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Abstract

The electrochemical oxidation of graphite is investigated to determine the relative influence of the composition of a molten carbonate electrolyte on a solid anode. The binary eutectics of sodium, lithium and potassium carbonates were investigated as well as ternary mixtures including the eutectic and combinations of systematically varied lithium content. It was seen that the combination of cations included in the carbonate melt can influence the electrochemical performance of graphite with binary combinations performing better than ternary in all cases. Very little change in the mechanistic behaviour was observed through tafel analysis; instead it is proposed that the observed kinetic effects are a combination of the catalytic role of all metal cations present as well as the intercalation of lithium into the solid graphite electrode. The effect of lithium intercalation is suggested to lead to a change in the graphite surface polarity which affects product gas bubble formation and dislodgement at the solid anode. Increased lithium concentration, and it is assumed intercalation, encourages smaller bubbles to form which are dislodged at a faster rate than surfaces with less lithium intercalation in the ternary electrolyte. A threshold lithium concentration is reached above approximately 65 % where the electrochemical behaviour is significantly changed and bubble formation behaviour is no longer observed.

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1. Introduction

1.1. Energy Generation

Coal fired power stations produce electricity through several energy transformations. Overall this has the consequence of being only ~40% efficient (1) in transforming chemical energy to electrical energy. Coal combustion is therefore a high carbon intensity energy generation method where large amounts of the greenhouse gas carbon dioxide (CO₂) is emitted, as well as other toxins such as sulfur dioxide (SO₂) and nitrous oxides (NO_x). CO₂ capture systems have been developed; however, with a CO₂ capture system the efficiency of coal fired power stations is further decreased due to parasitic energy use (2). Since coal is abundant and relatively inexpensive to obtain, the role of coal in the production of electrical energy is nevertheless likely to continue until renewable energy becomes viable and mining deposits are exhausted, predicted to occur within the 21st century (3).

1.2. The Direct Carbon Fuel Cell

The direct carbon fuel cell (DCFC) is a viable option as a replacement technology for coal fired power stations. As it is solid carbon which supplies the fuel for the DCFC, a variety of abundant fuels such as coke, tar, biomass, organic waste and of course coal can be used (1).

There are several DCFC arrangements possible (4). Of these, a hybrid design combining the technologies of the solid oxide fuel cell (SOFC) and molten carbonate fuel cell (MCFC) is the most promising arrangement, and can be seen schematically in Figure 1.

The cathode reaction occurs in contact with a solid electrolyte and an O²⁻ ionic conductor, which allows the transport of O²⁻ into the molten carbonate electrolyte. The molten carbonate in solution is assumed to be in equilibrium with O²⁻ and CO₂, as outlined in Figure 1. The carbon fuel provides the active material at the anode, combining with O²⁻ to form CO₂, as well as acting as the current collector in the case of a solid anode. The simplified reactions occurring at each electrode are:

It is the direct electrochemical oxidation of the solid carbon which enables the fuel utilization to be theoretically 100% as the solid carbon fuel and product gases are distinct phases which are easily separated. In reality, cell design limitations suggest a realizable efficiency of around 80% (1), still almost double that of coal fired power plants.

1.3. Molten Carbonate Electrolytes for the DCFC

The hybrid DCFC uses a molten carbonate electrolyte to enable transport of oxygen anions to the reaction site. The electrolyte generally consists of varying ratios of Li_2CO_3 , Na_2CO_3 and K_2CO_3 (1). The melting temperatures of the pure salts are 723 °C, 851 °C and 891°C, respectively, however melting point depression occurs when a mixture of these carbonates are used. Recently, modelling software based on thermodynamic principles has been used to draw a detailed phase diagram which was compared with past experimental results (5) where good general agreement was observed (6). Ternary phase diagrams have also previously been established by Janz et. al (7) and Pelton et. al (8). The ternary carbonate molar composition with the lowest melting point (397 ± 1 °C), i.e. the eutectic, has been found in all investigations to be 43.5:31.5:25.0, $Li_2CO_3:Na_2CO_3:K_2CO_3$ (LiNaK), respectively (6-8).

There are significant differences in the physical and thermal properties of varied compositions of the ternary carbonate and binary mixtures including viscosity and melting temperature, as well as there being influencing factors of the atmosphere to which it is exposed (6, 9). The influence of these varying properties on electrochemical results within a DCFC system has had limited investigation. Cantero-Tubilla et al. appear to be the only research group who have considered the electrochemical impact of variation in carbonate composition (10), where a DCFC arrangement using electrolyte-supported button cells was used to determine overall performance of a base-line carbon-black fuel in electrolytes of various composition. The brief investigation showed that electrolyte composition has a clear influence on the overall electrochemical performance. Both binary LiK and LiNa mixtures outperformed the ternary eutectic, the responses strongly influenced by operating temperature. The authors suggested a catalytic role of the potassium cation, similar to

its catalytic role in thermal carbon oxidation. Evidence for this was not strong however as the performance of LiNa and LiK were both higher than that of the NaK binary, and no further evidence for this was provided.

Within DCFC literature, the ratios of the carbonate mixture used as the electrolyte vary quite considerably and include both binary and ternary mixtures. Table 1 outlines some compositions that have recently been used in DCFC studies. The choice of the carbonate composition, whether it be ternary or binary appears to be relatively arbitrary where very few authors justify the use of a particular composition, typically related to the melting point of the electrolyte.

In some cases, other carbonates or additives have been used to enhance electrochemical behaviour. Kouchachvili et al. (13) observed that the ternary carbonate eutectic, when spiked with 20 wt.% Cs_2CO_3 , melted at a lower temperature than that of the eutectic. Electrochemical performance was also improved when using this additive in the DCFC with petroleum coke used as the carbon fuel. More recently, Liu et al. (21) investigated the use of a different cesium based binary eutectic mixture which included CsVO_3 and MoO_3 salts mixed with a traditional LiNaK ternary eutectic in different ratios. Using an anodic half-cell with a solid graphite working electrode, a high catalytic impact for inclusion of the CsVO_3 - MoO_3 eutectic in a 5:1 ternary:binary ratio was observed with the achievable current density at +0.5 V polarisation more than doubled. Electrochemical effects however were not seen with the addition of coal ash contaminants added to the carbon electrolyte in low concentrations (5wt%) (12), while Wang et al. showed an apparent catalytic effect of only 0.1% NiO added to a LiK binary (the eutectic composition was not used) (22). Clearly, the molten salt environment has the ability to impact on the electrochemistry of the carbon oxidation reaction in a way which is separate to changing the physical or thermal properties of the melt, influencing the oxidation kinetics and potentially the reaction mechanism.

1.4. This Work

Despite the clear impact of the molten salt environment on carbon oxidation, previous work has not considered the possible influence of the lithium ion on the electrochemistry of the anode. Li^+ ions are present in a lithium carbonate containing melt which are free to interact with the carbon fuel. These may pass through micro pores in the carbonaceous structure to lodge within. This process is termed 'lithium intercalation' and is

a well-known phenomenon in the study of Li-ion batteries (23). However, its effects have not been considered in relation to the electrochemistry of the DCFC, possibly due to the prevalence of slurry-type fuel arrangements and a lack of sensitive kinetic analysis at a solid carbon anode submersed in an excess of molten carbonate.

In this work, two series of systematically varied carbonate compositions have been investigated in an anodic half-cell arrangement using a solid graphite electrode at 750°C. In the first series, the lithium content of the electrolyte has been varied while keeping the sodium and potassium mole ratio constant. Compositions were chosen to also take into account the melting temperature as well as the lithium content to allow comparison of lithium content separately to the physical changes imposed through differences in melting temperature. In the second series, the binary eutectic compositions have been investigated and compared on both a mechanistic and kinetic level to determine possible reasons for differences in electrochemical performance of these carbonates and their role in the electrochemical oxidation of carbon.

2. Experimental

2.1. Binary and ternary carbonate electrolytes

Li_2CO_3 , Na_2CO_3 and K_2CO_3 (Sigma; > 99% pure) were dried in an oven (air) at 110°C prior to combining.

The mole ratios of the different electrolytes studied were determined keeping the Na and K composition in the same relative ratio (6:5, $\text{Na}_2\text{CO}_3\text{:K}_2\text{CO}_3$) while varying the lithium content. The final compositions for the “Lithium Series” and “Binary Series”, eutectic compositions determined from the work of Janz et al. (7), are shown in Figure 2[A] and [B], respectively, along with the ternary diagram for these combinations (Figure 2 [B])

The carbonate powders were milled using a mortar and pestle in the ratio specified in Figure 2 for a minimum of 5 min before ball milling (stainless steel balls and vessel) at 200 RPM for 40 minutes. The carbonate mixture was then placed in an alumina crucible and fused by taking the mix up to its melting temperature under a carbon dioxide atmosphere (CoreGas, Food Grade CO₂) and cooling back to room temperature prior to use in the electrochemical cell.

2.2. Anode construction

2.2.1. Graphite Pellet

Graphite (SFG44; Timcal, Timrex, Switzerland) pellets were manufactured in a 13 mm diameter pellet press (International Crystal Laboratories) and compressed at 740 MPa for 5 min. The graphite pellets were then sintered for 4 hours under a nitrogen atmosphere in a tube furnace at 500°C with no observable changes in appearance or mass.

2.2.2. Working Electrode

The essential structure of the working electrode used the design published by Tulloch et al. (12) and included a graphite pellet housed in an alumina tube, which had been specified to match the diameter of the graphite pellet. The pellet was cemented into the tube with a ceramic adhesive (Resbond 989, Ceramic Oxide Fabricators, Australia) and electrical contact to the graphite pellet was made through a chromel wire to ensure good electrical contact. The wire was cemented in place with a conductive Resbond-graphite glue mixture, of which was 50 wt. % SFG44 graphite powder. The electrode was then cured at 65°C in air for 12 hours. This procedure produced a working electrode with a cross sectional geometric area of 1.327 cm² which has been used for current density normalisation in this work.

2.3. Electrochemical Experiments

Electrochemical experimentation was performed using a portable WaveNow potentiostat from Pine Instruments with AfterMath electrochemical software. The experiments performed included the measurement of the open circuit potential (OCP), linear sweep voltammetry (LSV), and chronoamperometry (CA).

A three-electrode high temperature electrochemical anodic half-cell was constructed for the purpose of testing the graphite pellets in a molten carbonate electrolyte, outlined in earlier work (12).

The cell housed a molten electrolyte with a specially manufactured ceramic tile lid which allowed the working (WE), reference (RE) and counter (CE) electrodes to be placed in contact with the electrolyte while also being held securely in place. To maintain constant reference electrode conditions, a constant carbon dioxide atmosphere was maintained via the gas feed at a flow rate of 50 mL min^{-1} (at standard temperature and pressure). A muffle furnace was used to house the electrochemical arrangement and to reach a temperature of 750°C used for the electrochemical experiments performed.

The counter and reference electrode consisted of graphite rods which achieved electrical contact through internally inserted chromel twined wire of a width which formed a good fit upon forced mechanical insertion. The geometric surface area was approximately 4.5 times that of the working electrode (based on an electrolyte depth of 15 mm and electrode diameter of 10 mm).

Experiments were performed identically for each electrolyte studied using a new working electrode for every run. The electrochemical procedure included the insertion of the working electrode at 700°C (or after the fused carbonate salt had become molten) and a wait time of 1 h, after which the initial open circuit potential was measured. Three consecutive linear sweeps were then carried out at 5 mV/s . A slower 1 mV/s scan was then performed, as well as a stepped potential procedure where the electrode potential was sequentially stepped to 0.2 V and 0.5 V versus the reference potential to allow measurement and comparison of the current density. The cell was held at open circuit potential (OCP) for 2 min between each experiment. The applied potential profile used is shown in Figure 3, for example, using 0 V versus the reference as the example open circuit potential.

3. Results and Discussion

3.1. Reproducibility

The reproducibility of the experimental method was firstly investigated to ensure the elevated temperature used did not result in variation in reference system behaviour. Reproducibility of the quasi-reference system

used was confirmed using a graphite electrode immersed in the eutectic carbonate at 500°C (12); however, it is possible that at the increased temperatures necessary for the investigation of increased melting point (>700°C) mixtures will cause changes to the reference conditions due to the influence of Boudouard corrosion at higher temperatures (25). In order to ensure results are reproducible and do not vary in response to changes in the reference electrode and small changes to the working electrode surface and position, several carbonate compositions were repeated, examples of which are shown in Figure 4.

It was found that electrochemical behaviour is reproducible in terms of overpotential and the general shape of the LSV curve, however slight variations can be seen, in particular at high polarisation for the second lowest (SL) carbonate composition (Figure 4 [B]). In fact, this variation is not specific to runs carried out on different days, and variation in electrode behaviour was observed between LSV scans of a single run. Three consecutive linear sweeps, as well as the scan at 1 mV/s are shown for the ternary eutectic composition (LiNaK, E) in Figure 5. It can be seen in Figure 5 that scans carried out at a scan rate of 5 mV/s are very similar at low polarisation, however discrepancies increase with potential as indicated by the standard deviation (Figure 5 [B]). Despite these variations, the current density observed remains within a reproducible region, which is largely contained within current density variations observed when scanning at 1 mV/s, as shown in Figure 5 [A]. The average of the current density for each 5 mV/s scan can be seen to sit neatly in this region and therefore comparison of both the average of the three 5 mV/s scans, as well as the 1 mV/s scan, are able to be reasonably used for comparison of carbonate composition effects.

3.2. LSV Behaviour

LSV behaviour has been examined for carbonate mixtures with molar compositions outlined in Figure 2. A systematic electrochemical assessment has been carried out for each as described in Section 2.3. In order to take into account observed variation between scans, LSV data discussed here includes the current density of each carbonate mixture as the average of three consecutive scans carried out at 5 mV/s with a single 1 mV/s scan representing the region of oxidation current density observed for each. LSV results are shown in Figure 6 and have been grouped into the “Lithium Series”, which includes the ternary eutectic composition, as well as the “Binary series” as outlined in Figure 2.

It can be seen in Figure 6 that the carbonate composition has a clear effect on the electrochemical performance of graphite at 750°C. Differences are enhanced at increased polarisation where current instability is observed. This high potential region has been shown to be the region where mass transfer control starts to dominate in the case of carbon slurry arrangements (26). No diffusion plateau is observed in the case of solid carbon electrodes and the absence of diffusion limitation is also implied in the similarities between the current density achievable at each scan rate (comparison of scan rate shown clearly in Figure 5 [A]). Observed current instability at high polarisation could result from the formation of product gas bubbles at the anode surface which, in the case of the horizontal plane anode used in this study, may become trapped and lead to inhibition through blockage of surface active sites. It is likely that the bubble formation period goes through a nucleation, growth and coalescence period, where the final coalescence of a bubble is then overcome by buoyancy forces resulting in dislodgement and a consequent dramatic increase in available surface active sites, and therefore current density increase. It can be seen in Figure 6 that the scan rate influences the appearance of bubbles as clearly this is a time sensitive observation; i.e., peaks at high polarisation are much sharper and begin earlier for a slower scan rate.

Clear differences in performance can be seen for the carbonate compositions tested. These include changes to the maximum current density achieved and the extent of current instability (maxima/minima) change.

In order to quantify differences observed at low polarisation (prior to current instability), Tafel analysis of each data set was carried out (Figure 7). The Tafel plot was broken into three regions of oxidation where linear regression was carried out to find the Tafel slope in each case to give a maximum R^2 value, presented in Table 2 for each carbonate composition and analysis region. In cases where bubble formation occurred early within the third region (including E, SH and LiK and LiNa) the Tafel slope was calculated to the point where bubble formation begins to cause destabilisation in the Tafel plots.

The RDS indicated in Figure 7 [C] for Step 2 (first electron transfer step) and Step 3 (second electron transfer step) at 750°C have Tafel slopes of 0.406 mV/decade and 0.135 mV/decade respectively (11). These Tafel slopes were calculated theoretically using kinetic analysis of a 7 step oxidation mechanism derived in a

previous publication (11) which involves the adsorption and subsequent oxidation of two consecutive oxide anions as follows:

Region (I) oxidation sits between steps 2 and 3 while Region (II) is closer to Step 2 and Region (III) is not able to be described by the mechanism proposed in Ref. (11). It is inferred from these results however that mechanistic behaviour in each region does not vary significantly as a function of carbonate composition. Since results in Figure 6 show a definite influence of the carbonate on the LSV plot obtained, it is suggested therefore that the rate determining step does not change, however the kinetics of the reaction do change and at low polarisation, prior to current destabilisation, the effect of changing the carbonate composition is to enhance or reduce the electron transfer steps of the first oxide anion adsorbed.

The open circuit potential (OCP) also remains consistent for the carbonate compositions tested with some small variation, shown in Figure 8. It is expected that, due to the reference system used (graphite working electrode), the open circuit potential (OCP) will be approximately zero since reference and working electrodes are both graphite based. The deviation observed is likely to be a result of reference electrode exposure to the carbon dioxide atmosphere used. At lower temperatures this is not expected to influence the reference system; however at the temperature use of 750°C it is possible that the influence of Boudouard corrosion (25) on the exposed reference electrode surface will cause a difference from the working electrode, which is fully submerged in the carbonate melt.

3.2.1. Chronoamperometry and Bubble Formation

Potential hold experiments were also carried out on the graphite working electrodes, including holding at 0.5 and 0.2 V for a period of 2 min, as shown in Figure 9.

Current instability is clearly observed at high potentials (Figure 9 [B] and [D]) while small step changes are also observable at moderate polarisation in some cases (Figure 9 [A] and [C]). The shape of the current-time profile indicates a gradual decline in current density with time, followed by a sharp spike in current which is reproducible over more than once cycle in most cases. The average current density is compared for both potential hold regions over the two series of carbonate concentrations investigated is shown in Figure 10.

It can be seen that the average current density achieved, a general indication of the performance of the graphite electrode in individual carbonate, varies significantly over the lithium series investigated, especially at 0.5 V polarisation, while results in binary eutectics are mostly unchanged. The melting point of each carbonate investigated is also indicated in Figure 10 where the melt temperature varies from 397°C (ternary eutectic) to 710°C (NaK binary eutectic). It has been proposed previously that temperature above the melting point of the specific molten medium used will affect the performance of the carbon oxidation reaction (27). This is clearly not the case in Figure 10 where the experiments were conducted at the same operating temperature and had widely varied melting points as measured using DSC. Effects of the melting temperature are therefore only minor compared to chemical nature of the molten solution studied.

Current behaviour in Figure 10 can be further analysed for bubble formation trends. The area under the current-time curve can be used to calculate the total charge passed over the course of a bubble formation cycle as shown in Figure 11 for the ternary eutectic results at 0.5 V polarisation.

This charge can then be converted into a relative bubble volume making a number of assumptions including the reaction proceeding to carbon dioxide for a 4-electron transfer as per Eqn (1). One carbon dioxide molecule was therefore assumed to be produced for every 4 electrons passed, which was assumed to be at atmospheric pressure within the cell and at the operating temperature of 750°C. The use of atmospheric pressure in the ideal gas law will give an overestimate of the bubble volume since the slight pressurisation of the cell with carbon dioxide gas as well as the small head pressure expected above the working electrode

submerged in molten carbonate likely mean the pressure is higher than atmospheric pressure. The relative bubble volume for each cycle seen at 0.5 V can therefore be calculated as shown in Figure 12.

It is also possible that partial oxidation of carbon to carbon monoxide will occur electrochemically. This would result in a bubble volume twice as large as that of carbon dioxide since 2 electrons are consumed to generate one mole of carbon monoxide, compared to 4 electrons involved in carbon dioxide generation. However, the extent to which CO would be formed is expected to be minimal because of the substantial anodic polarization applied to the electrode, and the submersion of the carbon electrode in the molten carbonate electrolyte. The diameter of the theoretical bubble volume (assuming a sphere) in each case may in fact be larger than feasibly expected on an electrode of 13 mm diameter and indeed the actual bubble diameter will depend on several factors including the extent of bubble agglomeration and incomplete removal, wetting of gas produced with the carbon electrode surface, as well as physical properties of the molten carbonate including viscosity and hydrodynamic pressure (atmospheric pressure is assumed in calculation of relative bubble volume).

Other valuable information regarding the bubble formation behaviour is also indicated in Figure 12, including the period of bubble formation (time (s)) and the relative surface blockage resulting from bubble formed (Figure 12 [B]). Analysis of this information shows that there are several dependencies which can be observed. Figure 12 [A] shows a clear relationship between the bubble period, or time of a single cycle (taken as the average of observable full cycles in a two minute period) and the lithium content of the carbonate. Similarly, there is also a relationship between the bubble volume (presented in mm^3) and the lithium concentration with the same decreasing trend with increasing lithium content observed. This also reflects a relationship between the bubble period and the size of the bubble with large bubbles dislodging over extended time periods and shorter time period for small bubbles. An exception is the bubble volume observed for the SL carbonate composition, which also showed anomalous behaviour in terms of average current density (Figure 10).

Information can also be found from consideration of the relative surface blockage (Figure 12 [B]), which is defined here as the ratio of total charge passed during a single bubble period, and the charge passed only in the bubble formation region (regions defined in Figure 11):

$$\text{Relative blockage} = \frac{\theta_B}{\theta_{ASA}} = \left(\frac{Q_B}{Q_{TOT}} \right)_{\text{Single Cycle}} \quad (11)$$

Where θ_B (dimensionless) represents the active surface sites blocked by the bubble formation, θ_{ASA} is the active surface area, Q_B is the charge passed for a single bubble and Q_{TOT} is the charge passed for both the bubble formed as well as charge passed in the stable reaction region (see Figure 11). The relative blockage calculated represents the extent to which the formation of a product gas bubble limits the active surface sites available at the electrode surface. It can be seen in Figure 12 [B] that the relative surface area blocked by the bubbles formed increases to a plateau of around 30% for the “L” electrolyte.

3.3. Carbonate Medium Impact on Electrochemistry

The only variable which has been changed in this work using a DCFC anodic half-cell is the carbonate composition. All other variables including carbon fuel type and delivery method, operational temperature, pre-treatment and half-cell arrangement are all identical. Observed effects are therefore specific to the molten carbonate composition used. If the effect of changing the carbonate composition only is considered, results could be due to several factors.

3.3.1. Temperature above melting point

It has been observed for molten hydroxide eutectic carbon fuel cell designs (27) that in order to achieve desirable conductivities, the molten electrolyte must be heated to a minimum of 150°C above its melting point. However, in the solid electrode system used here, the temperature of the melt has been seen to have very little influence over the electrochemical activity as observed by comparison of the relative performance of NaK eutectic (MP 710°C) to the LiK eutectic (MP 488°C) where no difference in the average current density can be observed at the same polarisation (Figure 10).

3.3.2. Liquid viscosity changes

The specific carbonate composition effects on viscosity might be expected to play a role in the bubble formation behaviour since viscosity and surface tension can affect the size of carbon dioxide bubbles in a molten carbonate melt (28). All binary compositions are expected to have a higher viscosity than the ternary eutectic (29), with a higher lithium content having a small but notable increase in the viscosity of LiK binary mixtures at temperatures up to 650°C (30). Therefore, the viscosity likely increases slightly across the lithium series investigated here. However, bubble formation behaviour observed for this series (Figure 9) displays the opposite behaviour to that predicted based on viscosity effects alone. Bubble size is expected to be reduced when viscosity and surface tension are low (28); however, analysis of bubble behaviour (Figure 12 [A]) shows that the binary compositions tested result in bubbles which are smaller than the ternary lithium series and the bubble size and period show a clear trend of decreasing with increasing lithium concentration in the melt. At the high temperatures investigated therefore, the viscosity of the carbonate solution is expected to play little to no role in the bubble formation and dislodgement behaviour.

3.3.3. Catalytic effect of cations

The catalytic effect of metal cations on several thermal processes involving chemical reactions of carbon have previously been observed, including the catalytic effect of carbonates on pyrolysis (31) and catalytic effects of alkali metal carbonates on carbon gasification (32).

Recently, Cantero-Tublia et al. investigated the effect of the carbonate composition on the performance of a DCFC using carbon black fuel (10). These authors found the NaK binary performed very poorly over the temperature range investigated (650-800°C) compared to superior performance of LiK in particular (10). Only a small amount of carbonate (6 vol%) was used, with the majority of the anode mixture containing carbon black. The viscosity of the molten medium therefore plays a lesser role in the oxidation of carbon since the formation of a liquid phase is highly unlikely. The authors suggested instead a catalytic effect of the cations on the carbon oxidation mechanism with lithium having a strong catalytic effect which is enhanced in the presence of potassium.

Since the presence of the cations do not appear to change the mechanistic pathway of the oxidation, while changing the oxidation kinetics (Figure 7 [C] and Figure 10, respectively), it is reasonable to assume their

effect is catalytic. In the case of results shown here, binary eutectics have similar activity with no one cation showing specific catalytic activity over another. Certainly lithium seems to cause changes to the bubble formation behaviour, seen clearly in the comparatively stable LSV performance (Figure 5) and low level of destabilisation at high polarisation (Figure 9) of the NaK electrolyte; however, this is more likely to be a result of changes in the surface properties of the graphite, discussed in Section 3.3.4.

In fact it appears as though the cations do act catalytically, however that certain combinations enhance this catalytic performance. The three-way combination of LiNaK is apparently inhibiting to the catalytic activity, the electrolyte with an almost even molar combination of these (“SL”) showing the second lowest performance. Poor performance can also be seen when one cation has dominance over the others (i.e. “H” and “L”).

3.3.4. Lithium intercalation into graphite

Li^+ ions are free to interact with the solid carbon electrode in the molten system used. These may pass through micro pores in the carbonaceous structure to lodge within. This ‘lithium intercalation’ process is a well-known phenomenon in the study of Li-ion batteries, however little research has been conducted in its role in the operation of the DCFC.

He et al. (23) observed, by high energy in situ XRD, that the driving force, the potential, at the beginning of the intercalation process is high enough to overcome the van der Waals force between graphene layers, and there is negligible repulsive interaction between the intercalated lithium. As a result, lithium intercalates into graphite randomly. At higher concentrations of intercalation into the graphite structure, it was observed that the stronger repulsive interaction between the intercalated lithium forces them to become a uniformly ordered distribution among graphene layers (23).

From results shown here, it appears as though the intercalation of lithium into the graphite working electrode causes changes at the graphite electrode surface which influences the formation and dislodgement of product gas bubbles. The addition of lithium apparently causes an increase in the relative area of the electrode which is affected by bubble blockage since the NaK electrolyte shows blockage of only 6% of the electrode surface compared to >20% for all electrolytes containing lithium (Figure 12 [B]). An increase in intercalation of

lithium, assumed to occur with an increased lithium concentration electrolyte, also appears to cause bubbles formed to be small and easily dislodged (Figure 12 [A]). However beyond a threshold concentration of lithium (i.e. above 65 mol% lithium) intercalation appears to occur to such an extent that electrode activity is significantly reduced and that bubble formation no longer occurs to the extent that no inhibition and activation current density profiles can be observed (Figure 9). This could represent the maximum lithium intercalation possible and the high degree of intercalation forcing the lithium to become uniformly dispersed through the graphite and likely exfoliation of the graphite surface. It is seen here that the intercalation of lithium causes changes in the gas coverage and formation of gaseous bubbles at the electrode surface. It is possible that this observation is a result of a change in the wetting behavior of both the molten carbon and gaseous products formed with the carbon surface through changes to the carbon electrode polarity effected through lithium intercalation. It has previously been suggested that the inclusion of coal ash components such as kaolin (12) changes the wetting behaviour of the molten carbonate with graphite and the subsequent rate of oxidation through differences in electrode polarity. It is possible that a similar effect is being observed here.

4. Conclusion

It has been shown in this work that the impact of the carbonate electrolyte composition on the electrochemical performance of a solid graphite anode cannot be discounted. Effects are mainly observed at high polarisation where bubble formation behaviour occurs and clear destabilisation of the oxidation current can be seen. The effect of changing the cation concentration is thought to be a combined effect of the catalytic effect of the cations on the electrochemical oxidation reaction, as well as lithium intercalation into the solid anode surface changing surface properties of the anode. Each cation is thought to work catalytically for the electrochemical oxidation reaction; however, specific combinations appear to work to the best advantage, with the best results seen for binary eutectics. An increase in lithium concentration is thought to lead to an increase in lithium intercalation at the electrode surface which leads to formation of smaller product gas bubbles dislodged in a shortened time frame. A threshold lithium concentration is reached above approximately 65 mol% which leads to inhibition of oxidation behaviour as well as the disappearance of bubble formation trends.

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Figure 1: Hybrid DCFC arrangement

Figure 2: Carbonate compositions investigated including [A] Lithium Series with lithium content including: H – Highest, SH – Second Highest, E – Eutectic, SL – Second Lowest and L – Lowest and [B] Binary Series with binary eutectic compositions and [C] ternary composition diagram with compositions used in this work marked (graph method used in ref. (24))

Figure 3: Applied potential procedure used for electrochemical evaluation

Figure 4: LSV at 5 mV/s (third repetition) for [A] L and [B] SL compositions from the Lithium Series at 750°C at a graphite working electrode.

Figure 5: [A] LSV behaviour at 1 and 5 mV/s on a graphite electrode at 750°C (Ternary Eutectic composition) and [B] standard deviation between three scans carried out at 5 mV/s as a function of potential

Figure 6: LSV performance of “Lithium Series” at [A] 5mV/s and [B] 1 mV/s and “Binary Series” at [C] 5 mV/s and [D] 1 mV/s

Figure 7: Tafel performance of average 5 mV/s scan calculated at 750 C on graphite for [A] “Lithium Series” [B] “Binary Series”; [C] analysis of tafel slope as a function of carbonate composition for each region of oxidation outlined in [A] and [B].

Figure 8: Average OCP measurement for all measurements taken during electrochemical experiment period as described in Section 2.3.

Figure 9: Chronoamperometry (potential hold) experiments on graphite at 750°C for "Lithium Series" at [A] 0.2 V and [B] 0.5 V vs reference and “Binary Series” at [C] 0.2 V and [D] 0.5 V vs reference

Figure 10: Average current density during potential holding at 0.2 and 0.5 V versus reference as indicated for [A] “Lithium Series” and [B] “Binary Series” , melting point also indicated extrapolated from data of Janz et. al. (7)

Figure 11: Analysis of chronoamperometry results for bubble formation; ternary eutectic at 0.5 V

potential hold (750°C)

Figure 12: [A] Bubble period and relative size compared to lithium concentration of the carbonate composition investigated and [B] relative surface blockage calculated from charge passed during bubble formation as a function of bubble volume at 750°C

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Table 1: Carbonate compositions used commonly in the literature (mol%)

Li	Na	K	Ref
43.5	31.5	25.0	(11-13)
32.0	0.0	68.0	(14, 15)
62.0	0.0	38.0	(16-20)

Table 2: R^2 values for linear regression of Tafel slopes calculated

R^2	REGION I	REGION II	REGION III
L	98.3%	98.5%	99.0%
SL	99.6%	98.8%	99.8%
E	99.6%	98.3%	99.9%
SH	98.4%	99.3%	99.8%
H	98.7%	99.1%	99.7%