EFFECT OF VARIOUS TEMPERATURES AND VOLTAGE VARIATION ON ELECTRO-DEPOSITION OF CARBON USING $CaCO_3$-Li_2CO_3-LiCl SALT

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2018

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THESIS SUBMITTED IN FULFILMENT FOR THE DEGREE OF MASTER OF ENGINEERING

**FACULTY OF ENGINEERING
UNIVERSITI MALAYSIA SABAH**

2018

UNIVERSITI MALAYSIA SABAH

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DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, excepts, equations, summaries, and references, which have been duly acknowledged.

22 AUGUST 2018

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ACKNOWLEDGEMENT

This thesis is completed with the support and help from many individuals. I would like to extend my gratitude to all of them.

Foremost, I sing praises to God, the Father Almighty, for giving me the opportunity and strength to do this research and completing it. Without His wisdom, peace and strength, this thesis would not have finished in a good note.

I would like to express my deepest appreciation to my supervisor, Dr. Nancy Julius Siambun, for her continuous support, advice, guidance and to always steered me in the right direction whenever she thought I needed it. The door to her office was always open whenever I ran into a trouble spot or had a question about my research or writing. Without her unfaltering and persistence guidance, this thesis would not have been possible. I would like to thank my co-supervisor, Dr. Jidon Janaun for his advice and help in this research.

Special thanks to Ministry of Science, Technology, and Innovation (MOSTI) for Escience Fund, Universiti Teknikal Malaysia Melaka (UTeM) for allowing us to use their instruments, and Universiti Malaysia Sabah for the facility.

I also want to thank all FKJ laboratory staff for their help and guidance regarding this research. I also like to thank my dearest friends and peer who journey together with me throughout my study: Miss Noor Aemi Dawalih, Elnetthra Folly Eldy, Jessica William, Masnah Massuanna, Evelyn Yahin, and Adeline Jelung, thank you for listening to me and your continuous advice; Ricky Lee, thank you for all those crazy times; Leonora Pang and Christine Frank, thank you for understanding me; and to my Molten Salt Research Group mate, Miron Gakim, Saffuan Awg Bahrin and Mohd Zaim bin Mohd Zukeri, thank you for the wonderful experience to be in this research group. Also, to Madam Jamila Gumu, Mr. Borhan Masalin and Jester Ling for being a good friend of mine.

Finally, I must express my very profound gratitude to my parents and siblings for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis. This accomplishment would not have been possible without them. Thank you.

Karen Wong Min Jin
22 August 2018

ABSTRACT

Demand in carbon materials for various applications *i.e.* energy storage, biosensors and etcetera, calls the need to produced carbon materials especially nano-sized carbon. The microstructure, size and structure of the carbon materials are important in determining its possible application. One of the potential process to produced carbon materials is electrolysis of molten salt. Electro-deposition process is a preparation of solid carbon via electrolysis process using molten salt as electrolyte. The molten salt electrolyte has high melting temperature thus not economical. Furthermore, the electrolysis parameters; temperature and voltage play important role in determining the quantity and quality of carbon produced. Therefore, the aims of this research were to formulate salt mixture to obtain low melting temperature, to investigate the effects of electrolysis temperature and voltage on the amount of carbon, microstructure, purity, and carbon structure, and to determine the energy usage for electrolysis process. In this study, carbonate and chloride-based salts were properly selected to formulate a mixture with low melting temperature and with low electrochemical stability to ensure successful deposition of solid carbon via electrolysis process. Molten salt mixture containing $CaCO_3$, Li_2CO_3 and LiCl was successfully formulated with mole ratio of $CaCO_3$:Li_2CO_3:LiCl = 0.09:0.28:0.63 (*m.p.* = 495°C), that has much lower melting temperature compared to $CaCO_3$ (decomposes at 825°C), Li_2CO_3 (*m.p.* = 726°C) and LiCl (*m.p.* = 610°C) individually. In the electro-deposition process, electrolysis process was carried in two-electrode cell using AISI 304 stainless steel electrodes under CO_2 gas environment, with voltage 4 – 6V and temperature of 550, 650 and 750°C. The CO_2 gas was captured and electro-converted to solid carbon which then deposited on the cathode surface. Solid carbon was successfully deposited using the newly formulated salt mixture. For further understanding and comparison, electrolysis processes were also carried out for the individual salt electrolyte; $CaCO_3$, Li_2CO_3 and LiCl. It was found that only Li_2CO_3 and LiCl were able to deposit solid carbon. SEM images of solid carbon prepared in Li_2CO_3 electrolyte consisted of particles and tubes with diameter ranging from 0.05 to 0.2μm, whereas LiCl produced large flakes and small particles with size 0.5 to 6.5μm range. Carbon prepared in $CaCO_3$–Li_2CO_3–LiCl salt mixture revealed five dominant microstructures: grape-like, tubes, thread-like, spheres, and flakes. Nanotubes structures of 13 – 90nm outer diameter was also detected under TEM analysis. The size of the carbon microstructures decreased with elevation of temperature and enlarged when cell voltage increased. Elemental analysis had confirmed that electro-deposited products prepared in the newly formulated salt at various temperature and voltages have 69 – 82% carbon content. The XRD analysis had revealed carbon with amorphous structure for all carbon produced in various temperature and voltage. Electrolysis efficiency were calculated for processes carried out at 550°C (70 – 85%), 650°C (28 – 46%) and 750°C (59 – 79%) and had shown peculiar trend where 550°C give the highest efficiency, followed by 750°C and 650°C process. Higher electrolysis efficiency uses less energy thus the equivalent trend in the amount of energy usage was observed; electrolysis at 550°C (62 – 85kW.h/kg) uses lowest energy followed by electrolysis at 650°C (186 – 554kW.h/kg) and 750°C (70 – 126kW.h/kg).

ABSTRAK

KESAN VARIASI SUHU DAN KEPELBAGAIAN VOLTAN DALAM ELEKTRODEPOSISI KARBON MENGGUNAKAN GARAM CAMPURAN $CaCO_3$-Li_2CO_3-LiCl

Permintaan bahan karbon bagi pelbagai aplikasi i.e. penyimpanan tenaga, biosensor dan sebagainya, memerlukan penghasilkan bahan karbon terutamanya karbon bersaiz nano. Mikrostruktur, saiz dan struktur bahan karbon penting dalam menentukan jenis aplikasi bahan karbon tersebut. Salah satu proses yang berpotensi menghasilkan bahan karbon ialah elektrolisis garam lebur. Proses elektrodeposisi adalah satu proses penyediaan pepejal karbon melalui proses elektrolisis menggunakan garam lebur sebagai elektrolit. Takat lebur yang tinggi menyebabkan garam lebur tidak ekonomi. Parameter proses elektrolisis iaitu suhu dan voltan memainkan peranan penting dalam menentukan kuantiti dan kualiti karbon yang dihasilkan. Motivasi bagi kajian ini adalah untuk merumuskan campuran garam bagi mendapatkan suhu lebur yang rendah, mengkaji kesan suhu dan voltan proses elektrolisis pada jumlah karbon, morfologi, ketulenan, dan struktur karbon, dan menentukan penggunaan tenaga dalam proses elektrolisis. Dalam kajian ini, garam berasaskan karbonat dan klorida telah dipilih dengan teliti untuk merumuskan campuran dengan suhu lebur yang rendah dan dengan kestabilan elektrokimia yang rendah untuk memastikan pemendapan pepejal karbon melalui proses elektrolisis. Campuran garam yang mengandungi $CaCO_3$, Li_2CO_3 dan LiCl berjaya dirumuskan dengan nisbah mol $CaCO_3$:Li_2CO_3:LiCl = 0.09:0.28:0.63 (suhu lebur 495°C), di mana mempunyai suhu lebur yang lebih rendah berbanding $CaCO_3$ (terurai pada 825°C), Li_2CO_3 (suhu lebur 726°C) dan LiCl (suhu lebur 610°C). Dalam proses elektrodeposisi, proses elektrolisis dilakukan dalam sel dua elektrod menggunakan elektrod keluli tahan karat AISI 304 di dalam persekitaran gas CO_2, bekalan voltan sebanyak 4 – 6V dan suhu 550, 650 dan 750°C. Gas CO_2 ditangkap dan elektro-tukarkan kepada pepejal karbon yang kemudiannya didepositkan pada permukaan katod. Karbon telah berjaya dihasilkan menggunakan campuran garam yang baru dirumuskan. Untuk pemahaman dan perbandingan selanjutnya, proses elektrolisis juga dijalankan untuk elektrolit garam individu; $CaCO_3$, Li_2CO_3 dan LiCl. Didapati hanya Li_2CO_3 dan LiCl yang dapat menghasilkan karbon. Gambar SEM karbon yang terhasil daripada elektrolit Li_2CO_3 terdiri daripada 'particles' dan 'tubes' dengan diameter antara 0.05 hingga 0.2µm, manakala LiCl menghasilkan 'large flakes' dan 'small particles' dengan saiz 0.5 hingga 6.5µm. Karbon yang disediakan dalam campuran garam $CaCO_3$-Li_2CO_3-LiCl mendedahkan lima mikrostruktur dominan: 'grape-like', 'tubes', 'thread-like', 'spheres', dan 'flakes'. Struktur 'nanotubes' berdiameter luar 13 – 90nm juga dikesan menggunakan analisis TEM. Saiz mikrostruktur karbon mengecil dengan peningkatan suhu, dan membesar apabila voltan sel meningkat. Analisis unsur telah mengesahkan bahawa produk yang disediakan dalam garam yang baru dirumuskan pada pelbagai suhu dan voltan mempunyai kandungan karbon 69 - 82%. Analisis XRD telah menunjukkan pepejal karbon mempunyai struktur amorfus untuk semua sampel karbon. Kecekapan elektrolisis untuk proses yang dijalankan pada 550°C (70-85%), 650°C (28-46%) dan 750°C (59 – 79%), dan ia menunjukkan 'trend' yang aneh di mana 550°C memberi kecekapan tertinggi, diikuti oleh 750°C dan 650°C. Kecekapan elektrolisis yang lebih tinggi menggunakan tenaga yang kurang, sekaligus menunjukkan 'trend' yang sama bagi penggunaan tenaga; elektrolisis pada 550°C (62 – 85kW.h/kg) menggunakan tenaga terendah diikuti dengan elektrolisis pada 650°C (186 – 554kW.h/kg) dan 750°C (70 – 126kW.h/kg).

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LIST OF ABBREVIATIONS

SEM	-	Scanning Electron Microscopy
TEM	-	Transmission Electron Microscope
EDX	-	Energy-dispersive X-ray Spectroscopy
EA	-	Elemental Analyzer
XRD	-	X-ray Powder Diffraction
CV	-	Cyclic voltammogram
SSA	-	Specific surface area
BET	-	Brunauer – Emmett – Teller
CNT	-	Carbon nanotubes
OD/*o.d*	-	Outer diameter
i.d	-	Internal diameter
Temp.	-	Temperature
m.p.	-	Melting point
i.e.	-	In essence

LIST OF SYMBOLS

I	-	Current
t	-	Time
V	-	Voltage
R	-	Resistance

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

Molten salts are preferred electrolyte for electro-deposition process in collecting solid carbon. Molten salts compose a classification of liquids which are known as ionic liquids or molten electrolytes. Comparable to liquids at room temperature, these salts have differing characteristics. The liquid state of the salts is intermediate between the gaseous and solid states, therefore, it presents neither the structural regularity of solid crystals nor the typical disorder of gases (Galasiu, Galasiu, and Thonstad, 1999). Molten salts have high conductance and excellent medium for electrochemical reactions. It completely ionized into its respective ions when it melts (Chipperfield, 1999).

Molten carbonate salts which contains carbonate ions normally use as electrolyte for preparation of solid carbon via electrolysis process. Carbonate ions is the main element in the mechanism of solid carbon deposition (Ingram, Baron, and Janz, 1966; Ijije, Sun, and Chen, 2014; Mao *et al.*, 2016). Although carbonate salts are preferable due to the presence of carbonate ions in the salt, chloride salts would be able to produce solid carbon with the usage of graphite electrode (Chen *et al.*, 1998; Kaptay *et al.*, 2000; Schwandt, Dimitrov, and Fray, 2010; Schwandt, Dimitrov, and Fray, 2012) or with the addition of metal oxide with the introduction of CO_2 gas inside the system (Otake, Kinoshita, Kikuchi, and Suzuki, 2013; Li, Shi, Gao, Hu, and Wang, 2016).

1.2 Carbon Materials Demand in Various Applications

Nanocarbon or carbon based-nanomaterials such as carbon nanotubes, graphene, carbon fibres, fullerene, nano-diamonds and hollow carbon nanostructures had been broadly used in various industrial application *i.e.* energy storage, electronic nanodevices, flat panel displays, drug delivery, biosensors, conductive coatings and environment remediation, and etcetera. The nanocarbons properties was determined by its microstructure, size and structure. For instance, carbon nanotubes were used in supercapacitors due to its low electronic and ionic charge-transfer resistances, whereas for graphene, it possesses good electrical conductivity and high surface area (Zhang *et al.*, 2013; Mao *et al.*, 2017).

Production of high performance carbon materials had been one of the main studies in material science research, and electrolysis of molten salts is a promising process in which solid carbon could be obtained in micro- and nano- sized with wide variety of microstructures (Deng *et al.*, 2018). Therefore, for the carbon materials produced by using this process could be utilized in various application, intensive study was done on the carbon materials obtained.

1.3 Electro-deposition of Solid Carbon via Electrolysis in Molten Salt under CO_2 Gas Environment

Electrolysis is a process which involves the splitting of a substance when electrical energy was fed into the system (Silberberg, 2006: 941). Carbonaceous materials could be obtained by deposition of solid carbon on electrode with utilization of CO_2 gas as carbon source via electrolysis process, which also known as electro-deposition process. Electrochemical conversion of CO_2 gas into fuels or solid carbon has attracted the attention of many researchers, industries and governments due to its amenability to automation and the increasing interest towards renewable energy (Tang *et al.*, 2013). Therefore, the electro-conversion of CO_2 gas to solid carbon has been widely reported; mostly through a process using a molten salt electrolyte containing a carbonate (Ingram, Baron, and Janz 1966; Tang *et al*. 2013; Le Van *et al*. 2009; Yin *et al*. 2013; Ijije *et al*. 2014), or mixture of carbonate and chloride (Dimitrov, Chen, Kinloch, and Fray, 2002; Novoselova *et al*., 2008; Ge, Hu, Wang, Jiao, and Jiao, 2015; Deng *et al.*, 2018) in which solid carbon was deposited on the cathode surface. Various mixtures have been reported, including pure carbonate salt mixtures of Li_2CO_3–Na_2CO_3–K_2CO_3 (Groult *et al.*, 2006; Le Van *et al.*, 2009; Tang *et al.*, 2013), Li_2CO_3–K_2CO_3 (Gakim, Khong, Janaun, Yun Hsien, and Siambun, 2015; Ijije *et al.*, 2014), Na_2CO_3–K_2CO_3 and $CaCO_3$–Na_2CO_3–K_2CO_3 (Licht, 2012), and carbonate-chloride salt mixtures of K_2CO_3–KCl–LiCl (Kawamura and Ito, 2000), Li_2CO_3–LiCl (Dimitrov, 2003; Ge *et al.*, 2015), $CaCO_3$–$CaCl_2$–LiCl–KCl (Gakim *et al.*, 2015), Na_2CO_3–LiCl–NaCl (Ge, Wang, Hu, Zhu, and Jiao, 2016) and LiCl-KCl-$CaCO_3$ (Deng *et al.*, 2018). Despite the successful deposition of carbon being reported with one or more alkali or alkaline-earth metal carbonates in the presence of a molten salt (Dimitrov, 2003; Le Van *et al.*, 2009; Tang *et al.*, 2013; Yin *et al.*, 2013; Ijije *et al.*, 2014; Gakim *et al.*, 2015; Ge *et al.*, 2015), the selection of the salt mixture was not clearly explained by the researchers.

The vast selection of salts makes it challenging to identify the optimum salt mixture to use as a medium for the electro-conversion process, but most studies preferred to use an alkali carbonate. The presence of carbonate ions (CO_3^{2-}) has shown to substantially increase the amount of carbon deposited (Lantelme *et al.*, 1999). The carbonate ions were directly reduced to carbon and oxide ions at the cathode. In turn, the oxide ions reacted with CO_2 to regenerate the carbonate ions given CO_2 gas was supplied throughout the electrolytic process (Ijije *et al.*, 2014; Gakim *et al.*, 2015). In this research, the molten salt was formulated to have low electrochemical stability but with high ability to absorb and convert CO_2 to carbon. In addition, the melting temperature was low to reduce energy consumption.

It has been reported that both electrolysis voltage and temperature have a direct effect on the characteristics of the carbon produced. Using pure carbonate salt, Tang *et al.* (2013) and Yin *et al.* (2013) claimed that in the electro-deposition from a Li_2CO_3–Na_2CO_3–K_2CO_3 mixture, the carbon particle size decreased as the voltage increased. Similar observations were reported by Ijije *et al.* (2014) when using Li_2CO_3–K_2CO_3 mixture. In studies on the effect of electro-deposition temperature in a Li_2CO_3–Na_2CO_3–K_2CO_3 mixture by Tang *et al.* (2013) and Le Van *et al.* (2009), it was found that carbon particle size increased with increasing deposition temperature. By contrast, Ijije *et al.* (2014) reported that particle size reduced as temperature increased for carbon electro-deposition in a

Li_2CO_3–K_2CO_3 mixture. Ge *et al.* (2016) studied the effect of voltage and temperature variation for a carbonate-chloride mixture of Na_2CO_3–LiCl–NaCl and reported that the quasi-spherical particle shape changed as voltage increased. At high voltage and temperature, the current efficiency decreased due to formation of lithium carbide or alkali metals at high voltage. In addition, the accumulation of carbon debris at the bottom of the melt also affected the process performance. In this work, the effects of electrolysis temperature and voltage were examined in the newly formulated $CaCO_3$-Li_2CO_3-LiCl mixture to determine their impact on the carbon microstructure, elements, structure, current efficiency, and energy consumption for the process.

1.4 Problem Statement

Carbon materials especially nanocarbons had been widely used in various application *i.e.* energy storage, supercapacitors, biosensors and etcetera. The properties of carbon materials: microstructure, size and structure, are the important characteristics in determining its potential application. Electrolysis of molten salts could produce wide variety of carbon materials which have promising potential to be utilized in the related industries. Electrolyte with low melting temperature for production of solid carbon in electrolysis process is economical and the yield can be easily control. Temperature and voltage supply also play an important factor in the characteristics of the produced solid. However, the molten carbonate and chloride salts which often use as the electrolyte possesses high melting temperature that could lead to high usage of energy and production of undesired substance due to side reactions. Moreover, the variation on operating temperature and voltage supply was not vastly studied, therefore, the effect of the parameters on the produced solid was still vague. Formulating a mixture of carbonate-chloride salt as an electrolyte would lowered the melting temperature of the electrolyte, and, with varied operating temperature and voltage supply, the yield of solid deposition can be monitored. Optimization of process efficiency will lower the energy consumption during the electrolysis process and interesting structures of solid deposition could be obtained.

1.5 Aim and Objectives

The aim of this study is to formulate a molten salt mixture as the electrolyte for the electro-deposition process of solid carbon by electrolysis of molten salt in carbon dioxide gas. Mixture of carbonate-chloride salt have been suggested for the electrolysis process. The main objectives of the study are:

1. To formulate a novel low melting temperature carbonate-chloride salt mixture which enable to produce solid carbon via electro-deposition process by electrolysis of molten salt in carbon dioxide gas environment.
2. To study the effect of temperature and voltage variation in electro-deposition process via electrolysis of carbonate-chloride salt mixture.
3. To characterize the collected solid carbon by its microstructure, element, and structure.

1.6 Scope of Study

This study was limited to the electro-deposited solid carbon in electrolysis of formulated $CaCO_3$-Li_2CO_3-LiCl with CO_2 gas environment. Figure 1.1 shows the research flow chart of this study.

1. $CaCO_3$-Li_2CO_3-LiCl salt mixture was formulated in Molten Salt Laboratory Faculty of Engineering, UMS, to obtain a low melting temperature electrolyte for electro-deposition of solid carbon via electrolysis of molten salt.

2. The eutectic mixture contains both essential ions, Li^+ and CO_3^{2-} (Li_2CO_3-LiCl), whereas $CaCO_3$ was added as additive.

3. Preliminary experiment with single-salt electrolysis process was conducted to determine whether $CaCO_3$, Li_2CO_3 and LiCl could undergo electrolysis process and deposition of solid on cathode can be obtained.

4. The electrolysis of single-salt and $CaCO_3$-Li_2CO_3-LiCl electrolyte was conducted in laboratory scale.

5. Electrolysis process was carried out in a sealed retort chamber with purified CO_2 gas supply.

6. Electrolysis time was fixed to three hours to accumulate sufficient amount of solid deposition.

7. Stainless steel type AISI 304 was chosen as the electrodes and crucible due to its high corrosion resistance characteristic and inexpensive.

8. Electro-deposited solid obtained from single-salt electrolysis process was characterized by SEM/EDX and XRD to observe the microstructures and type of structure exhibit by the solid deposition.

9. The effect of operating temperature and voltage supply in electrolysis of $CaCO_3$-Li_2CO_3-LiCl electrolyte was studied in respect to the yield of solid deposited, its microstructures, elements, and structure.

10. Current efficiency and energy consumption in the electrolysis of $CaCO_3$-Li_2CO_3-LiCl electrolyte was observed due the variation of operating temperature and voltage supply.

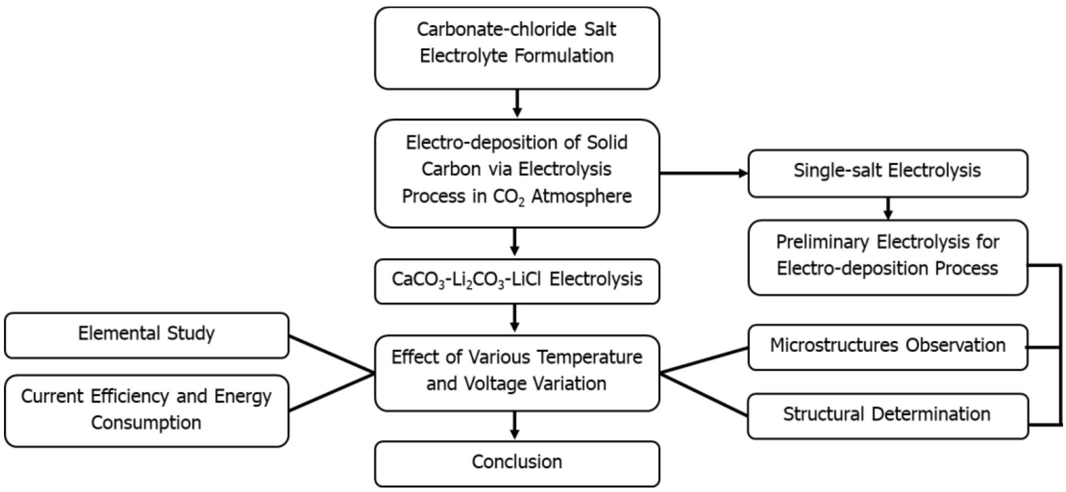

Figure 1.1: Research flow chart.