

An Investigation into Alkali Metal Carbonate Mixtures for Application in Direct Carbon Fuel Cells

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DECLARATION

STATEMENT OF ORIGINALITY

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ACKNOWLEDGEMENT OF AUTHORSHIP

I have received advice and guidance from my supervisors which has been within the scope of normal supervisor-student relations. Apart from their help, this thesis has been my own work.

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*Imagination is more important than knowledge. For knowledge is limited,
while imagination embraces the entire world, and all there will ever be to know and understand.*

Albert Einstein

Publications

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Abstract

This work is aimed at examining the properties of alkali metal carbonate mixtures, which are in turn related to their role in the DCFC. Properties of the individual alkali metal carbonates; i.e., Li_2CO_3 , Na_2CO_3 and K_2CO_3 are well understood. However, there are gaps in the literature and even contradictions when it comes to assessing mixtures. In the DCFC, alkali metal carbonate mixtures are commonly used as the secondary electrolyte. Hence, this experimental work begins with analysing simple binary mixtures. X-ray diffraction (XRD) and Differential thermal analysis (DTA) are used to examine the thermal and crystallographic properties respectively. Consideration is given to the formation of intermediate compounds; e.g., LiNaCO_3 , which are thought to be produced when the system is recrystallised from a molten state. A kinetic analysis was performed from the DTA data using the Friedman method. It was discerned that both a dominant and excess phases exist in the melt. Here DTA peaks were attributed to either melting or dissolution processes.

Following this a similar investigation was carried out in terms of ternary mixtures. It was found that intermediate compound formation also takes place. For ternary systems this generally leads to the formation of mixtures that exhibit a greater number of phases post thermal fusion compared to their binary counterparts. XRD was able to show several different phases, however FTIR unable to detect this. Therefore, it was deduced that changes resulting from thermal fusion affect the unit cell configuration over a range of greater than $\sim 10 \text{ \AA}$ and not individual bonding interactions. Fusion of the ternary eutectic under varied cooling rates and gas atmospheres; i.e., CO_2 versus N_2 , results in distinctly different XRD patterns for the resultant material. Thus indicating that preparation methods exert a significant effect upon the material produced. This is something that is suggested to contribute to conflict amongst literature findings. A kinetic analysis was performed using both the Freidman method, as was done for the binary mixtures, and the $1-\alpha$ model. The latter of which assumes that the system follows first order kinetics, as would be expected for a simple meting system. It was found that the $1-\alpha$ model is insufficient, therefore giving credence to the hypothesis that both melting and dissolution of distinctly separate phases are both occurring.

Coal has been shown to be a high performing fuel in the DCFC. During operation coal minerals leech into the molten carbonate, hence an investigation was carried out to examine how these minerals affect the mixture. The ternary eutectic was purposefully contaminated with several different inorganics; i.e., Fe_2O_3 , FeS , TiO_2 , CaCO_3 , CaSO_4 , SiO_2 and kaolin in separate experiments. The contaminated mixtures were examined by DTA and the results were compared to the unmodified eutectic. It was found that the contaminants cause liquid phase disruption, which effects the chemical potential of the system. This causes the melting point to shift due contaminant dissolution and the

colligative properties that are associated with solution formation. TiO_2 causes a large activation energy increase upon addition to the mixture. This is due to the rather large specific heat capacity of this compound, which acts as a heat sink and therefore is undesirable for DCFC operation.

The addition of SiO_2 was the only contaminant which caused a melting point increase. The area bound by the DTA peak was analysed over consecutive melt cycles. It was found that alkali metal silicate formation was progressively occurring. Evidence for this was also found from analysing the TGA response and the XRD patterns of systematically contaminated mixtures; i.e., 1, 2 and 5 wt% SiO_2 . Contamination of molten Na_2CO_3 by SiO_2 has been shown to elevate the decomposition temperature from the literature. Hence, this is another example of molten phase destabilization. These concepts were extended to explain the behaviour of kaolin, which caused the maximum melting point reduction of all of the contaminants analysed. The literature shows that adding kaolin to coal impregnated with K_2CO_3 leads to the formation of alkali alumina silicates. This actually deactivates K_2CO_3 as a gasification catalyst. Hence, it is likely that kaolin undergoes this transformation in the experiments presented here and in the DCFC. The product, which is termed ‘modified kaolin’ K_M has been shown to be the most effective electro oxidation catalyst over the course of several studies. The ternary eutectic was contaminated with yttria stabilized zirconia YSZ, which was found to be soluble, however the saturation limit is very low. Therefore it is suggested that the carbonate be purposefully contaminated with YSZ in DCFC operation in order to prevent the YSZ membrane disk from being thinned.

Interactions between carbon and the ternary eutectic were explored. This involved a DTA investigation under N_2 where graphite was used to purposefully contaminate the melt. The kinetic response indicates that graphite is an effective heat sink. This may present an issue for slurry arrangements where excess heat is required to melt the carbonate medium. A noisy response was noted for high loadings of 25 wt% and 50 wt% graphite. This is thought to be due to both the high heat capacity of the graphite interrupting the thermocouple function and activation of the graphite. Alkalies are known to be effective agents for producing activated carbon, the effect of which is to greatly enhance the BET surface area of the material. These contaminated mixtures were analysed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) to look for evidence of activation. The existence of distinctly different carbonate phases was validated. It is also evident that carbonate decomposition to form the corresponding oxide is facilitated at the interface where the melt contacted a graphite particulate. Oxide formation causes the system pH to increase, which further enhances activation.

This then transitioned into a series of gasification experiments where coal char was examined by thermogravimetric analysis (TGA). Samples were heated under N₂, then held isothermally for two hours, before the gas was switched to CO₂. Unmodified coal samples were systematically switched at temperatures between 500°C and 800°C in 50°C increments. Other separate samples were contaminated with the eutectic at loadings of 5, 10 and 25 wt% and the gas was switched at 700°C. It was found that under N₂ carbonate decomposition occurs and also carbothermic reduction leading to gasification. Under CO₂ carbonate reformation occurred, which is the reverse process of decomposition. The reverse Boudouard reaction also occurred under CO₂, causing a rapid mass loss.

A holistic mechanism was devised which integrates the processes of alkali metal carbonate catalysed gasification and electro oxidation. This mechanism was extended to encompass different fuels, such as pristine graphite versus coal, and the effects of adding kaolin to the system. Consideration is also given to enhanced electro oxidation which was noted to accelerate above 0.25 V, particularly in systems doped with kaolin. This is hypothesised to be due to the heterogeneous distribution of oxide in the melt, which is more responsive to the polarizing electric field compared to the carbonate.