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## 1. Introduction

Low carbon energy production is essential in order to meet future energy demands. Current practice for electrical energy generation is neither sustainable, nor globally responsible in terms of excessive carbon dioxide (and other) emissions. This is especially true of coal fired power stations (CFPS). Despite growing environmental concerns, coal remains an important economic resource for Australia and its export and use are projected to remain substantial over the coming decades [1]. Coal is also extensively used in developing nations such as China and India, and this expanding use could potentially result in the substantial release of carbon dioxide

to the atmosphere, even using current best practice. Reduction in emissions from the use of coal and carbon-based energy sources is therefore essential.

The direct carbon fuel cell (DCFC) is a low carbon technology option that converts the chemical energy contained in carbon fuels to electrical energy without combustion. Instead, the oxidation reaction key to releasing chemical energy in coal is carried out electrochemically. This electrochemical pathway is enabled by physical separation of the carbon oxidation and oxygen reduction reactions in an anode and cathode compartment, respectively; i.e.



\* Corresponding author.

E-mail address: [scott.donne@newcastle.edu.au](mailto:scott.donne@newcastle.edu.au) (S.W. Donne).



In order for the oxidation reaction to proceed, reactants must be separated where direct contact between carbon and oxygen will result in a chemical rather than electrochemical reaction. Several fuel cell arrangements have been investigated for this purpose, considered in detail in recent reviews of this area [2,3]. The most promising DCFC arrangement makes use of both a solid oxide membrane to separate the anode and cathode compartments, as well as molten carbonate media to aid in transport of oxide anions to the anode. This is often referred to as a hybrid DCFC arrangement as it makes use of both molten carbonate fuel cell as well as solid oxide fuel cell technology [3]. The use of coal as a fuel in such an arrangement has also been assessed with performance being far from optimized compared to achievable power outputs using similar arrangements with pyrolysed medium density fibreboard (MDF) as fuel [4,5].

Thermal degradation of coal in an oxygen-free atmosphere occurs at temperatures as low as 350 °C [6,7], changing both the overall composition of the solid material and structure of the remaining organic components [8]. Much work relating to coal pyrolysis to date has been for the express purpose of gasifying the coal to produce syngas [6,9]. Fast pyrolysis of the coal has therefore been studied in some detail since the speed of the pyrolysis process (heating rate) leads to the preferential production of a gaseous species at the expense of the solid char component [6,7,9,10].

Pyrolysis processing requirements are unique for application to the DCFC since gas production represents a loss in efficiency and is therefore desired to be limited. Maximising the solid char component of coal pyrolysis is essential for the efficient use of coal in the DCFC, as is stabilization of the char component at the preferred operating temperature.

Several studies have investigated coal in a DCFC arrangement [11–18]. Of these many do not consider the possible effect of thermal history of the coal fuel when examining its electrochemical performance [12,15–17]. One study has investigated the effect on performance of coal pre-treatment temperature in nitrogen and oxygen atmospheres [13]. The results of Li et al. [13] suggest that pyrolysis of the coal at higher temperatures results in a less electrochemically active coal char than that produced at lower temperatures.

In this work, the effect of several variables on the electrochemical oxidation of coal at a solid electrode has been examined. Variables examined include the pyrolytic pre-treatment temperature of the parent coal (500–900 °C), and the type of parent coal used (thermal and coking coals investigated). Electrochemical assessment has been carried out under identical conditions to allow systematic and reproducible investigations. Complimentary physical characterization has also been carried out to determine possible factors influencing activity towards electrochemical oxidation including elemental composition, chemical oxidation activity under both air and carbon dioxide, electrical resistivity, and BET surface area.

## 2. Experimental

### 2.1. Coal preparation

#### 2.1.1. Particle size

Two parent coal samples were used, sourced from NSW Australia coal deposits, including a bituminous coal used for thermal applications (noted as CT) and a traditional coking coal (CC). The coal samples were firstly milled and sieved repeatedly to obtain a particle size of <45 µm. A stainless steel bowl and balls were used

for milling in a Fritsch planetary monomill (Idar-Oberstein, Germany), while a shaker sieve platform was used for particle size separation. Larger fractions were milled until the required size was obtained for a full sample set. The temperature was kept below 100 °C during milling to avoid thermal degradation during this procedure.

#### 2.1.2. Pyrolytic pre-treatment of coal

Samples of the milled coal were weighed into alumina crucibles and inserted into a tube furnace under constant nitrogen flow. The program used included heating initially to 110 °C (to ensure sample is fully dried prior to pyrolysis) at a ramp rate of 10 °C/min, followed by a wait of 1 h at this temperature. Following drying, the sample was heated to the highest heating temperature (HHT) of interest at a heating rate of 6 °C/min, where it was held for 4 h. The furnace was then turned off and allowed to cool to room temperature naturally under a nitrogen flow. Samples were not removed from the inert atmosphere until temperatures reached below 100 °C. Once removed, samples were gently crushed to loosen prior to electrode preparation. Sample naming in this work consists of the parent coal identifier (CT or CC for thermal and coking coal, respectively) and the HHT of the char (500–900 °C).

## 2.2. Coal characterisation

### 2.2.1. Thermogravimetric analysis

A Perkin–Elmer (Massachusetts, USA) diamond TGA/DTA apparatus was used for sample analysis. In each case, a sample of ~20 mg was used, and samples were analysed in an alumina crucible set with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> used as a reference material. Samples were tested under both air flow (industrial grade, CoreGas) and under carbon dioxide flow (Food Grade, CoreGas) at 20 mL/min. In both cases, a heating rate of 15 °C/min was used, and changes in mass measured as a function of temperature.

### 2.2.2. Elemental analysis

Elemental analysis was carried out using an elemental analyzer (PerkinElmer PE2400 CHNS/O) using PE Datamanager 2400 and a PerkinElmer AD-6 ultra-micro balance. The instrument was run in CHNS and ash mode in duplicate with a sample size of 1–2 mg. Determination of the oxygen content was performed by difference in sample weight with other measured variables.

### 2.2.3. Resistivity measurements

The resistivity of graphite and coal chars was measured using a purpose built cell with a Keithley Multimeter (sensitive to 0.0001 Ω). Pellets of pure coal char were made in-situ from ~1 g of material in the resistance measurement cell. The cell consisted of two conducting plates lined with an insulating ceramic material which could be held together at constant pressure. The cell was pressurized to 140 MPa initially, to ensure consistent contact with the coal char, before the cell was secured at this pressure and removed from press for a period of 10 min. Resistance was then measured in ohms. The compressed length was also recorded at this point using calipers in order to calculate the electronic resistivity according to:

$$R_{TOT} = R_0 + \rho \frac{l}{A} \quad (4)$$

where  $R_{TOT}$  is the total measured resistance (Ω),  $R_0$  is the resistance measured with no coal char present (Ω),  $\rho$  is the electrical resistivity (Ω m),  $l$  is the pellet length (m), and  $A$  is the cross sectional area (m<sup>2</sup>).  $R_0$  was measured between each conductivity measurement to ensure there was no drift and was also measured after pressurizing

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