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School of Energy and Environment

Factors Affecting Anion Intercalation into Graphite

A thesis submitted to the City University of Hong Kong in partial fulfillment of the Bachelor degree of Engineering in Energy Science and Engineering

Prepared by
CHAN Cheuk Ying

Supervisor: Dr. Denis Y. W. YU
Moderator: Dr. Chun Hua LIU
Abstract

In the 21st century, Lithium ion battery (LIB) has widely been used and it is the most popular one among the secondary battery. However, the idea of dual carbon battery has emerged since it has potential to overcome the disadvantages of LIB. In dual carbon battery, both cathode and anode use carbon as active material while the cations and anions in electrolyte are acted as charge carrier.

In this thesis, anion especially PF$_6^-$ is studied with 5 factors which are, type of binder, active material, electrode composition, voltage range and electrolyte concentration affecting the performance of anion intercalation. The cells are tested with physical methods including cyclic voltammetry and ex situ XRD are used to investigate the mechanisms of charge-discharge process and identify the problems in anion intercalations. Consequently, electrochemical methods are used to study the improvement in charge-discharge, rate performance and self-discharge during resting time by varying the electrode compositions.
Acknowledgement

Firstly, I would like to express my sincere gratitude to my supervisor Dr. Denis Yu Y. W. from School of Energy and Environment for giving me a valuable opportunity to be part of his team as an FYP student. I am thankful for his endless support, sincere advice and immense knowledge on this research project. This experience is vital for me as an engineering student.

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Table of contents

Tables and Figures .............................................................................................................................. 5
List of Abbreviations .......................................................................................................................... 8

1 Introduction ................................................................................................................................ 8
   1.1 Background .............................................................................................................................. 8
   1.2 Objectives and Scope .............................................................................................................. 10

2 Literature Review ......................................................................................................................... 12
   2.1 Mechanism .............................................................................................................................. 12
      2.1.1 Anion intercalation ........................................................................................................... 12
      2.1.2 Electrolyte decomposition ............................................................................................... 14
   2.2 Different concentration of electrolyte .................................................................................. 15
   2.3 Different electrolyte solvent ................................................................................................. 16
   2.4 Plane distance of graphite material ..................................................................................... 17
   2.5 Rate performance of PF\textsubscript{6} intercalation ............................................................. 17
   2.6 Self-discharge problem in supercapacitor and Lithium-ion battery .................................. 18

3 Methodology ............................................................................................................................... 19

4 Experimental Design .................................................................................................................... 20
   4.1 Battery making ....................................................................................................................... 20
      4.1.1 Stage 1 – Electrode coating ............................................................................................... 20
      4.1.1.1 Preparation of slurry ................................................................................................... 21
      4.1.2 Stage 2 – Cell assembling ............................................................................................... 22
   4.2 Cell testing - Electrochemical analysis ................................................................................. 23
      4.2.1 Cyclic voltammetry (CV) ................................................................................................. 23
   4.3 Cell testing – physical analysis ............................................................................................... 24
      4.3.1 X-Ray Diffraction (XRD) ................................................................................................. 24
      4.3.2 Scanning Electron Microscopy (SEM) ............................................................................ 24

5 Results and Discussion .................................................................................................................. 25
   5.1 Electrode composition affecting anion intercalation ........................................................... 25
      5.1.1 Graphite materials ........................................................................................................... 25
   5.2 Improvement for PF\textsubscript{6} intercalation .......................................................................... 29
      5.2.1 Add AB to the active material ......................................................................................... 29
      5.2.2 Reduce the voltage range ............................................................................................... 32
      5.2.3 Increase the electrolyte concentration ......................................................................... 34
   5.3 Change of graphite material, binder and AB composition ................................................ 37
   5.4 Charge-discharge mechanism of PF\textsubscript{6} in graphite ...................................................... 43
      5.4.1 Ex situ XRD ..................................................................................................................... 43
      5.4.2 Cyclic voltammetry ........................................................................................................ 46
   5.5 Rate Performance of PF\textsubscript{6} intercalation ..................................................................... 50
      5.5.1 Change of graphite material, binder and AB amount .................................................... 51
   5.6 Self-discharge in anion intercalation ....................................................................................... 67

6 Conclusion ................................................................................................................................. 71

7 Future Works ............................................................................................................................. 72

8 List of Reference .......................................................................................................................... 73

9 Appendix ................................................................................................................................... 75
Tables and Figures

Table 1  List of abbreviations ............................................................................................................ 8
Figure 1  D/C of dual carbon battery and lithium-ion battery .......................................................... 10
Figure 2  Scope of study ................................................................................................................... 11
Figure 3  Summary of material needed in an electrode coating ......................................................... 20
Flowchart 1  The procedure of preparing a slurry ........................................................................... 21
Flowchart 2  The procedure of preparing electrode ......................................................................... 21
Figure 4  Compartment of a coin cell ............................................................................................... 22
Flowchart 3  The procedure of assembling a coin cell ...................................................................... 22
Flowchart 4  The procedure of cell testing for charge-discharge .................................................... 23
Figure 5  SEM images with 2000 magnification of (a) MTI artificial graphite, (b) Sigma graphite and (c) KS6 graphite respectively ..................................................................................... 25
Table 2  BET specific surface area of graphite materials ..................................................................... 26
Figure 6  1st cycle D/C curve of different graphite in PVdF at 3-5.3V .................................................. 27
Figure 7  Discharge capacity of graphite in PVdF at 3-5.3V ............................................................... 27
Figure 8  The relationship of 1st cycle discharge capacity and BET specific surface area .................. 28
Figure 13  1st cycle D/C curve of KS6 with AB and without AB ........................................................ 30
Figure 14  CE of KS6 with AB and without AB along 1st – 20th cycles .............................................. 30
Figure 15  Discharge capacity of KS6 with AB and without AB along 1st – 20th cycles ...................... 31
Figure 16  1st cycle D/C curve at 3-5.1V and 3-5.3V ........................................................................ 32
Figure 17  Discharge capacity of KS6:AB:PVdF at 3-5.1V and 3-5.3V ............................................. 32
Figure 18  CE of KS6:AB:PVdF at 3-5.1V and 3-5.3V ..................................................................... 33
Figure 19  1st cycle D/C curve of Sigma graphite in different concentration of LiPF6 in PVdF at 3-5.3V ......................................................................................................................... 34
Figure 20  1st cycle D/C curve of KS6:AB:PVdF in 1-3M LiPF6 at 3-5.1V .......................................... 35
Figure 21  Discharge capacity of KS6:AB:PVdF in 1-3M LiPF6 FECDEC .......................................... 35
Figure 22  Coulombic efficiency of KS6:AB:PVdF in 1-3M LiPF6 FECDEC ...................................... 36
Table 3  Summary of the combination of graphite material, AB amount and binder ......................... 37
Table 4  Summary of the comparisons of electrodes with respect to Table 3 and the results in D/C test ........................................................................................................................................ 38
Figure 24  Coulombic efficiency of different electrode composition in 20 cycles ................................. 39
Figure 25  Typical discharge capacity along 10th – 20th cycle of 8 electrode component .................... 39
Figure 26  Average CE along 10th – 20th cycle of 8 electrode component .......................................... 40
Figure 27  The positions of 6 stages in the charge-discharge curve for ex situ XRD test ................. 43
Figure 28  The arbitary unit vs 2θ of (00n) in the ex situ XRD test ..................................................... 44
Table 5  The summary of the relationship of 2θ and d_{00n} and the cumulative capacity ...................... 45
Figure 29  The change of cumulative capacity during charge-discharge ........................................... 45
Figure 30  Cyclic voltammetry profile of Sigma graphite with 1M LiPF6 ........................................... 47
Figure 31  Graph of normalized peak current versus square root of the scan rate ............................. 47
Figure 32 CV test for KS6:AB:CMC = 7:2:1 1M LiPF$_6$ FECDEC at 0.06 mV/s ....................... 48
Figure 33 CV test for KS6:AB:CMC 1-3M LiPF$_6$ FECDEC ........................................................ 49
Figure 34 Rate performance of Sigma graphite with 1M LiPF$_6$ and PVdF .............................. 50
Table 6 Summary of electrode component tested in rate performance ........................................ 51
Table 7 Electrodes for comparison and their factors to be compared ......................................... 52
Figure 35 Rate performance of KS6:AB:PvDF = 7:2:1 with 3M LiPF$_6$ .............................. 53
Figure 36 Rate performance of KS6:AB:CMC = 7:2:1 with 3M LiPF$_6$ ..................................... 53
Figure 37 Discharge capacity of KS6:AB:CMC = 7:2:1 and KS6:AB:PvDF = 7:2:1 with 3M LiPF$_6$ .............................................................. 54
Figure 38 Rate performance of KS6:AB:PAA = 85:5:10 with 3M LiPF$_6$ .............................. 55
Figure 39 Rate performance of KS6:AB:CMC = 85:5:10 with 3M LiPF$_6$ .............................. 55
Figure 40 Discharge capacity of KS6:AB:PAA = 85:5:10 and KS6:AB:CMC = 85:5:10 with 3M LiPF$_6$ .............................................................. 56
Figure 41 Rate performance of Sigma:CMC = 9:1 with 3M LiPF$_6$ ......................................... 57
Figure 42 Rate performance of Sigma:PAA = 9:1 with 3M LiPF$_6$ ........................................ 57
Figure 43 Discharge capacity of Sigma:CMC = 9:1 and Sigma:PAA = 9:1 with 3M LiPF$_6$ ..... 58
Figure 44 Rate performance of Sigma:AB:PvDF = 8:1:1 with 3M LiPF$_6$ ................................ 59
Figure 45 Rate performance of Sigma:AB:CMC = 8:1:1 with 3M LiPF$_6$ .............................. 59
Figure 46 Discharge capacity of Sigma:AB:PvDF = 8:1:1 and Sigma:AB:CMC = 8:1:1 with 3M LiPF$_6$ .............................................................. 60
Figure 47 Rate performance of KS6:AB:CMC = 7:2:1 with 3M LiPF$_6$ ..................................... 61
Figure 48 Rate performance of KS6:AB:CMC = 85:5:10 with 3M LiPF$_6$ .............................. 61
Figure 49 Discharge capacity of KS6:AB:CMC = 7:2:1 and KS6:AB:CMC = 85:5:10 with 3M LiPF$_6$ .............................................................. 62
Figure 50 Discharge capacity of Sigma:CMC = 9:1 and Sigma:AB:CMC = 8:1:1 with 3M LiPF$_6$ .............................................................. 64
Table 8 Summary of electrode showing the factor to be compared in the electrode in self-discharge in anion intercalation........................................ 67
Figure 51 The relationship between starting voltage after resting and resting time for Sigma:CMC = 9:1 and Sigma:AB:CMC = 7:2:1 in TFSI................................. 68
Figure 52 The relationship between starting voltage after resting and resting time for Sigma:PAA = 9:1 and Sigma:CMC = 9:1 in TFSI ........................................ 69
Figure 53 The relationship between starting voltage after resting and resting time for KS6:AB:PAA = 8:1:1 in PF$_6$ and KS6:AB:PAA = 8:1:1 in TFSI ................................................. 70
Figure 54 D/C curve of KS6:AB:CMC = 7:2:1 measured under 3-5.1V with 10 mA/g .......... 75
Figure 55 D/C curve of KS6:AB:CMC = 85:5:10 measured under 3-5.1V with 10 mA/g ........ 75
Figure 56 D/C curve of KS6:AB:CMC = 85:5:10 measured under 3-5.1V with 10 mA/g .......... 76
Figure 57 D/C curve of Sigma:CMC = 8:1:1 measured under 3-5.1V with 10 mA/g .......... 76
Figure 58 D/C curve of Sigma:CMC = 8:1:1 measured under 3-5.1V with 10 mA/g .......... 77
Figure 59 D/C curve of Sigma:CMC = 8:1:1 measured under 3-5.1V with 10 mA/g .......... 77
Figure 60 D/C curve of Sigma:CMC = 9:1 measured under 3-5.1V with 10 mA/g .......... 78
Figure 61 D/C curve of Sigma:CMC = 9:1 measured under 3-5.1V with 10 mA/g .......... 78
Figure 64 D/C curve of Sigma:PAA = 9:1 measured under 3-5.1V with 10 mA/g

Figure 65 1st cycle D/C curve of KS6:AB:CMC in 1-3M LiPF$_6$ at 3-5.1V

Figure 66 Discharge capacity of KS6:AB:CMC in 1-3M LiPF$_6$ FECDEC

Figure 67 Voltage drop of Sigma:CMC = 9:1 during different resting time between D/C

Figure 68 Voltage drop of Sigma:AB:CMC = 7:2:1 during different resting time between D/C

Figure 69 Voltage drop of Sigma:PAA = 9:1 during different resting time between D/C

Figure 70 Voltage drop of KS6:AB:PAA = 8:1:1 with PF$_6$ anion during different resting time between D/C

Figure 71 Voltage drop of KS6:AB:PAA = 8:1:1 with TFSI anion during different resting time between D/C
### List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviations</th>
<th>Full form</th>
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<tbody>
<tr>
<td>LIBs</td>
<td>Lithium ion batteries</td>
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<tr>
<td>D/C curve</td>
<td>Discharging and charging curve</td>
</tr>
<tr>
<td>CE</td>
<td>Coulombic efficiency</td>
</tr>
<tr>
<td>LiPF$_6$</td>
<td>Lithium hexafluorophosphate</td>
</tr>
<tr>
<td>TFSI</td>
<td>Bis(trifluoromethane)sulfonimide</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
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<tr>
<td>CMC</td>
<td>Carboxymethyl cellulose</td>
</tr>
<tr>
<td>PVdF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>PAA</td>
<td>Polyacrylic acid</td>
</tr>
<tr>
<td>AB</td>
<td>Acetylene Black</td>
</tr>
<tr>
<td>FEC/DEC</td>
<td>Fluoroethylene carbonate / diethyl carbonate</td>
</tr>
<tr>
<td>EC/DMC</td>
<td>Ethylene carbonate / dimethyl carbonate</td>
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<tr>
<td>Gr</td>
<td>Graphite</td>
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Table 1  List of abbreviations
1 Introduction

1.1 Background

Nowadays, with the technology advancement, electric car becomes more and more popular. Battery plays a major role in developing electric transport since battery works as the energy storage. However, battery remains a critical issue for the public because of the capacity, battery decay, safety problem and environmentally friendliness as well.

Traditionally, Lithium-ion battery is used and it is the most popular one among the secondary batteries. The mechanism of Li-ion battery is based on the transfer of Li\(^+\) ions between electrodes during charge and discharge. The transverse of Li\(^+\) ions between two interfaces during charge and discharge affects the rate performance of battery because the Li\(^-\) inserting process has a slower rate. The ionic diffusion in the solid electrodes in LIB also contributes to the rate-limiting factor in the battery power performance\(^1\). In order to solve this problem, decoupling of insertion and extraction processes by introducing anion are able to increase the power of the processes.

This idea has fostered the idea of dual carbon battery that anion reaction is introduced in the battery reactions. During charging, both anion and cation go into the electrodes while both types of ions comes out from the electrodes during discharging. The dual-ion battery performs a hybrid battery between flow battery and lithium ion battery. Since the feature of a dual-ion battery is that anion is introduced in the reaction, a cathode material is chosen to accept anions. The illustration of mechanism of both dual carbon battery and LIB are shown in Figure 1 below.

A material engineering company “Power Japan Plus” has announced plans to commercialize dual carbon battery\(^3\) which has the same energy density as LIB but less capacity loss and much safer as lithium metal is not used.

In the previous research, Lithium ion intercalation is studied but not the anion intercalation. It is vital to conduct research on anion intercalation in order to make headway to develop a powerful dual carbon battery.


1.2 Objectives and Scope

The aim of this project is to study the reasons of capturing anions especially PF$_6^-$ in cathode for batteries and how to achieve high capacity and cycle stability. Half-cell is made so as to investigate on the anion intercalation. On top of that, rate performance and self-discharge of anion intercalation will be discussed with the respective factors.

This study focuses on
1. Investigate the different types of graphite,
2. Choose an appropriate binder for coating the cathode,
3. Analyses the D/C mechanism of anion intercalation
4. Study how is the surface area of graphite, concentration of LiPF$_6$, AB to graphite ratio and binder selection and affect the battery capacity, cycle stability, rate performance and self-discharge,
5. Evaluate using different anion except PF$_6$ affecting the anion intercalation process

Figure 2  Scope of study
2 Literature Review

2.1 Mechanism

The working principle of a dual carbon battery is similar to the LIBs in a way that they require a pair of electrodes which are different in potential and they are able to undergo reversible redox reactions.

However, unlike LIBs, carbon is used as cathode and anode in dual carbon battery. When the reaction is taken place, cations and anions in the electrolyte are used to charge the electrode. For LiPF₆ is used as the electrolyte, the cation Li⁺ intercalates into the anode while the anion PF₆⁻ intercalates into the cathode. In LIBs, only Li⁺ intercalation is performed during redox reaction.

2.1.1 Anion intercalation

Among all the anions, PF₆⁻ is the most common anion to be studied in the previous research. In PF₆ intercalation, the operation of the cell is one of the main concerns of the study. For a dual carbon battery, two different intercalants are involved during charge and discharge and there are changes in the electrolyte concentration during the process. Therefore, cell potential is crucial for the determination the cell operation.⁴

During the operation of the cell, here are the half-cell equation and overall equation:

Anode: \( C + x\text{Li}^+ + x\text{e}^- \Leftrightarrow \text{Li}_x\text{C} \) \ [Equation 1]
Cathode: \( C + x\text{A}^- \Leftrightarrow \text{A}_x\text{C} + x\text{e}^- \) \ [Equation 2]
Overall equation: \( 2C + x\text{Li}^+ + x\text{A}^- \Leftrightarrow \text{Li}_x\text{C} + \text{A}_x\text{C} \) \ [Equation 3]

For $n$ Li atoms and $n$ A molecules are intercalated into electrodes, $n$ electrons are transferred in the external circuit. The cell potential is given by this equation:

$$-neV = n(\mu_{Li} - \mu_{Li^+}) + n(\mu_{A} - \mu_{A^-})$$  \[\text{Equation 4}\]

$\mu_{Li}$ is the chemical potential of Li intercalated in anode, $\mu_{Li^+}$ is the chemical potential of Li$^+$ in electrolyte, $\mu_{A}$ and $\mu_{A^-}$ are analogous quantities for A and A$^-$ respectively. For the $\mu_{Li^+}$ and $\mu_{A^-}$, they can be found by Nernst equation below.

$$\mu_{Li^+} = \mu_{\circ Li^+} + kT \ln[Li^+]$$, $\mu_{A^-} = \mu_{\circ A^-} + kT \ln[A^-]$  \[\text{Equation 5}\]

$\mu_{\circ}$ is the chemical potential of ion in 1M solution.

By combining Equation 4 and 5,

$$-eV = \mu_{Li} + \mu_{A} - \mu_{\circ Li^+} - \mu_{\circ A^-} - 2kT\ln[Li^+]$$  \[\text{Equation 6}\]

For the half-cell with Lithium metal as the anode,

$$-eV = \mu_{\circ Li} + \mu_{A} - \mu_{\circ Li^+} - \mu_{\circ A^-} - 2kT\ln[Li^+]$$  \[\text{Equation 7}\]

From the Nernst equations shown in the literature, it shows that the chemical potential depends on the solvent used and also the anion type. In the Equation 6 and 7, it shows that the concentration of the electrolyte affects the potential of the cell during operation.

Beside PF$_6^-$, TFSI$^-$ intercalation is also revealed. It is found that electrolyte with TFSI$^-$ intercalated into graphite cathode has a sufficiently high coulombic efficiency. This results are proved that it is dependent on the stability of the intercalated anion and the high oxidative stability of the electrolyte mixture$^5$.

---

2.1.2 Electrolyte decomposition

As mentioned, electrolyte in dual carbon battery provides charges to the electrode. This implies that the electrolyte drives the performance of the dual carbon battery. Therefore, electrolyte decomposition is essential to be minimized during charge and discharge.

Studies relate solvent with the reaction kinetics of LiPF$_6$ and water$^6$ which implies the factors affecting the chemical reaction rate. Different solvent used would have different effect in electrolyte decomposition with water. During storage of the electrolyte, there will be a small amount of water present and it causes the electrolyte to decompose. The electrolyte LiPF$_6$ dissociates to form PF$_5$ and it reacts with water to form hydroxides and oxides which are not ion conductive$^6$. Therefore, a lower water content is beneficial for dual carbon battery.

Different solvents have a different reaction rate because of the viscosity, polarity and the solvation of the solvent. In this study, the first two factors are investigated and it is concluded that relative permittivity contribute the most to the reaction. Solvents with high relative permittivity are more difficult for LiPF$_6$ to react with water and this affects the rate constant of electrolyte decomposition. For example, the relative permittivity of FEC is higher than EC$^7$. Another aspect of electrolyte decomposition is because of high voltage applied in the presence of solvents.

By obtaining the order of reaction rate from in the empirical equation, dielectric constants are obtained by the inverse proportion of reaction rate. EC/DMC has the highest dielectric constants and it has a more rapid ionization of LiPF$_6$. Hence it could suppress the reaction with water.


2.2 Different concentration of electrolyte

In order to achieve high energy density, concentration of the electrolyte in dual carbon battery has to be increased since the electrolyte not only provides the path for ion exchange but also the source of charges for both electrodes.

The effect of difference in maximum salt concentration in the electrolyte is calculated between both fully charged and discharged states\(^8\). The volumetric and gravimetric energy density is calculated by multiplying the average cell potential by the volumetric and gravimetric capacity. By plotting the specific energy verses the electrolyte concentration, it is found that increasing the electrolyte molarity increases the cell’s energy density. The result is more obvious when only electrodes and electrolyte are taken into account\(^9\). In a recent research, high energy density dual carbon battery is studied using different concentration of LiPF\(_6\) as the electrolyte in EC/DMC. The effect of the anion intercalation into graphite is determined through the capacity and the potential\(^9\).

In cathode, the capacity of the graphite KS6 increased with increasing concentration of LiPF\(_6\). However, the capacity decreases for anode when the concentration of LiPF\(_6\) increases. This implies that PF\(_6^-\) intercalation increases and the Li\(^+\) intercalation decreases when the concentration of LiPF\(_6\) increases. As for activation energy, it is almost the same for cathode in different concentrations of electrolyte.

From the Raman spectroscopy, it shows that increasing the concentration of LiPF\(_6\) would increase the amount of solvated Li\(^+\) while PF\(_6^-\) is a large anion and it will not solvate in organic electrolyte. So there would be interaction between PF\(_6^-\) and Li\(^+\) in concentrated LiPF6/DMC. The self-diffusion coefficient is also larger for PF\(_6^-\) than Li\(^+\) so the mobility of PF\(_6^-\) is high in concentrated LiPF\(_6\). As for Li\(^+\), it is solvated in increasing LiPF\(_6\) concentration. So the activation energy is higher for Li\(^+\) intercalation.

---


As a result, PF$_6^-$ intercalation is preferred in the presence of higher concentration of electrolyte in cathode. Therefore, it is necessary to investigate and justify the activation energy changes in different concentration of electrolyte in cathode in the future studies.

### 2.3 Different electrolyte solvent

Studies have revealed that different solvent in the presence of PF$_6$ has different effect on anion intercalation into graphite and the cycle performance. It is found that the battery performance has improved a lot when the EMC content is in a suitable ratio of sulfolane (SL)$^{10}$. The PF$_6^-$ ions can be inserted into graphite positive electrode efficiently. By using the cyclic voltammetry, it is verified that increasing the EMC concentration would accelerate the PF$_6^-$ intercalation kinetics. This implies that there is adequate PF$_6^-$ transfer across the graphite interface. Both XRD and Raman spectra indicates there is a two-phase region in stages 1 and 2 when the EMC is of 4vol.% of SL. Further analysis of interaction is done by IR and NMR spectra.

This explains that PF$_6^-$ can insert into graphite in cathode smoothly when anion in solvent SL is being interrupted by the attraction of Li$^+$ and PF$_6^-$ with appropriate amount of EMC.

Another literature has studied EMS as a solvent of LiPF$_6$ which has a better oxidation stability than EC$^{11}$. It is proved by using in situ XRD and CV for the cell using 2M LiPF6/EMS and 1M LiPF6 EC+DEC. They are charged up to 5.3-5.4V and 4.9-5.1V respectively. From the X-Ray pattern, the anion intercalation is reversible in the former cell while in the differential capacity measurements, the curves plotted shows that the cells with 1M LiPF6 EC+DEC cannot be charged up to 5.2V. It is probably due to the graphite structure is being destroyed and there is electrolyte decomposition. These support the fact that solvent affects the cell potential and performance of a dual carbon battery.

---


2.4 Plane distance of graphite material

Carbon structure is an influential factor for anion intercalation since anion is intercalated between layers of carbon during charge and anion is taken out during discharge. So carbon with smaller plane distance will have a larger capacity.

Crystallinity of carbon is a dominant factor that determines the PF$_6^-$ intercalation capacity$^{12}$. Higher crystallinity of carbon implies a smaller plane distance, $d_{002}$. With smaller $d_{002}$, the reversible intercalation capacity increased and the intercalation capacity is high. The graphitic carbon achieves the best performance is the one with 0.334nm as the plane distance.

2.5 Rate performance of PF$_6^-$ intercalation

In PF$_6^-$ intercalation into graphite, diffusion constant and activation energy determines the rate property. Both measurements are obtained by two electrochemical methods which are galvanostatic intermittent titration technique (GITT) and electrochemical impedance spectroscopy (EIS). It is found that the diffusivity of PF$_6^-$ in graphite is higher than that of Li$^+$ in LiFePO$_4$ or other oxide cathode material in LIB$^{13}$. The density functional theory (DFT) calculations suggested that PF$_6^-$ migrates along $<100>$ family of directions with an estimated activation energy of 0.23 eV. This shows that PF$_6^-$ is capable of achieving higher rate property than LIB. When higher current rate is applied, PF$_6^-$ intercalation is allowed to have stable cycle performance.


2.6 Self-discharge problem in supercapacitor and Lithium-ion battery

Self-discharge in a battery is referred to a decrease in voltage that take place when the battery is left in an open circuit. Usually, the self-discharge problem is occurred in supercapacitor and it is also the main problem in the use of storing energy over time period as stated in the journal paper\textsuperscript{14}. The reasons for having self-discharge problem are because there is current leakage through the double-layer at the electrolyte-carbon interface and due to the diffusion process.

Though it is stated that the self-discharge rate is low in the chemical cells, it is still a concern in dual carbon battery since the carbon in graphite form is present in the electrode and creates electrolyte-carbon interface. This increases the chance of current leakage and results in self-discharge.

3 Methodology

In this research, coin cells are produced. In each experiment, only one factor is changed so as to identify the effect of the variable factor which includes the active material, binder, concentration of electrolyte and electrolyte solvent.

Two characteristics are focused in the analysis of the coin cell namely electrochemical analysis and physical analysis. For the former one, battery capacity, cycle efficiency, cycle performance, rate performance and cyclic voltammetry are the prime indicators to determine the electrochemical properties. The latter one defines the physical properties of electrode as well as the material used. When the information of both sides is obtained, mechanism and effects of the variable factor can be evaluated.

For the electrochemical analysis, some important measurements are calculated and compared as follows:

Specific D/C capacity (mAh/g):

\[
\frac{\text{Current applied (mA) \times Time (h)}}{\text{Weight of the active material, graphite (g)}}
\]

[Equation 8]

Coulombic efficiency (%):

\[
\eta = \frac{\text{Discharge capacity}}{\text{Charge capacity}}
\]

[Equation 9]
4 Experimental Design

In order to investigate how to achieve high capacity and performance stability of PF$_6^-$ intercalation, electrodes are produced for assembling a cell and the results are interpreted electrochemically and physically.

4.1 Battery making

4.1.1 Stage 1 – Electrode coating

Since PF$_6$ intercalation is being investigated, cathode is needed to be prepared with the desired material. Aluminum foil is used as the current collector for the cathode because of its running potential. Graphite is used as the active material and the graphite from different manufacturer is tested in this thesis.

Figure 3 Summary of material needed in an electrode coating
4.1.1.1 Preparation of slurry

After preparing the material, slurry is made according to Flowchart 1. Then the electrode is prepared following the Flowchart 2.

Flowchart 1   The procedure of preparing a slurry

- Weigh the appropriate amount of active material
- Put the appropriate amount of binder and solvent
- Add suitable amount of solvent to adjust the viscosity
- Mix well with the mortar and pestle
- Coat the slurry onto the Aluminum foil with a doctor blade
- Dry the electrode for 30 minutes on the hot plate at 80°C under the fume hood

Flowchart 2   The procedure of preparing electrode

- Coat the slurry onto the Aluminum foil with a doctor blade
- Dry the electrode for 30 minutes on the hot plate at 80°C under the fume hood
- Press the electrode with a roll press machine with the gap of 200μm
- Punch the electrode with the diameter of 16mm
- Further press the electrode with the gap of 160μm
4.1.2 Stage 2 – Cell assembling

Figure 4 Compartment of a coin cell

Flowchart 3 The procedure of assembling a coin cell

Dry all the coin cell compartment in the Buchi Oven for 20 hours at 60°C to remove the moisture.

Put the dried compartments and dried electrode into the Argon-filled glovebox.

Assemble the cell based on the sequence from top to bottom in Figure 2.

Press the cell using the coin cell stamping machine to fix the compartment inside the cell.

Wipe the cell with Kimwipe to remove any excess electrolyte.
4.2  Cell testing - Electrochemical analysis

**Flowchart 4  The procedure of cell testing for charge-discharge**

By testing charge-discharge of the coin cell, specific capacity (mAh/g), first cycle efficiency, coulombic efficiency can be obtained. Rate performance of the coin cell can be measured by setting different current rate.

### 4.2.1 Cyclic voltammetry (CV)

CV is a technique to study the electrochemical properties of the cell. A cyclic potential is applied onto the electrode and the current is obtained. By recording the current in different scan rate, the kinetics and the diffusion of the electrode with the electrolyte is analyzed from the CV profiles.

For the sake of analyzing the different effect of concentration of electrolyte, CV is used to justify the results from the charge-discharge curve and details of PF$_6$ intercalation can be understood.
4.3 Cell testing – physical analysis

4.3.1 X-Ray Diffraction (XRD)

XRD is a technique used to identify the atomic and molecular structure by inserting an X-ray to the selected sample. The beam of incident X-ray is diffracted into different directions while the angles and intensities of the diffracted beams are measured. Information such as the average spacing between layers of atoms and orientation of a sample are acquired.

In order to study the PF$_6$ intercalation into graphite, it is of interest to know the amount and occupancy of PF$_6$ anion intercalated into the electrode during charge and discharge in different cycles. Therefore, ex situ XRD is performed to identify the expansion of the electrode. The coin cells with different potential are opened during charge-discharge process and record by the XRD.

4.3.2 Scanning Electron Microscopy (SEM)

SEM is an electron microscope that uses a focused beam of high-energy electrons to produce images by scanning the samples. The high-resolution images produced can reveal the information about the orientation of materials and crystalline structure of the sample. Magnification can be adjusted to suit the requirement of experiment.

By running SEM, the physical properties of the active materials used in cathode can be characterized. Image of electrode and the powder of active materials are recorded. This helps to define the choice of active material in cathode.
5 Results and Discussion

5.1 Electrode composition affecting anion intercalation

In PF$_6^-$ intercalation, PF$_6^-$ is intercalated into the electrode during charging and return to the electrolyte during discharge. Therefore, the electrode composition of the cell would affect the performance of anion intercalation. In this chapter, active material used and binder effect are discussed.

With the previous studies, it is found that the chemical potential and the amount of lithium intercalated into carbon are affected by the structure of carbon material while the same mechanism is applied in PF$_6^-$ intercalation. Therefore, it is important to identify the graphite material which performs the best. Apart from the graphite materials, different binder also results differently and affects the performance of the cell. In this part, two types of graphite and 2 binders are tested.

5.1.1 Graphite materials

Figure 5  SEM images with 2000 magnification of (a) MTI artificial graphite, (b) Sigma graphite and (c) KS6 graphite respectively
MTI Artificial graphite, Sigma graphite and KS6 graphite are analyzed. All of them have different physical characteristics. In the Figure 5, SEM images of the graphite material shows the particle size and shape of the materials while Table 2 shows the specific surface area of each material according to the information given by the manufacturer.

For MTI, it has the smallest specific area (4.2 m²/g) and the size is about 10-20 µm with spherical appearance. Sigma has 9 m²/g surface area and largest size (10-40 µm) in the form of flakes. KS6 has the largest surface area (20 m²/g) and the smallest size (2-4 µm) in the form of flakes. The electrolyte used in the study is 1-3M LiPF₆ with FEC/DEC (1:1) as the solvent while the binder chosen is PVdF.

<table>
<thead>
<tr>
<th></th>
<th>BET (m²/g)</th>
<th>Size and appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTI</td>
<td>4.2</td>
<td>10-20 µm (Spherical)</td>
</tr>
<tr>
<td>Sigma</td>
<td>9</td>
<td>10-40 µm (Flakes)</td>
</tr>
<tr>
<td>KS6</td>
<td>20</td>
<td>2-4 µm (Flakes)</td>
</tr>
</tbody>
</table>

Table 2  BET specific surface area of graphite materials
Figure 6 1st cycle D/C curve of different graphite in PVdF at 3-5.3V

Figure 7  Discharge capacity of graphite in PVdF at 3-5.3V
From the 1st cycle D/C capacity in Figure 6, the charge-discharge capacity increases with the specific surface area of graphite materials. Also, from the discharge capacity along cycles, KS6 with the largest specific surface area and the smallest particle size has a poor cycle performance among three materials. The discharge capacity of KS6 starts to drop in the 6th cycle and reduce to less than half of the discharge capacity in the 1st cycle shown in Figure 7. The discharge capacity in the 20th cycle for Sigma and MTI graphite is more or less the same as their 1st cycle. This results implies that larger surface area of graphite has a more vigorous reaction in the beginning but it is unstable along the cycles.

In Figure 8, it shows the relationship between the 1st cycle discharge capacity and the BET specific surface area that large particle surface area allows to have a higher discharge capacity in the 1st cycle. The reason is probably because the increase in surface area enhances the reaction with electrolyte.
5.2 Improvement for PF$_6^-$ intercalation

Among the three types of graphite, KS6 has the highest 1$^{st}$ charge-discharge capacity. Meanwhile the coulombic efficiency is the worst. Therefore, it is important to improve the cycle performance of KS6.

5.2.1 Add AB to the active material

One solution to solve the cycle performance problem is to add Acetylene Black (AB) into graphite powder since adding AB can enhance the electrical conductivity of electrode so as to improve the stableness of cycle performance. The experimental condition is changed as follows:

Electrode composition: KS6:AB:PVdF = 7:2:1
Electrolyte: 1M LiPF$_6$ FEC/DEC = 1:1
Voltage range and current applied: 3-5.3V and 10 mA/g

After adding AB, the 1$^{st}$ cycle discharge capacity is about the same as shown in Figure 9. However, the coulombic efficiency is lowered indicated in Figure 10 when AB is added. But the discharge capacity is improved with the present of AB shown in Figure 11. Therefore, adding AB to the active material is not enough to solve the problem of cycle performance.
Figure 9 1st cycle D/C curve of KS6 with AB and without AB

Figure 10 CE of KS6 with AB and without AB along 1st – 20th cycles
Figure 11 Discharge capacity of KS6 with AB and without AB along 1st – 20th cycles
5.2.2 Reduce the voltage range

In order to improve the coulombic efficiency, voltage range needs to be lowered. The 1st D/C curve is shown in Figure 12. When the voltage range is reduced from 5.3V to 5.1V, the discharge capacity is decreased. Yet, the cycle stability is improved with more stable discharge capacity and coulombic efficiency as shown in Figure 13 and Figure 14.

Figure 12 1st cycle D/C curve at 3-5.1V and 3-5.3V

Figure 13 Discharge capacity of KS6:AB:PVdF at 3-5.1V and 3-5.3V
This result implies that there is limit in voltage range when a stable cycle performance is required as lower voltage applied can minimize electrolyte decomposition. The voltage range should be lowered to 5.1V in order to achieve better performance of anion intercalation. So the following experiments would use 3-5.1V voltage range instead of 3-5.3V.

Figure 14 CE of KS6:AB:PVdF at 3-5.1V and 3-5.3V
5.2.3 Increase the electrolyte concentration

In the PF$_6^-$ intercalation, electrolyte determines capacity of the cell. With the increase in concentration of electrolyte, it is believed that the capacity would also increase. Figure 15 shows the 1-3M LiPF$_6$ used as electrolyte for Sigma graphite.

![Figure 15 1st cycle D/C curve of Sigma graphite in different concentration of LiPF6 in PVdF at 3-5.3V](image)

Using higher concentration of electrolyte results in higher charge and discharge capacity. For the first charging plateau, the 3M LiPF$_6$ curve is located at a lower potential than the other two. This indicates that lower potential is needed for a cell to charge up to the same capacity when the electrolyte concentration is higher.

The 2M LiPF$_6$ has a more significant increase than 3M LiPF$_6$. This probably implies that there is an optimal concentration for LiPF$_6$ in anion intercalation.
Figure 16 1st cycle D/C curve of KS6:AB:PVdF in 1-3M LiPF$_6$ at 3-5.1V

Figure 17 Discharge capacity of KS6:AB:PVdF in 1-3M LiPF$_6$ FEC/DEC
In the presence of AB, the extent of increase in discharge capacity is smaller than that without AB when the concentration of electrolyte increases. With the increase of salt content from 1 to 3M, the charge-discharge plateau is also shifted to lower potential throughout the cycles shown in Figure 16. The discharge capacity is slightly increased using increasing electrolyte concentration but the coulombic efficiency is almost the same in Figure 18.

The reason for smaller increase in discharge capacity is because AB is not part of the active material and it cannot perform anion intercalation. So the amount of PF$_6^-$ that the graphite can store decreased which would lead to a smaller extent of increase in capacity.
5.3 Change of graphite material, binder and AB composition

In order to improve the discharge capacity and the cycle performance of PF$_6^-$ intercalation, different electrodes with different composition with graphite material, AB and binder are tested. It is proved that adding AB can stabilize the cycle performance by enhancing the electrical conductivity. The binder also plays a role in the D/C performance that the ionic conductivity is strengthened. Therefore, it is crucial to understand how the electrode component changes with the results. And finally, come up with the best combination of the electrode when having D/C.

In the following experiment, 3M of LiPF$_6$ is used so as to attain the maximum capacity. The current and voltage range are kept constant which are 10 mA/g and 3-5.1V respectively. The discharge capacity along 20 cycles and their coulombic efficiency are measured. Table 3 summarizes the electrode composition with their typical capacity and the average coulombic efficiency in 10$^{\text{th}}$ to 20$^{\text{th}}$ cycle where the cells are in stable condition while Table 4 summarizes the comparisons and results. The D/C curve of each electrode compositions are shown in the Appendix while the discharge capacity and the coulombic efficiency are shown in Figure 19 and Figure 20 respectively.

<table>
<thead>
<tr>
<th>No. of</th>
<th>Electrode composition</th>
<th>Typical capacity (mAh/g)</th>
<th>CE (10-20$^{\text{th}}$ cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>KS6:AB:CMC = 7:2:1</td>
<td>~87.7</td>
<td>~78.6%</td>
</tr>
<tr>
<td>B</td>
<td>KS6:AB:CMC = 85:5:10</td>
<td>~84.1</td>
<td>~84.4%</td>
</tr>
<tr>
<td>C</td>
<td>KS6:AB:PAA = 85:5:10</td>
<td>~80.5</td>
<td>~89.2%</td>
</tr>
<tr>
<td>D</td>
<td>Sigma:AB:CMC = 7:2:1</td>
<td>~82.5</td>
<td>~85.1%</td>
</tr>
<tr>
<td>E</td>
<td>Sigma:AB:CMC = 8:1:1</td>
<td>~84.5</td>
<td>~91.9%</td>
</tr>
<tr>
<td>F</td>
<td>Sigma:AB:PVdF = 8:1:1</td>
<td>~75.6</td>
<td>~86.5%</td>
</tr>
<tr>
<td>G</td>
<td>Sigma:CMC = 9:1</td>
<td>~79.6</td>
<td>~91.4%</td>
</tr>
<tr>
<td>H</td>
<td>Sigma:PAA = 9:1</td>
<td>~78.3</td>
<td>~92.5%</td>
</tr>
</tbody>
</table>

Table 3 Summary of the combination of graphite material, AB amount and binder
<table>
<thead>
<tr>
<th>No. of comparisons</th>
<th>Electrodes</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A VS B</td>
<td>A: higher capacity, lower CE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B: lower capacity, higher CE</td>
</tr>
<tr>
<td>2</td>
<td>B VS C</td>
<td>B: higher capacity, lower CE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C: lower capacity, higher CE</td>
</tr>
<tr>
<td>3</td>
<td>D VS E</td>
<td>D: lower CE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>E: higher CE</td>
</tr>
<tr>
<td>4</td>
<td>E VS F</td>
<td>E: higher capacity and CE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F: lower capacity and CE</td>
</tr>
<tr>
<td>5</td>
<td>G VS H</td>
<td>G,H: similar capacity and CE</td>
</tr>
</tbody>
</table>

Table 4  Summary of the comparisons of electrodes with respect to Table 3 and the results in D/C test

![Discharge capacity of different electrodes](image)

Figure 19 Discharge capacity of different electrode composition in 20 cycles
Figure 20 Coulombic efficiency of different electrode composition in 20 cycles

Figure 21 Typical discharge capacity along 10th – 20th cycle of 8 electrode component
Figure 22 Average CE along 10th – 20th cycle of 8 electrode component


In order to compare the discharge capacity and the coulombic efficiency of the electrode components, Figure 21 and Figure 22 shows the distributions respectively. In these two figures, electrodes like KS6:AB:CMC = 7:2:1 and KS6:AB:CMC = 85:5:10 have high discharge capacity while perform unsatisfactorily in cycle performance. From these two electrodes, the only difference is the AB amount which causes different ratio with the Gr material and the binder. With more AB amount, the discharge capacity increases and the coulombic efficiency reduces.

The effect is the same when binder PAA is used. Concerning the electrode KS6:AB:CMC = 85:5:10 and KS6:AB:PAA = 85:5:10, KS6:AB:PAA has a lower discharge capacity and higher coulombic efficiency.

Comparison 3: Sigma:AB:CMC = 8:1:1 VS Sigma:AB:PVdF = 8:1:1

For the electrodes Sigma:AB:CMC = 8:1:1 and Sigma:AB:PVdF = 8:1:1, it is clear that using CMC is more superior than PVdF since the discharge capacity and CE is both higher than those using PVdF.

Comparison 4: Sigma:AB:CMC = 8:1:1 and Sigma:AB:CMC = 7:2:1

And for the amount of AB added in Sigma and CMC, both discharge capacity and coulombic efficiency is higher in Sigma:AB:CMC = 8:1:1 than Sigma:AB:CMC = 7:2:1. This results implies that the ratio 7:2:1 exceeds the optimal amount of AB needed.

Comparison 5: Sigma:CMC = 9:1 and Sigma:PAA = 9:1

For the last two electrodes Sigma:CMC = 9:1 and Sigma:PAA = 9:1, the results agree with the conclusion that PAA has better cycle performance with lower discharge capacity than using CMC.
In the above results, only Sigma and KS6 are compared. The graphite materials KS6 and Sigma have different surface area. KS6 is 20 m$^2$/g and Sigma is 9 m$^2$/g that the surface area of KS6 is more than twice as Sigma. From the above data, it is shown that increasing the surface area of graphite material causes higher discharge capacity, yet lower CE. Therefore, Sigma is preferred for D/C since CE is of more importance when the cells is run for a long time with large amount of cycles.

To propose the best electrode component, Sigma:AB:CMC 8:1:1 is suggested since it has a relatively high discharge capacity and CE among all the tested electrodes. With the limited data, the best electrode component is still unknown as binder PAA has not been tested with Sigma and AB. But from the data generated, Sigma:AB:CMC 8:1:1 is preferred.
5.4 Charge-discharge mechanism of PF$_6$ in graphite

To further understand the charge-discharge mechanism of PF$_6$ in graphite, \textit{ex situ} XRD is done in different stages of charge-discharge cycle and cyclic voltammetry is analyzed with different concentration of electrolyte and different scan rate.

5.4.1 \textit{Ex situ} XRD

In \textit{ex situ} XRD, the x-ray diffraction is done when the cell is charged or discharged in different stages. The cell is stopped and opened so as to take out the electrode to undergo XRD test. The green curve represents the charging state while the red curve represents the discharging state in Figure 23.

![The positions of 6 stages during charge-discharge](image)

Figure 23 The positions of 6 stages in the charge-discharge curve for \textit{ex situ} XRD test
With the results obtained by XRD in Figure 24, the related $d_{00n}$ spacing is obtained in Table 5. From the relationship of cumulative capacity and the $d_{00n}$ spacing in stages A-F, it shows that $d_{00n}$ spacing is decreased from 26 to 24 during charging and back to 26 when it is discharging. Besides, there is difference of cumulative capacity between stage A and F indicated in Figure 25 and it is probably caused by self-discharge of the electrolyte with the electrode because there would be chances of current leakage which causes voltage drop when the current scan rate is slow. Hence, more experiment would be done to explore about self-discharge problem in anion intercalation in Chapter 5.6.
<table>
<thead>
<tr>
<th>State</th>
<th>Cumulative capacity (mAh/g)</th>
<th>$\theta$ of (00n)</th>
<th>$d_{00n}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
<td>26.51</td>
<td>3.359</td>
</tr>
<tr>
<td>B</td>
<td>40</td>
<td>25.41</td>
<td>3.502</td>
</tr>
<tr>
<td>C</td>
<td>80</td>
<td>24.72</td>
<td>3.599</td>
</tr>
<tr>
<td>D</td>
<td>120</td>
<td>24.04</td>
<td>3.698</td>
</tr>
<tr>
<td>E</td>
<td>80</td>
<td>25.14</td>
<td>3.540</td>
</tr>
<tr>
<td>F</td>
<td>40</td>
<td>26.42</td>
<td>3.371</td>
</tr>
</tbody>
</table>

Table 5 The summary of the relationship of $\theta$ and $d_{00n}$ and the cumulative capacity

![The change of cumulative capacity during charge-discharge](image)

Figure 25 The change of cumulative capacity during charge-discharge
5.4.2 Cyclic voltammetry

Apart from the *ex situ* XRD study, cyclic voltammetry measurement is done. The redox equation of PF₆⁻ intercalation into graphite is as follows:

\[
C + x \text{PF}_6^- \rightarrow C (\text{PF}_6)_x + x e^-
\]  

[Equation 10]

Cyclic voltammetry is tested for the 1M LiPF₆ using Sigma Graphite. Figure 26 shows the relationship of specific current and potential with different scan rate. The normalized peak current with square root of scan rate is plotted in Figure 27. Each slope represents different current peak in two scan rate. For the scan rate 0.06 mV/s, peak 5 disappears. This agrees with the rate performance with 100 mA/g results which is due to electrolyte decomposition. From the slope, the diffusion coefficient can be obtained, as shown in Equation 11\(^{15}\)

\[
i_p = 0.4463 F \left( \frac{F}{RT} \right)^{1/2} C^* v^{1/2} AD^{1/2}
\]  

[Equation 11]

Figure 26  Cyclic voltammetry profile of Sigma graphite with 1M LiPF6

Figure 27  Graph of normalized peak current versus square root of the scan rate
In addition to Sigma with PVdF being tested, KS6:AB:CMC = 7:2:1 is tested with 1M LiPF$_6$ at scan rate 0.06 mV/s is also undergoes CV test and the result is shown in Figure 28.

![CV test with KS6:AB:CMC = 7:2:1 at 0.06 mV/s](image)

**Figure 28** CV test for KS6:AB:CMC = 7:2:1 1M LiPF$_6$ FECDEC at 0.06 mV/s

Theoretically, the reduction reaction is the opposite mechanism of the oxidation. In CV test, the number of peaks during oxidation should equal to that during reduction. From the Figure 28, it shows the CV test with KS6:AB:CMC = 7:2:1 in 1M LiPF$_6$. There are 5 oxidation peaks indicated as “I to V”. However, the reduction peaks are not clear at this point. Some of the peaks may be overlapped and the number of peaks are not consistent with the oxidation peaks.
The change of LiPF$_6$ concentration is investigated. By keeping the scan rate at 0.06 mV/s, the characteristic is revealed. The oxidation and reduction peaks of the CV curve shifted to the left during oxidation and reduction when the concentration of electrolyte increases. The shapes of the curve are the same. It shows that the mechanism of charge-discharge with different concentration of electrolyte is the same. The result is consistent with the Nernst equation that the cell potential is affected by the salt concentration. The Nernst equation is stated below.

$$
\Delta E = \Delta E^\circ - 2 \frac{RT}{F} \ln \left[ \frac{a_{PF_6}}{a_{PF_6}^o} \right]
$$

[Equation 12]
5.5 Rate Performance of PF₆ intercalation

To understand the characteristics of the cell during charging and discharging at high current rate, rate performance is being done. Figure 30 shows the rate performance of Sigma graphite in 1M LiPF₆ with PVdF. The current rates are 20 mA/g, 30 mA/g, 40 mA/g, 50 mA/g and 100 mA/g. The cell performs well under different current rate since the irreversible capacity is similar to each other. For the 100 mA/g scan rate, the charging plateau indicated by the arrow disappears. This is probably due to electrolyte decomposition. Still, more rate performance with higher concentration of electrolyte is needed to carry out so as to make comparisons.

![Figure 30 Rate performance of Sigma graphite with 1M LiPF6 and PVdF](image)
5.5.1 Change of graphite material, binder and AB amount

In rate performance test, binder would affect the coulombic efficiency in different current rate since different binder have different strength of facilitating ion transfer. In this session, different combinations of electrode materials with different types of binder are compared. For the concentration of electrolyte, 3M of LiPF₆ is used since the discharge capacity and the coulombic efficiency is the best among 1-3M LiPF₆ done in previous part. In Table 6 and 7, it presents the summary of comparisons of types of binder in rate performance test and the results.

<table>
<thead>
<tr>
<th>No. of electrode</th>
<th>Electrode component</th>
<th>Ratio of electrode material</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>KS6:AB:PVdF</td>
<td>7:2:1</td>
</tr>
<tr>
<td>B</td>
<td>KS6:AB:CMC</td>
<td>7:2:1</td>
</tr>
<tr>
<td>C</td>
<td>KS6:AB:PAA</td>
<td>85:5:10</td>
</tr>
<tr>
<td>D</td>
<td>KS6:AB:CMC</td>
<td>85:5:10</td>
</tr>
<tr>
<td>E</td>
<td>Sigma:CMC</td>
<td>9:1</td>
</tr>
<tr>
<td>F</td>
<td>Sigma:PAA</td>
<td>9:1</td>
</tr>
<tr>
<td>G</td>
<td>Sigma:AB:PVdF</td>
<td>8:1:1</td>
</tr>
<tr>
<td>H</td>
<td>Sigma:AB:CMC</td>
<td>8:1:1</td>
</tr>
</tbody>
</table>

Table 6 Summary of electrode component tested in rate performance
<table>
<thead>
<tr>
<th>No. of comparisons</th>
<th>Electrodes with respect to Table 6</th>
<th>Factors to be compared</th>
<th>Results (Rate property comparison)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A VS B</td>
<td>Binder: PVdF, CMC (Gr used: KS6)</td>
<td>CMC has better rate property</td>
</tr>
<tr>
<td>2</td>
<td>C VS D</td>
<td>Binder: PAA, CMC (Gr used: KS6)</td>
<td>PAA has better rate property</td>
</tr>
<tr>
<td>3</td>
<td>E VS F</td>
<td>Binder: CMC, PAA (Gr used: Sigma)</td>
<td>PAA has better rate property</td>
</tr>
<tr>
<td>4</td>
<td>G VS H</td>
<td>Binder: PVdF, CMC (Gr used: Sigma)</td>
<td>CMC has better rate property</td>
</tr>
<tr>
<td>5</td>
<td>B VS D</td>
<td>AB amount (Gr used: KS6) Ratio: 7:2:1, 85:5:10</td>
<td>KS6:AB:CMC=7:2:1 performs better</td>
</tr>
<tr>
<td>6</td>
<td>E VS H</td>
<td>AB amount (Gr used: Sigma) Ratio: 8:1:1, 9:1</td>
<td>Sigma:AB:CMC=8:1:1 performs better</td>
</tr>
</tbody>
</table>

Table 7 Electrodes for comparison and their factors to be compared

Figure 31 Rate performance of KS6:AB:PVdF = 7:2:1 with 3M LiPF₆

Figure 32 Rate performance of KS6:AB:CMC = 7:2:1 with 3M LiPF₆
In Figure 31 and 32, KS6:AB:PVdF = 7:2:1 and KS6:AB:CMC = 7:2:1 in FEC/DEC being compared respectively. In Figure 31, the discharge capacity of high current rate decreases gradually as indicated when PVdF is used. To understand more about the change of discharge capacity, Figure 33 shows the comparison of discharge capacity of both binders used change with the current rate. In 200 mA/g, the discharge capacity of PVdF decreases with the largest extent. This shows that the rate performance of PVdF is worse than CMC.

Figure 34 Rate performance of KS6:AB:PAA = 85:5:10 with 3M LiPF$_6$

Figure 35 Rate performance of KS6:AB:CMC = 85:5:10 with 3M LiPF$_6$
For these two electrodes, binder PAA and CMC is compared when the KS6 to AB to binder ratio is 85:5:10. From the D/C curves in Figure 34 and 35, the rate property has a better performance in PAA than that in CMC. Under the current rate at 10 mA/g which has undergone high current charge-discharge for CMC as indicated in Figure 35, the discharge capacity has decreased a lot. This result demonstrates that CMC has a lower potential in switching high and low current rate while keeping the discharge capacity the same. For rate property of these two binder, PAA is more superior than using CMC.
Comparison 3: Sigma:CMC = 9:1 VS Sigma:PAA = 9:1

Figure 37 Rate performance of Sigma:CMC = 9:1 with 3M LiPF₆

Figure 38 Rate performance of Sigma:PAA = 9:1 with 3M LiPF₆
Apart from using KS6 as the active material, Sigma graphite is also tested. Firstly, Sigma:CMC and Sigma:PAA with the ratio 9:1 is compared. In Figure 37, the discharge capacity decreases to about half of the original capacity when 100 mA/g is applied and even decreases to 0 when the current rate is 200 mA/g as indicated in the figure. On the contrary, when PAA is used, the coulombic efficiency improves in Figure 38. The change of discharge capacity with different current rate is indicated in Figure 39. Sigma:CMC electrode starts to have a significant decrease in discharge capacity when the current rate is increased to 100 mA/g. It is concluded that PAA performs better with Sigma graphite as the active material in rate performance test.

Figure 39 Discharge capacity of Sigma:CMC = 9:1 and Sigma:PAA = 9:1 with 3M LiPF$_6$
Comparison 4: Sigma:AB:PVdF = 8:1:1 VS Sigma:AB:CMC = 8:1:1

Figure 40 Rate performance of Sigma:AB:PVdF = 8:1:1 with 3M LiPF₆

Figure 41 Rate performance of Sigma:AB:CMC = 8:1:1 with 3M LiPF₆
Figure 42 Discharge capacity of Sigma:AB:PVdF = 8:1:1 and Sigma:AB:CMC = 8:1:1 with 3M LiPF$_6$

With the presence of AB, binder PVdF and CMC is compared when Sigma is used. In Figure 40 and 41, Sigma:AB:PVdF has a poor rate property than Sigma:AB:CMC since the discharge capacity is low when the current rate is switched from 200 mA/g to 10 mA/g as indicated. The same situation did not happen to Sigma:AB:CMC. The discharge capacity did not reduce when high current rate is switched to low current rate. However, the overall discharge capacity of electrode using PVdF is higher than CMC as shown in Figure 42.

Figure 43 Rate performance of KS6:AB:CMC = 7:2:1 with 3M LiPF$_6$

Figure 44 Rate performance of KS6:AB:CMC = 85:5:10 with 3M LiPF$_6$
Figure 45 Discharge capacity of KS6:AB:CMC = 7:2:1 and KS6:AB:CMC = 85:5:10 with 3M LiPF₆.

The electrode KS6:AB:CMC = 85:5:10 has a discharge capacity drop when the current rate is changed from high to low as indicated in Figure 44 while the electrode in ratio 7:2:1 does not have the same problem. The discharge capacity is stable and a bit higher than KS6:AB:CMC = 7:2:1 as shown in Figure 45.
Comparison 6 Sigma:CMC = 9:1 VS Sigma:AB:CMC = 8:1:1

Figure 46 Rate performance of Sigma:CMC = 9:1 with 3M LiPF$_6$

Figure 47 Rate performance of Sigma:AB:CMC = 8:1:1 with 3M LiPF$_6$
To understand AB amount in the presence of Sigma and CMC, the rate performance of Sigma:CMC = 9:1 and Sigma:AB:CMC = 8:1:1 is compared in Figure 46 and 47. Without AB, Sigma:CMC cannot perform charge-discharge under high current rate. The discharge capacity drops to 0 when 200 mA/g is used indicated in Figure 48. After adding AB in the ratio of 8:1:1, the performance improves and the rate property enhances.

Figure 48 Discharge capacity of Sigma:CMC = 9:1 and Sigma:AB:CMC = 8:1:1 with 3M LiPF$_6$
In general, the electrode using KS6 as the active material has higher discharge capacity than using Sigma since three of the electrodes with highest discharge capacity shown in Figure 49 are KS6 electrodes. It shows that the surface area of active material determines the rate property. Larger surface area of graphite has a superior rate property than smaller ones.

However, the Sigma electrode with AB and CMC in the ratio of 8:1:1 also attains relatively high discharge capacity than the others. So this shows that the combination of Sigma, AB and CMC could be able to achieve high capacity in rate performance. More experiments need to be done to verify the justification.
The use of AB can enhance the conductivity of graphite that the discharge capacity would be more stable. However, the amount of AB added is also crucial for the stableness of the discharge capacity when the current rate is switching from high to low. KS6:AB:CMC = 7:2:1 electrode is the best ratio comparing with 85:5:10. Therefore, the ratio of graphite to AB and binder affect the rate performance of cells.

For the use of binder, it is concluded that PAA is the best binder for rate property while CMC comes the second and PVdF is the worst. PVdF is unstable that the discharge capacity of electrodes drops when the current rate is high or switching from high to low but PAA performs well in both aspects. PAA is the best binder for facilitating the transport of PF$_6^-$ between electrolyte and electrode. However, PAA is only tested with KS6 and AB in the ratio of 85:5:10. So the electrode composition with optimal rate performance has not been obtained and will continue as future work.
5.6 Self-discharge in anion intercalation

In anion intercalation, there is a problem of self-discharge that the length of resting time between charge and discharge would result in differences in voltage drop. The reasons would be the leakage of current or anions. The characteristic of self-discharge of different electrodes are shown below.

<table>
<thead>
<tr>
<th>No. of combination</th>
<th>Electrode composition</th>
<th>Anion used</th>
<th>Factors to be investigated</th>
<th>Results (Electrode with less voltage drop)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sigma:CMC = 9:1 VS Sigma:AB:CMC = 7:2:1</td>
<td>TFSI</td>
<td>AB amount</td>
<td>Sigma:CMC=9:1</td>
</tr>
<tr>
<td>2</td>
<td>Sigma:PAA 9:1 VS Sigma:CMC 9:1</td>
<td>TFSI</td>
<td>Binder</td>
<td>Sigma:CMC=9:1</td>
</tr>
</tbody>
</table>

Table 8 Summary of electrode showing the factor to be compared in the electrode in self-discharge in anion intercalation.
Combination 1: Sigma:CMC = 9:1 and Sigma:AB:CMC = 7:2:1 in TFSI

Figure 50 The relationship between starting voltage after resting and resting time for Sigma:CMC = 9:1 and Sigma:AB:CMC = 7:2:1 in TFSI

To compare the difference of the use of AB in TFSI anion, the electrode Sigma:CMC = 9:1 and Sigma:AB:CMC = 7:2:1 are tested. From Figure 50, it shows that the electrode with AB present in the active material has a higher rate of self-discharge during resting time since Sigma:AB:CMC = 7:2:1 has a larger reduction in voltage when the resting time is 36 hours. Therefore, AB has a negative effect in self-discharge.
Combination 2: Sigma:PAA = 9:1 and Sigma:CMC = 9:1 in TFSI

Figure 51 The relationship between starting voltage after resting and resting time for Sigma:PAA = 9:1 and Sigma:CMC = 9:1 in TFSI

This experiment compares the effect of binder in the presence of Sigma and TFSI anion in self-discharge. From Figure 51, Sigma:CMC performs a little bit better than Sigma:PAA. For 36 hours resting time, Sigma:CMC is 0.1V higher than that of Sigma:PAA only. So binder plays an insignificant role in self-discharge during resting time.

Figure 52 The relationship between starting voltage after resting and resting time for KS6:AB:PAA = 8:1:1 in PF₆ and KS6:AB:PAA = 8:1:1 in TFSI

This combination compares different anions in self-discharge of the KS6:AB:PAA = 8:1:1 electrode. When TFSI⁻ is used, the starting voltage after resting decreases continuously while the starting voltage stopped reducing when the resting time is 12 hours or above when PF₆ anion is used. When the number of resting hours increases to 36 hours, the difference of starting voltage between using TFSI and PF₆ is more than 3V as indicated.

Among all the combination of self-discharge test, it is clearly shown that anion PF₆ has smaller self-discharge than using TFSI⁻. And CMC is a better binder than PAA. However, more experiments using PF₆- with both graphite materials and binders need to be done in order to make comparisons and come up with the combination of electrode with the least self-discharge problem.
To conclude, three main experiments of anion intercalation are investigated in this thesis which are namely improvement of charge-discharge of PF$_6^-$ intercalation, rate performance of PF$_6^-$ and self-discharge of anion intercalation. For charge-discharge reactions, Sigma:AB:CMC = 8:1:1 is the best among all the tested composition of electrodes while the rate property of KS6 with AB and PAA is the ideal one for the tested electrodes. For the self-discharge problem in anion intercalation, it is known that TFSI$^-$ is worse than PF$_6^-$, however, more experiments with PF$_6^-$ are necessary to be carried out to provide more details about the proof.

Among all the experiments done, electrolyte decomposition and self-discharge are the dominant factors that affect the performance of anion intercalation. It is important to overcome this problem in the long term development of anion intercalation. Therefore, instead of using graphite in the form of carbon as the active material of cathode, other forms of material with the cage structure could be used so that lower voltage is needed to apply on the cells during charge-discharge and this can minimize electrolyte decomposition. Also, more experiments on self-discharge needs to be done.
7 Future Works

(1) Try Sigma:AB:PAA and Sigma:AB:CMC = 85:5:10 with D/C test so as to compare with the results of Sigma:AB:CMC = 8:1:1 which is the best results generated.

(2) Compare KS6:AB:PAA and Sigma:AB:CMC with different ratio and test for rate performance.

(3) Use other anion such as BF$_4^-$ and TFSI$^-$ to do perform cycle performance, rate performance and self-discharge test so as to compare with the result of PF$_6^-$.

(4) Use another solvent mixing with electrolyte because only FEC/DEC is investigated in this thesis.

(5) Perform surface coating on graphite particles and investigate whether it is able to suppress electrolyte decomposition and self-discharge problem.

(6) Use material other than graphite to carry out anion intercalation such as Fe$_7$(CN)$_{18}$ which is in a cage structure that allows to store more ions for reactions so that the voltage range could be set lower to achieve the same discharge capacity while minimizing electrolyte decomposition.
8 List of Reference


Appendix

Charge-discharge test:

Figure 53 D/C curve of KS6:AB:CMC = 7:2:1 measured under 3-5.1V with 10 mA/g

Figure 54 D/C curve of KS6:AB:CMC = 85:5:10 measured under 3-5.1V with 10 mA/g
Figure 55 D/C curve of KS6:AB:PAA = 85:5:10 measured under 3-5.1V with 10 mA/g

Figure 56 D/C curve of Sigma:AB:CMC = 7:2:1 measured under 3-5.1V with 10 mA/g
Figure 57 D/C curve of Sigma:AB:CMC = 8:1:1 measured under 3-5.1V with 10 mA/g

Figure 58 D/C curve of Sigma:AB:PVdF = 8:1:1 measured under 3-5.1V with 10 mA/g
Figure 59 D/C curve of Sigma:CMC = 9:1 measured under 3-5.1V with 10 mA/g

Figure 60 D/C curve of Sigma:PAA = 9:1 measured under 3-5.1V with 10 mA/g
Figure 61 1st cycle D/C curve of KS6:AB:CMC in 1-3M LiPF$_6$ at 3-5.1V

Figure 62 Discharge capacity of KS6:AB:CMC in 1-3M LiPF$_6$ FECDEC
Self-discharge test:

Figure 63 Voltage drop of Sigma:CMC = 9:1 during different resting time between D/C

Figure 64 Voltage drop of Sigma:AB:CMC = 7:2:1 during different resting time between D/C
Figure 65 Voltage drop of Sigma:PAA = 9:1 during different resting time between D/C

Figure 66 Voltage drop of KS6:AB:PAA = 8:1:1 with PF₆ anion during different resting time between D/C
Figure 67 Voltage drop of KS6:AB:PAA = 8:1:1 with TFSI anion during different resting time between D/C