



# 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.

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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 CO<sub>2</sub> 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, CO<sub>3</sub><sup>2-</sup>. As such the carbonate species must dissociate within the double layer at the current collector/carbon/electrolyte interface prior to reaction; i.e.,

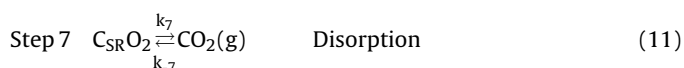
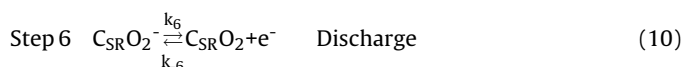
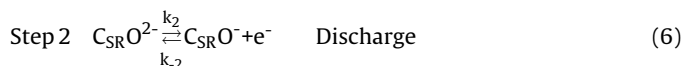


Despite extensive work investigating the electrochemical oxidation of carbon in molten medium [3,5–9], there still exists great uncertainty around the mechanism of this oxidation reaction. This reaction has been shown to have an onset potential sensitive to several parameters within the system, with 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

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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), the  $O^{2-}$  ion is proposed to adsorb at a surface reactive sites on the carbon ( $C_{SR}$ ). The adsorbed  $C_{SR}O^{2-}$  species can then undergo two, single electron transfers to form  $C_{SR}O$ . The relatively stable  $C_{SR}O$  carbon site, it is suggested, then adsorbs a second  $O^{2-}$  adsorption to form  $C_{SR}O_2^{2-}$ . To finish the oxidation reaction the  $C_{SR}O_2^{2-}$  species then undergoes two sequential single electron transfer reactions to form  $C_{SR}O_2$ , 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 Fig. 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 Fig. 2. The adsorption of the oxide anion is shown in Fig. 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.

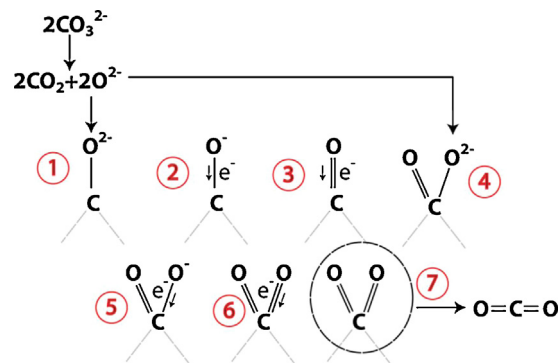


Fig. 1. Possible reaction pathway for carbon oxidation from a single reactive surface site.

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  $CO_2$  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 ( $\alpha_a$ ) as these are easily measured using the experimental design developed in previous work [14]. These derived parameters are then compared to experimental data

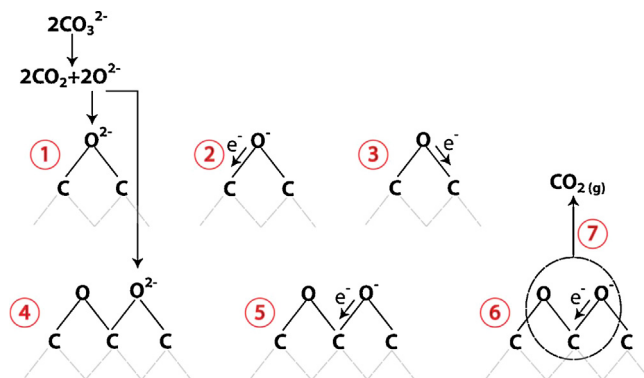


Fig. 2. Possible reaction pathway for carbon oxidation from two reactive surface sites (Originally proposed by Cherepy et al. [17][1]).

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