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Kinetic Analysis of the Anodic Carbon Oxidation Mechanism in a Molten Carbonate Medium

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Abstract

The oxidation mechanism for carbon in a carbonate melt was modelled using an electrochemical kinetic approach. Through the Butler-Volmer equation for electrode kinetics, a series of expressions was derived assuming each step of the proposed carbon oxidation mechanism is in turn the rate determining step (RDS). Through the derived expressions the transfer coefficient and Tafel slope were calculated for each possible RDS of the proposed mechanism and these were compared with real data collected on carbon based electrodes including graphite and coal. It was established that the RDS of the electrochemical oxidation process is dependent on both the carbon type and the potential region of oxidation. The simplified kinetic analysis suggested that the RDS in the main oxidation region is likely to be the first or second electron transfer on a graphite electrode surface, which occurs following initial adsorption of an oxygen anion to an active carbon site. This is contrary to previous suggestions that adsorption of the second anion to the carbon surface will be rate determining. It was further shown that use of a coal based carbon introduces a change in mechanism with an additional reaction region where a different mechanism is proposed to be operating.

Keywords: mechanistic analysis, carbon oxidation, direct carbon fuel cell, molten carbonate

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1. INTRODUCTION

The direct carbon fuel cell (DCFC) is able to convert the chemical energy contained in carbon bonds into an electrical energy output through separation of carbon oxidation and oxygen reduction steps in a fuel cell arrangement. The anodic and cathodic reactions involved are shown in Eqns (1) and (2); i.e.,

The overall equation is no different to the chemical oxidation of carbon; i.e.,

Coal fired power stations are nearing the maximum thermal efficiency attainable via the Carnot (steam) cycle due to metallurgical and engineering constraints. This limits the efficiency of coal-electrical energy conversion to around 42-43% (higher heating value basis) for new plants and gives little scope for reducing the CO₂ intensity of coal-based electricity generation via improvements in thermal efficiency. However, since the DCFC can transform chemical energy contained in a carbonaceous material directly to electrical energy, it is theoretically 100% efficient [1] with realisable efficiencies upwards of 80% of incoming carbon material, depending on the system configuration [1-3].

The molten carbonate DCFC is one of many possible cell configurations able to achieve electrical energy outputs through Eqns (1) and (2). The molten carbonate medium facilitates oxygen ion transfer to the carbon for reaction [4].

The oxygen ion is thought to exist as a part of the carbonate carrier species, CO₃²⁻. As such the carbonate species must dissociate within the double layer at the current collector/carbon/electrolyte interface prior to reaction; i.e.,

Despite extensive work investigating the electrochemical oxidation of carbon in molten medium [3, 5-9], there still exists great uncertainty around the mechanism of this oxidation reaction. This

reaction has been shown to have an onset potential sensitive to several parameters within the system, with the largest influence apparently the type of carbon undergoing oxidation [10]. The attainable power output of a DCFC is highly variable with the reaction shown to be more facile on an amorphous, unstructured carbon surface [5, 11-13] compared to a graphitic structure where limited oxidation activity can be observed [6, 14]. Recently, it has been shown by our research group that the oxidation activity of graphite can be significantly enhanced by inclusion of clays commonly found in coal, such as kaolin and montmorillonite, when this material is incorporated at the carbon surface [14]. Other research efforts have also shown sensitivity of the cell activity to the incorporation of various materials instead into the molten carbonate phase [6]. It is therefore possible to affect oxidation kinetics both at the carbon reaction site and also by incorporating materials into the oxide conducting medium. Investigations where the mechanism has been assessed have not been able to satisfactorily match theoretical mechanistic proposals with observed experimental behaviour [3, 6, 15].

A general oxidation mechanism involving single electron transfer steps and transformation of single species per step was envisaged as early as 1981 by Haupin and Frank [16], where the oxidation mechanism of carbon was established within cryolite for the production of aluminium. This mechanism was originally applied to the DCFC by Cherepy et al. [17] and has been broadly accepted in the literature [1, 2, 10]. Cherepy et al. justify the adaptation of Haupin and Frank's mechanism on the basis of the strong dissociation of the ternary carbonate to the O^{2-} ion at the electrode surface [17]. The mechanism proposed is shown in Eqns (5)-(11).

Following dissociation of the anion from its carrier (carbonate in the case of the current study ~~MC~~ ~~DCFC~~), the O^{2-} ion is proposed to adsorb at a surface reactive sites on the carbon (C_{SR}). The adsorbed $\text{C}_{\text{SR}}\text{O}^{2-}$ species can then undergo two, single electron transfers to form $\text{C}_{\text{SR}}\text{O}$. The relatively stable $\text{C}_{\text{SR}}\text{O}$ carbon site, it is suggested, then adsorbs a second O^{2-} adsorption to form $\text{C}_{\text{SR}}\text{O}_2^{2-}$. To finish the oxidation reaction the $\text{C}_{\text{SR}}\text{O}_2^{2-}$ species then undergoes two sequential single electron transfer reactions to form $\text{C}_{\text{SR}}\text{O}_2$, which is then discharged from the bulk carbon surface. This sequence has been visualised for the purpose of this work in a schematic, shown in Figure 1.

It is interesting to note that although Eqns (5)-(11) are commonly cited as the reaction pathway, indicating a single reactive surface site, initial representations of the mechanism in fact show adsorption of a single oxide anion to two active carbon sites. This is also shown schematically in Figure 2. The adsorption of the oxide anion is shown in Figure 2 to occur over two carbon surface sites initially in a C_2O type adsorption, which was not reflected in the mechanistic proposal developed by Cherepy et al. [17], although a dual reaction site scheme was outlined in the work of Wang et al. [6]. The initial adsorption is followed by a second adsorption, including the first carbon site and an adjacent site in a C_3O_2 arrangement. This arrangement results from proposals made by Cherepy et al. which are consistent with the more fully understood mechanism of the chemical oxidation of carbon in air [18]. It has been proposed that the relative stability of the C_2O group compared to C_3O_2 causes the main reaction product to be carbon dioxide rather than carbon monoxide, which reflects DCFC experimentation where carbon dioxide was found to be the favoured reaction species under most electrochemical conditions. Chemical formation of CO via the Boudouard reaction of carbon and carbon dioxide is thought to occur chemically and only when no potential is directly applied to the carbon species – for example in carbon slurry type arrangements

[16, 17].

Regardless of single or double carbon site involvement, the second adsorption step (Eqn (8)) has previously been proposed to be kinetically hindered, requiring a considerable over-potential, and has been presented as the rate determining step (RDS) in the carbon oxidation mechanism [6, 16, 17]. This proposal has not been supported by experimental evidence being based instead on the expected difficulty of physically attaching a second anion to the electrode surface. It is thought that after fast initial adsorption of oxide to preferred sites, liberation of CO₂ cannot proceed until less favourable sites located next to the initial adsorption are also occupied. This has been suggested to result in an increase in the driving potential required for oxidation and therefore a shift in the OCP away from that calculated thermodynamically [15].

In this work, expected kinetic parameters for the proposed oxidation mechanism have firstly been derived using the Butler-Volmer approach for oxidation steps laid out in Eqns (5)-(11). Parameters of specific interest include the Tafel slope (b) and the anodic transfer coefficient (α_a) as these are easily measured using the experimental design developed in previous work [14]. These derived parameters are then compared to experimental data gathered on carbon based electrodes in order to give experimental evidence to kinetic limitations proposed.

2. EXPERIMENTAL

2.1. Carbon Pellet Preparation

Carbon pellets were prepared using the procedure outlined previously [14]. This consists generally of pressing carbon powders in a 13 mm diameter pellet press under 740 MPa for 5 minutes. Pellets formed were then, independent of material used, sintered under nitrogen for a period of 4 hours at 500°C and fitted to an alumina tube for electrochemical testing (see [14] for more details). Graphite pellets were produced with no further additives (using SFG15; Timcal Timrex®) and formed a pellet of high strength and conductivity (resistivity of the pellets measured

to range from 8.0-9.3 $\mu\Omega\text{m}$).

The coal used was an Australian black coal sourced from a sub-bituminous deposit. Further characterisation was carried out in previous work [14] where the coal used in this study is 'Coal B'. Coal based pellets required addition of graphite in order to manufacture a stable pellet of high conductivity. The final coal to graphite ratio (w/w) of the pellet was 78:12 and its behaviour is therefore expected to be predominantly that of the coal. The coal pellet was also sintered under N_2 for a period of 4 hours to allow volatile material to be driven off prior to electrochemical testing. The coal used in this study was therefore partially pyrolysed in nature.

2.2. Electrochemical Arrangement

Solid carbon electrodes were manufactured from graphite and coal. These were submersed in an alumina crucible containing a pre-fused ternary carbonate eutectic (Na_2CO_3 , Li_2CO_3 and K_2CO_3 , Sigma >99% pure) at 500°C in a muffle furnace. For anode investigations a graphite counter and reference electrode were used, with the reference electrode equilibrium consisting of the $\text{C}/\text{CO}_2/\text{CO}_3^{2-}$ potential. Linear sweep voltammetry (LSV) was performed in order to obtain Tafel plots using an EG&G - Princeton Applied Research (PAR) 273A Potentiostat/Galvanostat. Detailed information regarding the set-up has been described in a previous publication [14]. LSV was performed at a scan rate of 1 mV/s in all cases presented here, beginning from the measured open circuit potential (measured over a period of 2 minutes). A constant carbon dioxide (BOC grade 4.5) atmosphere was maintained within the cell via an external gas feed line flowing at a rate of 50 mL/min (STP) in order to maintain constant reference electrode conditions.

2.3. Eutectic Preparation

The ternary eutectic was prepared from a mixture of Li:Na:K carbonates in the mole ratio 43.5:31.5:25 (m.p. 397°C [19]). The eutectic was gently combined using a mortar and pestle and dried under vacuum at 110°C for at least 24 hours. The eutectic was then pre-fused in a platinum

crucible at 450°C for a period of 40 minutes under CO₂ (BOC grade 4.5).

3. RESULTS AND DISCUSSION

3.1. Derivation of Rate Constant Expressions

The proposed mechanism through which the electrochemical oxidation of carbon is thought to occur is a series of chemical and electrochemical (charge transfer) steps ultimately resulting in the evolution of CO₂ (see Figure 2 and Eqns (5)-(11)). The Butler-Volmer model and equation for electrode kinetics allows the calculation of a predicted electrical current on an electrode as a function of the potential of that electrode. The high field approximation takes into account only the anodic region of the voltammogram (away from equilibrium) and can be used for assessment of the oxidation of carbon. The Butler Volmer high field approximation can be written as:

$$i = i_0 \exp\left(\frac{\alpha_a \eta F}{RT}\right) \quad \dots(12)$$

$$i = nFv = nFk_a [C_A] \exp\left(\frac{(1-\alpha)\eta F}{RT}\right) \quad \dots(13)$$

where i is the electrode current density (A/m²), i_0 is the exchange current density (A/m²), α is the charge transfer coefficient, η is the overpotential (V), F is the faradaic constant (C/mol), R is the universal gas constant (J/K/mol), T is the absolute temperature (K), k_a is the anodic reaction rate constant (/s), C_A is the concentration of the reactant being oxidised (mol/m³), and v is the rate of reaction (mol/m³/s). The value of $(1-\alpha)$ can also be referred to as α_a which is the overall anodic charge transfer coefficient.

Through the application of the anodic high field Butler-Volmer equation on the proposed mechanism, the transfer coefficient α_a can be calculated sequentially assuming each step of the electrochemical reaction mechanism is the rate determining step (RDS). Further assumptions that this approach makes are that all reactions/steps before the RDS are in quasi-equilibrium, there is only one reaction or step that controls the rate of the reaction, no step can have more than two

chemical reactants, and that charge transfer steps are a one electron transfer step only.

The rate of reaction (v) depends on three main driving forces including:

1. The rate constant (k_a), specific to the reaction taking place.
2. The amount of the reacting species available. This can be either the concentration of the ionic species in solution, available surface sites for adsorption or alternatively the coverage of the electrode surface with a species formed in previous steps.
3. If the reaction is electrochemical, it will also have a potential dependent driving force (involves the transfer coefficient).

The reaction scheme shown in Eqns (5)-(11) is heavily dependent on species adsorption and transformation at the carbon surface. Therefore, the surface coverage of the O^{2-} species on the reactive carbon sites needs to be defined. It can be assumed that not all of the reactive carbon sites are occupied at steady state and there is equilibrium between the occupied and non-occupied sites, and the fraction of occupied reactive sites can be expressed as a function of the surface coverage; i.e.,

$$\theta_T = \frac{\Gamma}{\Gamma_{\max}} \quad \dots(14)$$

where θ_T indicates the coverage of the electrode with adsorbed species, Γ the actual surface coverage of species on the active sites and $\Gamma_{\max}$ is the total number of reaction sites. It should be noted that $\Gamma_{\max}$ varies considerably depending on the carbon type used. In the case of graphite, this will be much smaller than a more porous and disordered material such as activated carbon or even coal [11, 20].

The surface coverage (θ_T) can be further defined as the sum of the occupied reactive sites throughout the entire reaction mechanism as Steps (1)-(7) occur through the same reactive site; i.e.,

$$\theta_T = \theta_{C_{SR}O^{2-}} + \theta_{C_{SR}O^-} + \theta_{C_{SR}O} + \theta_{C_{SR}O_2^{2-}} + \theta_{C_{SR}O_2^-} + \theta_{C_{SR}O_2} \quad \dots(15)$$

At a point far from the equilibrium potential where the anodic oxidation is occurring at steady state, it is assumed for this analysis that the coverage of the electrode (θ_T) does not change and that,

beyond this point, the total coverage will not change with increasing potential. It is further noted that θ_T will tend towards being equal to the coverage of species involved in the rate determining step as this species will remain at the electrode surface for a longer period of time than other more quickly consumed reactants.

The output of this analysis (full derivation available in Appendix A) is a current prediction based on which step of the oxidation mechanism is the rate determining step (RDS). A summary of these outputs (assuming a temperature of 500°C (773.15 K)) is shown in Table 1.

This data can be used to analyse experimental outputs for any molten carbonate systems to compare observed outputs with those predicted using the proposed mechanism of Cherepy et al. [17] and the derivation carried out here. Generally, the Tafel slope and transfer coefficient are used to determine the relative rate of charge transfer for a specific reaction. Changes in the Tafel slope can indicate changes in the reaction mechanism since this will be related to a change in the charge transfer rate at the electrode surface and may be indicative of a changed RDS or mechanistic pathway. In this work, the Tafel slope and anodic transfer coefficient have been used for comparison to theoretically derived values in order to indicate possible rate determining pathways of the oxidation reaction.

3.2. Mechanistic Analysis using Fixed-Carbon Working Electrodes

LSV was carried out on both graphite and coal based working electrodes in order to observe changes to the Tafel behaviour of the respective carbon types. The LSV and respective Tafel plot for a pure graphite working electrode are shown in Figure 3. The LSV behaviour for the electrochemical arrangement used to produce the data in this figure has previously been observed to be highly reproducible and stable [14]. Tafel analysis reveals two oxidation regions. The first is at low polarisation, close to the reversible potential of the system. The second continues over a wide potential region (between -0.1 V to 0.2 V vs C/CO₂/CO₃²⁻) and is reflective of the main oxidation reaction occurring on the graphite electrode. Results shown here are consistent with the analysis of

Cooper et al. who found two distinct oxidation regions occurring over experiments conducted by others under widely varied conditions [3]. However, Cooper et al. did not examine Tafel behaviour and instead suggested an inflection point from polarisation curves.

Results for the performance of a coal based working electrode are shown in Figure 4. The coal based working electrode far outperforms that of the graphite with close to a two-fold increase in current density (9.97 and 19.95 mA/cm² at 0.2 V vs C/CO₂/CO₃²⁻ on graphite and coal, respectively). The improved performance of coal materials compared to graphite has not been observed to this extent previously, although improved behaviour on carbon with high surface functionalization has been previously investigated and found to have improved oxidative behaviour compared to graphitic counterparts [11].

Coal also shows different Tafel behaviour. In this case there are three clear Tafel regions at low, mid and high potentials. The mid and high potential regions make up the majority of the oxidative activity occurring on the electrode while the low potential region may not have reached equilibrium where the Butler-Volmer model applies. A summary of observed Tafel slopes along with calculated anodic transfer coefficient and corresponding RDS is given in Table 2 for both graphite and coal working electrodes.

It can be seen in Table 2 that the RDS for coal and graphite varies depending on the potential region. Under low polarisation, both materials tend towards limiting steps related to the second oxygen anion adsorption step, as previously suggested for the mechanism [6]. However the major RDS for graphite appears to fall within the region of the initial charge transfer. This is also the case for the mid-range potential region for coal. Oxidation on coal also has a further reaction region where the Tafel slope and anodic transfer coefficient do not fall within the range predicted by the derivation carried out here. This may be a result of variation in the coal surface as it is consumed, however is more likely to stem from a change in the reaction mechanism.

All assumptions relating to the oxidation mechanism have previously assumed that the mechanism involves the oxide anion and that fast dissociation of the oxide in the carbonate melt

occurs at the electrode double layer. However, it may be that the carbonate is in fact directly involved in the oxidation without dissociation to its oxide anion in the case of a carbonate melt. This could involve direct adsorption of the carbonate to the electrode surface and subsequent dissociation, or could be more complex involving replacement of surface functional groups. Since the change is specific to coal and not observed on graphite, it is likely to be related to the functionalised nature of the carbon undergoing oxidation.

4. CONCLUSIONS

Kinetic analysis of the oxidation of carbon in a carbonate media can give valuable kinetic information able to be used for quantitative assessment of the oxidation mechanism of carbon. Here, it has been shown that mechanistically, coal and graphite have similar behaviour at potentials close to the equilibrium potential. However the large deviation at high polarisation, with coal exhibiting an additional oxidation region, has not been previously observed and is likely indicative of a change in the oxidation mechanism at this point. The evidence shown here also supports mechanistic investigations which suggest that charge transfer and not oxide adsorption is a rate determining factor in the achievable current density of graphite in a carbonate melt. This behaviour is also shown in a similar polarisation regime on coal.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- [1] T. M. Gür; Critical Review of Carbon Conversion in “Carbon Fuel Cells”. *Chem. Rev.*, 2013. 113(8): p. 6179-6206.
- [2] S. Giddey, S. P. S. Badwal, A. Kulkarni and C. Munnings; A comprehensive review of direct carbon fuel cell technology. *Prog. Energy Comb. Sci.*, 2012. 38(3): p. 360-399.
- [3] J. F. Cooper and J. R. Selman; Analysis of the carbon anode in direct carbon conversion fuel cells. *Int. J. Hydrogen Energy*, 2012. 37(24): p. 19319-19328.
- [4] J. F. Cooper; Direct Conversion of Coal Derived Carbon in Fuel Cells, in *Recent Trends in Fuel Cell Science and Technology*, S. Basu, Editor. 2007, Anamaya Publishers: New Delhi, India.
- [5] X. Xu, W. Zhou, F. Liang and Z. Zhu; Optimization of a direct carbon fuel cell for operation below 700°C. *Int. J. Hydrogen Energy*, 2013. 38(13): p. 5367-5374.
- [6] C. Q. Wang, J. Liu, J. Zeng, J. L. Yin, G. L. Wang, D. X. Cao; Significant improvement of electrooxidation performance of carbon in molten carbonates by the introduction of transition metal oxides. *J. Power Sources*, 2013. 233: p. 244-251.
- [7] A. Elleuch, J. Yu, A. Boussetta, K. Halouani and Y. Li; Electrochemical oxidation of graphite in an intermediate temperature direct carbon fuel cell based on two-phases electrolyte. *Int. J. Hydrogen Energy*, 2013. 38(20): p. 8514-8523.
- [8] B. Cantero-Tubilla, C. Xu, J. W. Zondlo, K. Sabolsky and E. M. Sabolsky; Investigation of anode configurations and fuel mixtures on the performance of direct carbon fuel cells (DCFCs). *J. Power Sources*, 2013. 238: p. 227-235.
- [9] X. Li, Z. Zhu, R. De Marco, J. Bradley and A. Dicks; Modification of Coal as a Fuel for the Direct Carbon Fuel Cell. *J. Phys. Chem. A*, 2010. 114(11): p. 3855-3862.
- [10] D. Cao, Y. Sun and G. Wang; Direct carbon fuel cell: Fundamentals and recent developments. *J. Power Sources*, 2007. 167(2): p. 250-257.
- [11] X. Li, Z. Zhu, J. Chen, R. De Marco, A. Dicks, J. Bradley and G. Lu; Surface modification of carbon fuels for direct carbon fuel cells. *J. Power Sources*, 2009. 186(1): p. 1-9.

- [12] X. Li, Z. H. Zhu, R. De Marco, A. Dicks, J. Bradley, S. Liu and G. Q. Lu; Factors That Determine the Performance of Carbon Fuels in the Direct Carbon Fuel Cell. *Ind. Eng. Chem. Res.*, 2008. 47(23): p. 9670-9677.
- [13] R. D. Weaver, Direct Electrochemical Generation of Electricity from Coal: Quarterly Progress Report. 1979: Stanford Research Institute.
- [14] J. Tulloch, J. A. Allen, L. Wibberley and S. W. Donne; Influence of selected coal contaminants on graphitic carbon electro-oxidation for application to the direct carbon fuel cell. *J. Power Sources*, In Press (2014).
- [15] H. Li, Q. Liu and Y. Li, A carbon in molten carbonate anode model for a direct carbon fuel cell. *Electrochim. Acta*, 2010. 55(6): p. 1958-1965.
- [16] W. E. Haupin and W.B. Frank, Electrometallurgy of Aluminium, in *Comprehensive Treatise of Electrochemistry*, J.O.M. Bockris, et al., Editors. 1981, Plenum Press: New York. p. 301-325.
- [17] N. J. Cherepy, R. Krueger, K. J. Fiet, A. F. Jankowski and J. F. Cooper; Direct conversion of carbon fuels in a molten carbonate fuel cell. *J. Electrochem. Soc.*, 2005. 152(1): p. A80-A87.
- [18] G. Blyholder and H. Eyring, Kinetics of graphite oxidation. *J. Phys. Chem.*, 1957. 61(5): p. 682-688.
- [19] G. J. Janz and M. R. Lorenz; Solid-Liquid Phase Equilibria for Mixtures of Lithium, Sodium, and Potassium Carbonates. *J. Chem. Eng. Data*, 1961. 6(3): p. 321-323.
- [20] X. Li, Z. Zhu, R. De Marco, J. Bradley and A. Dicks; Evaluation of raw coals as fuels for direct carbon fuel cells. *J. Power Sources*, 2010. 195(13): p. 4051-4058.

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Table 1. Equations derived for prediction of current, transfer coefficient and Tafel slope for each step as the RDS.

Table 2. Summary of Tafel behaviour, anodic transfer coefficient and rate determining step of the anodic oxidation on graphite and coal

Figure 1. Possible reaction pathway for carbon oxidation from a single reactive surface site.

Figure 2. Possible reaction pathway for carbon oxidation from two reactive surface sites (Originally proposed by Cherepy et al. [17] [1]).

Figure 3. Graphite working electrode oxidation with a scan rate of 1 mV/s at 500°C in the low melting temperature Li/Na/K eutectic.

Figure 4. Coal based working electrode oxidation with a scan rate of 1 mV/s at 500°C in the low melting temperature Li/Na/K eutectic.

Table 1. Equations derived for prediction of current, transfer coefficient and Tafel slope for each step as the RDS.

RDS	Predicted Current	α_a	$\partial V/\partial \log(j)$
(1)	$j_1 = 4Fk_1[O^{2-}](1 - \theta_T)$	-	-
(2)	$j_2 = \frac{4Fk_2k_1}{k_{-1}}[O^{2-}](1 - \theta_T) \exp\left\{\frac{(1 - \alpha)VF}{RT}\right\}$	0.5	0.307
(3)	$j_3 = \frac{4Fk_3k_2k_1}{k_{-2}k_{-1}}[O^{2-}](1 - \theta_T) \exp\left\{\frac{(2 - \alpha)VF}{RT}\right\}$	1.5	0.102
(4)	$j_4 = \frac{4Fk_4k_3k_2k_1}{k_{-3}k_{-2}k_{-1}}[O^{2-}]^2(1 - \theta_T) \exp\left\{\frac{2VF}{RT}\right\}$	2.0	0.077
(5)	$j_5 = \frac{4Fk_5k_4k_3k_2k_1}{k_{-4}k_{-3}k_{-2}k_{-1}}[O^{2-}]^2(1 - \theta_T) \exp\left\{\frac{(3 - \alpha)VF}{RT}\right\}$	2.5	0.061
(6)	$j_6 = \frac{4Fk_6k_5k_4k_3k_2k_1}{k_{-5}k_{-4}k_{-3}k_{-2}k_{-1}}[O^{2-}]^2(1 - \theta_T) \exp\left\{\frac{(4 - \alpha)VF}{RT}\right\}$	3.5	0.044

The Tafel slope was calculated using constants R (universal gas constant) and F (Faradays constant) with a temperature of 500°C (773.15 K).

Table 2. Summary of Tafel behaviour, anodic transfer coefficient and rate determining step of the anodic oxidation on graphite and coal

	POTENTIAL REGION	$\delta V/\delta \log(j)$	α_a	RDS
GRAPHITE	LOW (<0.1 V)	0.076	2.0	Step 4
	HIGH (0.1<E<0.3)	0.250	0.6	Step 2-3
COAL	LOW (<-0.2 V)	0.045	3.5	Step 6
	MID (-0.2<E<0 V)	0.208	0.74	Step 2-3
	HIGH (0.4<E<0.1)	0.646	n/a	n/a

APPENDIX A: Kinetic Derivation

A1. Step (1) as RDS

To begin the Butler-Volmer approach we assume Step (1) is the RDS, and since it is a chemical step then the rate of the reaction, (v) can be described by,

$$v_1 = k_1[O^{2-}](1 - \theta_T) \quad \dots(A1)$$

Thus the current from Step (1) as the RDS can be defined by,

$$j_1 = 4Fk_1[O^{2-}](1 - \theta_T) \quad \dots(A2)$$

This implies that if Step (1) is the RDS then the electrochemical reaction would give a constant current irrespective of the overpotential.

A2. Step (2) as RDS

Next, Step (2) is assumed to be the rate determining step for the mechanism. This presumes that Step (1) is in quasi-equilibrium; i.e.,

$$v_1 = v_{-1} \quad \dots(A3)$$

Substituting for v from (A1) and assuming the desorption depends on the coverage of O^{2-} yields,

$$k_1[O^{2-}](1 - \theta_T) = k_{-1}\theta_{C_{SR}O^{2-}} \quad \dots(A4)$$

$$\theta_{C_{SR}O^{2-}} = \frac{k_1}{k_{-1}} [O^{2-}](1 - \theta_T) \quad \dots(A5)$$

As Step (2) is an electrochemical step, its rate will be defined by both the $\theta_{C_{SR}O^{2-}}$ occupied reactive carbon sites, and the overpotential; i.e.,

$$v_2 = k_2\theta_{C_{SR}O^{2-}} \exp\left\{\frac{(1 - \alpha)VF}{RT}\right\} \quad \dots(A6)$$

Substitution of $\theta_{C_{SR}O^{2-}}$ from Eqn (A4) into Eqn (A6) using Eqn 9, and assuming $n=4$, gives a current which can be defined by,

$$j_2 = \frac{4Fk_2k_1}{k_{-1}} [O^{2-}](1 - \theta_T) \exp\left\{\frac{(1 - \alpha)VF}{RT}\right\} \quad \dots(A7)$$

Taking the log of both sides of the above expression and assuming the oxide anion concentration,

occupied active sites and rate constants are not potential dependent results in a combined constant, named K_2 , i.e.,

$$\log(j_2) = \log(K_2) + \frac{(1 - \alpha)VF}{2.303RT} \quad \dots(A8)$$

Differentiating the above expression with respect to V yields,

$$\frac{\partial V}{\partial \log(j)} = \frac{2.303RT}{(1 - \alpha)F} \quad \dots(A9)$$

This result indicates that $\alpha_a = 1 - \alpha = 0.5$ (assuming $\alpha = 0.5$ for an electrochemical reaction step). At a temperature of 500°C, the gradient of the V versus $\log(j)$ curve will have a slope of 0.307 were Step (2) the RDS of the system.

A3. Step (3) as RDS

Next, let Step (3) be the rate determining step for the mechanism. This presumes that Steps (1) and (2) are in quasi-equilibrium; i.e.,

$$k_2 \theta_{C_{SR}O^{2-}} \exp\left\{\frac{(1 - \alpha)VF}{RT}\right\} = k_{-2} \theta_{C_{SR}O^-} \exp\left\{\frac{-\alpha VF}{RT}\right\} \quad \dots(A10)$$

Substituting $\theta_{C_{SR}O^{2-}}$ from Eqn (A5) and solving for $\theta_{C_{SR}O^-}$ gives:

$$\theta_{C_{SR}O^-} = \frac{k_2 k_1}{k_{-2} k_{-1}} [O^{2-}] (1 - \theta_T) \exp\left\{\frac{VF}{RT}\right\} \quad \dots(A11)$$

As Step (3) is an electrochemical step, its rate will be defined by the $\theta_{C_{SR}O^-}$ occupied reactive carbon sites, and the overpotential; i.e.,

$$v_3 = k_3 \theta_{C_{SR}O^-} \exp\left\{\frac{(1 - \alpha)VF}{RT}\right\} \quad \dots(A12)$$

Substitution of $\theta_{C_{SR}O^-}$ from Eqn (A11) into Eqn (A12) using Eqn 9, and assuming $n=4$, gives a current which can be defined by:

$$j_3 = \frac{4Fk_3 k_2 k_1}{k_{-2} k_{-1}} [O^{2-}] (1 - \theta_T) \exp\left\{\frac{(2 - \alpha)VF}{RT}\right\} \quad \dots(A13)$$

Taking the log of both sides and differentiating with respect to V (again, assuming no potential

dependence of coverage value) yields,

$$\frac{\partial V}{\partial \log(j)} = \frac{2.303RT}{(2 - \alpha)F} \quad \dots(A14)$$

This result suggests that $\alpha_a = 2 - \alpha = 1.5$, or the gradient of the V versus $\log(j)$ curve will have a slope of 0.102 were Step (3) the rate determining step of the system.

A4. Step 4 as the RDS

Next, Step (4) is assumed to be the rate determining step for the mechanism. This presumes that Steps (1), (2) and (3) are in quasi-equilibrium; i.e.,

$$k_3\theta_{\text{C}_{\text{SR}}\text{O}^-} \exp\left\{\frac{(1 - \alpha)VF}{RT}\right\} = k_{-3}\theta_{\text{C}_{\text{SR}}\text{O}} \exp\left\{\frac{-\alpha VF}{RT}\right\} \quad \dots(A15)$$

Substituting $\theta_{\text{C}_{\text{SR}}\text{O}^-}$ from Eqn (A11) and rearranging of Eqn (A15) gives:

$$\theta_{\text{C}_{\text{SR}}\text{O}} = \frac{k_3k_2k_1}{k_{-3}k_{-2}k_{-1}}[O^{2-}](1 - \theta_T) \exp\left\{\frac{2VF}{RT}\right\} \quad \dots(A16)$$

As Step (4) is a chemical step its rate is not dependent on the potential but rather the adsorption of the O^{2-} on the number of $\text{C}_{\text{SR}}\text{O}$ sites, as such it can be defined by:

$$v_4 = k_4\theta_{\text{C}_{\text{SR}}\text{O}}[O^{2-}] \quad \dots(A17)$$

Substitution of $\theta_{\text{C}_{\text{SR}}\text{O}}$ from Eqn (A16) into Eqn (A17) and using Eqn 9 results in the current from

Step (4) as the RDS being defined by:

$$j_4 = \frac{4Fk_4k_3k_2k_1}{k_{-3}k_{-2}k_{-1}}[O^{2-}]^2(1 - \theta_T) \exp\left\{\frac{2VF}{RT}\right\} \quad \dots(A18)$$

Taking the log of both sides of Eqn (A18) and differentiating with respect to V yields:

$$\frac{\partial V}{\partial \log(j)} = \frac{2.303RT}{2F} \quad \dots(A19)$$

This result suggests that $\alpha_a = 2$ or the gradient of the V versus $\log(j)$ curve will have a slope of 0.077 if Step (4) was the RDS of the system.

A5. Step 5 as RDS

Next, Step (5) is assumed to be the rate determining step for the mechanism. This presumes that Steps (1), (2), (3) and (4) are in quasi-equilibrium; i.e.,

$$k_4 \theta_{\text{C}_{\text{RS}}\text{O}} [\text{O}^{2-}] = k_{-4} \theta_{\text{CO}_2^{2-}} \quad \dots(\text{A20})$$

Rearrangement of Eqn (A20) and substitution for $\theta_{\text{C}_{\text{SR}}\text{O}}$ from Eqn (A16) gives,

$$\theta_{\text{C}_{\text{SR}}\text{O}_2^{2-}} = \frac{k_4 k_3 k_2 k_1}{k_{-4} k_{-3} k_{-2} k_{-1}} [\text{O}^{2-}]^2 (1 - \theta_{\text{T}}) \exp \left\{ \frac{2VF}{RT} \right\} \quad \dots(\text{A21})$$

As Step (5) is an electrochemical step, its rate will be defined by the $\theta_{\text{C}_{\text{SR}}\text{O}_2^{2-}}$ occupied reactive carbon sites, and the overpotential; i.e.,

$$v_5 = k_5 \theta_{\text{C}_{\text{SR}}\text{O}_2^{2-}} \exp \left\{ \frac{(1 - \alpha)VF}{RT} \right\} \quad \dots(\text{A22})$$

Substitution of $\theta_{\text{C}_{\text{SR}}\text{O}_2^{2-}}$ from Eqn (A21) into Eqn (A22) using Eqn 9 to define current density leaves expression:

$$j_5 = \frac{4Fk_5 k_4 k_3 k_2 k_1}{k_{-4} k_{-3} k_{-2} k_{-1}} [\text{O}^{2-}]^2 (1 - \theta_{\text{T}}) \exp \left\{ \frac{(3 - \alpha)VF}{RT} \right\} \quad \dots(\text{A23})$$

Taking the log of both sides and differentiating the above expression with respect to V yields:

$$\frac{\partial V}{\partial \log(j)} = \frac{2.303RT}{(3 - \alpha)F} \quad \dots(\text{A24})$$

This result suggests that $\alpha_a = 3 - \alpha = 2.5$ or the gradient of the V versus $\log(j)$ curve will have a slope of 0.061 were step (5) the RDS of the system.

A6. Step 6 as RDS

Finally, Step (6) is assumed to be the rate determining step for the mechanism. This presumes that Steps (1), (2), (3), (4) and (5) are in quasi-equilibrium; i.e.,

$$k_5 \theta_{\text{C}_{\text{SR}}\text{O}_2^{2-}} \exp \left\{ \frac{(1 - \alpha)VF}{RT} \right\} = k_{-5} \theta_{\text{C}_{\text{SR}}\text{O}_2^-} \exp \left\{ \frac{-\alpha VF}{RT} \right\} \quad \dots(\text{A25})$$

Rearrangement of Eqn (A25) and substitution for $\theta_{\text{C}_{\text{SR}}\text{O}_2^{2-}}$ from Eqn (A21) gives:

$$\theta_{\text{C}_{\text{SR}}\text{O}_2^-} = \frac{k_5 k_4 k_3 k_2 k_1}{k_{-5} k_{-4} k_{-3} k_{-2} k_{-1}} [\text{O}^{2-}]^2 (1 - \theta_T) \exp\left\{\frac{3VF}{RT}\right\} \quad \dots(\text{A26})$$

As Step (6) is an electrochemical step, its rate will be defined by the $\theta_{\text{C}_{\text{SR}}\text{O}_2^-}$ occupied reactive carbon sites, and the overpotential; i.e.,

$$v_6 = k_6 \theta_{\text{C}_{\text{SR}}\text{O}_2^-} \exp\left\{\frac{(1 - \alpha)VF}{RT}\right\} \quad \dots(\text{A27})$$

Substitution of $\theta_{\text{C}_{\text{SR}}\text{O}_2^-}$ into Eqn (A27) yields:

$$v_6 = \frac{k_6 k_5 k_4 k_3 k_2 k_1}{k_{-5} k_{-4} k_{-3} k_{-2} k_{-1}} [\text{O}^{2-}]^2 (1 - \theta_T) \exp\left\{\frac{(4 - \alpha)VF}{RT}\right\} \quad \dots(\text{A28})$$

Thus the current from Step (6) as the RDS can be defined by,

$$j_6 = \frac{4F k_6 k_5 k_4 k_3 k_2 k_1}{k_{-5} k_{-4} k_{-3} k_{-2} k_{-1}} [\text{O}^{2-}]^2 (1 - \theta_T) \exp\left\{\frac{(4 - \alpha)VF}{RT}\right\} \quad \dots(\text{A29})$$

Taking the log of both sides of the above expression and combining the constants results in:

$$\log(j_6) = \log(K_6) + \frac{(4 - \alpha)VF}{2.303 RT} \quad \dots(\text{A30})$$

Differentiating the above expression with respect to V yields:

$$\frac{\partial V}{\partial \log(j)} = \frac{2.303RT}{(4 - \alpha)F} \quad \dots(\text{A31})$$

This result suggests that $\alpha_a = 4 - \alpha = 3.5$ or the gradient of the V versus $\log(j)$ curve will have a slope of 0.044 were step (6) the RDS of the system.

Figure 1. Possible reaction pathway for carbon oxidation from a single reactive surface site.

Figure 2. Possible reaction pathway for carbon oxidation from two reactive surface sites (Originally proposed by Cherepy et al. [17]).

Figure 3. Graphite working electrode oxidation with a scan rate of 1 mV/s at 500°C in the low melting temperature Li/Na/K eutectic.

Figure 4. Coal based working electrode oxidation with a scan rate of 1 mV/s at 500°C in the low melting temperature Li/Na/K eutectic.