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Modeling of the Electrochemical Oxidation of Contaminated Carbon in a Molten Carbonate Electrolyte

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Like all fuel cell devices the DCFC produces electrical energy through the reduction of a species, most commonly O_2, within the cathodic side of the cell, with oxidation of the fuel source within the anodic side. Constant supply of oxidant and fuel to these respective compartments within the cell ensures continued power output from these devices.

The proposed mechanism through which the electrochemical oxidation of carbon is thought to occur is a mechanism that was adapted from earlier works of Haupin and Frank [1], which a series of chemical and electrochemical (charge transfer) steps ultimately resulting in the evolution of CO_2, i.e.,

$C_{SR} + O^{2-} \rightarrow C_{SR}O^{2-}$	Chemical	(1)
$C_{SR}O^{2-} \rightarrow C_{SR}O^{-} + e^{-}$	Electrochemical	(2)
$C_{SR}O^{-} \rightarrow C_{SR}O + e^{-}$	Electrochemical	(3)
$C_{SR}O + O^{2-} \rightarrow C_{SR}O_2^{2-}$	Chemical	(4)
$C_{SR}O_2^{2-} \rightarrow C_{SR}O_2^{-} + e^{-}$	Electrochemical	(5)
$C_{SR}O_2^{-} \rightarrow CO_{2\,(g)} + e^{-}$	Electrochemical	(6)

where, C_{SR} is a reactive site on the carbon surface at which the oxidation reaction can occur.

As such the Butler-Volmer model and equation for electrode kinetics (below), allows the calculation of a predicted electrical current on an electrode on the basis of the potential of that electrode, considering both the cathodic and anodic reactions occur at the electrode.

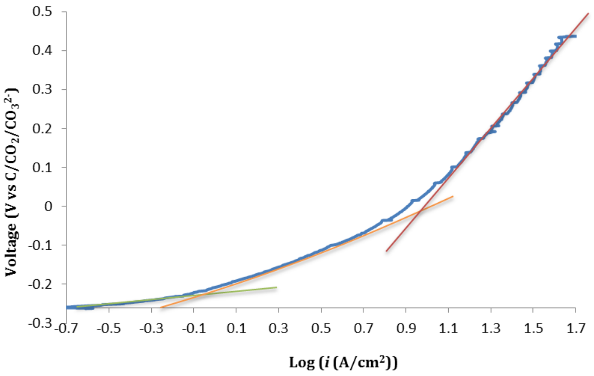
$$i = i_o\left\{\exp\left(\frac{\alpha_a VF}{RT}\right) - \exp\left(-\frac{\alpha_c VF}{RT}\right)\right\}$$

However, the Butler-Volmer equation in this form accounts for both the anodic and cathodic regions of the voltammogram. In the potential sweeps performed during the experimental course of this work, only the carbon oxidation or anodic region of the voltammogram was of interest, with the cathodic component essentially having no influence. As such the Buttler-Volmer could be expressed in its High Field Approximation form.

$$i = i_o\left\{\exp\left(\frac{\alpha_a VF}{RT}\right)\right\}$$

From this analysis a set of values were determined for the series of reactions in the proposed mechanism, which then could be used to determine the rate determining step (RDS) of the carbon oxidation reaction within a specifically designed electrochemical cell.

By analyzing the electrochemical data form the cell in the form of a tafel plot, the tafel slopes were used to determine the RDS



From the mechanism analysis and calculations and results from the tafel plot it was clear that the RDS of the electrochemical oxidation mechanism is notably sensitive to changes in either the carbon type/functionality, or the any contaminants that constitutes the carbon working electrode in the electrochemical cell.

[1] W. E. Haupin and W. B. Frank, in Comprehensive Treatise of Electrochemistry, Electrochemical Processing, Volume 2, J. O'M. Bockris, B. E. Conway, E. Yeager, and R. E. White, Editors, Pages 301-325, Plenum Press, New York ,1981.