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Carbonate Reduction and the Properties and Applications of Carbon Formed Through Electrochemical Deposition in Molten Carbonates: A Review

Matthew A. Hughes, Jessica A. Allen and Scott W. Donne*

Discipline of Chemistry, University of Newcastle, Callaghan NSW 2308, Australia

Abstract

The electrochemical conversion of CO₂ to carbon through the reductive electrolysis of molten carbonate-containing salts has been studied by a range of groups. These groups have examined the yields, mechanisms of deposition and physical characteristics of carbon synthesized through electrolysis using a variety of electrolytes, substrates, temperatures, current densities and deposition potentials. The findings of these research groups have been compiled and compared, with particular significance being placed on findings relating to the influence of variables on the physical properties of carbon obtained in this manner. Research on potential applications of carbon derived from the electrolysis of molten carbonate-containing salts has been presented and the energetics of these carbons have been discussed. The possibility of using this form of carbon synthesis as a manner of permanent waste CO₂ sequestration has been considered.

*Communicating author

Email: scott.donne@newcastle.edu.au; Ph: +61 2 4921 5477; Fax: +61 2 4921 5472

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1. Advanced Carbon Materials

Carbon is the element which provides the basis of all life on Earth and, beyond this, carbon is vital for a range of technological and industrial applications¹. Carbonaceous materials, including activated carbons, graphite, carbon black and biomass, are used extensively in processes such as the electrochemical production of fluorine^{2,3}, combustion for heat and electricity⁴, the formation of gas and liquid fuels⁴, the production of drugs and synthetic materials¹, and in the construction of lithium-ion batteries and supercapacitors⁵⁻⁷. This versatility of use for carbon materials is a direct result of its diverse interactions both with itself and other elements, resulting in the formation of a range of structurally diverse organic compounds with widely varying properties¹. Elemental carbon exists in two natural allotropes, these being diamond, a crystalline network of sp^3 hybridised carbon, and graphite, crystalline networks of sp^2 hybridised carbon¹. The diverse binding potential of carbon has allowed for the discovery of several synthetic carbon allotropes including the fullerenes in 1985¹, carbon nanotubes in 1991^{1,8} and graphene in 2004^{1,9} (Figure 1).

Of the commonly recognised carbonaceous materials, two dimensional graphene has been identified as an interesting electrode material for energy storage and conversion devices (batteries for example) due to physical properties that differentiate it from other forms of carbon. The characteristic properties of graphene include high specific surface area^{6,7} of around $2600\text{ m}^2\text{g}^{-1}$, good electrical^{6,7} and thermal conductivities⁷, superior charge-carrier mobility at room temperature¹ and a structural composition consisting of single-atom-thick, nearly two-dimensional sp^2 hybridised carbon lattices arranged in parallel sheets^{1,7}. These properties combine to form a material that is highly suited for use in batteries, capacitors and transparent conductive electrodes such as those used in touch screens¹. The close stacking of graphene sheets in a lattice does however lead to reductions in the effective surface area of the material available for ion diffusion from an electrolyte to graphene electrodes, and therefore decreases the electrochemical performance of graphene from what may otherwise be expected⁷. Graphite too is a form of carbon often used in the creation of electrode and supercapacitor materials, the basis for which is that the theoretical specific discharge

capacity of pure graphite^{10, 11} is quite high (372 mAhg⁻¹) corresponding to the formation of the intercalation compound LiC₆. However, the applied performance of graphite and other carbonaceous material as supercapacitors is affected by the method of preparation^{7, 11, 12}. Due to this, an expanding region of research deals with the preparation methods of carbonaceous materials for use as a supercapacitor material^{7, 11-14}.

The influence of preparation method on the product of carbon synthesis is a huge area of research and remains an area of major innovation and study¹⁵⁻¹⁹. A range of methods have been used to prepare carbon for industrial and chemical use. The most widely researched of these methods is the synthesis of carbon from biomass using the pyrolytic^{17, 18}, hydrothermal^{15, 16} or vapour-deposition¹⁹ pathways. It was, however, known as far back as 1966 that it was possible to synthesise carbon using the electrolytic reduction path detailed above for carbonate-containing melts of salts²⁰. This electrolytic path of carbon deposition is of interest as a medium temperature (>400°C) method of producing carbonaceous products with unique physical properties that depend heavily on the exact conditions of deposition and on post-deposition treatments^{5, 11, 14, 21-25}.

2. Electrochemical Deposition from Molten Carbonate Salts

Recent research into the reduction of carbonate-containing materials has begun to examine the electrolytic reduction of molten carbonate containing salts for the formation of carbonaceous products^{5, 11, 13, 14, 20-31}. Unlike reduction in aqueous media there is no water present during this form of electrolytic reaction, hence the mechanism of carbonate reduction is demonstrated by Eqn (1); i.e.,

which shows the redox couple for the electrolytic reduction of molten carbonate salts⁵. This is a reaction of particular interest not only for its potential as a method of waste CO₂ consumption by way of the Eqn (2), but also due to the carbonaceous product of the electrodeposition reaction.

Research into the electrodeposition of carbon from carbonate-containing melts is summarized in Table 1. Successful deposition was first reported as early as 1966 when Ingram *et al.*²⁰ detailed the cathodic deposition of carbon onto gold, platinum, silver and stainless steel substrates from several different fused carbonates across a range of temperatures under both CO₂ and Ar atmospheres.

Ingram *et al.*²⁰ focused heavily on the yield of carbon in the system and its dependence on atmosphere, temperature, substrate and electrolyte, however they focussed very little on characterisation of the carbon products using the typical methods for carbon characterisation described in Table 2. It was proposed that, in a ternary eutectic of Li₂CO₃-Na₂CO₃-K₂CO₃ at 600°C under an Ar atmosphere, the yield of carbon deposition, based on the charge-based yield, onto a gold cathode was close to 100%. Carbon yields were found to significantly decrease under a CO₂ atmosphere, at low deposition currents and at elevated temperatures²⁰.

2.1. Effect of Temperature Variation

The effects of temperature variations on the charge-based carbon yield of electrodeposition from molten carbonate salts have not been widely considered since the work of Ingram *et al.*²⁰. Recent research from Ijije *et al.*²⁵ reported a slight decrease in the current efficiency of carbon deposition from molten carbonate salts at increased temperatures. Several research groups have, however, investigated the effects of temperature variation on the physical characteristics of carbon synthesised in this manner. Ijije *et al.*²⁵ examined the structure of carbon samples deposited via electrolysis at 3-4 V onto mild steel using a stainless steel anode in molten Li₂CO₃-K₂CO₃ (in a 62:38 mole ratio) at temperatures between 540°C and 700°C using TEM and HRTEM imaging (Figure 2 a-b). Ijije *et al.*²⁵ found that flat sheets of carbon were more often observed in samples deposited at elevated temperatures, and that spherical morphologies were observed more often at lower deposition temperatures. Research was also undertaken into the specific surface areas (SSA) and combustion activation energy (E_a) of carbon samples deposited at various temperatures, finding that the average combustion activation energy of carbon samples deposited at lower temperatures

were greater than those of samples deposited at higher temperatures, and that carbon samples deposited at lower temperatures tended to have greater BET SSA. In general, BET SSA for samples were found to vary between 278-585 m²g⁻¹, with the greatest BET SSA belonging to samples deposited with low deposition temperatures and more negative deposition potentials.

This result was consistent with those obtained on the trends in the BET SSA of carbons deposited from molten carbonate salts by Le Van *et al.*⁵ who obtained samples with BET SSA between 900-1300 m²g⁻¹ after heat treatment at 600°C that exhibited greater BET SSA both at more negative deposition potentials and at lower deposition temperatures. Le Van *et al.*⁵ also showed using SEM that carbon particle size increases drastically with increased deposition temperature and that the apparent porosity of carbon samples deposited at higher temperatures were lower than those of samples deposited at lower temperatures. This was further confirmed using SEM⁵, which showed that, at elevated temperatures of deposition from ternary carbonate eutectics, carbon particles generally elongated, showed decreased porosities and exhibited higher BET SSA.

The research of Le Van *et al.*⁵ continued on to suggest, based on XRD, that there was no consistent pattern in the crystalline nature of samples and that, independent of the temperature of deposition, there were always amorphous, graphitised domains with random orientations, and graphitised domains with clear orientations present in all carbon samples derived from the electrolytic reduction of molten carbonate salts. Furthermore, the interlayer spacing between the edges of graphitised domains with clear orientation across carbon samples deposited at all temperatures of deposition were found to be close to that of pure graphite, which was consistent with the findings of Yin *et al.*¹³ and Lantelme *et al.*²¹. These findings were inconsistent with early research by Ingram *et al.*²⁰, which examined the physical characteristics of carbon deposited from a ternary carbonate eutectic using only XRD, and thereby showed carbon deposits to only consist of amorphous carbon across a range of deposition temperatures.

2.2. Structural Identification of Carbon Products

The physical characterization of carbon samples derived from the electrolytic reduction of

molten carbonate salts under specific conditions is itself an area that has received considerable interest since the work of Ingram *et al.*²⁰. Research from Baker *et al.*²⁴ studied carbon deposits obtained from deposition at 1100°C onto a graphite cathode from molten CaF₂-CaCl using TEM and found that carbon samples prepared in this manner consisted entirely of parallel sheets of crystalline carbon with an occasional deformity. This finding clashed with that of Massot *et al.*²³ who found, using Raman spectroscopy and SEM, that carbon deposited onto a copper electrode at 800°C from molten LiF-NaF-Na₂CO₃ salt contained only amorphous, sp² hybridised deposits. The hybridisation of carbon derived from the electrolysis of molten carbonate salts was further examined by Ijije *et al.*¹⁴, who showed using TEM and XPS (X-ray photoelectron spectroscopy) that, irrespective of electrode material, carbon deposited from molten LiF-NaF-KF-K₂CO₃ was largely amorphous with a sp² hybridised structure and some surface sp³ hybridisation corresponding to functionalised surface groups. The research of Groult *et al.*¹¹ gave an in depth overview on the properties of carbon obtained from the electrolytic reduction of carbonate in a eutectic melt of Li₂CO₃-K₂CO₃-Na₂CO₃ at 450°C onto a nickel substrate under a CO₂ atmosphere. Groult *et al.*¹¹ showed, using AFM imaging, that carbon synthesised under these conditions formed quasi-spherical nanoparticles of between 40-80 nm and, using TEM, that carbon samples contained graphitised layers with 0.34 nm sheet separation, which is close to the d₀₀₂ value of pure graphite. Groult *et al.*¹¹ also used Raman spectroscopy to indicate that carbon samples experienced increased surface disordering at increasing temperatures of heat treatment and demonstrated that the intensity of the XRD peak for amorphous phase decreased with increased treatment temperatures. Hence heat treatment may be used to increase the graphene-like properties of carbon deposits. This finding was consistent with that presented by Groult *et al.*³² at an earlier time. The research of Groult *et al.*¹¹ also used SIMS to detect sodium and lithium fused to the powder surface of carbon samples, which Ingram *et al.*²⁰ attempted to locate through chemical testing but failed to detect. The presence of these elements on the surface of carbon deposits was also noted in the research of Kaplan *et al.*³³ whom used XPS to identify the possible presence of Li₂O, Li₂CO₃ and LiOH on the surface of

carbon deposits.

Explaining the huge variation in the observed morphology of carbons prepared through the electrolysis of molten carbonates is still an area of modern research, with headway being made through an increased understanding of the role that deposition substrates and electrolytes hold in the electrodeposition of carbon from molten carbonate-containing salts.

2.3. Effect of Substrate Variation

Ingram *et al.*²⁰ found that the mechanism of electrolytic carbon deposition from molten carbonate salts was largely independent of the substrate onto which deposition was occurring. This was attributed to the formation of a thin carbon layer on electrodes at the start of deposition reactions onto which further deposition occurred. Electrodeposition onto gold, 80:20 Au:Pd, platinum, silver and stainless steel electrodes was found to occur in all cases close to -2.5 V vs a silver wire immersed in molten electrolyte. Lantelme *et al.*²¹, however, studied the deposition of carbon onto aluminium, gold, platinum and copper electrodes and found that the potential of carbon deposition and the shape of the cyclic voltammogram (CV) for a system was dependent on the nature of the working electrode. Ijije *et al.*³⁴ observed, based on CV profiles and changes in the ratio of cathodic to anodic charge with time, that a nickel electrode initially showed greater current flow than a platinum one for the deposition of carbon at the same potential, but that over time the deposition current became closer to equivalent as a carbon coating forms on each substrate. This was said to imply that the nature of the working electrode is irrelevant for the reductive electrodeposition of carbon from molten carbonate salts over a lengthened duration, so long as the electrode is stable in a molten salt³⁴.

This was expanded upon by the research of Kamali *et al.*²⁹ who examined the effects of the initial structure of carbon anodes on the physical properties of carbon deposited electrochemically onto carbon cathodes using a molten LiCl electrolyte. The research of this group found that carbon deposited using a carbon anode with planar grains led to the formation of tubular carbonaceous

deposits under SEM and that carbon deposited using anodes with irregular grain structures formed deposits with spherical nanostructures under SEM. This demonstrated that, in spite of the mechanism of deposition being apparently the same in all cases, the nature of the electrode does effect the physical properties of the carbon deposit. This result was further confirmed by the research of Song *et al.*³⁰ who concluded, based on observations of differences in carbon films deposited onto titanium and oxide-scale-coated titanium substrates for 6 hours at -1.8 V vs Ni and at 500°C from a LiCl-KCl-Na₂CO₃ electrolyte as observed via SEM (Figure 3 a-b), that the morphology of carbon films prepared by electrochemical methods was significantly dependent on the substrate onto which the carbon was deposited.

Song *et al.*³⁰ found that the morphology and porosity of carbon deposits on titanium electrodes with different surface conditions were notably different in spite of each deposit consisting of porous quasi-spherical aggregates. Song *et al.* went on to characterise the carbon samples synthesised in this manner using Raman spectroscopy and XRD, ultimately finding Raman spectra across each sample characteristic of sp² hybridised carbon, and XRD spectra showing both an amorphous phase and a d₀₀₂ peak similar to that of graphite, which is consistent with the findings of both previous and subsequent groups^{5, 11, 13, 21}. This indicated the morphology of carbon deposited from molten carbonate-containing melts to be dependent on the substrate of deposition, as was also concluded by Kamali *et al.*²⁹.

The findings of these groups were, however, contradicted by the research of Kaplan *et al.*³³ who compared the physical characteristics of carbon deposited onto glassy carbon and nickel substrates. Kaplan *et al.*³³ found, using SEM and XRD, that the substrate of deposition had no major influence on the morphology of deposited carbons, with particles aggregating into quasi-spherical conglomerates of less than 100 nm diameter consisting of both amorphous and graphitised carbon across both substrates. In all cases the fringe separation of graphitised sheets were found to be close to 0.34 nm, the d₀₀₂ value of pure graphite.

2.4. Influence of Electrolyte Composition on Deposition

Ingram *et al.*²⁰ investigated the effects of electrolyte composition on the electrolysis of molten carbonate salts, finding that the identity of the electrolyte had a major influence on the results of the electrolysis. Notably the potential of deposition was found to be dependent on the electrolyte in which deposition occurred, with deposition in a Li_2CO_3 electrolyte at 750°C being found to occur at less negative potentials than deposition in a $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic melt. This was supported by the research of Lawrence³⁵ who found that carbon electrodeposition occurred at the cathodic limit of carbonate electrolytes on the condition that Li_2CO_3 was present. Lawrence³⁵ also noted that, when using $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ and $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ electrolytes, which exhibit similar CV profiles on stainless steel working electrodes, similar electrochemical reactions occur in either case.

The importance of Li_2CO_3 to the electrolytic deposition of carbon from carbonate-containing melts is explained through thermodynamic consideration of the reactions involved. The deposition of carbon in a system containing Li^+ will occur prior to the deposition of Li metal with intermediate formation of Li_2O , however in the absence of Li^+ ions other carbonates, including the commonly used Na_2CO_3 (Figure 4), have thermodynamic deposition potentials such that metal deposition (Eqn (3)) occurs prior to carbon deposition (Eqn (1)); i.e.,

The necessity of Li^+ ions for the electrolytic deposition of carbon from molten carbonate melts was experimentally confirmed by Ijije *et al.*¹⁴, who suggested the deposition mechanism to be independent of electrolyte identity on the condition that Li^+ ions were present, Ingram *et al.*²⁰ and by Le Van *et al.*⁵ who supplied a thermodynamic explanation for the phenomenon.

Le Van *et al.*⁵ theorized that reactions like in Eqns (1) and (3) may both occur at the cathode during the reduction of molten carbonate salts. Assuming the reaction at the graphite anode to be:

Le Van *et al.*⁵ determined that, in the event of the cathodic reaction in Eqn (3), overall reactions

were of the form:

The Gibbs energy and standard potential versus a $\text{CO}_3^{2-}/\text{CO}_2$, O_2 reference system are given by:

$$\Delta G^\circ(\text{Li}^+ / \text{Li}) = \Delta G_f^\circ(\text{CO}_2) - \Delta G_f^\circ(\text{Li}^+) \quad \dots(6)$$

$$E^\circ(\text{Li}^+ / \text{Li}) = -\frac{\Delta G^\circ(\text{Li}^+ / \text{Li})}{2F} \quad \dots(7)$$

Le Van *et al.*⁵ continued on to state that, in the event of the cathodic reaction in Eqn (1), the overall reaction was of the form shown in Eqn (8), hence the Gibbs energy and standard potential versus a $\text{CO}_3^{2-}/\text{CO}_2$, O_2 reference electrode were given to be of the form shown in Eqns (9) and (10), respectively; i.e.,

$$\Delta G^\circ(\text{CO}_3^{2-} / \text{C}) = 3\Delta G_f^\circ(\text{Li}_2\text{O}) + 2\Delta G_f^\circ(\text{CO}_2) - \Delta G_f^\circ(\text{Li}_2\text{CO}_3) \quad \dots(9)$$

$$E^\circ(\text{CO}_3^{2-} / \text{C}) = -\frac{\Delta G^\circ(\text{CO}_3^{2-} / \text{C})}{4F} \quad \dots(10)$$

Based on values presented in literature³⁶ Le Van *et al.*⁵ used these expressions to compare the Gibbs energy and standard potentials of conversion from Li_2CO_3 , Na_2CO_3 and K_2CO_3 to alkali metals and carbon at temperatures between 450°C and 700°C (Table 3). From this Le Van *et al.*⁵ determined that across all temperatures, the deposition of carbon from molten Li_2CO_3 occurred at significantly lower potentials than the deposition of lithium metal. This was not the case for the deposition of carbon from Na_2CO_3 or K_2CO_3 , which either competes with the deposition of the corresponding alkali metals, or occurs at more negative potentials so is not favourable. Based on this Le Van *et al.*⁵ concluded that, in the absence of lithium ions, the electrolytic deposition of carbon from molten carbonate salts will either not be observed or will proceed at a severely reduced rate.

2.5. Effect of Deposition Current Variation

The effect of current variation on the reductive electrodeposition of carbon from carbonate-

containing melts has been researched very little since the work of Ingram *et al.*²⁰, which found a slight positive correlation between current and yield for electrodeposition reactions. The subject was touched upon in the 2003 work of Massot *et al.*²⁶ who examined the effects of current and temperature variation on the growth of carbon clusters at the surface of gold working electrodes in a molten LiF/NaF eutectic at 670°C-750°C, to which Na₂CO₃ pellets were introduced. Massot *et al.*²⁶ found that carbon deposition proceeds by progressive generation of carbon clusters (nucleation) followed by diffusion-controlled nuclei growth. Increased deposition temperatures and current density were found to increase the rate of nucleation, but not the rate of nuclei growth.

2.6. Effect of Gaseous Atmosphere

The effects of atmospheric composition on the electrodeposition of carbon from carbonate containing melts has been studied in some detail^{5, 14, 25, 34}, with most research on the matter being directed towards the comparison of using an Ar atmosphere to a CO₂ or mixed CO₂-Ar atmosphere. The research of Le Van *et al.*⁵ studied the effects of a CO₂ atmosphere on the reduction and oxidation of carbon in a Li₂CO₃-Na₂CO₃-K₂CO₃ eutectic mix at 450°C with a vitreous carbon working electrode and a silver reference electrode. This group examined the mechanism of carbon reduction and oxidation in such a system through the use of CV, finding there to be minimal alteration in the electrochemical oxidation and reduction peaks of a system under a CO₂ atmosphere at a partial pressure of 1 atm as compared to those under an Ar atmosphere. This was used to indicate that a CO₂ atmosphere does not participate directly in the deposition of carbon from carbonate containing melts. The mechanism of reaction was determined from the position of oxidation peaks for the system at 450°C (Figure 5) to be that previously described by Eqns (1) and (2), where Eqn (2) enables replenishment of consumed carbonate ions in the carbonate melt. This mechanism agrees with the findings of several other groups working with a range of electrolytes and a variety of working electrodes including Kawamura and Ito²², Massot *et al.*²³, Song *et al.*³⁰, Novoselova *et al.*²⁷ and Ijije *et al.*¹⁴.

A recent paper from Ijije *et al.*³⁴ studied the effect of varying partial pressures of CO₂ on the electrodeposition of carbon in a CaCl₂-CaCO₃-LiCl-KCl melt at 579°C onto a mild steel working electrode under a potential difference of 4 V. This study found that electrolysis current increased with increasing partial pressures of CO₂, which was taken to support the occurrence of Eqns (1) and (2) as the accepted mechanism by which carbon electrodeposition occurred in carbonate containing melts under a CO₂ atmosphere. Additionally, it was found that some CO was produced during the deposition process³⁴. The effect of high partial pressures of CO₂ on the electrolytic deposition of carbon from molten carbonate salts was later studied by Ijije *et al.*¹⁴ who reported the direct conversion of CO₂ to carbon and oxygen without the involvement of carbonate in a NaCl-KCl melt at 750°C under 1.0 MPa of CO₂ partial pressure via Eqn (11):

Ijije *et al.*¹⁴ concluded that this reaction mechanism only led to carbon deposition at extremely high partial pressures of CO₂, whereas at lower partial pressures deposition proceeds by way of Eqns (1) and (2). The earlier research of Novoselova *et al.*²⁷ failed to observe the direct conversion of CO₂ to C and O₂ at high partial pressures of CO₂; however, it did note that increased partial pressures of CO₂ corresponded to less negative deposition potentials of carbon from an equimolar melt of NaCl and KCl in the range of 750°C to 850°C.

Ijije *et al.*¹⁴ also examined the relative effects of an Ar and CO₂ atmosphere on the electrodeposition of carbon in a CaCl₂-CaCO₃-LiCl-KCl melt at 579°C onto a mild steel working electrode under a potential difference of 4 V. Under an Ar atmosphere the yield was found to be 97% but current efficiency was found to markedly decrease in a CO₂ atmosphere to 67%. This result was consistent with the previous research of Ingram *et al.*²⁰. The work of Ijije *et al.*¹⁴ continued beyond the scope of that previously presented, however, and found that, under a mixed CO₂-N₂ atmosphere, the rate of carbon deposition increased with rising partial pressures of CO₂. This finding was supported by a second study on the same subject by Ijije *et al.*²⁵ which reached the same conclusion.

2.7. Influence of Deposition Potential

Lantelme *et al.*²¹ examined the effects of deposition potential variation on the deposition of carbon onto a nickel substrate from a molten ternary $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ eutectic at 450°C . The group found that more negative deposition potentials corresponded to increased charge-based yields and that, as deposition potentials became more negative, the BET SSA of carbon samples increased. This was supported by the research of Groult *et al.*³⁷ who additionally noted that increased deposition potentials tended to lead to the increased microporosity and increased amorphous character in carbon deposited from molten carbonate salts. Groult *et al.*³⁷ also noted no major changes in particle size with changing deposition potentials. The increasing amorphous character of carbon samples with increasingly negative deposition potentials noted by Groult *et al.*³⁷ has not been observed in other research and contradicts the previous research of Groult *et al.*³² which found, based on XRD, that the amorphous character of carbon tended to decrease with increasingly negative deposition potentials.

The finding that the BET SSA of carbon samples derived from the electrolytic reduction of molten carbonates increases with increasingly negative deposition potentials has been challenged by Kaplan *et al.*³³ who found that carbon samples synthesised through the electrolytic reduction of molten ternary carbonate eutectic had a BET SSA which decreased with increasingly negative potentials of deposition, varying between $850\text{ m}^2\text{g}^{-1}$ at -2.4 V to $500\text{ m}^2\text{g}^{-1}$ at -6.0 V . Kaplan *et al.*³³ also observed that, at highly negative deposition potentials, the deposition of carbon competes with the formation of Li_2O and lithium carbides, which leads to the filling of nano-pores in deposited carbon. This was used to explain the decrease in the BET SSA of carbon samples at more negative deposition potentials observed by this group.

Kawamura and Ito²² expanded on knowledge of the influence of deposition potential on the electrolytic deposition of carbon from molten carbonate salts in a system of $\text{LiCl-KCl-K}_2\text{CO}_3$ with an aluminium working electrode, a carbon counter electrode and a Li^+/Li reference. Under these

conditions deposition was found to occur close to 0.7 V. Deposition potentials were varied in the interval of 0.6-1.2 V relative to the Li^+/Li reference and it was found that deposition at potentials greater than 0.8 V resulted in rough, coarse and easily stripped deposits, whereas deposition below this limit led to smoother, finer and harder to strip carbon deposits. In contrast to this macroscopic result, SEM imaging showed that, as deposition potentials increased, the microscopic structure of the deposits became smoother and more regular. Kawamura and Ito²² went on to determine, based on Raman spectroscopy, in agreement with the results previously, that carbon deposits largely consisted of sp^2 hybridised carbon, and confirmed using XPS and X-ray excited atomic emission spectroscopy (XAES) that the surface atoms of deposits were oxidised by air to a sp^3 hybridised state.

The conclusions presented above were, to a degree, challenged in a later publication by Le Van *et al.*⁵ which indicated, based on SEM results, that the potential of deposition had a negligible effect on the physical characteristics of carbon deposits and, using TEM, that, irrespective of the deposition potential, carbon deposits consisted of aggregates of particles with size between 30-50 nm. The potential of deposition was, however, found to have a noticeable effect on the porosity and BET SSA of carbon deposits, with more negative deposition potentials corresponding to increased micro-porosity, decreased macro-porosity and increased BET SSA⁵. The research of Song *et al.*³⁰ initially appears to contradict the results presented by Le Van *et al.*, with variation in the deposition potential of carbon samples appearing to alter the morphology of the deposited carbon (Figure 6 a-c).

Song *et al.*³⁰ explains this contradiction in terms of charge per unit area, where over time the morphologies would equalise due to approximately equivalent charge per unit area having passed through each point on the electrode, and therefore concludes, in agreement with Le Van *et al.*⁵, that the potential of deposition has a negligible influence on the morphology of carbon deposits over an extended duration of deposition. The research of Ijije *et al.*²⁵ expanded upon that of the various groups noted above, exploring various aspects of the effects of potential variation on carbon

deposition from molten carbonate salts. The research of this group contradicts the earlier finding of Lantelme *et al.*²¹ in that no clear correlation is noted between the potential of deposition and the charge-based carbon yield of deposition. Combustion activation energies of carbon samples across a range of deposition potentials were investigated by Ijije *et al.*²⁵ (Table 4) who noted a pattern of increased combustion activation energy at more negative deposition potentials. The research of Ijije *et al.*²⁵ goes on to show, based on TEM and HRTEM imaging, that increased deposition potential leads to an increase in the flat-sheet structure of carbon samples and a decrease of sphere-like microscopic aggregates in a similar manner to elevated deposition temperature²⁵. In agreement with the findings of Le Van *et al.*⁵, Groult *et al.*³⁷ and Lantelme *et al.*²¹, the work of Ijije *et al.*²⁵ also concludes, based on porosity and adsorption studies, that increasingly negative deposition potentials correspond to the deposition of more porous carbon samples with greater BET SSA.

3. Applications and Electrochemical Properties

Carbonaceous materials find regular use as materials in the construction of supercapacitors and batteries. The reasonably high BET SSA and surface functionalization of carbon synthesised through the reductive electrolysis of molten carbonate salts make it a material of interest for potential applications of this form, and to this end various research groups have studied the capacitive and electrochemical properties of these carbons.

Groult *et al.*¹¹ examined the irreversible capacitance of carbon samples derived from electrodeposition in a eutectic melt of $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ onto a nickel sheet under a CO_2 atmosphere. This group found the maximum irreversible capacitance to be, after heat treatment at 400°C , 1080 mAhg^{-1} in a $1\text{M LiPF}_6\text{-EC:DEC:DMC (2:1:2)}$ system, a value much greater than that of pure graphite (372 mAhg^{-1}). This result was a reproduction of the results of earlier research from Groult *et al.*³² which noted the same maximum irreversible capacitance of 1080 mAhg^{-1} in the same cell setup, but additionally observed that the maximum irreversible capacitances were obtained by carbon samples with low surface disordering and low levels of hydrogen at the carbon surface.

The capacitive behaviour of carbon samples from electrolytic reduction in molten carbonate salts was also investigated by Yin *et al.*¹³. This group examined the physical properties of carbon prepared through the electrolytic reduction of a eutectic $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3$ melt onto a nickel cathode at 500°C . This method was found¹³ to produce carbon nanoparticles that were electronically conductive and which had BET SSA of between $414\text{-}616\text{ m}^2\text{g}^{-1}$, values which were comparable to those reported previously. The greatest specific capacities were obtained for carbons prepared at a potential difference of 4 V which showed, in a three electrode cell in 1 M H_2SO_4 , specific capacities of 270, 330, 376 and 400 Fg^{-1} at 5, 2, 0.5 and 0.2 Ag^{-1} current densities respectively, values stated to be superior to commercially available active carbons. There was also noted to be a correlation between increased BET SSA and increased capacitances for tested carbon samples.

The capacitance of deposited carbon from carbonate containing melts was more recently investigated by Ijije *et al.*¹⁴ who used carbon powders prepared at 4V under a CO_2 atmosphere in $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ and $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ to form pellets and construct symmetrical two electrode supercapacitors which had their performance in 3 M KCl electrolyte evaluated by analysis of the shape and area under CVs (Figure 7). In all cases good reversibility and capacitive behaviour was observed, with samples prepared in $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ melts at 600°C having an average SSA of $535\text{ m}^2\text{g}^{-1}$ and specific capacitance of 100 Fg^{-1} , and those prepared in $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$ melts at 623°C an average SSA of $236\text{ m}^2\text{g}^{-1}$ and specific capacitance of 71 Fg^{-1} . This study also lent validation to the effect of electrolyte on the physical characteristics of the deposited carbons. The large variation between the capacitances of carbon samples synthesised and tested by Ijije *et al.*¹⁴ and those of carbon samples synthesised and tested by Yin *et al.*¹³ may be attributed in part to the differences between the methods of carbon preparation used by each group, including the use of different electrolytes, producing carbons with different morphologies. A further and perhaps more influential factor in the variation of recorded capacitance values for carbon synthesised from the electrolytic reduction of molten carbonate salts is the use of different electrolytes in the testing cells in each

case, with Ijije *et al.*¹⁴ making use of 3M KCl and Yin *et al.*¹³ utilising 1M LiPF₆-EC:DEC:DMC. The capacitance of an electrical double layer capacitor (EDLC) such as graphite has been shown to be influenced to a large degree by the nature of the electrolyte³⁸. The ability of an EDLC to store charge is dependent on the storage of ions from the electrolyte by the EDLC, this being in turn dependent on the accessibility of pores on the surface of the EDLC to these ions³⁸. Therefore, for each EDLC there is an optimal size for electrolyte ions, and as ion size approaches this the ability for an EDLC to store charge increases. Based on this, the variation in the capacitance values presented by Ijije *et al.*¹⁴ and Yin *et al.*¹³ may be attributed largely to carbon samples acting as EDLCs and to effects of the electrolyte used by each research group.

The research of Ijije *et al.*¹⁴ extended to a brief investigation of the potential uses for the carbon deposition process, with proposals including CO₂ waste consumption and the production of supercapacitor and battery materials. The investigation also proposed several further uses for carbon derived in this method such as steel carburising, the production of transitional metal carbides and, perhaps most interestingly, for the storage of excess energy from power plants in the form of carbon, which may be oxidised to CO₂ to release electrical energy when required during periods of reduced demand¹⁴. Research¹⁴ into the process of converting electrodeposited carbon back to CO₂ via anodic re-oxidation has shown process energy efficiencies of 34-95% depending on cell setup. Carbon is itself easy to store and transport so the high charge-based efficiency of anodic re-oxidation allows for the reductive synthesis of carbon from molten carbonate salts to be a potential manner for energy storage.

4. Energetic Considerations and Costs

The production of carbon by the electrolysis of molten carbonate salts is a reversible energy-consuming process. While this gives rise to the potential use of the process as a method of energy storage it also means that use of the process as a method of CO₂ transformation relies on the input of an energy which does not generate comparable amounts of CO₂ during its production. Yin *et al.*¹³

theorized that, if powered by a renewable energy source, molten salt CO₂ capture and electrochemical transformation (MSSC-ET) would be a viable method of CO₂ transformation (Figure 8). It has been noted¹³ that this method of electrochemical transformation relies on the use of an inert anode (such as SnO₂, Ni, Ir or Pt¹³) at which carbonate ions are converted to oxygen and CO₂ by way of Eqns (12) and (13)

Yin *et al.*¹³ went on to examine the energetic requirements of the electrochemical transformation of CO₂ to carbon through the electrolysis of molten carbonate salts, finding that, on a nickel electrode, the lowest energy consumption occurred when depositing at potentials of 3 V. At this potential, energy consumption for the production of carbon from CO₂ was found to be 38 kWhkg⁻¹C⁻¹ (or 10.4 kWhkg⁻¹CO₂⁻¹). Yin *et al.*¹³ went on to state, based on high current densities of approximately 50 mA cm⁻², that the electrochemical reactions involved in the deposition of carbon from molten carbonate salts appear to proceed at a relatively rapid rate¹³, so kinetic limitations are not a major factor. Ijije *et al.*²⁵ also examined the energy requirements of the reductive conversion of CO₂ to carbon in a molten carbonate system. Based on samples deposited at potentials of 4.0 V the energy of conversion from CO₂ to C was determined to be 39.7 kWhkg⁻¹C⁻¹ (10.8 kWhkg⁻¹CO₂⁻¹). This is comparable to the energies of conversion previously reported by Yin *et al.*¹³ for carbon prepared at 3.0 V potentials. The slight increase in the magnitude of energy consumption for the electrochemical conversion of CO₂ to carbon as reported by Ijije *et al.*²⁵ compared to the values reported by Yin *et al.*¹³ may be attributed to increased energy consumption at potentials greater than 3.0 V (Figure 9). Figure 9 shows that, at a 4.0 V deposition potential, the results of Yin *et al.*¹³ are extremely similar to those of Ijije *et al.*²⁵.

The potential use of a renewable energy source to supply the energy requirements for the electrolytic conversion of CO₂ feedstock to carbon in molten carbonates has been investigated through the use of solar step simulators³⁹. The conversion of CO₂ to carbon in molten Li₂CO₃

between 750-950°C has been successfully simulated, leading to the conclusion that the process is an area of interest for further study³⁹. This lends validity to the statement that the conversion of waste CO₂ to carbon through the electrolysis of molten carbonate salts is potentially viable.

5. Conclusions

Research from a range of groups has demonstrated that the electrolytic deposition of carbon from molten carbonate-containing salts is a potential method of permanent CO₂ sequestration. Solar step simulation has demonstrated that the use of solar power to supply the energy requirements for this process is potentially viable. This method of CO₂ sequestration has been shown to only proceed in the presence of lithium ions and the reasons for this have been explained in terms of the Gibbs energies and standard reduction potentials involved. The carbon yield of electrolytic depositions from molten carbonate salts has been indicated to be close to quantitative under an Ar atmosphere, but to decrease significantly under a CO₂ atmosphere, possibly due to the formation of CO. Yields have also been shown to decrease slightly at elevated temperatures of deposition, possibly due to the formation of lithium carbides and lithium oxide, and with decreased deposition current. Carbon yields have also been for the most part shown to increase with more negative deposition potentials.

The morphology of carbonaceous deposits from the electrolysis of molten carbonate salts has been shown to be dependent on the temperature, substrate, electrolyte, potential, and current of deposition. The structure of deposited carbons has been largely concluded to consist of amorphous, disordered graphitised and ordered graphitised domains which show, for the most part sp² hybridisation. Some surface sp³ hybridisation is present in carbons synthesised by the reductive electrolysis of molten carbonate salts and this has been shown to be due to surface functionalization. The BET SSA of carbon samples have been shown to decrease with increased deposition temperatures and to increase with more negative potentials of deposition, with BET SSA in the range of 500 m²g⁻¹ being reported regularly. More negative deposition potentials have also been shown to correspond to increased micro-porosity and decreased macro-porosity in carbonaceous

deposits. The reversible capacitance and porosities of carbonaceous deposits have been shown to decrease with decreased BET SSA, and so to decrease with increasing deposition temperature. The maximum reversible capacitance of 400 Fg^{-1} has been reported at a current density of 0.2 Ag^{-1} , which is superior to the reversible capacitance of commercially available active carbons.

The combustion activation energies of carbonaceous deposits from the electrolytic reduction of molten carbonate salts has been shown to increase with increased deposition potential and to decrease with increased deposition temperature, with maximum reported combustion activation energies reaching 171 kJ mol^{-1} at deposition potentials of 5.0 V and temperatures of 540°C .

The potential applications of carbon derived from the electrolytic reduction of molten carbonate salts has been shown to include use as a supercapacitor or battery material, in steel carburising, in the production of transitional metal carbides, and as an energy storage material. A brief overview of the energy requirements for the conversion of waste CO_2 to carbon through the electrolysis of molten carbonate salts has shown the potential of powering the process through a renewable energy source such as solar power, however the monetary cost of such a method has not been estimated at this point.

Overall, many aspects of the electrolytic deposition of carbon from molten carbonate-containing salts have been examined, however there still exists contention in the literature as to the level of influence that variables, such as the potential of deposition, have on the efficiency of carbon deposition and on the properties of deposited carbons. Furthermore there exists much room for expanded knowledge on the influence that deposition substrate and electrolyte have on the properties of carbon deposited from molten carbonate-containing salts, on the effectiveness of such carbons when applied in various manners and on the effects of treatments on the properties of carbons gained in this manner.

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Figure 1. The progression of synthetic carbon allotrope discovery, with reference to the potential of future allotrope discoveries. Reproduced with permission¹.

Figure 2. TEM and HRTEM images of carbon deposited at (a) 540°C and 3.0 V, (b) 700°C and 3.0 V from molten $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ for 1 hour. Reproduced with permission²⁵.

Figure 3. SEM images of carbon films deposited onto (a) bare titanium substrate and (b) oxide-scale-coated titanium substrate at -1.8 V vs Ni for 6 hours from $\text{LiCl-KCl-Na}_2\text{CO}_3$ electrolyte at

500°C. Reproduced with permission³⁰.

Figure 4. Thermodynamic deposition potentials calculated for carbon in carbonate salts including lithium (left), sodium (right). Thermodynamic values from NIST Standard Reference Database Number 69³³.

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Figure 6. SEM images of carbon films deposited onto oxide-scale-coated titanium from molten $\text{LiCl-KCl-K}_2\text{CO}_3$ at 500°C under (a) -1.2 V, (b) -1.6 V, (c) -2.0 V. Reproduced with permission³⁰.

Figure 7. CVs of symmetrical cells constructed using carbon powders deposited at 4 V under a CO_2 atmosphere in (a) $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ (62:38 mol%) at 600°C and $\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$ (52:48 mol%) at 632°C (b) Li_2CO_3 with scan rates of 10 mV s^{-1} and 3 M KCl electrolyte. Reproduced with permission¹⁴.

Figure 8. Schematic path for the MSSC-ET process. Reproduced with permission¹³.

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Table 4. Comparison of the variables involved in the electrodeposition of carbon from molten carbonate salts considered by major research groups.

Research Group (Year)	Experimental Variable						
	Substrate	Atmosphere	Temperature	Electrolyte	Current	Potential	P(CO ₂)
Ingram <i>et al.</i> (1966) ²⁰	✓	✓	✓	✓	✓		
Lantelme <i>et al.</i> (1999) ²¹	✓					✓	
Kawamura and Ito (2000) ²²						✓	
Kaplan <i>et al.</i> (2002) ³³	✓					✓	
Massot <i>et al.</i> (2003) ²⁶					✓		
Groult <i>et al.</i> (2003) ³²						✓	
Novoselova <i>et al.</i> (2003) ²⁷							✓
Le Van <i>et al.</i> (2009) ⁵		✓	✓			✓	
Kamali <i>et al.</i> (2011) ²⁹	✓						
Song <i>et al.</i> (2012) ³⁰	✓					✓	
Ijije <i>et al.</i> (2014) ¹⁴	✓	✓	✓	✓			✓
Groult <i>et al.</i> (2014) ³⁷			✓			✓	
Ijije <i>et al.</i> (2014) ³⁴	✓	✓	✓				✓
Ijije <i>et al.</i> (2014) ²⁵		✓	✓			✓	

Table 2. Comparison of the techniques used by various research groups to examine the physical characteristics of carbon samples synthesized by electrodeposition in molten carbonate salts.

Research Group (Year)	Characterization Technique								
	TEM	SEM	BET	Raman	XRD	XPS	XAES	SIMS	Electrochemical
Ingram <i>et al.</i> (1966) ²⁰					✓				
Baker <i>et al.</i> (1970) ²⁴	✓								
Lantelme <i>et al.</i> (1999) ²¹			✓		✓				
Kawamura and Ito (2000) ²²		✓				✓	✓		
Massot <i>et al.</i> (2002) ²³		✓		✓					
Kaplan <i>et al.</i> (2002) ³³	✓	✓	✓		✓	✓			
Massot <i>et al.</i> (2003) ²⁶		✓							
Groult <i>et al.</i> (2003) ³²				✓		✓			✓
Groult <i>et al.</i> (2006) ¹¹		✓		✓	✓			✓	✓
Le Van <i>et al.</i> (2009) ⁵	✓	✓	✓						
Kamali <i>et al.</i> (2011) ²⁹		✓							
Song <i>et al.</i> (2012) ³⁰		✓		✓	✓				
Yin <i>et al.</i> (2013) ¹³		✓		✓	✓				✓
Ijije <i>et al.</i> (2014) ¹⁴	✓		✓			✓			✓
Groult <i>et al.</i> (2014) ³⁷	✓	✓	✓	✓	✓	✓		✓	
Ijije <i>et al.</i> (2014) ²⁵	✓		✓		✓				

Table 5. Gibbs energies and standard potentials for the disassociation of Li, Na and K carbonates to corresponding alkali metals and to alkali oxides and carbon. Reproduced with permission⁵.

Temperature (°C)	Metal (M)	$\Delta G^0(\text{M}_2\text{CO}_3/\text{M})$ (kJ mol ⁻¹)	$E^0(\text{M}_2\text{CO}_3/\text{M})$ (V)	$\Delta G^0(\text{M}_2\text{CO}_3/\text{C})$ (kJ mol ⁻¹)	$E^0(\text{M}_2\text{CO}_3/\text{C})$ (V)
450	Li	602.5	-3.12	687.4	-1.78
	Na	522.6	-2.71	1007.2	-2.61
	K	534.9	-2.77	1217.4	-3.15
540	Li	581.3	-3.01	661.4	-1.71
	Na	500.3	-2.59	978.1	-2.53
	K	511.0	-2.65	1181.8	-3.06
620	Li	562.5	-2.91	638.4	-1.65
	Na	480.5	-2.49	952.1	-2.47
	K	489.7	-2.54	1150.1	-2.98
700	Li	543.6	-2.82	615.3	-1.59
	Na	460.7	-2.39	926.2	-2.40
	K	468.5	-2.43	1118.4	-2.90

Table 6. Average combustion activation energies for carbon samples deposited from molten $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ between 540°C-700°C for potentials of 3.0V-5.0V. Reproduced with permission²⁵.

Temperature (°C)	Cell Voltage (V)		
	3.0	4.0	5.0
	E_a (kJ mol ⁻¹)		
540	158	165	171
593	152	158	160
700	131	142	148

Figure 3. The progression of synthetic carbon allotrope discovery, with reference to the potential of future allotrope discoveries. Reproduced with permission¹.

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