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

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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.

KEYWORDS: Direct carbon fuel cell, carbon electro-oxidation, coal, coal ash catalysis

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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.

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 $< 45\ \mu\text{m}$. 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 $10^{\circ}\text{C}/\text{min}$, 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 $6^{\circ}\text{C}/\text{min}$, where it was held for 4 hours. 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 α -Al₂O₃ 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 minutes. 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), ρ is the electrical resistivity ($\Omega.m$), l is the pellet length (m), and A is the cross sectional area (m^2). R_0 was measured between each conductivity measurement to ensure there was no drift and was also measured after pressurizing the cell to 140 MPa.

2.2.4. Gas Adsorption

Approximately 0.2 g of each coal char was degassed under vacuum for a minimum of 8 hours at 300°C. The sample was then returned to room temperature and weighed in order to ensure adsorption measurements for the dry weight of the char added. The sample was then analysed using a Micrometrics ASAP 2020 Surface Area Analyser. Adsorption isotherm data was collected using carbon dioxide as the adsorbate submersed in an ice-water bath (0°C). Average pore size was weighted based on volume adsorbed for specific pore size, calculated using the Frenkel-Halsey-Hill method. A value of 0.17 nm² was used as the cross sectional area of the CO₂ molecule.

2.3. Electrochemistry

2.3.1. Electrode Preparation

Coal pellets for electrochemical assessment were formed using a mixture of graphite (SFG44 Timrex, Timcal Switzerland) and pyrolysed coal, using 25 wt% (dry basis) coal char for all pyrolysis temperature investigations. 0.8 g of the carbon mix in all cases was pressed into a pellet using an International Crystal Laboratories (Garfield, USA) 13 mm pellet die press under a pressure of 740 MPa. Once pressed, pellets were sintered at 500°C for 4 h under nitrogen flow. Pellets were then

inserted into alumina electrode holders using the ceramic adhesive Resbond 989 (Ceramic Oxide Fabricators, VIC, Australia) and a paste of 1:1 Resbond 989 to graphite (weight percent) was compressed onto the back of the pellet over an electrical contact to ensure good connection (see also Ref. [19] for a schematic).

2.3.2. Anodic Half-Cell Arrangement

The electrochemical half-cell used consisted of the working electrode as described above with counter and reference electrodes made from graphite rods. The rods were used several times and sanded back between experiments to refresh the surface, as well as renewing electrical connections which were inserted into a small hole drilled in the graphite rod. The electrodes were submersed in a pre-fused ternary carbonate eutectic once molten in an alumina bath with a weighted lid.

The eutectic was prepared from a mixture of lithium carbonate (Li_2CO_3 , >99%), sodium carbonate (Na_2CO_3 , >99%) and potassium carbonate (K_2CO_3 , >99%, all Sigma-Aldrich) in the mole ratio 43.5:31.5:25 (eutectic composition [20]). The carbonates were firstly dried in air at 110°C for several days to remove moisture before being weighed separately and combined using a mortar and pestle. The eutectic was finally ball milled to ensure proper mixing (apparatus as described in Section 2.1.1). The eutectic was then fused at a temperature of 500°C in an alumina crucible before cooling.

Carbon dioxide (CO_2 , Coregas, food-grade) was allowed to flow over the surface of the carbonate during electrochemical testing to maintain a carbon dioxide atmosphere (50 normal L/min flow rate, nitrogen basis) to ensure a stable reference electrode. Detailed cell and electrode drawings are provided in an earlier publication [19].

2.3.3. Electrochemical Test Procedure

In order to ensure consistent analysis, the same electrochemical method was used for assessment of all electrodes. Electrodes were at first partially inserted in the electrochemical half-cell to sit above

the fused solid eutectic at room temperature. Carbon dioxide flow was started and the cell was heated at 6°C/min to the electrochemical assessment temperature of 600°C. The electrodes were immersed in the carbonate melt at 500°C prior to continuing to 600°C where the anode was held for 1 hour at open circuit potential (OCP) prior to testing to ensure good wetting of the carbon surface [21] and stable conditions within the cell (i.e., no temperature fluctuations from opening and closing the furnace door or movement of molten eutectic from insertion). Electrochemical testing was then carried out including sweeping of the electrode potential from the measured OCP to an overpotential of 0.5 V. Sweep rates of 1 and 5 mV/s were investigated.

For this work, the electrochemical apparatus used was a Pine Research Instrumentation (Durham, USA) WaveNow portable potentiostat, with AfterMath electrochemical software used for data collection. Current measured has been normalized for the geometric surface area of the pellet of 1.327 cm² (13 mm diameter) in all cases.

3. Results and Discussion

3.1. Coal Characterisation

3.1.1. Coal Char Composition

The coal samples used are NSW Australia bituminous thermal (CT) and coking (CC) coals. Elemental analysis is shown in Table 1 along with the atomic H/C and O/C ratios measured from coal char samples.

Table 1: Elemental analysis of coal and coal chars investigated (wt% dry basis)

	C	H	N	S	O	Ash	O/C	H/C
CT-RAW	62.58%	3.61%	1.53%	0.36%	9.51%	22.43%	0.152	0.686
CT-500	62.87%	2.30%	1.58%	0.29%	6.50%	26.47%	0.103	0.435
CT-600	64.22%	1.66%	1.55%	0.31%	4.33%	27.95%	0.067	0.307
CT-700	64.67%	1.03%	1.39%	0.21%	4.16%	28.55%	0.064	0.190
CT-800	65.50%	0.54%	1.29%	0.24%	3.41%	29.03%	0.052	0.098
CT-900	65.69%	1.18%	1.22%	0.09%	3.63%	28.20%	0.055	0.214
CC-RAW	78.73%	4.35%	1.60%	0.40%	5.48%	9.45%	0.070	0.658
CC-500	79.15%	3.16%	1.94%	0.29%	5.46%	10.01%	0.069	0.476
CC-600	79.45%	2.07%	1.77%	0.17%	5.54%	11.00%	0.070	0.310
CC-700	79.80%	2.40%	1.76%	0.22%	4.78%	11.05%	0.060	0.358
CC-800	82.25%	1.27%	1.74%	0.20%	3.13%	11.42%	0.038	0.183
CC-900	83.17%	1.43%	1.22%	0.09%	2.55%	11.56%	0.031	0.204

Raw CT can be seen in Table 1 to have a substantial ash content (>20 wt% dry basis) while raw CC has a smaller ash content (<10 wt% dry basis). The ash is not removed from the solid product during pyrolysis and therefore the composition of ash will increase as the pyrolysis yield decreases. The carbon content of the char for both CC and CT chars is also seen to increase systematically with pyrolysis HHT.

Increased pyrolysis temperature also results in a reduction in the oxygen and hydrogen containing groups present in the char. This is expected since more volatile material will be driven off with increasing temperatures during conversion to syngas and coal tars. These products contain large amounts of hydrogen and oxygen derived from the original parent coal [7] and their production will reduce the remaining functional groups. As functional groups are driven off, the coal char becomes more carbonized as indicated by comparison of H/C and O/C ratios for each char. Since aromaticity increases linearly as H/C ratio decreases [22], an increase in aromatic carbon groups and therefore partial graphitization of the carbon remaining is expected at higher pyrolysis temperatures [8].

Sulfur content is seen to change only slightly as the HHT increases for both parent coal types investigated and in both cases the sulfur content is almost identical. The sulfur is seen to change dramatically above a temperature of 900°C where it is presumably evolved during pyrolysis.

The measured pyrolysis yields for the bulk samples produced for testing in the DCFC half-cell are compared in Figure 1. Both the dry basis (db) and the dry ash free (daf) yields are shown in Figure 1 for each coal investigated. The pyrolysis char yield is seen in Figure 1 to decrease as a function of HHT with an almost linear relationship observed for both coal types investigated. CT, however, demonstrates a plateau above 700°C while CC shows a consistent linear decrease with HHT, although the overall yield for each parent coal (db) is within 5wt% of each other. The yield of CT calculated on an ash free basis (daf) however is much lower than CC. In the case of CT-900 less than 70% of the organic matter present in the coal remains, while in CC almost 90% is retained. This difference is likely a result of the coking coal being of higher rank than the thermal coal, with high starting carbon content (see Table 1), this carbon content exacerbated as pyrolysis temperature increases.

3.1.2. Gasification Response

Each coal char generated has been investigated using thermogravimetric analysis in air and carbon dioxide to assess and compare activity towards chemical oxidation. Simplified reactions are shown in Eqs (4) and (5) respectively along with gasification agent:

The mass loss profiles of each char generated on an ash-free basis is shown as a function of temperature using both air and carbon dioxide in Figure 2 where a heating rate of 15°C/min was used. Yield has been calculated in Figure 2 assuming 0% conversion at 110°C (i.e., starting point with dry coal). Clearly, oxidation in air results in a much larger loss of organic material compared to carbon dioxide. In the majority of chars examined, final yields in air of close to 0% organic matter at 900°C (i.e. only inorganic ash remains) while more than 80% of the starting material remains under

CO₂ up to a higher temperature of 950°C. This result is not unexpected as the relatively sluggish kinetics of coal gasification by CO₂ compared to combustion in air has been known for some time [23].

Difference between coal chars based on both parent coal and pyrolysis temperature can be observed in Figure 2 [A] and [C] under air. CT shows the majority of mass loss under air in the region 500-600°C with near complete conversion of organic material achieved by 700°C for all coal chars. CC however shows a slower oxidation process for all coal chars tested, excepting CC-500, with complete conversion not reached in the majority of cases in the temperature range shown. Differences in mass loss profiles are also observed between CC and CT examined under carbon dioxide. CC coal chars display two clear reaction regions starting at approximately 500°C and 700°C, the extent of conversion within each region varies with coal char HHT. CT chars however generally show a single large mass loss beyond approximately 700°C which is not seen in the case of CC. The exception to these observations is the CT-500 which appears to be very similar in shape to CC-500. This material was the only coking coal char to approach similar mass loss to the thermal coals tested.

In order to assess performance quantitatively, the yield obtained in air and carbon dioxide has been assessed at 600°C and 950°C respectively (indicated in Figure 2) for comparison. At these temperatures, the coal chars are still undergoing gasification and have not stabilized. These values are plotted as a function of HHT of the original coal char in Figure 3.

Both sets of coal chars investigated show a general trend of increasing yield with increase in pyrolysis temperature in both air and carbon dioxide. Activity towards chemical oxidation of coal and carbon materials in air is known to involve surface functional groups, with more highly functionalized materials showing comparatively faster kinetics [13, 24]. This does not however encompass all influences on chemical oxidation of carbon materials. As mentioned in Section 3.1.1, the increased ash material present in the thermal coal investigated might be expected to lead to a

lower yield and better oxidation kinetics for thermal coal chars as observed due to the catalytic role of ash materials in chemical oxidation [25].

Coals chars reacted in carbon dioxide show large yields with relatively little variation, suggesting only small reactivity towards Boudouard gasification (chemical formation of carbon monoxide through reaction of carbon and carbon dioxide) which does not vary significantly with changes in pyrolysis temperature for the regime investigated here ($<1000^{\circ}\text{C}$). CC chars investigated are seen to show a similar pattern towards activation under carbon dioxide as under air. CT chars tested however did not follow the same pattern, with a decrease in yield (increased activity) observed between 500 - 600°C and no observed increase in activity for CT-900.

Coal char gasification by carbon dioxide is not a new area of study [26], and it has been shown that coal type, based on rank generally (carbon content), has a significant effect on reaction kinetics with low rank coals performing better than high rank as a result of the presence of more oxygen-containing functional groups and inorganic ash components [26]. The inorganic matter components contained in coal can act as catalysts for the gasification reaction [27], with the ash type and composition, as well as pyrolysis conditions all contributing to the final gasification behavior [26].

Overall, CT coal is seen to be more active towards chemical oxidation by both air and carbon dioxide for all pyrolysis conditions assessed here and both coals show a general trend of decreasing activity towards oxidation with increasing pyrolysis temperature.

3.1.3. BET surface area

The BET surface area of each char investigated was determined from a carbon dioxide adsorption isotherm. The measured BET surface area for each coal char produced is shown in Table 2 along with average pore size.

Table 2: Surface area and average pore size from CO₂ adsorption isotherm

Pyrolysis HHT	BET SA / m ² g ⁻¹		D _{AV} (Å)	
<i>Parent Coal</i>	<i>CC</i>	<i>CT</i>	<i>CC</i>	<i>CT</i>
500°C	57.8	59.2	1.957 ± 0.774	2.195 ± 0.861
600°C	98.9	89.3	2.966 ± 1.732	2.258 ± 0.931
700°C	69.7	96.1	2.280 ± 0.966	2.680 ± 1.035
800°C	66.3	98.1	1.532 ± 0.582	2.566 ± 1.118
900°C	36.7	74.2	2.492 ± 1.174	2.571 ± 1.260

The BET surface area and average pore diameter (with standard deviation) measured for coal chars produced at low pyrolysis temperatures (< 700°C) exhibit little variation between each parent coal type. Increasing the pyrolysis temperature for both CT and CC chars from 500 to 600°C causes a distinct increase in BET surface area. CT chars are further shown to display an increase in BET surface area to a pyrolysis HHT of 800°C. Heat treatment of bituminous coal has previously been shown to increase BET surface area with pyrolysis HHT in the range investigated here [28]. Conversely, CC shows a sudden decrease in BET SA between 600 and 700°C which is not recovered at higher pyrolysis treatment temperatures. Surface area has been shown to influence the chemical oxidation activity of carbon materials [23] and indeed some correlation between the BET surface area and activity towards chemical oxidation activity can be observed, especially in the case of CT. Overall however the BET SA does not vary significantly with pyrolysis HHT or parent coal type (i.e. all chars have the same order of magnitude surface area).

3.1.4. Electrical Resistivity

The measured electrical resistivity of each coal char investigated is shown in Figure 4. An 8-order of magnitude variance in resistivity from coal char formed at 500°C to that at 900°C can be seen for both parent coals investigated. These results concur with a 5-order of magnitude drop in electrical resistance observed between 600 and 900°C HHT for biomass chars [29], where a similar experimental set-up was used. A higher pressure was applied in the chars investigated here; however the results of Mochidzuki et al. suggest little variation to measured resistance using this method

beyond a pressure of 7 MPa [29].

In general the resistivity of the coal char pyrolysed at temperatures higher than 700°C show much smaller variation than those pyrolysed at lower temperatures (Figure 4). This is especially true in the case of CC chars pyrolysed at HHT 800 and 900°C where the electrical resistance approaches that expected for pure graphite.

3.1.5. Summary of Physical Properties

CT and CC coal chars studied here show similar general trends with increasing pyrolysis HHT including:

- i. Increasing solid yield under air and carbon dioxide (lower chemical reactivity)
- ii. Decreasing functionalization (including O/C and H/C ratios)
- iii. Decreasing electrical resistance, and,
- iv. Small changes in surface area and pore size

Comparison of the coking (CC) and thermal (CT) coal chars show that the thermal coal had higher ash content, as well as higher activity towards chemical oxidation in both air and carbon dioxide, especially for low pyrolysis HHT. The pyrolysis yield was also lower for CT chars suggesting a larger initial volatile composition for the parent thermal coal, which is also reflected in the lower carbon content of the thermal coal. Overall, the thermal coal also had higher surface area and average pore size than the coking coal, especially for char treated at pyrolysis temperatures above 600°C, although overall no large variation in pore size was observed. Degree of functionalization was similar between coal types pyrolysed at the same temperature with only small differences in H/C and O/C ratios observed between CC and CT. The exception is CC-700 which showed a larger H/C ratio than the equivalent CT, which may also account for non-linear behaviour observed for chemical activity, where CC-700 was seen to be more active than CC-600 under both air and carbon dioxide.

3.2. Electrochemistry of Coal

3.2.1. Comparative Performance versus Reference

The electrochemical activity of each coal char generated was assessed using a solid anode arrangement. The anode consisted of 25 wt% coal char with graphite as a binder. Since coal is expected to be more active than graphite [17, 30, 31], comparison of the 25 wt% loaded electrode will demonstrate key differences in electrochemical oxidative behavior for coal chars. Activity was assessed in a ternary carbonate eutectic ($\text{Li}_2\text{CO}_3\text{:Na}_2\text{CO}_3\text{:K}_2\text{CO}_3$) at 600°C in all cases for comparison. The same electrochemical procedure was used for consistency and included allowing the electrode to equilibrate at open circuit in the molten carbonate at temperature for 1 h. Three LSV sweeps were carried out consecutively (two at 5 mV/s followed by one at 1 mV/s) with a 2 minute wait at OCP between each. Results for CC-500 are shown in Figure 5.

Comparison of scan rates used shows no dependence on diffusion of reactants to the electrode, as expected in the carbonate/oxide rich electrolyte used here. In the potential region investigated the oxidation of carbon further occurs without reaching a diffusion plateau, commonly seen in slurry arrangements [32]. Standard deviation between the three LSVs measured in Figure 5 increases with polarization, reaching $\sim 1.3 \text{ mA cm}^{-2}$ at a polarisation of 0.45 V positive of the OCP (indicated in Figure 5). In order to encompass variations between LSV sweeps, it can be seen in Figure 5 that taking the average current density at 25 mV intervals, along with the standard deviation at a specific point, can be effectively used to encompass possible deviations in LSV curves observed with polarization. This has been done for each coal char produced as well as for pure graphite, shown in Figure 6.

Each coal char investigated shows differences in OCP and in the maximum current density obtained. Variation in the stability (smoothness of curve) and general shape of the LSV can also be observed between chars. To compare overall performance, the current density at 0.1 V versus the reference

(indicated by dashed line in Figure 6) has been plotted as a function of HHT. The standard deviation can also be included in this analysis, as outlined in Figure 5, in order to show the reproducibility of the current density measured for each coal char at this polarization, results shown in Figure 7.

A clear activation can be observed for CC-700 and CT-800, also observed to a lesser extent for CT-500 and CC-800. A systematic decrease in activity can be seen for CT chars between 500 and 700°C HHT, while little to no difference is observed between CC chars below the activation HHT of 700°C. Both coal chars treated at 900°C HHT show limited activity. All coal chars investigated are shown in Figure 7 to perform better than graphite versus the reference system at the same polarization, this is in agreement with results found using slurry-type arrangements for the increased activity of coal materials compared to relatively inert graphite [3, 33].

3.2.2. OCP Assessment

Average OCP, measured between each LSV, as a function of pyrolysis HHT is shown for each parent coal type in Figure 8. In the case of CT chars, the activation of the electrode apparently decreases with pyrolysis HHT while CC chars display an increase in relative activity, as marked in Figure 8. Change in the OCP could be due to (i) the presence of a mixed potential at the electrode surface, and/or (ii) change in the relative “activity” of solid carbon at the electrode surface.

Temperature, carbonate composition and carbon dioxide flow rate/partial pressure can affect the open circuit potential through the Nernst equation (Eq 7) for electrochemical carbon oxidation in molten carbonate (Eq 6) [21]:

$$E = E^0 - \frac{RT}{4F} \ln \left(\frac{a_c a_{CO_3^{2-}}^2}{p_{CO_2}^3} \right) \quad (7)$$

Where standard terms include E as the equilibrium potential and E^0 as the standard potential (V), R is

the universal gas constant ($\text{J mol}^{-1}\text{K}^{-1}$), T is the temperature (K) and F is Faradays constant (C/mol).

The activity of carbon and carbonate is described by a_C and $a_{\text{CO}_3^{2-}}$ respectively. Many investigations assume activity for both carbon and either carbonate or the oxide anion as unity, meaning the OCP is predicted to be affected only by the partial pressure of CO_2 . Since, in our system, all variables are constant, the only variant is in fact the carbon source. Carbon activity was discussed by Li et al. [34] where changes in the OCP were modelled based on a calculated value for carbon activity. In this work, carbon activity was defined in limited terms by considering a model carbon (graphene) with the number of active carbon atoms defined as a function of several factors including the distance between two active carbon atoms, the diameter of the crystallites and carbon particle size. Although this idealized system is difficult to apply to results shown here, the systematic change in the OCP observed for CT chars as pyrolysis temperature increases suggests possible graphitization of the char and therefore a reduction in surface activity. In the case of the reference system used here, this causes the OCP to approach 0 V versus the reference since the reference electrode is also graphite.

Carbon activity with respect to relative graphitization however cannot be used to explain changes observed for the coking coal char investigated where increasing HHT appears to increase activity of the coal char, decreasing the OCP, until a HHT of 900°C where activity is lost. This is despite results suggesting that the carbon component of the coal char is also undergoing some degree of graphitization and presumably reduced carbon “activity” as defined by Li et al. [34]. Changes to the coking coal char OCP are also to a greater degree than that observed for the thermal coal investigated with variation of almost 0.3 V between most and least active OCP. It is therefore likely that a different effect on the OCP is observed in the case of CC compared to CT chars.

Chen et al. demonstrated that the open circuit potential is strongly affected by the extent of contact of the carbon sample tested (graphite) and the binary Li/K molten carbonate used by the authors, showing a sudden change in OCP of 0.3 V after flooding of a graphite sample at 650°C [21]. The

authors discussed the OCP as representing a mixed/corrosion potential where the surface undergoes simultaneous reduction of carbon dioxide and oxidation of carbon, depending on whether the surface was wetted or not. They attributed large variation in OCP to progressive coverage of carbon by the molten carbonate and the subsequent generation of CO via the reverse Boudouard reaction, which can be electrochemically reduced to carbon. It is therefore likely that large variation in OCP observed for coking coal, in particular between 500 and 600°C HHT results from variation in the wetting of the coal char, possibly influenced by a change in properties of the ash component of the coking coal between these temperatures. It has previously been suggested that coal contaminants cause variation in the electrode polarity and therefore wettability with carbonate [19]. It is therefore suggested that pyrolysis of coal causes changes to the ash structure and distribution, effecting changes in the wetting behavior and therefore observed OCP of the electrode.

3.2.3. Comparative Performance versus Overpotential

It is useful to compare results independent of the OCP to assess the kinetic performance of the electrodes. Comparison of chars produced versus their respective overpotential is therefore shown in Figure 9. Comparison of results irrespective of OCP shows very similar behavior for the majority of coal chars to each other, as well as to a standard graphite electrode, also included in Figure 9 [A]-[C] for comparison. In the case of activated electrodes, CC-700 and CT-800 behaviour deviates from low overpotentials showing much faster kinetics for these activated electrodes which appear to follow a similar catalytic pathway to each other with a clear transition between low and high polarization, the change occurring at ~0.25 V. In the case of coal chars generated at 900°C, performance is almost identical between parent coals tested, both of which show an inhibited oxidative response at high polarization compared to graphite, again in the high potential region where instability is observed for activated electrodes (>0.25 V). Similarly to Section 3.2.1, comparison of performance at the same polarization (OCP + 0.45 V) can be assessed including standard deviation calculated as described in

Figure 5. This is shown in Figure 10.

When expressed as overpotential it can be seen clearly that the kinetics of coal char oxidation only vary significantly in the case of the activated cases of CC-700 and CT-800. Other coal chars result in very little variation where performance appears similar to, or, in most cases, inhibited from, graphite. The activated electrodes also show a high degree of standard deviation for activated coal chars at this polarization, most likely as a result of CO₂ bubble formation and dislodgement which has previously been observed on graphite at more elevated temperatures (750°C) [35]. Based on these observations it is suggested that the mechanism of oxidation on the activated electrodes follow an identical catalytic pathway, while inactive coal chars follow a similar mechanism to pure graphite.

3.2.4. Electrochemical Activation of Coal Chars

A clear relationship between the specific surface area and electrochemical activity of a slurry activated carbon system was observed by Cao et al. [36], the authors also suggesting changes in the relative ‘acidity’ or ‘basicity’ of the surface to effect electrochemical oxidative activity as a result of variation in surface functional groups. Increasing the surface functionalization of ashless carbon material, for example through chemical pre-treatment, has been suggested in the literature to lead to higher electrochemical activity for molten carbonate suspended carbon fuels [13, 36]. The importance of conductivity in a solid electrode has also been previously suggested by Hackett et al. when investigating solid carbon electrodes of various compositions [12], as might be expected when using the carbon fuel as a current collector also.

The performance of coal chars examined here can be explained to some extent using these observations for ashless carbon electro-oxidation including the importance of surface functional groups, BET surface area and, in the case of a solid anode, char resistivity. Performance can generally be explained in Figure 11 showing three regions of reaction which are influenced by properties shown here.

For a coal char of low conductivity but high functionalization and BET surface area, areas outlined in Figure 11 would correspond to:

- A. Low resistivity and low activity
- B. Low resistivity and high activity
- C. High resistivity and high activity

Performance is initially low for high resistance CT chars (CT-500 and CT-600). This is likely due to the high electrical resistivity of these chars limiting oxidation to Area (B) in Figure 11 where CT-500 outperforms CT-600 despite higher resistivity due to the higher functionalization and therefore

activity of this char at the interface between graphite and coal char. When pyrolysed excessively; i.e., to a HHT of 900°C, activity of the carbon drops to that of graphite due to low levels of surface functionalization; i.e., Area (A) in Figure 11. The most active char however was CT-800, which might be a result of the further reduced resistivity for this char at a pyrolysis temperature of 800°C compared to 700°C (Figure 4). This seems unlikely however since similar activation is also observed for CC char at 700°C which has higher electrical resistivity than CT-800. The relative activation of CT-800 could be related to higher porosity (Table 2), as suggested for ashless carbons [37], however the observed reduction in porosity through the plasticization stage of coking coal examined between HHT of 600 and 700°C apparently activated the coking coal tested here, meaning no clear relationship with porosity can be made.

The functionalization, surface area, porosity and electrical resistance do not appear to be the defining factor to cause a catalytic electrochemical pathway to be followed in the case of high ash coals investigated here. All of these conditions could be described to be necessary, but not sufficient for activation of coal chars electrochemically. Instead, it is suggested that ash type influences the electrochemical performance considerably for high ash coals. This is possibly a result of the interfacial mixing of carbon and ash. The dependence of this activation on pyrolysis temperature further suggests a change in the ash distribution and character with thermal treatment. In the case of CC chars, activation occurs at lower temperatures than CT chars and allows for a larger active window before destruction of activity at 900°C HHT for both coal types. The effect of coal ash pyrolysis has been investigated for gasification applications where it is established that coal ash acts catalytically and, further, that catalytic coal ash properties are affected by thermal treatment [26, 27]. For example iron oxides, which are known catalysts for coke gasification [38], are proposed to act as oxide mediators, enhancing gasification through the pathway [26]:

The oxidation state of the iron catalyst is dependent on thermal treatment conditions, including both gas atmosphere and temperature [26]. Eq (9) also suggests contact of the metallic catalyst with solid carbon is essential for activity, implying distribution and contact of the carbon and catalyst is a determining factor for activation.

4. Conclusion

Activity of coal chars cannot be simplified to optimization of porosity, surface functional groups or resistivity as, although trends in these properties do clearly occur, no definitive pattern for activation based on one or more of these factors can be observed for the two very different coal types investigated in this work. Instead it is suggested here that the ash composition and distribution in the coal particle plays a dominant role in catalytic activation, possibly through effect of ash on carbonate wettability and oxide mediation at the surface of the ash. Specific thermal treatment of the coal and coal ash appears to change these properties and lead to promotion of a catalytic reaction pathway at the solid carbon electrode.

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6. REFERENCES

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Figure 1: Pyrolysis yield as a function of HHT for CT and CC coal types on both dry basis (db) and dry ash free basis (daf)

Figure 2: Dry ash free yield of coal chars (CC-[A] and [B], CT- [C] and [D]) during gasification by air ([A] and [C]) and carbon dioxide ([B] and [D]) at a heating rate of 15°C/min. Note y-axis limits are different for CO₂ and air experiments.

Figure 3: Solid yield of dry ash free coal char remaining for CC and CT in [A] air at 600°C and [B] carbon dioxide at 950°C. Note y-axis limits are different for CO₂ and air experiments

Figure 4: Electrical resistivity of coal chars under 140 MPa at room temperature

Figure 5: CC-500 electrochemical performance including LSV's at 1 and 5 mV/s, average current density at 0.025 V intervals and standard deviation at each potential

Figure 6: Comparative performance of each coal char investigated to an overpotential of 0.5 V for [A] CT chars and [B] CC chars

Figure 7: Average current density at 0.1 V vs reference from LSV results of 25 wt% coal chars at 600°C in ternary carbonate eutectic

Figure 8: Average OCP measured versus reference for 25 wt% coal char working electrodes submersed in ternary carbonate eutectic at 600°C

Figure 9: Comparison of CT and CC chars at different pyrolysis temperatures versus over-potential (OCP) [A] 500 and 600°C HHT, [B] 700 and 800°C HHT and [C] 900°C HHT

Figure 10: Average current density at 0.45 V vs OCP from LSV results of 25wt% coal chars at 600°C in ternary carbonate eutectic

Figure 11: Defining regions of activity proposed for low conductivity, highly functionalized coal char

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11