Effective Electrolyte Additives for Dual-Ion Batteries

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Abbreviations

AN  Acetonitrile
BETI⁻  Bis(pentafluoroethanesulfonyl) imide
BMIM  1-butyl-3-methylimidazolium
CD  Charge discharge
CE  Coulombic efficiency
CFP  Carbon fibre paper
CGP  Conductive graphite powder
CV  Cyclic voltammetry
DARb  Diaminorubicene
DEC  Diethylene carbonate
DIB  Dual ion battery
DIME  Dual intercalating molten electrolytes
DLD  Delay line detector
DMC  Dimethyl carbonate
DMF  Dimethyl formamide
DMPI⁺  1,2-dimethyl-3-propylimidazolium
DMSO  Dimethyl sulfoxide
EB  Binding energy
EC  Ethylene carbonate
EEG  Electrochemically exfoliated graphene
EMC  Ethyl methyl carbonate
EMIm⁺  1-ethyl-3-methylimidazolium
EMS  Ethyl methyl sulfone
ES  Ethylene sulfite
EV  Electric vehicle
FEC  Fluoroethylene carbonate
FSI⁻  Bis(fluorosulfonyl) imide
FTFSI⁻  Fluorosulfonyl-(trifluoromethanesulfonyl) imide
GCD  Galvanostatic charge/discharge
GDIB  Graphite dual ion battery
GIC  Graphite intercalation compound
GO   Graphene oxide
HCE  Highly concentrated electrolyte
HFIP Tris(hexafluoro-iso-propyl)phosphate
HOMO Highest occupied molecular orbital
IL   Ionic liquid
KE   Kinetic energy
KS4  KS4 synthetic graphite powder by Timrex
KS6  KS6 synthetic graphite powder by Timrex
KS6-L KS6-L synthetic graphite powder by Timrex
LFP  Lithium iron phosphate
Li2DAnT Dilithium 2,5-(dianilino)terephthalate
LIB  Lithium-ion battery
LMO  Lithium manganese oxide
LNMO Lithium nickel manganese oxide
LUMO Lowest unoccupied molecular orbital
MCMB Mesocarbon microbead graphite
MOF  Metal organic framework
NatG Natural graphite
NBD  Nitrobenzenediazonium
NiMH Nickel metal-hydride
NMC  Lithium nickel manganese cobalt oxide
NMP  N-methyl-2-Pyrrolidone
PAH  Polycyclic aromatic hydrocarbons
PC   Propylene carbonate
PP14+ 1-butyl-1-methylpiperidinium
PVDF Polyvinylidene fluoride
PXRD Powder X-Ray diffraction
RE   Reference electrode
SEI  Solid electrolyte interphase
SL   Sulfolane
SP1  SP1 graphite powder
<table>
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<tr>
<td>TBA⁺</td>
<td>Tetrabutylammonium</td>
</tr>
<tr>
<td>TFSI</td>
<td>Bis(trifluoromethane-sulfonyl) imide</td>
</tr>
<tr>
<td>TM</td>
<td>Transition metal</td>
</tr>
<tr>
<td>VC</td>
<td>Vinylene carbonate</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>XPS</td>
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Abstract

This work identifies and evaluates effective electrolyte compositions for dual-ion batteries with carbon-based cathodes, supporting the simultaneous intercalation and deintercalation of Li\(^+\) and PF\(_6^-\). The electrolytes were investigated in a variety of dual-ion configurations; aluminium dual-ion, dual-graphite, and lithium half-cells, using electrochemical characterisation techniques such as galvanostatic charge/discharge and cyclic voltammetry to determine their effectiveness during cycling.

Dual graphite cells display the most reliable results, enabling prolonged cycling performance over 350 cycles with a 100 % capacity retention when the electrolyte is ethyl methyl carbonate (EMC) 2 M LiPF\(_6\) + 3 % vinylene carbonate (VC). Both VC and fluoroethylene carbonate (FEC) additives (3 %) were trialled in an EMC 2 M LiPF\(_6\) electrolyte displaying notable performance improvements in Li-half cells, with a ~20 % increase in the discharge capacities observed in comparison to the control electrolyte without the presence of the additives. The best Li-half cell performance is achieved when the cathode material is low-defect content graphite (SP1 graphite), resulting in a coulombic efficiency > 95 %. The improved performance of the VC and FEC containing Li-half cells indicates that these additives sufficiently stabilise the cathode/electrolyte interface. Enabling sustained anion intercalation into graphite whilst minimising the degree of parasitic reactions at the cathode due to electrolyte degradation at highly oxidising potentials. However, the transfer of the FEC containing electrolyte into a dual-graphite cell does not significantly improve the cell performance, indicating that the increase in cathode stability as a result of FEC addition is detrimental to the anode stability when a second graphite electrode is introduced. Alternatively, the addition of VC improved the dual-graphite cell performance with a discharge capacity of 61 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) reported after 350 cycles when the cathode is SP1 graphite.

Finally, the importance of high-quality carbon-based cathode materials, that facilitate reversible anion storage, is highlighted throughout this work regardless of the dual-ion cell configuration.
Declaration

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1 Literature Review and Background

1.1 Background

1.1.1 Introduction

In 2018 fossil fuel resources accounted for 65 % of global electricity generation, with CO\textsubscript{2} emissions from these sectors reaching a record high in the same year. In light of this there is a desire to reduce fossil fuel dependence to less than 20 % by 2040, if sustainable development policies are adhered to.\textsuperscript{1} To accommodate for such rapid growth in renewable energy markets and given that we are currently only capable of storing 1 % of the renewable energy we consume globally, it is vital that the capacity of energy storage systems is vastly increased.\textsuperscript{2} Furthermore, intermittent renewable energy sources, such as solar and wind, rely on low-cost, localised high-performance energy storage systems in order to maximise their efficiencies. Alternatively, failure to keep up with energy storage requirements will result in the need for a global reduction in energy consumption. A growing global population and increasing energy requirements per capita make it difficult to imagine such drastic reductions in energy consumption are possible in a short period of time, emphasizing the importance of shifting from a fossil-fuel economy to a more sustainable, renewables-based economy.

Lithium-ion batteries (LIBs) have revolutionised the energy storage sector since their inception in the early 1990’s, changing the way modern society functions on a daily basis. The development of such versatile, rechargeable energy storage devices induced a technological boom with significant progress made towards the production of portable electronic devices, ranging from mobile phones to electric vehicles (EVs). The evolution of energy storage systems from aqueous electrolyte systems, such as lead acid (Pb-acid) and nickel metal-hydride (NiMH) batteries, to non-aqueous electrolyte LIBs has resulted in significant performance developments given their much greater operating voltages (1.2 V NiMH vs. 3.7 V LIB). NiMH batteries are nowadays restricted to stationary applications as a result of their lower coulombic efficiencies (CE) of ~ 65 %, lower energy densities of ~ 80 Wh kg\textsuperscript{-1} and slower charge rates in comparison to LIBs.\textsuperscript{3} Current state-of-the-art LIBs display energy densities greater than 250 Wh kg\textsuperscript{-1} along with CEs in excess of 99 %. Fig.1 displays the increasing energy
densities of LIBs since their commercialisation in 1991, with values increasing by ~ 300 % over 29-years.⁴

![Graph showing increasing gravimetric energy density trend of LIBs](image)

*Figure 1 – A graph displaying the increasing gravimetric energy density trend of LIBs since their commercialisation in 1991. Adapted from [ref.4].*

Such rapid performance growth has proven challenging to maintain with traditional host materials approaching their limits of capacity and gravimetric energy density due to limited charge storage sites. Furthermore, LIBs face challenges as a result of material scarcity and safety. Diminishing lithium reserves combined with energy intensive recycling efforts have led to predictions of a Li shortage in coming years, with significant proportions of the Li in LIBs being unrecoverable upon the end of the batteries lifespan.⁵ The future of LIBs hinges on the research of sustainable host materials with increasing number of crystallographic storage sites for charge carriers. As such, further developments are still required before successful global implementation of high-performance battery technologies in large grid scale energy storage facilities and mass fleets of reliable EVs. To realise these goals the key requirements worthy of consideration are high gravimetric energy density, high power and charge capabilities, and long-term cycling stability, whilst maintaining high levels of safety and low cost.

Many alternative battery systems have grown out of LIB research, with varying degrees of performance observed depending on their specific applications.⁶,⁷ Of these alternative
systems, dual ion batteries (DIBs) have shown potential for grid-scale applications thanks to their low cost, environmental benignity, long term cycling stability and the ability to achieve high energy densities comparable to LIBs in some cases. These batteries do not rely on typically expensive transition-metal based positive electrode (cathode) materials, instead utilising sustainable materials such as graphite as the cathode. In doing so, these systems are considered readily recyclable whilst maintaining affordability.

Table 1 - An overview of the advantages and disadvantages most commonly associated with LIBs and DIBs.

<table>
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<tr>
<th>Lithium-ion Batteries</th>
<th>Dual-ion Batteries</th>
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<tr>
<td><strong>Advantages</strong></td>
<td><strong>Advantages</strong></td>
</tr>
<tr>
<td>- High cyclic stability and excellent reversibility</td>
<td>- High operating potentials (&gt; 4.5 V)</td>
</tr>
<tr>
<td>- High energy density</td>
<td>- Environmentally benign materials</td>
</tr>
<tr>
<td>- Extensively researched</td>
<td>- Reduced costs associated with dual carbon systems</td>
</tr>
<tr>
<td><strong>Disadvantages</strong></td>
<td><strong>Disadvantages</strong></td>
</tr>
<tr>
<td>- Increasing scarcity of TMs and depletion of Li reserves</td>
<td>- Poor reversibility due to:</td>
</tr>
<tr>
<td>- Capacity limitations prevent further energy density</td>
<td>- Electrolyte decomposition at high potentials</td>
</tr>
<tr>
<td>improvements</td>
<td>- Graphite exfoliation during intercalation</td>
</tr>
<tr>
<td>- Currently rely on toxic materials</td>
<td>- Not as extensively researched as LIBs</td>
</tr>
</tbody>
</table>

### 1.1.2 DIB Functionality

The basic configuration of both DIB and LIB systems are similar in that they consist of positive and negative electrodes (cathode and anode respectively) positioned either side of a porous polymer separating membrane and electrolyte. Whilst there are similarities in configuration there are significant differences in their energy storage mechanisms arising from differing behaviours of ionic species in the cells. Eq.1-3 and Eq.4-6 display examples of the reactions that take place within LIBs and DIBs respectively, with the forward reactions representing charging and the reverse discharging.\(^8\)
Negative electrode: $x\text{Li}^+ + xe^- + C \leftrightarrow \text{Li}_x\text{C}$ \[1\]
Positive electrode: $\text{LiCoO}_2 \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$ \[2\]
Overall: $\text{LiCoO}_2 + C \leftrightarrow \text{Li}_{1-x}\text{CoO}_2 + \text{Li}_x\text{C}$ \[3\]

Negative electrode: $C + x\text{Li}^+ + xe^- \leftrightarrow \text{Li}_x\text{C}$ \[4\]
Positive electrode: $C + x\text{A}^- \leftrightarrow \text{A}_x\text{C} + xe^-$ \[5\]
Overall: $x\text{Li}^+ + x\text{A}^- + 2C \leftrightarrow \text{Li}_x\text{C} + \text{A}_x\text{C}$ \[6\]

LIBs take on a traditional rocking chair cell operation where, during charging, Li$^+$ are transported from the positive electrode and intercalate into the interlayer spacing of the graphite negative electrode (Eq.2). During the discharge process Li$^+$ is deintercalated from the negative electrode and intercalates back into the positive electrode (Eq.1). In these systems only the cationic species (Li$^+$ in this case) are active charge carriers and are initially present in the positive electrode material and electrolyte. The most common cathodes (positive electrodes) are lithium containing transition metal oxides such as lithium nickel manganese cobalt oxide ($\text{NMC} = \text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, where $x + y + z \approx 1$ i.e. $\text{NMC811 LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$), lithium cobalt oxide ($\text{LCO} = \text{LiCoO}_2$) and lithium manganese oxide ($\text{LMO} = \text{LiMn}_2\text{O}_4$).\textsuperscript{9-13}

In DIBs both cations and anions are active charge carriers and are typically present in the electrolyte salt, as opposed to the positive or negative electrodes being the source, with carbonaceous materials typically applied as both electrodes. Exceptions to this configuration are possible with Li metal negative electrodes also providing a source of Li$^+$. During the charge process the cations are intercalated into the graphite negative electrode and anions intercalated into the graphite positive electrode, evacuating the electrolyte of all active charge carriers upon reaching a full state of charge. Whereas, during the discharge process deintercalation from the electrodes occurs releasing anions and cations back to the electrolyte. This simultaneous transport and intercalation of ionic species results in varying concentrations of anions and cations in the electrolyte depending on the state of charge. As such, the electrolyte can be considered active material in the energy storage process, influencing performance parameters such as energy density and storage capacity.\textsuperscript{14} Fig.2 illustrates the mechanisms of energy storage in LIBs and DIBs during operation.
Figure 2 – A schematic displaying the operation of: A) a LIB with a graphite anode and Li-containing metal oxide cathode. B) a DIB with graphite anode and cathode (GDIB configuration). Highlighting the intercalation and deintercalation of ions during charging and discharging.

Alternatively, the electrolyte within LIBs solely acts as a charge transport medium for ionic species between anode and cathode and is not active material in the energy storage process. The concentration of cationic species in the electrolyte of LIBs only decreases when side reactions occur at the electrolyte/electrode interface forming a solid electrolyte interphase (SEI), this is a key aspect to LIB functionality.\textsuperscript{15,16} In order to maximise energy density in LIBs a thin separating membrane (10-20 µm) is employed, whereas a thickness in excess of 100 µm is employed in DIBs due to a greater amount of electrolyte being stored between the electrodes. This increase in solution requires thick separators with high porosity to accommodate the active electrolyte material and ensure sufficient transport can occur – this highlights the importance of optimising the electrolyte environment to maximise cell performance.\textsuperscript{7,17}

The operating cell potentials (V) of DIBs (V\textsubscript{DIB}) and LIBs (V\textsubscript{LIB}) are determined by calculating the chemical potential difference of the positive electrode (µ\textsubscript{P}) and negative electrode (µ\textsubscript{N}), displayed in Eq.7.\textsuperscript{18}
\[ neV = n(\mu_N - \mu_P) \]  

Where \( n \) corresponds to the number of anions and cations intercalated in the electrodes, such that this is equal to the amount electrons flowing through the external circuit.

Considering the intercalation/deintercalation processes at both electrodes, and applying Eq.7, the following potential changes can be derived for LIBs and DIBs in Eq.8 and Eq.9 respectively.

\[
\Delta V_{LIB} = \frac{(\mu_{N(Li^+)} - \mu_{N(Li)}) - (\mu_{P(Li^+)} - \mu_{P(Li)})}{e} \\
\Delta V_{DIB} = \frac{(\mu_{N(Li^+)} - \mu_{N(Li)}) + (\mu_{P(A^-)} - \mu_{P(A)})}{e} 
\]  

Where \( \mu_{N(Li)} \) and \( \mu_{P(Li)} \) are the chemical potentials of Li\(^+\) intercalation into the negative electrode and positive electrode respectively, \( \mu_{P(A)} \) is the chemical potential of anion intercalation at the positive electrode. The chemical potential of free anions in solution/electrolyte at the cathodic side is given by \( \mu_{P(A^-)} \). Furthermore, the chemical potential of the cations in solution/electrolyte are represented by \( \mu_{N(Li^+)} \) and \( \mu_{P(Li^+)} \) on the anodic and cathodic sides. Considering Eq.8 and with the knowledge that the chemical potential of Li\(^+\) in electrolyte is a function of concentration we can deduce Eq.10, given that the concentration of Li\(^+\) in the electrolyte of a LIB is constant.\(^{19}\)

\[
\Delta V_{LIB} = \frac{(\mu_{P(Li)} - \mu_{N(Li)})}{e} 
\]  

Derivation for the chemical potentials of Li\(^+\) and A\(^-\) intercalation processes in DIBs requires application of the Nernst equation, as stated in Eq.11 and Eq.12.\(^{20}\)

\[
\mu_{N(Li^+)} = \mu_{N(Li^+)}^0 + kTln[Li^+] \\
\mu_{P(A^-)} = \mu_{P(A^-)}^0 + kTln[A^-] 
\]
Where $[\text{Li}^+]$ and $[\text{A}^-]$ are the activities of $\text{Li}^+$ and $\text{A}^-$ in electrolyte, $\mu^0_{N(\text{Li}^+)}$ and $\mu^0_{P(\text{A}^-)}$ are the standard chemical potentials in 1 M solution of electrolyte. Applying Eq.11 and Eq.12 to Eq.9 a final definition can be determined for the cell potential of DIBs.

$$\Delta V_{\text{DIB}} = \frac{\mu_{P(\text{A})} + \mu_{N(\text{Li})} - \mu^0_{N(\text{Li}^+)} - \mu^0_{P(\text{A}^-)} - kT \ln[\text{Li}^+] - kT \ln[\text{A}^-]}{e}$$  \[13\]

Comparing the cell potentials of LIBs and DIBs, Eq.10 and Eq.13, it is noted that cell potential of LIBs is not dependant on electrolyte factors such as salt concentration as the cathode materials are the source of $\text{Li}^+$. Whereas, DIB operational cell potential is heavily dependent on the type of ionic species and their concentrations, further confirming that the electrolyte is active material within the cell and influences cell performance.
1.1.3 History and Development of DIBs: An Overview

Early research into acceptor type graphite intercalation compounds (GICs) provided the basis for the future developments in DIBs, first reported in the 1840’s by Schafhäutl.\textsuperscript{21,22} At the 2D level, the individual graphene layers that make up graphite, the electronic structure of the $\pi$ bands allow for amphoteric redox properties – meaning the material is capable of functioning as an electron donor or acceptor. Acceptor GICs are formed when electronegative species accept electrons from the $\pi$-system of the graphite, such a process occurs at cathodic graphite materials during intercalation of anions. Alternatively, graphite can accept electrons, stabilising its antibonding $\pi^*$-band through the intercalation of cations forming donor type GICs.\textsuperscript{23,24} The development of donor type GICs laid the foundations for lithium intercalated graphite, the most widely implemented anode material in modern day LIBs. Following on from Schafhäutl’s early work with the formation of $\mathrm{H}_2\mathrm{SO}_4$-GICs, similar findings were reported for alternative acceptor GICs namely $\mathrm{HClO}_4$-GIC and $\mathrm{HNO}_2$-GIC by Spröesser, and Creighton and Ogden respectively.\textsuperscript{7,25}

Thereafter, research into electrochemical anion intercalation increased and the mechanism of the rocking chair cell was first reported by Rüdorff and Hofmann in 1938. This early rocking chair cell consisted of two graphite electrodes and a concentrated sulfuric acid electrolyte. The reversible intercalation and deintercalation of $\mathrm{HSO}_4^-$ in graphite allowed for the transport of the anions from one graphite electrode to the other during operation, forming the initial operating principles of the LIB.\textsuperscript{26} Significant development in DIBs began to proceed in the 1970’s with numerous studies conducted into the electrochemical properties of various acceptor type GICs, and the efficacy of new and alternative anions for intercalation. The shift to non-aqueous electrolytes intercalation of new anions, $\mathrm{ClO}_4^-$, $\mathrm{BF}_4^-$ and $\mathrm{CF}_3\mathrm{SO}_3^-$, as reported by Dunning’s group in 1977 was the first systematic study into the reversible intercalation of anions into graphite in a Li/graphite cell.\textsuperscript{27} Thereafter, Jobert and Touzain investigated the electrochemical intercalation of $\mathrm{PF}_6^-$, $\mathrm{AsF}_6^-$ and $\mathrm{SbF}_6^-$ into graphite from a propylene carbonate (PC) electrolyte, reporting the staging mechanisms of anion intercalation into GICs with stoichiometry of $\mathrm{C}_{24}\mathrm{A}^-$ at 5.2 V vs Li$^+$/Li, reported through the use of powder X-Ray diffraction (PXRD).\textsuperscript{28} This study highlighted the potential for GICs to be applied as cathode materials in
high energy density batteries operating at increased voltages, thanks to their high operating potential of 5.2 V vs Li. Similar work was conducted by Billaud et al. into the staging of AsF$_6^-$ reporting a stoichiometry of C$_{24}$A$_3$F$_6^-$ at 4.6 V vs Li$^+$/Li.$^{29}$

In 1989 McCullough et al. reported the first rechargeable DIB with two carbon electrodes and LiClO$_4$ in PC non-aqueous electrolyte. In this early model Li$^+$ intercalation formed the donor type GIC and subsequently ClO$_4^-$ intercalation at the opposing electrode forms the acceptor type GIC of the system.$^{30}$ Whilst McCullough’s early DIB was the first to utilise the dual intercalation mechanism, the system was far from optimised given PC’s poor compatibility with graphite. PC molecules solvate the ions in solution and co-intercalate into the graphite, resulting in extensive exfoliation of the graphitic structure and decreasing the reversibility of anion intercalation.$^{31}$ In the following years numerous studies altered and optimised McCullough’s early DIB model, with many investigating alternative electrolytes that would yield high degrees of reversibility in the dual ion intercalation process. In 1994 Carlin et al. studied the reductive and oxidative intercalation of room temperature ionic liquids (ILs) in a DIB configuration, terming these systems as dual intercalating molten electrolyte (DIME) batteries. A combination of molten salts was comprehensively trialled, consisting of imidazolium cationic species 1-ethyl-3-methylimidazolium (EMI$^+$) or 1,2-dimethyl-3-propylimidazolium (DMP$I^+$), and anionic species AlCl$_4^-$, BF$_4^-$, PF$_6^-$, CF$_3$SO$_3^-$, or C$_6$H$_5$CO$_2^-$.$^{32}$ It was reported that AlCl$_4^-$ containing IL electrolytes resulted in less exfoliation of the graphite electrodes and its application in a (DMP$I^+$)(AlCl$_4$) electrolyte resulted in a coulombic efficiency of 85 % and an open circuit voltage of 3.5 V.$^{32}$ From 1995 to 1997 Santhanam and Noel reported the effects of various solvent/salt compositions on DIB intercalation/deintercalation efficiencies when using polypropylene-graphite composite electrodes. Monovalent cations (Li$^+$, Na$^+$, K$^+$ and tetrabutylammonium, TBA$^+$) and anions (ClO$_4^-$ and BF$_4^-$) were investigated in solvents optimised for their cationic (DMSO, DMF and PC) or anionic (PC and AN) intercalation purposes.$^{33,34}$

In 2000, Dahn and Seel were the first to report the staging mechanism of PF$_6^-$ anions via electrochemical intercalation into graphite with organic solvents such as ethyl methyl sulfone (EMS) and various carbonate electrolytes with LiPF$_6$ salt. Staging of PF$_6^-$ intercalation was investigated via in-situ XRD using Li/graphite cells with either EMS or ethylene carbonate (EC)
and diethylene carbonate (DEC) electrolytes, with stage II intercalation of graphite being achieved. Further intercalation, stage I, was not achieved due to the decomposition of the electrolytes at such high potentials, with the carbonate electrolytes oxidatively unstable above 5.2 V and as such poor coulombic efficiencies were observed. The reported stage II intercalation of PF$_6^-$ into graphite corresponds to a stoichiometry of PF$_6$C$_{16}$ and a capacity of 140 mAh g$^{-1}$ between 3.5 and 5.5 V for EMS electrolytes with these values being the first energy calculations reported for DIBs, paving the way for further research into practical DIBs.\textsuperscript{14,20}

Following on from these early developments of DIBs much research has been conducted into the improvements of individual cell components, with significant progress made in terms of electrolyte/salt combinations and the focus on novel cathode materials. Examples of such are discussed in the following component sections.
1.2 Components of DIBs

1.2.1 Developments of Cathode Materials in DIBs

Typically, in electrolytes the anions (i.e. PF$_6^-$) are significantly greater in size than the cations (i.e. Li$^+$) as seen in Table 2. This corresponds to a greater number of possible cation intercalation sites at the anode and fewer anion intercalation sites at the cathode. For that reason, cathode materials are considered as limiting factors in cell performance given that a reduced number of storage sites directly correlates to a reduction in cell capacity. For comparison, Li$^+$ intercalation into graphite anodes corresponds to a stoichiometry of LiC$_6$ with a theoretical capacity of 372 mAh g$^{-1}$, whereas PF$_6^-$ intercalation into the graphite cathode forms C$_{16}$PF$_6$ with a theoretical capacity of 140 mAh g$^{-1}$. Furthermore, intercalation and deintercalation of such large anions causes significant volumetric changes in the cathode (>100 % for anion intercalation vs. ~10 % for Li$^+$ intercalation) with this becoming more prominent after repeated cycling, resulting in reduced structural integrity of the cathode material.

These challenges facing cathode materials have resulted in extensive research into alternative cathode materials to graphite, as well as optimised graphitic materials. The challenges and developments that have accompanied them are discussed in the following section.

<table>
<thead>
<tr>
<th>Ion Dimensions (Å)</th>
<th>Theoretical Capacity (mAh g$^{-1}$)</th>
<th>Volume Expansion of Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Lithium Cation (Li$^+$)</strong></td>
<td>0.73 (radius)</td>
<td>372 (LiC$_6$)</td>
</tr>
<tr>
<td><strong>Hexafluorophosphate Anion (PF$_6^-$)</strong></td>
<td>3.5 x 3.5</td>
<td>140 (PF$<em>6$C$</em>{16}$)</td>
</tr>
</tbody>
</table>

Table 2 – Comparison of anion and cation dimensions, corresponding theoretical capacities and volumetric expansions associated with full intercalation.$^{8,22,35}$
1.2.1.1 Graphite

Graphite is composed of stacked layers consisting of \( sp^2 \) hybridised carbons in a repeating arrangement of hexagonal units, with the units held together through strong covalent carbon-carbon bonds, and the layers held together through weak van der Waals interactions with an interlayer spacing of 3.35 Å. Where the plane of the covalently bonded carbon atoms is referred to as the basal plane, layers are stacked perpendicularly in the c-axis. This configuration of carbon atoms gives rise to many remarkable properties ideal for applications in energy storage such as high electron mobility due to delocalised \( 2p_z \) orbitals that lie perpendicular to the basal plane, furthermore the stacked configuration allows for the accommodation of ionic species through electrochemical intercalation. The weak nature of the Van der Waals interactions can be overcome when a large enough potential is applied, driving ions between these layers. Anion intercalation processes into the ABAB stacked graphene layers occurs in via a ‘stage’ mechanism, where the stage number corresponds to the number of graphene layers between alternate intercalated layers. Stage 1 intercalation corresponds to a repeating unit of one intercalated layer and one graphite layer, Stage 2 intercalation corresponds to a repeating unit of one intercalated layer and 2 layers of graphite, and so on, stage 1 represents the highest charge capacity due to complete intercalation.

This approach to the staging of intercalation assumes that graphite maintains a rigid and defect free structure within its interlayer arrangement during intercalation. As seen in Fig.3A. However, this staging model was adjusted by Daumas and Herold who proposed a model with a more flexible approach to the behaviour of the graphene layers when intercalated with bulky anions, as seen in Fig.3B. Flexibility of the graphene layers explains the presence of domains with different stages within intercalated graphite structures, where the intercalation process occurs by the diffusion of anions into accessible sites.
The degree of anion intercalation can be observed through the use of several electrochemical techniques such as cyclic voltammetry (CV) and galvanostatic charge and discharge (GCD), where anion intercalation occurs at known potentials (> 4.4 V vs. Li/Li⁺) with distinct potential plateaus representing stage transition, allowing for the determination of interfacial kinetics and impedance characteristics. To achieve higher stages generally a higher cell potential is required, however numerous factors influence this behaviour, such as anion type and size, electrolyte composition, and cut off potential of the cathode. In order to achieve stage 1 intercalation of graphite cathodes high operating potentials in excess of 5.0 V are required, this has been reported in many works investigating anion intercalation in DIBs.\(^{35,37,38}\)

Intercalation of anions between graphene layers increases the d-spacing between said layers, also referred to as gallery expansion (Δd), allowing investigations into the degrees of staging through XRD analysis.\(^{35,39}\) The progress of staging can be monitored through observing the intensity of the (002) dominant peak, corresponding to pristine non-intercalated graphite, and the introduction of (00n+1) and (00n+2) peaks. Typically, as a result of anion intercalation the (002) dominant peak will reduce with the intensity of (00n+1) and (00n+2) peaks increasing. Determining the d-spacing ratio of these additional peaks, \(\frac{d_{00n+1}}{d_{00n+2}}\), indicates the stage of intercalation, \(n\). Studies conducted by Placke and Schmuelling’s groups investigated the staging mechanisms of several common anions, including PF₆⁻ and
bis(trifluoromethane-sulfonyl) imide (TFSI\(^-\)), through the use of in-situ XRD techniques.\(^{35,39}\) Increasing the cut-off potential from 4.8 – 5.2 V in increments of 0.1 V whilst conducting in-situ XRD displayed the disappearance of the (002) peak, and an increase of the d-spacing ratio, \((d_{00n+1}/d_{00n+2})\), as well as increased \(\Delta d\) upon stage 1 intercalation at 5.2 V. Furthermore, it was confirmed that a greater anion size results in lower discharge capacities and an increased degree of gallery expansion, with TFSI\(^-\) intercalation into KS6 graphite resulting in a volumetric expansion of approximately 140 %. For comparison, an expansion of 10 % is experienced when Li\(^+\) is intercalated into KS6 graphite, highlighting the significant volumetric stress that occurs at graphite when electrochemically intercalated with bulky anions such as TFSI\(^-\).

Figure 4 – In situ Raman spectra for [PF\(_6\)] intercalation during charging A, and deintercalation during discharging B.
Raman spectroscopy is an alternative in-situ technique commonly applied when investigating the electrochemical intercalation of anions into graphitic materials, where the ratio of $E_{2g}(i)$ and $E_{2g}(b)$ intensities are used to determine the stage of intercalation. Pristine graphite materials exhibit a G-band at 1584 cm$^{-1}$, this band arises due to the planar arrangement of the strongly bonded sp$^2$ carbons within graphite.\textsuperscript{40,41} Upon intercalation of anions this G-band splits to two bands, $E_{2g}(i)$, the vibrational mode of the inner graphene layer adjacent to other graphene layers, and, $E_{2g}(b)$, the vibrational mode of the boundary graphene layer adjacent to the intercalated layer. Upon further intercalation, and a decrease in stage number, these bands are shifted to higher wavenumbers. Once the desired cut-off potential has been reached, and the potential is reversed, the deintercalation of anions results in the intensities of the $E_{2g}(i)$ and $E_{2g}(b)$ bands decreasing as well as their wavenumbers, indicating reversibility of the intercalation/deintercalation process as seen in Fig.\textsuperscript{42}

Graphitisation, as a process, is the structural transformation of amorphous carbons to more ordered, graphitic products through heating to temperatures in excess of 2500 °C.\textsuperscript{43} The term degree of graphitisation (DoG) is widely used to refer to carbonaceous materials and their graphite crystallinity, with a higher degree of crystallinity assigned to a greater DoG. This property is associated with an increased anion uptake leading to improved discharge capacities. Ishihara et al. investigated the electrochemical intercalation of PF$_6^-$ into 10 different carbon cathodes, reporting for the first time the influence of the DoG on anion intercalation in carbon cathodes.\textsuperscript{44} Amorphous carbons and C$_{60}$ exhibited high initial charge capacities followed by significantly decreased discharge capacities. Capacity decreases of 65 % and 77 % for C$_{60}$ and amorphous carbons respectively highlights the poor reversibility of anion storage in low DoG carbon cathodes. Graphite particles with diameters of 6 µm and 4 µm displayed capacity retentions of ~ 45 % during initial charge/discharge, whilst maintaining favourably high capacities in comparison to non-graphitic carbons. An increase in crystallinity and DoG results in decreased (002) plane spacing, with the reversibility of anion uptake maximised when (002) spacing of 3.35Å was achieved using graphite particles, Fig.\textsuperscript{5}. 44
Further work into the impact of carbon-type on electrochemical intercalation behaviour of anions was conducted by Placke et al., where TFSI\(^{-}\) anions were investigated alongside cathodes with varying degrees of graphitisation at 20 and 60 °C. \(^{45}\) Particle size, specific surface area and the ratio of basal plane to non-basal plane surface area all directly influence the degree and reversibility of anion intercalation into graphite. Given that anion intercalation only takes place via edge or defect sites the ratio of basal to non-basal surface area is an important characteristic to observe, a greater degree of non-basal surface area allows for increased anion intercalation. However, at 60 °C the degree of non-basal surface area only had a minor influence on overall cell performance and no correlation was found between discharge capacity and non-basal plane surface area. Whereas at 20 °C an increase in discharge capacity was observed for graphite materials with increased non-basal surface area and reduced particle size, such as synthetic graphite produced by Timrex (KS4 and KS6L). A lack of correlation between first cycle efficiency and particle size/specific area of the graphite material was reported as being due to the fact that no SEI layer forms at graphitic cathodes at the operating potentials investigated. \(^{45}\) Further correlations between particle size and capacity were deduced by Märkle et al., reporting that smaller graphite particles are better at accommodating PF\(_6^{-}\) due to less volume expansion caused by exfoliation. \(^{46}\) The trend is
dependent on electrolyte composition with the effects more prominent when the electrolyte was PC/EMC compared to EC/DMC, due to increased solvent co-intercalation with PC molecules.

1.2.1.2 Organic Cathode Materials

Redox active organic materials dominate alternative cathode research – metal organic frameworks (MOFs), p-type organic compounds, and hydrocarbons are a few leading examples - these research avenues, however, are in their early stages and further developments and progress are required to replace graphite as the dominant cathode material in DIBs. The benefits and performance in DIBs of these examples will be discussed in detail in this section.

The redox active MOF Fe$_2$(dobpdc) (dobpdc$^{4-} = 4,4'$-dioxidobiphenyl-3,3'$-dicarboxylate) reported by Aubrey and Long (Fig.6) was investigated as a cathode material in a sodium anode-containing half-cell with the weakly coordinating anions PF$_6^-$ and BF$_4^-$, tested in the potential range 2.00 to 3.65 V vs Na$^+$/Na. An initial discharge capacity of ~ 90 mAh g$^{-1}$ was achieved after 10 cycles, with this value remaining relatively constant over the subsequent 50 cycles with a CE of 99 % being reported, confirming that PF$_6^-$ is capable of being reversibly hosted within the pores of the MOF structure. These results are comparable with some graphite cathode materials previously reported, however at significantly lower potential range. As such, these lower operating potentials allow for the implementation of electrolytes that would usually be unstable in DIBs operating at higher potentials (> 5.0 V in many cases).

![Figure 6 - 4,4'$-dioxidobiphenyl-3,3'$-dicarboxylate metal organic framework structure](image-url)
Alternatively, Speer et al. investigated functionalised-thianthrene as a high-voltage cathode material for DIB, which undergoes two oxidation processes with the first, more reversible oxidation occurring at 4.09 vs Li/Li$. The second oxidation of thianthrene requires dry conditions and as such is not suitable for application in DIBS. Utilisation of the first reversible oxidation state of thianthrene in a carbon composite electrode within a lithium half-cell provides a discharge capacity of $\sim 65$ mAh g$^{-1}$ and a CE of 96 % after 9 cycles. $^{48}$ However, this level of performance was not maintainable and significant capacity fade was observed after 15 cycles with a reduced capacity of 20 mAh g$^{-1}$, possibly due to poor mechanical strength and durability during repeated anion intercalation. Aside from the poor stability, the capacity value reported corresponds to an estimated energy density of $\sim 275$ Wh kg$^{-1}$, approximately half of the energy density of LiCoO$_2$ cathodes in LIBs, this value may be exceeded if reversible oxidation and reduction of the second oxidation state could be achieved within a cell configuration.$^8$ Whilst this example of a redox active molecule participates through an active sulphur centre, p-type organic radical compounds that are nitrogen based have been discussed as organic cathode materials.

Diaminorubicence (DARb) has been investigated as an anion-insertion cathode, with its p-type nature arising due to the presence of two redox active amino groups that enable reversible uptake and release of anions, as such facilitating the transfer of two electrons per molecule.$^{49}$ However, the authors report that the bulky rubicene structure prevents full utilisation of the multi-electron redox process with a capacity of 115 mAh g$^{-1}$ achieved, only 75 % of its reported theoretical capacity of 150 mAh g$^{-1}$, and this capacity decreases further to 75 mAh g$^{-1}$ after 60 cycles, with an upper cut-off voltage of 4.0 V vs Li/Li$. Cell performance of the DARb cathode was best when smaller anions were implemented, with these capacities reported using a LiPF$_6$ EC:DMC electrolyte.$^{49}$ Further work by Deunf et al. reported the reversible intercalation of ClO$_4^-$, PF$_6^-$ and TFSI$^-$ into the layered aromatic amine compound, dilithium 2,5-(dianilino)terephthalate (Li$_2$DAnT). Reversible anion intercalation was reported in the potential range 2.8 – 3.5 V, corresponding to single anion uptake from electrolyte, with a reversible capacity of $\sim 80$ mAh g$^{-1}$ with a LiClO$_4$/PC electrolyte. However, the uptake of a single anion in theory should result in a capacity half of the theoretical capacity for a two-electron process (148 mAh g$^{-1}$), indicating that PC may have been co-intercalating into the Li$_2$DAnT structure. Further tests were conducted excluding carbon from the cathode
composition, reducing the capacity to ~ 60 mAh g\(^{-1}\) with a CE of 90-95 % throughout the first 100 cycles. Subsequent long-term cycling saw a 33 % capacity retention after 400 cycles.\(^{49,50}\) This impressive reversibility throughout the initial 100 cycles is reported as being the first example of a carbon-free organic cathode material that is capable of undergoing electrochemical anion intercalation reversibly over many cycles.

Polycyclic aromatic hydrocarbons (PAH) possess similar structures to the graphene layers within traditional graphite cathodes, a repeating arrangement of C\(_6\) rings stacked to form 3D sheet-like structures held together by van der Waals forces. As such, PAHs exhibit redox amphoteric properties to a similar degree as graphite, capable of hosting delocalised electrons or electron holes. Commercially available coronene was investigated by Rodriguez Pérez et al. as cathode material for use in DIBs, revealing that PF\(_6^-\) can be successfully and reversibly stored within its layered structure.\(^{51}\) Such reversible anion intercalation was achieved with LiPF\(_6\) in EC/DEC electrolyte, displaying a capacity of ~ 40 mAh g\(^{-1}\) at a cut off potential of 4.2 V as seen in Fig.7. The operating potential reported is significantly lower than what is required for graphite cathodes, allowing for the use of additive-free organic electrolytes that would not usually be viable in DIBs due to operating potentials in excess of 4.5 V vs Li\(^+\)/Li. Furthermore, ex-situ analysis revealed that the coronene structure became fully amorphous after 50 cycles, potentially due to the coronene molecules not exhibiting covalent bonding between one another as the C\(_6\) rings within graphene layers do, resulting in decreased crystallinity following repeated anion intercalation and deintercalation. Despite this, impressive cycling stability is reported by the authors in the original paper with a capacity of 35 mAh g\(^{-1}\) and CE > 95 % after 960 cycles, and also a gradual capacity increase through 2000 cycles has been reported a year later in a Perspective published by the authors.\(^{51,52}\)
1.2.1.3 Cathode Summary

Currently graphitic materials are the benchmark for anion-intercalation cathodes owing to their excellent electrical conductivity, redox amphoteric nature and high mechanical durability. Whilst these intrinsic properties are advantageous for graphite’s application as an electrode material, the performance of DIBs is still limited by anion intercalation behaviour at the cathodic graphite, suffering from reduced anion storage sites and volume expansion. Until now, many of the organic cathode materials reported have failed to display superior cell performance when compared to their graphite counterparts, with low capacities and reduced long term cycling stabilities. However, organic cathodes present alternative anion storage processes that remain promising for future developments in superseding capacity-limited graphite cathodes in DIBs.
1.2.2 Developments of Anode Materials in DIBs

Despite the cathode being the limiting factor in DIB performance, the anode plays a significant co-factor in the degree of performance achieved in these systems. Anodes must provide sufficient capacity to balance the performance of anion storage at the cathode, known as mass balancing, preventing excess metal plating on the anode surface and increasing safety of the cells.\(^{53}\) Currently graphite intercalation anodes are regarded as the leading option for anodes in energy storage systems, LIBs and DIBs alike, where the energy storage mechanisms in these systems operate through the storage and release of cations during charging and discharging. Graphite is widely used thanks to its stability during repeated intercalation and deintercalation of cations, this gives it remarkable reversibility for such applications. Despite this, drawbacks such as poor initial coulombic efficiencies due to the formation of an SEI at the anode/electrolyte interface, and in some cases, low capacities due to the reduced degree of crystallographic sites accessible to cations, have led to novel approaches for alternative anode materials. These alternative approaches typically operate through non-intercalation cell chemistries, where solid-state processes such as conversion, alloying/plating and adsorption/desorption have been of particular interest, offering improvements to energy density with the potential to succeed that of graphite intercalation-type anodes.

1.2.2.1 Alternative Intercalation Type Materials

Alternative intercalation-type anodes have been investigated widely with the aim of minimising capacity loss after the initial formation of the SEI, with continual electrolyte degradation proving detrimental to the energy density of DIBs given that the electrolyte is active material.\(^{54}\) Orthorhombic niobium (V) oxide (Nb\(_2\)O\(_5\)) undergoes reversible structural changes during charging and discharging processes, unlocking a reversible capacity due to the redox nature of Nb (V). A KS6-Graphite/Nb\(_2\)O\(_5\) cell with LiPF\(_6\) in EC/DMC was investigated at various lower and upper cut-off potentials.\(^{55}\) Operating in the range 0.0 – 3.5 V a maximum first discharge capacity of 55 mAh g\(^{-1}\) was achieved, with poor capacity retention visible after 20 cycles and a retention of 54 % after 50 cycles. When the lower cut-off potential was increased to 1.5 V the initial discharge capacity was reduced to < 50 mAh g\(^{-1}\), however capacity
retention was significantly improved with a retention of 85 % after 50 cycles. In a lithium metal half-cell configuration, a clear voltage plateau was observed between 1.9 and 1.0 V with an initial discharge capacity of 186 mAh g\(^{-1}\), this capacity reduced to 165 mAh g\(^{-1}\) during the second cycle due to electrolyte degradation during the first cycle as seen in Fig.8. Upon further charge/discharge cycles a capacity retention of 90 % was observed indicating potential for high energy density values due to the decreased operating potential of the anode.\(^{55}\)

![Figure 8 – Charge discharge curve for a Li half-cell with a Nb₂O₅ cathode and 1 M LiPF₆ EC/DMC (1:2) electrolyte, at a current density of 100 mA g\(^{-1}\) between 1.0 – 3.0 V. \(^{55}\)](image)

Furthermore, anode materials with reduced safety concerns have been considered, with Gunawardhana et al. reporting a dual ion system with a KS6 graphite cathode and MoO₃ anode.\(^{56}\) Such a configuration allows for operation between 1.5 – 3.5 V vs Li/Li\(^+\), avoiding lithium plating and subsequent dendrite formation at the anode. An initial discharge capacity of 81 mAh g\(^{-1}\) and capacity retention of 90 % was reported after 200 cycles, with the majority of this capacity arising due to the intercalation of PF\(_6^-\) into the KS6 cathode. Increased capacity was observed when the voltage exceeded 2.2 V, correlating to increased intercalation of anions at the cathode, whereas a sudden increase in potential was observed up to 2.2 V with little capacity increase in the first charge cycle indicating anions were adsorbed to the edge planes of the graphite but not fully intercalated.\(^{53,56}\) MoO₃ undergoes a structural change from orthorhombic to an amorphous state, with in-situ XRD suggesting only partial
amorphization occurs and as such does not negatively influence the long term cycling stability of the MoO$_3$ anode.

1.2.2.2 Conversion Type Materials

The previously discussed alternative intercalation-type anodes have displayed relatively low capacities when applied in full cell configurations, therefore conversion-type anodes have received increased interest due to their high theoretical capacities in excess of 800 mAh g$^{-1}$. This type of anode material typically operates through reversible redox reactions between Li$^+$ and transition metal oxides and sulphides. High theoretical capacities as well as high relative abundance of some conversion type anode materials, such as Fe$_3$O$_4$ and MnO$_2$, suggests that these materials have great potential in overcoming the limitations of intercalation-type anode materials.

Despite these positives, conversion type anodes still face many hurdles to overcome before being successfully implemented in production level energy storage systems. A well-known downfall of conversion-type anode materials is the poor long-term cycling stability and rate capability as a result of repeated structural rearrangement during charging and discharging, such conformational changes result in volumetric expansions up to 200 $\%$. Reducing the dimensions of particles to the nanoscale increases contact with the electrolyte and reduce the diffusion pathway of ions, whilst reducing structural strain due to the large degrees of volumetric expansion experienced. Cobalt oxide (Co$_3$O$_4$) nanosheets on carbon fibre paper (CFP) substrates have been implemented in DIBs. The integrated electrode, Co$_3$O$_4$/CFP, can effectively buffer the volumetric expansion experienced during charging and discharging, improving the long-term cycling stability of the anode. In a half-cell configuration the initial discharge capacity is 766 mAh g$^{-1}$ at a current density of 50 mA g$^{-1}$ in the potential window 0.5 – 3.0 V vs. Li/Li$^+$. with this capacity dropping to 662 mAh g$^{-1}$ after 50 cycles at varying current densities. Whilst this highlights the exceptional potential of Co$_3$O$_4$/CFP as an anode material, such high capacity is not reproducible in a DIB configuration, with a first discharge capacity of $\sim$ 30 mAh g$^{-1}$ at a current density of 10 mA g$^{-1}$ being reported. The reduced performance in a DIB system is displayed in Fig.9. This work displays that whilst
impressive anode performance is achievable, the overall cell performance of DIBs is still greatly hindered by the intercalation of anions into graphite cathodes.

Figure 9 – A) Cell operation and configuration of DIB with carbon fibre paper/Co$_3$O$_4$ electrodes. B) Galvanostatic charge discharge profiles at 100, 50 and 10 mA g$^{-1}$. C) Cycling performance at a current density of 10 mA g$^{-1}$.

1.2.2.3 Adsorption/Desorption Type Materials

Alternatively, adsorption/desorption processes can be utilised in the storage of cations at anodes for DIBs. These examples display improved rate capabilities and long-term cycling as cations are not intercalated into the anode structure, rather they are adsorbed onto the anode. Porous materials with large surface areas are generally considered for adsorption/desorption anodes, allowing for the fast uptake and release of cations from the electrolyte.$^{18}$ Shi et al. proposed a hybrid adsorption-type DIB system with a reduced graphene oxide (rGO) anode, graphite cathode and an IL electrolyte, (EMIm)$^+$PF$_6^-$.$^{61}$ Whilst PF$_6^-$ anions were intercalated into the graphite cathode, (EMIm)$^+$ was absorbed onto the rGO
anode surface as illustrated by a rectangular CV curve in the potential range -1.8 – 0.2 V, displaying capacitive behaviour as seen in Fig.6. The CV corresponding to the intercalation of PF$_6^-$ displayed clear redox peaks assigned to the intercalation/deintercalation processes in the potential range 0 – 2.1 V. The integration of adsorption and intercalation processes yielded an energy density of 70 Wh kg$^{-1}$ at an ultra-high power density of 1333 W kg$^{-1}$, with an energy density retention of 74 % after 50 cycles.$^{61}$ Energy density values for DIBs reported in literature are in the range of 50 – 120 Wh kg$^{-1}$ at varying power densities, whilst the value reported here is mid-range in terms of energy density the high power density is a significant advantage over other DIBs reported.$^{7,14}$

*Figure 10 - A) Schematic of the adsorption of EMIm$^+$ cations on rGO surface and the intercalation of PF$_6^-$ anions into graphite. B) Corresponding CV curves for the individual processes.*$^{61}$
1.2.2.4 Alloying Type Materials

The most successful alternative to intercalation-type anodes would be those based on alloying processes, most commonly through the implementation of metal anodes such as Al, Sn and Si.\textsuperscript{62–64} Alloying processes offer the potential for high capacities, Al-Li alloying for example, has a theoretical capacity of 993 and 2235 mAh g\textsuperscript{-1} for LiAl and Li\textsubscript{9}Al\textsubscript{4} phases respectively.\textsuperscript{65} Whilst alloying-type metal anodes have many intrinsic properties owing to their impressive potential as DIB anodes they suffer from severe volumetric expansion during the alloying/dealloying process (e.g. up to \sim 300 \% for Sn-Li alloying, and \sim 420 \% for Sn-Na alloying) resulting in repeated SEI formation, and as such, significantly reduced long term cycling stabilities and poor coulombic efficiencies are commonly reported.\textsuperscript{64–66} As a consequence, many surface modification techniques and additives have been implemented in these DIBs.\textsuperscript{67,68}

An aluminium-graphite DIB was reported by Tang et al., where Al foil operated as the anode and current collector, with a graphite cathode and a 4 M LiPF\textsubscript{6} in EMC electrolyte with 2 \% vinylene carbonate (VC) as an SEI forming additive.\textsuperscript{66} During charging Li\textsuperscript{+} cations are deposited on the Al anode forming an Al-Li alloy and PF\textsubscript{6}\textsuperscript{-} anions are intercalated into the graphite cathode, upon discharging the reverse processes occur, replenishing the electrolyte of Li\textsuperscript{+} and PF\textsubscript{6}\textsuperscript{-}. The replacement of graphite as an anode removes the requirement for a current collector, reducing dead weight in the cell and vastly improving the energy density of the DIB to values close to those reported in commercial LIBs. A specific energy density of 222 Wh kg\textsuperscript{-1} at a power density of 132 W kg\textsuperscript{-1} was reported for the Al-DIB, the authors compared this value to commercial LIB with an energy density of \sim 200 Wh kg\textsuperscript{-1} at 50 W kg\textsuperscript{-1}. Impressive rate capability and long-term cycling stability was achieved through the addition of 2 \% VC in the electrolyte, with a discharge capacity of \sim 100 mAh g\textsuperscript{-1} at a current rate of 200 mA g\textsuperscript{-1} over the potential window of 3.0 − 5.0 V, and capacity retention of 88 \% after 200 cycles. Furthermore, a cell constructed without the presence of VC suffered from dramatic capacity fade with a capacity of \sim 30 mAh g\textsuperscript{-1} after 20 cycles, thus supporting the importance of the VC additive for long term cycling.\textsuperscript{66}
Further surface modifications can be achieved through coating the metal anodes with various materials, from polymer coatings to carbon coatings, forming a diverse range of possible composite materials with improved mechanical and electrochemical properties in an attempt to suppress the volume expansion experienced during cycling. A carbon-coated, porous aluminium foil anode was investigated by Tang et al. The porous nature of the Al anode increased ion diffusion, whilst alleviating the mechanical stress experienced as a result of Al-Li alloying, vastly improving the rate capability of the DIB compared to non-coated and non-porous Al anodes. This synergistic relationship resulted in a reversible capacity of 93 mAh g\(^{-1}\) and a capacity retention of 90% after 1000 cycles at 200 mA g\(^{-1}\), corresponding to an energy density significantly greater than what is reported for commercial LIBs at high power densities (204 Wh kg\(^{-1}\) at 3084 W kg\(^{-1}\)).

Metal alloying anodes are not limited to aluminium, or lithium-DIBs, with a promising tin-graphite DIB with a sodium-containing electrolyte reported by Tang et al., operating on the same basis as an Al-Li DIB with a Na-Sn alloy forming at the anode and PF\(_6^-\) intercalation taking place at the cathode. In an attempt to minimise the degree of volumetric expansion during cycling a reduced stage of Sn-Na alloy was formed, Na\(_9\)Sn\(_4\), with a theoretical capacity of 226 mAh g\(^{-1}\). Whilst a high degree of alloying at the anode, such as Na\(_{15}\)Sn\(_4\), provides high theoretical capacities, significant volume expansions of 420% are observed.

Although these alloying anodes appear promising, the long-term cycling stability of metal anodes and their large volume expansions leading to unstable SEI formation still require further optimisation for scalable, commercial applications.

**1.2.2.5 Anode Summary**

The anode chemistries highlighted in this section have displayed the potential for alternative anode materials in DIBs, with alloying-type anode materials appearing the current leading alternative. These materials pose great potential not only as a result of their superior cell performance, but also thanks to their naturally abundant nature and high intrinsic electrical conductivities, furthermore the ability to reduce the overall cell mass through the removal of the current collector yields great benefits in terms of energy density.
1.2.3 Electrolyte Developments

Electrolyte composition requires careful consideration when designing DIBs, given that the electrolyte supplies the active ions for energy storage whilst simultaneously serving as the charge migration medium during operation. The main contributing factor being the stability of the electrolyte at high oxidising potentials (> 4.5 V vs. Li/Li⁺ for anion intercalation at graphite cathodes), such high oxidative stability is imperative and can be intrinsic to the solvent or achieved through the use of electrolyte additives. The electrochemical window of stability is defined as the difference between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the electrolyte, illustrated in Fig.11. When the electrochemical potential of the cathode (µP) is below the HOMO of the electrolyte, the electrolyte is oxidised, and when the electrochemical potential of the anode (µN) is above the LUMO of the electrolyte, the electrolyte is reduced. Whilst efforts are made to avoid oxidation of the electrolyte at the cathode, a significant capacity contribution can be attained when exceeding 5 V, rendering many traditional LIB carbonate electrolytes unsuitable. Furthermore, the formation of an effective, stable SEI layer is necessary for optimal cell performance. Anion-solvent interactions, such as solvation energy, self-aggregation and ion pair formation, directly influence the maximum reversible capacity that can be achieved. These properties should be considered alongside the size of anions implemented in the salt of choice, small anions may appear favourable due to a greater packing density at the cathode, however the anion-solvent interactions may negate the benefits of reduced anion size. Moreover, the simultaneous process of anion and cation storage at the respective electrodes must be contemplated, referred to as “crosstalk”; if anions cannot be stored at the cathode, this has a knock-on effect at the anode preventing cation storage, and vice versa.

Electrolyte properties can vary throughout cell operation depending on the state of charge, when the state of charge is high the salt content of the electrolyte is reduced, and when the state of charge is low the salt content increases. For this reason, it is common practice to add excess salt to the electrolyte in an attempt to maintain suitable ionic conductivity for optimal performance. However, the addition of excess salt can reduce the energy density of the cell,
thus, identifying a balance between the amount of excess salt required and the performance output is critical.

![Diagram of potential window](image)

**Figure 11** – Illustration of the potential window that determines the electrochemical stability of the electrolyte, highlighting that the electrode potentials of the anode and cathode ($\mu_N$ and $\mu_P$ respectively) must remain within the constraints of the LUMO and HOMO values.

### 1.2.3.1 Organic Electrolytes

Organic electrolytes are widely implemented in LIBs and have been extensively researched throughout the years, with low cost, wide liquid ranges and high dielectric constants among a few of the favourable properties exhibited by them.\textsuperscript{70} Carbonate-based solvents are the most commonly used organic solvents in DIB and LIB electrolytes, possessing excellent SEI forming capabilities, high ionic conductivities, along with reasonable electrochemical windows of stability (> 5.0 V vs. Li/Li\textsuperscript{+}).\textsuperscript{71} Many studies include ethyl methyl carbonate (EMC) as either a co-solvent, or primary solvent, due to its superior electrochemical properties in comparison to other carbonates such as DMC and diethyl carbonate (DEC).\textsuperscript{31,72,73}

Various organic solvents (including EMC, DMC, EC and PC) and their interactions with LiPF\textsubscript{6} salt were investigated by Liu et al., identifying EMC as the best solvent for PF\textsubscript{6}\textsuperscript{-} intercalation.\textsuperscript{74} It was reported that EMC forms an optimal degree of van der Waals interactions with PF\textsubscript{6}\textsuperscript{-},
allowing de-solvation of the anion, whereas PC was found to form a high degree of van der Waals interactions with the PF$_6^-$ preventing de-solvation and resulting in co-intercalation into the graphite cathode. Furthermore, of the carbonate solvents investigated, 1 M LiPF$_6$ in EMC achieved the highest discharge capacity of 70 mAh g$^{-1}$ with a CE of 98 % after 450 cycles, whereas DMC and PC achieved capacities below 60 and 40 mAh g$^{-1}$ respectively.$^{74}$ The poor compatibility of PC with graphite anodes has been discussed extensively in both LIB and DIB applications.$^{75-77}$

Whilst EMC alone provides superior electrochemical performance, it is often the case that a mixture of organic solvents is used in order to tailor the properties of the electrolyte, cyclic carbonates such as ethylene carbonate (EC) are often added to improve the dielectric constant, increasing salt dissolution, and linear carbonates such as DMC provide increased ionic conductivity.$^{78}$ Seel and Dahn studied the intercalation of PF$_6^-$ into graphite using EC/DEC and pure ethyl methyl sulfone (EMS) electrolytes. EMS was reported to reversibly support PF$_6^-$ intercalation up to 5.5 V, whereas the EC/DEC electrolyte suffered from severe oxidative degradation above 5.2 V and as such did not support reversible intercalation of PF$_6^-$. In situ XRD indicated that the staging of PF$_6^-$ intercalation deteriorated over prolonged cycling, with a reduction in the peak corresponding to stage 2 intercalation, followed by the disappearance of said peak. This suggests that the graphite suffers from degradation potentially as a result of electrolyte decomposition, or co-intercalation of EC or DEC. In this case, EC co-intercalation is assumed to be a significant factor given that EC strongly solvates the PF$_6^-$ anions. Addition of EMC to EC electrolytes vastly improves performance and long term stability of the cells, this is attributed to EMC molecules competing with EC in bonding with PF$_6^-$, allowing for more favourable intercalation into graphite due to the linear nature of EMC and its solvation/de-solvation energies with PF$_6^-$.$^{22,79}$ Whilst EMC facilitates the intercalation of PF$_6^-$ into graphite electrodes, the same level of performance is not applicable to other anions such as BF$_4^-$, as illustrated by Wang et al.$^{80}$ An electrolyte consisting of 1.25M LiPF$_6$ in EMC achieved a specific capacity of 80 mAh g$^{-1}$ at the graphite electrode with an upper cut off potential of 5 V. Switching the salt to LiBF$_4$ results in a drastic decrease in capacity to 6 mAh g$^{-1}$. The authors suggest that a ‘special solvation state’ occurs when EMC solvates BF$_4^-$ anions, reducing mobility and intercalation at the graphite electrode, furthermore a strong affinity between
Li\(^+\) and BF\(_4^-\) reduce dissociation of the ions, as such reducing the amount of free BF\(_4^-\) available for intercalation.\(^{80}\)

The introduction of fluorinated species, either as co-solvents or additives, increases oxidative stability of the electrolyte at the cathode and can promote the formation of a stable SEI, vastly improving long term cycling performance. Fluorinated solvents and additives have been widely researched in LIBs as film forming additives due to their low flammability and SEI forming abilities.\(^{81,82}\) Read et al. reported a highly effective DIB with tris(hexafluoro-isopropyl)phosphate (HFip) additive in an EMC/fluoroethylene carbonate (FEC) electrolyte containing 1.7M LiPF\(_6\), where a Li/MesoCarbon MicroBead graphite (MCMB) half-cell achieved a stable capacity of 85 mAh g\(^{-1}\) and exhibited a CE in excess of 96% throughout 250 cycles at a high operating potential window of 4.0 – 5.2 V.\(^{37}\) When employed in a full graphite cell a specific capacity of 65 mAh g\(^{-1}\) is initially observed, with this dropping to ~ 40 mAh g\(^{-1}\) after 50 cycles as seen in Fig.12. Despite poor capacity retention in the full cell configuration the CE was reported to increase with every cycle, with a CE of ~ 98% reported after the 50\(^{th}\) cycle. Unsatisfactory capacity performance in a full dual graphite cell originates due to increasing impedance during cycling and given the good electrode-electrolyte stability it is expected that some form of inhibiting interactions between salt and solvent occurs. A non-fluorinated EC-EMC DIB was cycled under the same conditions, exhibiting poor cycling stability, not exceeding 10 cycles.\(^{37}\)
Sulfone-based electrolytes, like fluorinated species, offer increased oxidative stability thanks to their electron-withdrawing sulfonyl moiety. Whilst attractive from the perspective of redox stability, these solvents have not been extensively investigated in DIBs potentially due to their short liquid ranges, high viscosity and poor SEI formation, limiting their practical applications.83 As discussed previously, Seel and Dahn investigated EMS as an electrolyte solvent in a Li/graphite half-cell with 2 M LiPF₆ solvated, showing that such a cell could be operated to a high voltage of 5.45 V producing a reversible capacity of 140 mAh g⁻¹.20 Such a capacity corresponds to stage II intercalation, with a stoichiometry of (PF₆)₀.₅Cs₈, with this only achievable when employing a high charge-discharge rate in order to prevent electrolyte decomposition that occurs at lower rates.20 Poor viscosity and liquidity of sulfones such as sulfolane (SL) can be combated through the incorporation of EMC in a small quantity, as reported by Fan et al..41 EMC reduces the solvation of the PF₆⁻ within the SL solvent and aids with intercalation at the graphite electrode. In a Li/graphite cell with 1 M LiPF₆ in SL and 20 vol.% EMC, an initial capacity of 112 mAh g⁻¹ was reported in the potential range 3.0 – 5.4 V at a specific current of 200 mA g⁻¹, with a capacity of ~ 63 mAh g⁻¹ and CE > 98 % after 1000 cycles.41 Such excellent long-term stability and cycling performance is promising for future applications of sulfone-carbonate hybrid electrolytes.

Figure 12 – Dual graphite cell performance when the electrolyte is 1.7 M LiPF₆ in EMC/FEC (4:6) + 5 mM HfIP, as reported by Read et al.. a) specific capacity (mAh g⁻¹) b) coulombic efficiency.37
In order to fully achieve the full potential of DIBs, highly concentrated electrolytes (HCEs) have been pinpointed as a key avenue to pursue, achieving high reversibility, impressive long-term cycling performance, and high energy densities. Such electrolytes offer excellent oxidative stability at high cathode potentials, whilst forming uniform and well-developed SEI layers at the anodes allowing for repeated intercalation and deintercalation, yielding increased capacities as a result. The formation of a robust SEI protective layer prevents dissolution of the anodic Al current collectors, further improving long-term cycling of DIBs. Heckmann et al. demonstrated the impressive performance of HCEs, investigating HCEs based on LiPF₆ and LiTFSI in DMC, EMC and DEC. Li/graphite half-cells with HCEs exhibited higher capacities than their dilute counterparts, experiencing a reduced anion intercalation potential despite having reduced ionic conductivities in comparison to dilute electrolytes. An example of such impressive performance can be seen through the comparison of the specific discharge capacities of 4 M LiPF₆ in DMC vs. 1 M LiPF₆ in DMC, in Li/graphite cells at an operating potential range of 3.5 – 5.0 V and a charge/discharge current of 50 mA g⁻¹. The 4 M half-cell displayed an initial discharge capacity of ~85 mAh g⁻¹, reducing by 3 mAh g⁻¹ after 20 cycles, whereas the dilute 1 M half-cell displayed a capacity of ~55 mAh g⁻¹, reducing by 40 mAh g⁻¹ after 20 cycles. A similar trend is observed for 3.5M LiPF₆ and 1 M LiPF₆ in EMC. However, despite the many advantages associated with using HCEs, low ionic conductivity and high costs in comparison to dilute electrolytes may hinder their progress and further research as DIB electrolytes.

1.2.3.2 Ionic Liquid Electrolytes

Ionic liquids (ILs) possess many intrinsic properties that benefit them in their function as electrolytes for DIBs, primarily their wide electrochemical windows of stability often beyond the 5.0 V operating potentials of DIBS. Additionally, the impressive safety associated with these electrolytes owing to their high thermal stability, low flammability and low volatility; combined with ionic conductivities on par, or exceeding, organic electrolytes have resulted in these molten salt-based electrolytes being the focus of increasing research. ILs were first reported as DIB electrolytes by Carlin et al. in 1994 investigating various combinations of anions and cations, confirming their operation in such systems, however no results confirming
or discussing the long-term cycling performance were reported. In 2012 Placke et al. reported a 1-Butyl-1-methylpyrroloidinium bis(trifluoromethylsulfonyl)imide (Pyr$_{14}$TFSI)/LiTFSI electrolyte in a lithium/graphite half-cell reporting high CE of > 99 % after 500 cycles with an upper cut off potential of 5.0 V.  

Although ILs possess greater stability over a wide operating potential window, thus greater anodic stability, graphite anodes often experience significant exfoliation as a result of the formation of a thin SEI layer that allows the permeation of large cations between the graphite layers. Improving the coulombic efficiencies of IL-based DIBs is a key area of research interest in order to maximise their overall cell performance, whilst electrolyte additives such as VC and FEC are highly effective when implemented in organic electrolytes, such additives are less effective at preventing irreversible capacity loss with IL electrolytes. Rothermel et al. reported a coulombic efficiency of > 99 % after 50 cycles in a Li/graphite half-cell with an IL electrolyte of Pyr$_{14}$TFSI/LiTFSI with ethylene sulfite (ES) additive, suggesting that ES is an effective SEI forming additive that is compatible with IL electrolytes, thus allowing reversible Li$^+$ and [TFSI]$^-$ intercalation and deintercalation. To further support the effectiveness of ES a pure IL electrolyte, without the addition of ES, displayed a discharge capacity of ~ 50 mAh g$^{-1}$, approximately half the discharge capacity achieved with the ES-IL electrolyte, 97 mAh g$^{-1}$. The authors also stated that whilst discharge capacity nearly doubled with the use of ES, anion intercalation proceeded at a lower onset potential due to reduced coordination of Li$^+$ to [TFSI]$^-$ in the presence of ES. Initial cycling displayed relatively low coulombic efficiency of 55 %, arising due to a combination of SEI formation at the anode and due to formation/activation processes at the cathode. Such an activation process at the cathode is attributed to the intercalation of [TFSI]$^-$, given that the large anions must overcome the van-der-Waals forces between graphene layers before intercalating.

Due to the varying sizes of cations in ILs, it has been suggested that larger cationic species contribute to a reduced capacity and smaller anions are reversibly intercalated and deintercalated more successfully. Meister et al. supported this claim through observations made when comparing two IL-based DIB systems, one with a fluorosulfonyl-(trifluoromethanesulfon) imide, [FTFSI]$^-$, anion and the other a [TFSI]$^-$ anion. It was reported that the smaller anion, [FTFSI]$^-$ (0.65 nm), displays higher specific capacities at all of
the cut-off potentials investigated, ranging from 4.8 V to 5.2 V vs. Li/Li⁺, when compared to the larger [TFSI]⁻ anion (0.8 nm). A maximum capacity of 99 mA h g⁻¹ after 50 cycles was achieved for the intercalation of [FTFSI]⁻ at a cut off potential of 5.2 V, however this high cut off potential resulted in poor coulombic efficiency of 92 %. Poor coulombic efficiency of the [FTFSI]⁻ DIBs is due to the reduced stability of FTFSI electrolyte, with [TFSI]⁻ displaying superior CEs at all of the cut-off potentials investigated.⁹³ In a later study, the same authors reported the effects of anion size on the anion intercalation potential. Fig.13 displays the cyclic voltammograms of various imide-based ILs, bis(pentafluoroethanesulfonyl) imide (BETI⁻), TFSI⁻, FTFSI⁻, and bis(fluorosulfonyl) imide (FSI⁻) (largest – smallest), with the following descending trend observed for the onset potential of anion intercalation: BETI⁻ > FSI⁻ > FTFSI⁻ > TFSI⁻. BETI⁻, the largest anion, displays no clear onset potential indicating poor intercalation properties. Aside from this, the smallest anion, FSI⁻ displayed the highest onset potential (4.53 V vs. Li/Li⁺), this trend was due to a combination of factors related to electrolyte-anion interactions, not only anion size. It was reported that ion-pair formation and self-aggregation of the smaller anions results in a greater overpotential for anion intercalation, and that the ionic conductivity of the electrolyte is a less important factor.⁶⁹,⁹³
Further studies into alternative IL electrolytes have been conducted by various groups, namely Fan et al. and Li et al., with the intentions of improving anodic stability and increasing CE through the use of 1-butyl-1-methylpiperidinium cations (PP$_{14}^+$).$^{94,95}$ These studies investigated pure PP$_{14}$TFSI electrolyte in dual-graphite DIBs, with capacities of 50-60 mAh g$^{-1}$ reported at current density of 40 mA g$^{-1}$ over the potential range 0.1 V – 5.0 V after 100 cycles. Furthermore, Fan et al. reported an impressive CE of 97 % after 100 cycles, far superior to Pyr$_{14}$TFSI DIB with a CE of 82 % after 10 cycles. PP$_{14}$TFSI possesses great potential for DIB applications, with high CEs as reported, and also an optimum viscosity and conductivity that is reported to support ion transport whilst preventing self-deintercalation, thus reducing the effects of self-discharge.$^{94}$
1.3 Summary

DIBs are exciting next generation secondary energy storage systems capable of operating at high potentials and generally operating with two carbon-based electrodes, these factors contribute towards their impressive cell performance and their sustainable nature. In comparison to LIBs, lower capacities (< 60/70 mAh g⁻¹) and reduced reversibility (LIBs CE > 99 %, DIBs CE ~ 90 %) prevent current DIBs from superseding LIBs as the state-of-the-art energy storage system. Overcoming these issues requires improved cathode materials, either through the development of novel organic materials with high theoretical capacities, or by optimising the anion storage capabilities of current graphite cathodes. Metals, namely Al, can operate as current collector and anode simultaneously, reducing inactive mass within the cell. Alloying anodes can suffer from the formation of unstable SEI layers and large volume expansion during operation, yet surface modifications can suppress these effects providing coulombic efficiency improvements.

High operating potentials of DIBs generally exceed the working potentials of many traditional organic electrolytes, therefore identifying suitable high voltage electrolytes that are compatible with graphitic electrodes is crucial for taking DIBs to the next level. Moreover, HCEs possess excellent redox stabilities at these increased operating potentials and have the ability to form robust SEI layers at both electrodes. Vast improvements to the energy density of DIBs can be achieved through reducing the amount of electrolyte solvent required. The reversible capacity of HCE DIBs is generally greater than the capacities achieved when dilute electrolytes are applied, however these electrolytes possess low viscosity due to their high salt content. Likewise, ILs exhibit high oxidative stability, but poor compatibility with graphite anodes due to the intercalation of large cations from ILs which results in significant capacity fading during extended cycling. Whilst HCEs and ILs provide impressive performance increases to DIBs, high costs may thwart their applications in commercial DIBs. Electrolyte additives can provide a cost-effective approach to improving cell performance, such as the CE through stabilising the anode/electrolyte interfaces. High-voltage LIBs often employ electrolyte additives with significant amounts of research previously conducted in this area, the crossover of these additives to DIBs has not received as much interest yet. Of these
additives fluorinated species have great potential, possessing excellent oxidative stability and have received a small degree of interest in DIBs already, as reported by Read et al.

Research into DIBs has attracted significant interest in recent years as a result of these batteries possessing great potential for both EV and large-scale stationary storage applications. To achieve these commercial development goals further research into electrolyte compositions, electrode materials, and electrolyte/electrode pairings must be extensively conducted to identify the optimal balance between cost and performance.
2 Experimental Methods

2.1 Synthesis of Electrochemically Exfoliated Graphene (EEG) and Nitrobenzenediazonium Functionalised Graphene (NBD-Graphene)

Electrochemical exfoliation of graphite, and its subsequent functionalisation to produce NBD-Graphene, was carried out in a 3-electrode system with a graphite rod working electrode, graphite counter electrode and silver wire reference electrode. For the non-functionalised synthesis method 0.3 M CsClO₄ dissolved in DMSO was prepared as the electrolyte. For the functionalised graphene, 4-nitrobenzenediazonium tetrafluoroborate was dissolved in the same electrolyte composition at a concentration of 40 mM. A potential of −4.0 V vs. Ag was applied to the system for 2 hours whilst stirred, and the surface of the electrolyte was purged with N₂ throughout. The exfoliated product was filtered under vacuum and washed thoroughly with excess acetone, deionised water and acetone again. The filtered and washed product was then dried under vacuum at 60 °C for 24 hours.

2.2 Electrode Preparation: Slurry & Casting

2.2.1 Slurries for Negative Electrodes

Polyvinylidene fluoride (PVDF) (0.1 g) was added to N-methyl-2-Pyrrolidone (NMP) (2.5 g), stirring until fully dissolved after ~ 1 hour. The active material (0.8 g) and carbon black (0.1g) were added gradually whilst continuously stirring to ensure a homogeneous slurry. The resultant slurry was left to stir for 12 hours before being cast onto copper foil with a doctor blade at a thickness of 100 µm resulting in an average mass loading of 0.7 mg.

2.2.2 Slurries for Positive Electrodes

Active material, carbon black and sodium alginate were combined in a weight ratio of (8:1:1) with 3 times its weight of deionised water (eg. 1.0 g dry ingredients mixed with 3.0 g of water). To ensure a homogeneous slurry was produced mixing was carried out using a vortex mixer with the settings displayed in Table 3. The resultant slurries possessed honey-like
consistencies and were cast onto carbon coated aluminium foil with a doctor blade at a thickness of 50-150 µm, resulting in mass loadings between 1.0 – 3.5 mg.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>30</th>
<th>90</th>
<th>120</th>
<th>90</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed (rpm)</td>
<td>500</td>
<td>1500</td>
<td>2000</td>
<td>1500</td>
<td>500</td>
</tr>
</tbody>
</table>

The difference in binders for the negative and positive electrodes is due to the difference in the intercalating cation/anion sizes. The atomic radii of Li⁺ and PF₆⁻ are 0.73 Å and 1.75 Å respectively. The positive electrodes undergo significantly more mechanical stress during PF₆⁻ intercalation and therefore requires a more robust and flexible binder to accommodate the large volumetric expansion. Sodium alginate has been reported previously in literature as being an effective positive electrode binder, with alginate electrodes experiencing significantly less disintegration of the surface coating in comparison to PVDF electrodes.

The cast foils were dried at 80 °C for 24 hours before being calendared to a thickness of 20 µm, cut into 1.5 cm diameter electrodes and weighed. The resultant electrodes were dried in a vacuum oven at 80 °C for a further 24 hours and transferred to an Ar-glovebox.

Active materials and their respective mass loadings and thicknesses are seen in Table 4. Further discussion on the type of electrode materials, highlighting the significance of KS4 and SP1 graphite, can be found in section 4.2 (Characterisation of Materials).

<table>
<thead>
<tr>
<th>Electrode Material</th>
<th>Coating Thickness and Average Mass Loading</th>
<th>Material Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS4 Graphite on Cu</td>
<td>100 µm, 0.7 mg</td>
<td>Imerys</td>
</tr>
<tr>
<td>Natural Graphite on Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KS4 Graphite on Al</td>
<td>100 µm, 1.2 mg</td>
<td>Imerys</td>
</tr>
<tr>
<td>SP1 Graphite on Al</td>
<td>150 µm, 2.5 mg</td>
<td>Agar Scientific</td>
</tr>
<tr>
<td>Electrochemically Exfoliated Graphene on Al</td>
<td>200 µm, 3.5 mg</td>
<td>Self-produced</td>
</tr>
<tr>
<td>NBD-Functionalised Graphene on Al</td>
<td></td>
<td>Self-produced</td>
</tr>
</tbody>
</table>

Table 4 – A table displaying electrode material coating details and source of materials.
2.3 Electrolyte Preparation

All electrolytes were prepared and stored in an Ar-glovebox with O$_2$ < 20 ppm and H$_2$O < 0.5 ppm.

Fluorinated additive in an EMC/FEC based electrolyte - EMC/FEC (6:4) 2 M LiPF$_6$ + 5 mM HFiP$^{37}$

EMC and FEC were mixed in a volume ratio of 4:6 and stirred for ~ 1 hour before dissolving LiPF$_6$ at a concentration of 2 M. The solution was mixed for a further ~ 2 hours until the salt was fully dissolved, upon which 5 mM HFiP was added and stirring was continued for ~ 8 hours.

EMC with additive variations (AlF$_3$, VC & FEC)

The EMC based electrolyte compositions seen in Table 5 were prepared by the following method.

LiPF$_6$ was dissolved in EMC at a concentration of 2 M, stirring for ~ 1 hour. The additive(s) of choice was added to the solution, stirring for a further ~ 8 hours before being stored for later use.

<table>
<thead>
<tr>
<th>Solvent + Salt</th>
<th>Additive(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMC 2 M LiPF$_6$</td>
<td>2 % AlF$_3$ + 3 % VC</td>
</tr>
<tr>
<td></td>
<td>2 % AlF$_3$</td>
</tr>
<tr>
<td></td>
<td>3 % VC</td>
</tr>
<tr>
<td></td>
<td>3 % FEC</td>
</tr>
<tr>
<td></td>
<td>No additive</td>
</tr>
</tbody>
</table>

2.4 Coin Cell Assembly

In an Ar-glovebox, CR2032 coin cells were constructed with a negative electrode (lithium chip, aluminium foil or graphite on copper – depending on the type of cell), a graphite/graphene on aluminium foil positive electrode, a microfiber filter separator (250 μm) and 150 μL
electrolyte. Coin cell separator discs and spring were also included in the cell to maximise electrode contact Fig.14. The coin cells were sealed using a hydraulic coin cell press (MSK-60E) within the glovebox before being removed for electrochemical testing.

![Figure 14 - Figure showing the components of a CR2032 coin cell. The negative electrode is one of: Graphite on Cu, Aluminium foil or Lithium disc.](image)

2.5 3-Electrode Studies of EMC 2 M LiPF₆ +/- 3 % VC Electrolyte

A 3-electrode system with a glassy carbon working electrode, lithium reference electrode and lithium counter electrode was assembled within an Ar-glovebox. The electrolytes investigated were EMC 2 M LiPF₆ with 3 % VC and without VC. The lithium counter and reference electrodes were equally immersed in approximately 2 ml of electrolyte. Cyclic voltammetry of the 3-electrode system was carried out within the potential ranges of 2.7 – 5.2 V and 2.7 – 0.1 V vs. Li/Li⁺, at a scan rate of 5 mV s⁻¹* using an Autolab potentiostat.

* Full CV scans carried out in the potential range of 0.1 – 5.2 V were also conducted following the same method and scan rate.

2.6 Cell Testing: Cyclic Voltammetry and galvanostatic Charge Discharge

Cyclic voltammetry of coin cells was carried out within the potential range of 2.5 – 5.2 V vs. Li/Li⁺ at a scan rate of 1 mV s⁻¹ using an Autolab potentiostat.
Galvanostatic charge/discharge tests were measured from 2.5 – 5.0 V and 2.5 – 5.2 V vs. Li/Li⁺ with the following current density regime:

**Cycles 1-35:** 2.5 – 5.0 V vs. Li/Li⁺, with 20 cycles at 2 A g⁻¹ followed by 3 cycles at each of: 1, 0.5, 0.3, 0.2 and 0.1 A g⁻¹. The initial 20 cycles at 2 A g⁻¹ are used to aid the formation process that occurs at the cathode as a result of electrolyte degradation. Faster rates are typically used, reducing the amount of time that the electrolyte is at highly oxidising potentials whilst forming the initial SEI layer. A similar process is used in the formation of the anode in LIBs, albeit lower rates are typically used to prevent the formation of Li-dendrites at the graphite anode.

**Cycles 36 – 53:** 2.5 – 5.2 V vs. Li/Li⁺, with 3 cycles at each of: 1, 0.5, 0.3, 0.2 and 0.1 A g⁻¹.

**Cycles 54+:** 2.5 – 5.2 V vs. Li/Li⁺, 0.1 A g⁻¹.

The number of cycles at 0.1 A g⁻¹ is listed in relevant figures/results. Likewise, any deviations from this regime are specified in the relevant sections.
3 Characterisation Methods

3.1 Galvanostatic Charge Discharge

Galvanostatic charge discharge (GCD) is a popular electrochemical characterisation technique that can provide valuable insights into the performance of a cell over time. During GCD testing the cell is charged and discharged within a set voltage range at a constant current (A g\(^{-1}\)), measuring the voltage response over time (Fig.15). Typically, the process is repeated over many cycles and with varying current rates in order to determine the rate capability. The resulting plot of time vs. voltage ideally displays distinct plateaus corresponding to the intercalation and deintercalation processes occurring during cell operation. Capacity values are typically reported in the unit mAh g\(^{-1}\) and are calculated by multiplying the charge/discharge time step by the current applied during that duration.

Further to this, the average operating potential of a cell during both the charging and discharging processes can be determined and visualised from GCD profiles, with the difference between these two values defined as the polarisation value. An increase in the polarisation typically occurs as cell performance decreases, this can be attributed to an increase in charge transfer resistance at the electrode/electrolyte interfaces as electrolyte degradation reactions occur during cycling.

![Figure 15 – A typical time vs potential GCD graph.](image-url)
3.2 Cyclic Voltammetry

Cyclic voltammetry (CV) is a valuable electrochemical characterisation technique that measures the current response across a linearly swept voltage range at a constant scan rate. CV is useful in determining the redox behaviour and kinetics of electron-transfer reactions in a system. The presence of two redox peaks, one peak present during charging and the other when discharging, is indicative of a reversible redox process, such as the intercalation and deintercalation of ions into host materials in a DIB, an example is highlighted in Fig.16. In an ideal system if the redox couple is reversible the oxidation and reduction peaks would have similar shapes and equal areas under their respective peaks, corresponding to a high coulombic efficiency. In reality this is not always the case as electrolyte decomposition is a common issue with dual ion cells given the high operating potentials required for anion intercalation. If an electrolyte is unstable within the voltage range, a peak may be observed during charging with no reciprocal peak seen during discharge, this indicates irreversible degradation of the electrolyte. This behaviour is often observed during the initial cycle of a cell during CV tests and is attributed to the formation processes that occur at the electrolyte-electrode interface during the first cycle(s).

Figure 16 - A CV displaying the reversible intercalation and deintercalation processes in a dual graphite cell.
Three electrode cyclic voltammetry is often implemented to study the behaviour and performance of an electrode-electrolyte pairing at specific currents and voltages. A three electrode system consists of a working electrode (WE), reference electrode (RE) and a counter electrode (CE), as seen in Fig. 17. Where the working electrode is typically the electrode material of interest and the reference electrode is one that is stable under the operating conditions with a known standard electrode potential. During operation the current flows between the WE and CE, with the potential difference being measured between the WE and RE. Allowing for the determination of the current response of an electrode of interest in relation to a known reference electrode.

**Figure 17** – Diagram of a three electrode electrochemical cell setup consisting of working electrode (WE), reference electrode (RE) and counter electrode (CE).
3.3 X-ray Photoelectron Spectroscopy

X-Ray Photoelectron Spectroscopy (XPS) is a surface analytical technique capable of quantitatively determining elemental composition, chemical states and electronic states of elements present at the surface of a material. During XPS analysis a monochromatic beam of X-rays (~ 1.5 keV) is focused onto the sample under ultra-high vacuum conditions. These X-rays irradiate the surface, exciting core electrons that are subsequently ejected from the sample. The ejected electrons, photoelectrons, are measured as a function of their kinetic energy (KE) – where the KE of the electron is dependent upon the photon energy (E_{hv}) and the binding energy (E_B) of the electron to the parent atom. As such the KE is characteristic of the element of the parent atom, Eq.13.

\[ KE = E_{hv} - E_B \]  \[13\]

Elastically scattered photoelectrons contribute towards the photoelectron peak, with the intensity of the peak proportional to the number of electrons of the specific KE detected. Inelastic scattering of electrons before emission from the sample reduces the KE of the resulting photoelectrons, resulting in the detection of peaks with reduced intensities – contributing to the spectral background. The position and intensity of peaks can provide valuable information on the chemical state of the surface atoms and shifts in the E_B can indicate changes in the local environment of surface atoms and the element’s oxidation state. Relative intensities of elements can be interpreted by integrating the areas under each element’s respective peak, such analysis allows for the determination of material purity. For example, the relative ratio of carbon to oxygen in a graphite sample is an indicator of graphite purity – a low C:O ratio would correspond to a higher purity with less defect sites (C=O etc.).

XPS was performed using a Kratos Axis Ultra DLD spectrometer with a monochromatic Al K_{\alpha} X-ray source (E = 1486.6 eV, 10 mA emission), a hemispherical electron energy analyser and a multichannel plate and delay line detector (DLD). The analysis area of the samples was 300 \( \mu \)m x 700 \( \mu \)m. Survey spectra were collected as well as high resolution spectra for the C1s peak, and F1s peak where relevant. Charge neutralisation was used for all samples.
3.4 Raman Spectroscopy

Raman spectroscopy is a non-destructive analytical technique capable of determining chemical and structural information of a material through the interactions of its bonds with light. Materials can interact with light in many different ways – through transmission, reflection, or scattering. Raman spectroscopy focuses on the scattering process, specifically the elastic and inelastic scattering of light. The most common outcome when light interacts with a molecule, elastic scattering (Rayleigh scattering), is when the energy of the molecule remains unchanged after a photon interaction and the energy of the scattered photon is equal to that of the incident photon. Alternatively, for inelastic scattering (Raman scattering) the energy of the scattered photon is not equal to the energy of the incident photon. This occurs as a result of a transfer of energy between the molecule and the scattered photon. When the molecule loses energy after the photon interaction relaxation of the molecule to a lower vibrational state occurs, and the incident photon’s energy increases thus decreasing its wavelength. This is known as Anti-Stokes scattering. Alternatively, Stokes scattering occurs when the molecule gains energy from the interacting photon – reducing the photon’s energy and increasing its wavelength. Of the two Raman scattering processes, Stokes Raman scattering is more common and is therefore usually the measured process in Raman spectroscopy. For a Raman signal to be detected the molecule in question must undergo a change in its polarisability in relation to the vibrational modes of the bonds. The intensity and wavenumber of the scattered light make up the Raman shift, where the intensity is proportional to the degree of change in polarisability.

Graphite exhibits a strong peak at ~ 1580 cm$^{-1}$ known as the G-band, this unique band arises due to the planar arrangement of the strongly bonded sp$^2$ carbons within graphite. Contrastingly, the presence of defect/edge sites in a graphite sample results in the presence of a peak at ~ 1350 cm$^{-1}$, this is the D-band. This peak is an indication of structural disorder in the graphite and is referred to as the defect band. The G-band appears at a higher frequency as a result of the higher bond energy between sp$^2$ carbon atoms, increasing the vibrational frequency of the bonds. The intensity of the D-band in relation to the intensity of the G-band, $\frac{I_D}{I_G}$, provides a quantitative measure of the defect density in a sample, where a value close to 0 indicates less defects. Finally, the Raman spectra of graphene contains a G-band as well.
as a more intense G’ (2D band). This band is also present in graphite, where downshifting of the G-band and changes in the shape have been reported as a method of determining the number of graphene layers in a sample.\textsuperscript{98} Fig.18 illustrates the band positions in a typical Raman spectra of a graphene sample.

![Raman spectra of a graphene sample](image)

\textit{Figure 18 - Raman spectra of a graphene sample, highlighting the relevant Raman bands (D, G, D’ and 2D) typically observed in graphene & graphite.}\textsuperscript{99}

Raman measurements were performed using a Renishaw inVia Microscope with a 532 nm (2.33 eV) excitation laser at a power of 1 mW with a 100x objective. A grating of 1800 per mm was used giving a spectral resolution of ~ 1 cm\textsuperscript{-1}. 
4 Results and Discussion

4.1 Initial Plan: Identifying a Suitable DIB Electrolyte

The focus of this project was to identify an electrolyte composition that supports dual ion intercalation of Li$^+$ and PF$_6^-$, whilst matching or improving on the performance of other systems previously reported in literature. Initially an aluminium dual ion battery (Al-DIB) was used, which consisted of an aluminium anode and carbon-based cathode, whilst it was also important for the electrolyte to operate effectively in a dual graphite configuration (GDIB). Once such an electrolyte and additive combination was identified it was important to understand the role of the additive and solvent on the intercalation/deintercalation and SEI forming processes involved during full cell operation.

Two key parameters were used to determine whether an electrolyte was suitable, discharge capacity and coulombic efficiency (CE). Studies in literature have reported capacity values of 40-100 mAh g$^{-1}$ and coulombic efficiencies greater than 95% (Table 6), providing a benchmark for the results reported herein.
Table 6 - A table displaying some examples of the best performing DIBs in literature alongside the 3 best performing cells reported in this research.

<table>
<thead>
<tr>
<th>Electrolyte composition &amp; cell configuration</th>
<th>Reported cell performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>EMC/FEC (6:4) 2 M LiPF₆ w/ 5 mM HFiP</strong></td>
<td>Initial capacity 60 mAh g⁻¹ @ 100 mA g⁻¹, dropping to 40 mAh g⁻¹ after 50 cycles. CE &gt; 98 % after 50 cycles.</td>
<td>37</td>
</tr>
<tr>
<td>[Coin cell: CGP-Graphite anode, MCMB cathode]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EMC 1 M LiPF₆</strong></td>
<td>Capacity: 70 mAh g⁻¹ @ 100 mA g⁻¹. CE &gt; 98 % after 500 cycles.</td>
<td>74</td>
</tr>
<tr>
<td>[Pouch cell: MCMB anode, expanded graphite cathode]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EMC 1 M LiPF₆ w/ 20 % SL</strong></td>
<td>Pouch cell capacity: 139 mAh g⁻¹ @ 100 mA g⁻¹. 88 % capacity retention after 3000 cycles. (prelithiation of the anode boosts full cell performance)</td>
<td>41,100</td>
</tr>
<tr>
<td>[Pouch cell: Prelithiated-MCMB anode &amp; MCMB cathode]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EMC/DMC (1:1) 3 M LiPF₆ w/ 3 % VC &amp; 2 % AlF₃</strong></td>
<td>Initial capacity 100 mAh g⁻¹ @ 100 mA g⁻¹. CE &gt; 99 % after 600 cycles.</td>
<td>63</td>
</tr>
<tr>
<td>[Al-DIB: Aluminium foil anode, natural graphite cathode]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EMC 2 M LiPF₆ + 3 % VC</strong></td>
<td>Discharge capacity of 83 mAh g⁻¹ @ 0.1 A g⁻¹ &amp; CE 91 % after 150 cycles.</td>
<td>This work</td>
</tr>
<tr>
<td>[Li half-cell: Li anode, SP1 graphite cathode]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EMC 2 M LiPF₆ + 3 % VC</strong></td>
<td>Discharge capacity of 61 mAh g⁻¹ @ 0.1 A g⁻¹ &amp; CE 94 % after 350 cycles.</td>
<td>This work</td>
</tr>
<tr>
<td>[GDIB: KS4 graphite anode, SP1 graphite cathode]</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>EMC 2 M LiPF₆ + 3 % FEC</strong></td>
<td>Discharge capacity of 84 mAh g⁻¹ @ 0.1 A g⁻¹ &amp; CE 96 % after 350 cycles.</td>
<td>This work</td>
</tr>
<tr>
<td>[Li half-cell: Li anode, SP1 graphite cathode]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹ Acronyms: EMC (ethyl methyl carbonate), FEC (fluoroethylene carbonate), HFiP (tris(hexafluoro-isopropyl)phosphate), MCMB (mesocarbon microbead), SL (sulfolane), DMC (dimethyl carbonate), VC (vinylene carbonate).
4.2 Characterisation of Materials

It is well known from previous literature, relevant to LIBs and DIBs, that numerous factors play a part in determining the electrochemical performance of graphite anodes and cathodes, such as morphology, particle size and defectiveness. A brief summary of the carbon-based cathode materials discussed in this research is seen below. From herein, these materials will typically be referred to by their given acronyms.

The D/G ratio and elemental composition of the cathode materials are seen in Table 7, with the corresponding Raman and XPS figures displayed in Fig.19 and Fig.20. From this table it can be deduced that SP1 graphite contains the lowest degree of defect sites, closely followed by KS4 graphite, given their low D/G ratios and low oxygen contents. Where KS4 is a synthetic graphite with small particle size (D90 = 4.9 µm) and high specific surface area produced by Timcal. SP1 is a high quality (low oxygen content) natural flake graphite.

The “quality” of the cathode materials follows the trend:

\[
\text{SP1} > \text{KS4} > \text{NatG} > \text{EEG} \approx \text{NBD}
\]

Where the cell performance, and anion intercalation capacity, is directly related to the “quality” of the cathode material. An increase in defects on the surface of the cathode can reduce the anion intercalation and deintercalation capacities due to a number of factors, i) blocking of anion transport pathways reduces the intercalation density of the material. ii) the electrical conductivity of the electrodes is lowered in the presence of defect groups. iii) oxygen groups can repulsively interact with PF$_6^-$, increasing the overpotential required to achieve low stage intercalation phases (ie. To achieve the stage I intercalation phase).

The D/G ratio and elemental compositions of EEG and NBD are similar, with the low N content of the NBD graphene suggesting that the degree of functionalisation was minimal. To compare, Ejigu et al. reported a N content of 4.8 % when a concentration of 40 mM NBD was used during production. Further similarities between these cathode materials are reported in the Li-half cell and GDIB GCD performance and CVs when an EMC 2 M LiPF6 + 3 % VC electrolyte was used, Appendix 1 and Appendix 2. Given the similar cell performance and
characterisation results of the EEG and NBD systems, the NBD functionalised graphene cathodes are not discussed further in this report.

Table 7 - Table showing the D/G ratio and elemental composition (%) obtained through Raman and XPS. D/G ratios are an average across 5 points on the same sample.

<table>
<thead>
<tr>
<th>Material</th>
<th>I_D/I_G</th>
<th>Elemental Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP1 Graphite</td>
<td>0.124</td>
<td>C: 99.17 %; O: 0.83 %</td>
</tr>
<tr>
<td>KS4 Graphite</td>
<td>0.147</td>
<td>C: 98.44 %; O: 1.56 %</td>
</tr>
<tr>
<td>Natural Graphite</td>
<td>0.212</td>
<td>C: 98.22 %; O: 1.78 %</td>
</tr>
<tr>
<td>Electrochemically Exfoliated Graphene</td>
<td>0.525</td>
<td>C: 98.35 %; O: 1.65 %</td>
</tr>
<tr>
<td>NBD-Graphene</td>
<td>0.511</td>
<td>C: 98.00 %; O: 1.52 %; N: 0.49 %</td>
</tr>
</tbody>
</table>

Figure 19 – X-Ray Photoelectron spectra for the 5 carbon-based cathode materials trialled in this work. Displaying the elemental compositions of the materials.
4.3 Fluorinated Additive in an EMC/FEC Based Electrolyte

This section focuses on the application of a high voltage electrolyte, EMC/FEC (6:4 v/v) 2 M LiPF$_6$ + 5 mM HFiP, capable of supporting PF$_6^-$ intercalation at 5.2 V in both a lithium half-cell configuration and dual graphite cells, first reported by Read et al.. This early report was one of the first to investigate the performance of a GDIB when using a fluorinated electrolyte/additive combination in an attempt to increase the oxidative stability of the electrolyte. This section discusses the performance of this electrolyte in an Al-DIB, not previously reported by Read et al., and in a GDIB configuration with varied carbon-based cathodes.

4.3.1 Al-DIB Results

The electrochemical performance of the EMC/FEC (6:4) electrolyte in an Al-DIB can be seen in Fig.21 where in both graphs the first 20 cycles are at a rate of 2 A g$^{-1}$, followed by 3 cycles at each of the following rates: 1 A g$^{-1}$, 0.5 A g$^{-1}$, 0.3 A g$^{-1}$, 0.2 A g$^{-1}$ and 0.1 A g$^{-1}$. Typically, the
decrease in capacity and fluctuation in CE across the first 10/20 cycles can be attributed to the initial anion uptake and SEI formation processes that occur during charging and discharging. Where such formation processes are required to overcome the kinetic barrier of anion intercalation into the cathode whilst forming a sufficient protective SEI through the decomposition of the electrolyte.\textsuperscript{45}

Initially the Al-DIBs were cycled to 5.0 V before subsequent testing to 5.2 V. \textbf{Fig.21A} displays the cell performance when the cells were cycled to 5.0 V, where the general performance trend is SP1 Graphite > KS4 Graphite > Natural Graphite > Electrochemically Exfoliated Graphene. This trend correlates directly to the purity and degree of defects in the cathode material, as seen previously in \textbf{Table 7}. Observing the rate capabilities of the 4 carbon-based cathodes when cycled to 5.0 V, only KS4 and SP1 graphite experience an increase in their capacity when the rate is decreased. A reversible capacity of 20 mAh g\textsuperscript{-1} at 2 A g\textsuperscript{-1} increases to 30 mAh g\textsuperscript{-1} at 0.1 A g\textsuperscript{-1} for KS4 graphite. Likewise, a reversible capacity of 25 mAh g\textsuperscript{-1} at 2 A g\textsuperscript{-1} increases to 35 mAh g\textsuperscript{-1} at 0.1 A g\textsuperscript{-1} for SP1 graphite. EEG and NatG cathodes performed unfavourably, with the capacity continuously decreasing when cycling at varying rates. High defect cathode materials are prone to capacity drop off through the blocking of anion intercalation/deintercalation pathways and the formation of strong interactions between PF$_{6}^{-}$ and defect sites.\textsuperscript{42} Through increasing the upper cut off potential one can expect an increase in the discharge capacity, contributing to a significantly improved energy density of the batteries in question.\textsuperscript{81} The improved capacities of DIBs when cycling beyond 5.0 V vs. Li/Li$^{+}$ is attributed to the formation of a stage I intercalation phase between 5.0 and 5.2 V. This transition has been studied by Read, noting that the specific capacity of PF$_{6}^{-}$ intercalation into SP1 graphite cathodes increases by $\sim$ 20 mAh g\textsuperscript{-1} between 5.0 V and 5.2 V as the phase transition from stage II (C$_{24}$PF$_{6}$) to stage I (C$_{20}$PF$_{6}$) occurs.\textsuperscript{101} Both KS4 and SP1 graphite Al-DIBs were cycled up to 5.2 V with their cell performance displayed in \textbf{Fig.21B}, where a significant drop in the discharge capacities as well as poor rate performance is seen in comparison to the 5.0 V tests. These results are contrary to those expected, with the poor cell performance when cycled to 5.2 V a result of electrolyte degradation at the increased cut off potential.
The CVs of both the KS4 and SP1 Al-DIBs are depicted in Fig. 22, where the initial scans were carried out up to 5.0 V followed by subsequent scans to 5.2 V. This allowed for the investigation of the redox behaviour of the EMC/FEC electrolyte within the Al-DIB configuration. Cycle 1 in both Fig. 22A and Fig. 22B displays an upshifted cathodic scan as a
result of the initial increased overpotential required to intercalate anions into the cathode for the first time, as well as the formation of the SEI layer. Three clear reversible redox pairs can be identified during cycle 2 and 3 in both Fig.22A and Fig.22B, suggesting that the intercalation/deintercalation of PF$_6^-$ into the graphite cathodes occurs via a staging mechanism.$^{101}$ When the upper cut off potential is increased to 5.2 V, Fig.22C and Fig.22D, the initial peak of the cathodic scan (~ 4.3 V vs. Li/Li$^+$) is shifted to a more positive value from cycle 4 to cycle 5, before reducing significantly in cycle 6. Likewise, the reverse peak on the anodic scan (~ 3.9 – 4.0 V vs. Li/Li$^+$) is present in cycle 4 and disappears thereafter in both CVs. The disappearance of the initial redox peaks suggests the loss of stage 2/3 anion intercalation when cycling to 5.2 V, correlating to a reduced anion intercalation density and thus a reduced capacity is observed for KS4 and SP1 Al-DIBs in Fig.21.$^{102}$ Furthermore, by calculating the area under the respective CVs it can be seen that the coulombic efficiency of the intercalation/deintercalation processes decreases significantly, from 78 % to 53 % for cycles 4 and 6 of Fig.22C, and from 90 % to 71 % for cycles 4 and 6 of Fig.22D. To determine the efficiency values the charging region (above the x-axis) and discharging region (below the x-axis) of the CV curves are integrated, resulting in values for the charge input ($Q_{\text{charge}}$) and output ($Q_{\text{discharge}}$) during the cycle. The coulombic efficiency is then defined as the ratio between the charge output and charge input ($Q_{\text{discharge}}/Q_{\text{charge}}$).
After 35 cycles the capacity values, 25 – 35 mAh g\(^{-1}\), and coulombic efficiencies, \(\sim 90\%\), reported here are significantly lower than the original values reported by Read et al., where the anion intercalation capacity was reported to be 80 mAh g\(^{-1}\) with a CE greater than 95 % after 100 cycles in a lithium half-cell.\(^{37}\) Given that the initial report implemented the electrolyte system within a Li-half cell with a MCMB-graphite cathode suggests that, in this case, the aluminium anode is detrimental to the cell performance. With this significant decrease in capacity being attributed to the poor stability of the aluminium during the alloying process that occurs during charging and discharging. Aluminium anodes face many challenges in their applications within DIBs, with Li-dendrite formation during charging a common issue given the metallic nature of the anode. Dendrite formation depletes the lithium reserves of the electrolyte reducing the cycling lifetime and eventually leading to short circuiting of the cell, with these effects more prominent at current densities greater than 1 Ag\(^{-1}\).\(^{103}\) Furthermore, it has been reported that the protective oxide layer that forms on the surface of aluminium can reduce the electrochemical activity at the anode surface, reducing the efficiency of the alloying process that typically occurs at the Al-anode in Al-DIBs.\(^{62,104}\) To
circumvent this issue pre-treatment of aluminium has been explored – with polishing the aluminium in an inert atmosphere and immersion in acidic solution being two potential methods. Wang et al. pre-treated anodes by immersing aluminium in acidic AlCl₃/1-butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid for 24 hours, subsequently removing any oxide film on the Al-anode surface. The findings of which confirmed that cells with pre-treated Al-anodes performed better than cells with untreated anodes. The significant aluminium oxide (Al₂O₃) film on the untreated anode surface prevented the deposition of Al³⁺ resulting in a discharge capacity of 0.1 mAh g⁻¹ at 0.1 Ag⁻¹ after 3 cycles, when using an ionic liquid electrolyte and a V₂O₅ cathode. In comparison, a cell with the pre-treated anode displayed a capacity of 35 mAh g⁻¹ after 3 cycles.¹⁰⁴

Application of this electrolyte within an Al-DIB appears to be limited, attempting to implement the pre-treatment methods discussed above may have the potential to improve the cycling stability of the aluminium anode, or through the addition of an anode/Al modifying additive. Whilst these methods may improve results, the electrolyte composition itself may require further optimisation to achieve discharge capacity values closer to those reported in literature (> 80 mAh g⁻¹) and the theoretical capacity of PF₆⁻ intercalation into graphite cathodes.

4.3.2 GDIB Results

Fig.23 shows the full cell performance of the EMC/FEC (6:4) 2 M LiPF₆ + 5 mM HFIP electrolyte where the capacity and CE trends resemble those observed in the Al-DIB setup in Fig.21, with SP1 and KS4 cathodes displaying the greatest discharge capacities after 50 cycles (41 mAh g⁻¹ and 33 mAh g⁻¹ respectively). The decreasing CE seen for the KS4 GDIB is likely a result of the decreasing current density every third cycle and the increase in capacity attributed to this change. The transition from an Al-DIB to a GDIB sees a marginal improvement in the discharge capacity of the KS4 (3 mAh g⁻¹) and SP1 (6 mAh g⁻¹) cells at 0.1 Ag⁻¹ after 50 cycles, despite this increase all of the GDIBs tested display signs of capacity fade at cycle 50. CD profiles of KS4 and SP1 GDIBs at differing current densities can be seen in Appendix 3 displaying the
initial increase in capacity as the current density decreases to 0.2 \( \text{Ag}^{-1} \) for the KS4 GDIB and 0.3 \( \text{A g}^{-1} \) for the SP1 GDIB, with the discharge capacity decreasing thereafter.

![Graph showing capacity and coulombic efficiency performance of GDIBs](image)

*Figure 23 – Capacity and coulombic efficiency performance of GDIBs with varying carbon-based cathodes and EMC/FEC (6:4) 2 M LiPF_6 + 5 mM HFiP electrolyte. Where the first 35 cycles are cycled between 2.5 – 5.0 V, with the remaining 15 cycles between 2.5 – 5.2 V.*

The CD profiles for KS4 and SP1 GDIBs, *Fig.24A* and *Fig.24B*, highlight the increase in capacity when the cut off potential is increased from 5.0 V to 5.2 V – such behaviour was not observed for Al-DIBs with the HFiP electrolyte, further supporting the previous discussion that the aluminium anode was detrimental to the Al-DIB cell performance. Adding to this, comparisons can be drawn between the CVs of the GDIBs (*Fig.24C* and *Fig.24D*) and Al-DIBs (*Fig.22C* and *Fig.22D*) with KS4 and SP1 cathodes – where the CVs for both KS4 and SP1 GDIBs do not display a significant loss or reduction in the redox peaks corresponding to the intercalation and deintercalation processes when the cut-off potential is increased to 5.2 V.
The capacity and coulombic efficiency results reported for GDIBs with EMC/FEC (4:6) 2 M LiPF$_6$ + 5 mM HFiP electrolyte are consistent with those originally reported by Read et al., where cell performance decreases significantly after 50 cycles. This reduced performance may be attributed to the lack of an effective graphite-SEI forming additive, resulting in continuous electrolyte degradation at the electrodes during operation. Whilst HFiP has been studied as an electrolyte additive for LiBs with high voltage cathodes such as NMC-111 and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO), reports on its ability to form an effective SEI at a graphite cathode in a DIB system are scarce.\textsuperscript{105,106} Read et al. drew no conclusion between the relevance of the HFiP additive and the overall cell performance, instead suggesting that the partial oxidation of EMC may protect the cathode.

Furthermore, the reduced capacities reported when using this electrolyte in both Al-DIB and GDIBs may stem from the solvent and co-solvent choice and ratio. EMC is reported as a key component in DIB electrolytes, supporting the intercalation and deintercalation of PF$_6^-$ whilst being more oxidatively stable than alternative carbonate based electrolyte solvents such as
EC, thus reducing continuous electrolyte degradation once a compact SEI layer is formed.\textsuperscript{73,79} On the other hand, FEC is a common additive in LIBs and in some cases DIBs, capable of further improving the oxidative stability of the electrolyte and aiding in the formation of a stable SEI layer. Studies implementing FEC within their DIB electrolyte typically do so with less than ~10\% by volume, fitting the role of an electrolyte additive.\textsuperscript{107-109} In this instance 40\% of the electrolyte is FEC (60:40 EMC FEC by volume), reducing the amount of EMC molecules available in the electrolyte. During intercalation and deintercalation of anions into graphite EMC has been reported to have a lubricant-like effect – coordinating to anions and co-intercalating into the graphite electrode, subsequently ejecting the existing EMC molecules within the graphite (Fig.25). The co-intercalation of EMC molecules does not result in the excessive exfoliation of the cathode material, unlike previously reported PC based electrolytes. With fewer EMC molecules available in solution PF\textsubscript{6}– – EMC interactions become stronger, enabling intercalation into the graphite cathode and hindering the deintercalation process.\textsuperscript{102} Therefore, a shortage of EMC molecules within an electrolyte can greatly reduce the capacity and coulombic efficiency values of a DIB.

Figure 25 - Schematic illustrating the role of EMC molecules during the intercalation and deintercalation of anions into graphite layers.\textsuperscript{102}
4.4 Application and Adaptation of an EMC Based Electrolyte

The first report of an Al-DIB in literature implemented an EMC based electrolyte, EMC 2 M LiPF$_6$ + 3 % VC. Producing impressive results, with a capacity of ~ 100 mAh g$^{-1}$ and a CE of 88 % after 200 cycles at 0.1 A g$^{-1}$. Further to this, other studies have included the additive AlF$_3$ (EMC 2 M LiPF$_6$ + 3 % VC and 2 % AlF$_3$) in order to improve the stability of the aluminium anode during the cycling process. It was reported that without the presence of AlF$_3$ the Al negative electrode of the cell is visibly damaged when observed post-cycling, as a result of the large volumetric changes that occur during alloying to form AlLi$_x$. In addition to acting as a protecting agent, AlF$_3$ contributes to the overall capacity as a result of the formation of AlF$_4$ in solution. Dissolved Al$^{3+}$ and F$^-$ readily form the complex AlF$_4$ that is subsequently intercalated alongside PF$_6$ during charging. Wang et al. reported a capacity of 100 mAh g$^{-1}$ with a CE greater than 99 % after 600 cycles at 200 A g$^{-1}$ using this electrolyte in an Al-DIB. Whilst many studies have highlighted the impressive performance of EMC based electrolytes for Al-DIBs and Li-half cells, there have been fewer reports replicating such performance in GDIBs (full cell configuration).

4.4.1 EMC 2 M LiPF$_6$ + 3 % VC & 2 % AlF$_3$

4.4.1.1 Al-DIB Results

The Al-DIB electrochemical performance of the VC and AlF$_3$ containing electrolyte can be seen in Fig.26. In terms of capacity performance (Fig.26A), a significant improvement is seen in comparison to the HFiP electrolyte investigated in the previous section (86 mAh g$^{-1}$ vs. 26 mAh g$^{-1}$ @ 0.1 A g$^{-1}$ after 50 cycles between 2.5 – 5.2 V). Whilst the trend in cathode performance remains the same, with the less defective graphite (SP1 & KS4) outperforming the more defective examples. The coulombic efficiency values reported in Fig.26B decrease for KS4, NatG and EEG cathodes as the number of cycles increases, coinciding with the decrease in discharge capacity seen with these cathodes.
Figure 26 - A) Discharge capacity and B) coulombic efficiency performance of Al-DIBs with varying carbon-based cathodes and EMC 2 M LiPF$_6$ + 3 % VC & 2 % AlF$_3$ electrolyte. Cycles 1-35: 2.5 – 5.0 V. Where the first 20 cycles are at a rate of 2 A g$^{-1}$, followed by 3 cycles each at 1.0, 0.5, 0.3, 0.2 and 0.1 A g$^{-1}$. Cycles 36-53: 2.5 – 5.2 V. 3 cycles at 2.0, 1.0, 0.5, 0.3, 0.2 and 0.1 A g$^{-1}$.

From the CVs of the Al-DIBs with the VC & AlF$_3$ electrolyte (Fig.27A and Fig.27B) it can be seen that the redox peaks corresponding to anion intercalation (~ 4.3 – 4.8 V) remain when the cut-off potential is increased to 5.2 V, confirming that this electrolyte supports PF$_6^-$.
intercalation at potentials > 5.0 V in an Al-DIB configuration; unlike the HFiP electrolyte discussed previously.

![Figure 27](image)

**Figure 27** – Cyclic voltammograms of Al-DIBs with EMC 2 M LiPF<sub>6</sub> + 3 % VC & 2 % AlF<sub>3</sub> electrolyte, at a scan rate of 1 mV s<sup>-1</sup>.  
_A) K54 2.5 - 5.0 V (red) and 2.5 - 5.2 V (black), B) SP1 2.5 - 5.0 V (red) and 2.5 - 5.2 V (black)._  

**Fig.27** displays the discharge capacities and CEs over 100 cycles for the VC & AlF<sub>3</sub> electrolyte in a GDIB, where the cell performance is stable over 100 cycles with only a small degree of capacity fade observed. As a result, this electrolyte composition was subsequently altered in order to optimise its performance in a GDIB configuration, the results are discussed in the following section.
4.4.1.2 Removal of AlF₃ for GDIB

Given that the key role of AlF₃ is to stabilise the bare Al negative electrode in an Al-DIB, it is therefore deemed unnecessary in a full cell GDIB due to both electrodes being carbon based with no exposed aluminium. Further to this, the formation of the intercalating anion AlF₄⁻ has a negligible effect on the overall discharge capacity of a GDIB, seen in Fig.29, where in fact the discharge capacity is 2 mAh g⁻¹ greater without AlF₃ (whilst still containing VC). The AlF₃ electrolyte, without the presence of VC, only marginally improved cell performance when comparing to the electrolyte without additives. Both electrolytes suffered from continuous capacity fade as the number of cycles increased, such behaviour is not observed in the VC containing systems. This trend can be associated to the lack of formation of a stable SEI in the non-VC containing GDIBs resulting in continuous and excessive electrolyte degradation.

Whilst on a coin cell scale the addition of 2 % AlF₃ may not appear too detrimental to overall cell performance, yet when considering the scalability of a system it is favourable to reduce
unnecessary mass within it. In this case, the removal of a 2 % wt. additive would be a favourable step towards maximising the energy density of the system.

![Discharge capacity and coulombic efficiency performance of KS4 GDIB with and without additives (VC & AlF₃) in an EMC 2 M LiPF₆ electrolyte. Cycles 1 – 35: 2.5 – 5.0 V. Cycles 35 – 50: 2.5 – 5.2 V.](image)

**Figure 29 – Discharge capacity and coulombic efficiency performance of KS4 GDIB with and without additives (VC & AlF₃) in an EMC 2 M LiPF₆ electrolyte. Cycles 1 – 35: 2.5 – 5.0 V. Cycles 35 – 50: 2.5 – 5.2 V.**

4.5 EMC 2 M LiPF₆ + 3 % VC & EMC 2 M LiPF₆ + 3 % FEC

4.5.1 Li Half-Cell Performance

To investigate the effects of the VC and FEC additives on the intercalation and deintercalation of PF₆⁻ into graphite, lithium half cells with graphite cathodes were constructed with the EMC 2 M LiPF₆ electrolyte – whilst varying the additive (3 % VC/3 % FEC/no additive). Initially the cells were cycled following the GCD regime discussed in previous sections followed by 100 cycles at a constant current density of 0.1 A g⁻¹.

Prior to the assembly of these cells, values for the anion intercalation capacity of the cathode materials were determined using Al-DIBs. Given the unreliability and variable results attained when using the Al-DIB cell setup, it was important to gain a more representative value for the
anion intercalation capacities of the cathode materials in question. Doing so allows for a more accurately mass balanced GDIB, maximising the capacity whilst reducing excess electrode material. The discharge capacities for the EMC 2 M LiPF₆ 3 % VC electrolyte with varying cathode materials are seen in Fig.30A. After 150 cycles the graphite cathode materials (KS4, SP1 and NatG) displayed similar capacities of 74-80 mAh g⁻¹, despite their differences in oxygen and defect content. EEG displayed a significantly lower anion intercalation capacity of 65 mAh g⁻¹ after 150 cycles due to its large defect content. Whilst KS4 graphite displayed a greater discharge capacity than natural graphite throughout cycling (78 vs. 74 mAh g⁻¹ at cycle 150), the lower coulombic efficiency values (77 % vs. 82 % at cycle 150), Fig.30B, suggest that the initial SEI formed in the KS4 cells did not prevent further electrolyte degradation. On the other hand, the SP1 graphite cathode maintained a coulombic efficiency > 90 % throughout cycling. Given the greater discharge capacities of the KS4 and SP1 graphite cells, the comparison between VC and FEC electrolyte additives focused solely on cells with these positive electrode materials.
Following from this, Fig.31A and Fig.31B display the discharge capacities of KS4 and SP1 lithium half cells respectively, when varying the additive. During the initial 20-30 cycles cells with no additive equal, or better, the performance of cells with VC or FEC. However, for Li-SP1 cells (Fig.31B) without additive the rate capability is reduced, with the capacity declining...
as the current density is increased throughout cycling. Likewise, the initial capacity values reported for the VC electrolyte in an SP1 cell are lower than expected – with a value of 35 mAh g\(^{-1}\) reported after 22 cycles, with this increasing to 71 mAh g\(^{-1}\) after 36 cycles as the current density is decreased to 0.1 A g\(^{-1}\). The capacity recovers to a stable value of ~ 82 mAh g\(^{-1}\) after 75 cycles, the initial low and sporadic capacity values can be attributed to the formation of the SEI. In both cases, cells without VC or FEC present in their electrolyte suffered from a greater degree of capacity fade over 150 cycles, with capacity retentions of 91 % and 95 % for KS4 and SP1 cells. In comparison, VC and FEC significantly improved the capacity retention in both KS4 and SP1 lithium half cells, with the effects more prominent in the SP1 cells. Both VC and FEC electrolytes displayed a 100 % capacity retention after 150 cycles in the SP1 half-cell, with capacity retentions of 96 % (VC) and 98 % (FEC) observed for the KS4 cells.
Figure 31 – Discharge capacities of A) Li-KS4 and B) Li-SP1 half cells with EMC 2 M LiPF₆ electrolyte, with 3% VC/3% FEC/no additive.

The coulombic efficiencies of the Li half-cells, seen in (KS4) Fig.32A and (SP1) Fig.32B, align with the discharge capacity trends observed previously. Both KS4 and SP1 cells without additives display lower CE values during cycling in comparison to those with VC and FEC electrolytes. The addition of FEC significantly improved the CE in both cells, with a CE of 96%
observed after 150 cycles for cells with SP1 graphite cathode. A greater CE in Li-SP1 cells vs. Li-KS4 cells is no surprise when considering the defectiveness of the graphite cathodes given that defects at the cathode surface can result in the irregular formation of the SEI layer and increase the time in which a stable layer is formed. Therefore, low-defect SP1 graphite is likely to form a more uniform and compact SEI layer in comparison to the more defective KS4 graphite with a greater oxygen content.
The CD profiles in Fig.33A and Fig.33B are a valuable tool for visualising the reversibility of the Li-half cells in question, along with the effects of VC and FEC on the intercalation and deintercalation of PF$_6^-$ anions into KS4 and SP1 graphite cathodes. All 6 CD profiles display a high voltage plateau at ~ 4.9 V during the charging process, with this plateau significantly
more prominent in Li-SP1 cells. This voltage plateau corresponds to a two-phase transition during the intercalation of anions, with the stage II GIC transitioning to a stage I GIC upon further intercalation of anions. Furthermore, Li-SP1 cells also display a more defined plateau at ~ 4.4 V that is attributed to the onset of anion intercalation and formation of the initial stage 4 GIC. The nature of this plateau indicates that SP1 graphite offers more accessible anion intercalation pathways in comparison to the Li-KS4 cells. The stage transitions of anion intercalation observed in Fig.33 are defined as follows:

Stage IV – III: 4.4 V – 4.6 V. Stage III – II: 4.6 V – 4.9 V. Stage II – I: 4.9 V – 5.2 V.

As mentioned previously, Li-KS4 half-cells experience more capacity fade after 150 cycles than the Li-SP1 half-cells with the same electrolyte. The CD profiles for the Li-KS4 half-cells (Fig.33A) display an increased charge capacity (> 100 mAh g⁻¹ for all Li-KS4 half-cells) with the corresponding discharge capacities typically ~ 80 mAh g⁻¹ depending on the electrolyte composition. The half-cells were constructed with excess electrolyte (150 µL) in order to minimise the effects of anion and cation depletion due to electrolyte degradation/SEI formation, on the discharge capacity. Given that the Li-KS4 cells appear to irreversibly consume significantly more charge per cycle explains the origin of the faster rate of capacity fade.

The good overlap of the CD profiles for SP1 graphite cells with VC and FEC (Fig.33B middle & bottom), combined with the low electrochemical polarisation values calculated in Table 8, highlights the impressive reversibility of the anion intercalation and deintercalation process. The increased capacity and decrease in polarisation for SP1 FEC cells after 150 cycles may be a result of a reconfiguration of the SEI layer in order to maximise the efficiency of the anion transport pathways. This redistribution process occurs readily in the presence of lower defect graphite samples that promote more uniform SEI growth, explaining the capacity increase for SP1 cathodes (VC and FEC) and not for KS4 cathodes.
On the other hand, Li-SP1 cells with VC electrolyte displayed a lower capacity than the FEC counterpart, along with a larger electrochemical polarisation after 150 cycles. However, the degree of polarisation did not increase from cycle 60 to cycle 150 suggesting the formation of a stable SEI. Despite this, the lower capacity and larger polarisation in comparison to the FEC cells suggests that the VC electrolyte results in a thicker cathode SEI that increases the anion intercalation/deintercalation pathway. Similar conclusions can be drawn from the electrochemical polarisation values of the no additive electrolytes – in both KS4 and SP1 Li half-cells the electrolyte without additives displays the greatest increase in its polarisation.
values. This is attributed to the continuous electrolyte degradation that occurs during cycling without an SEI forming additive such as VC or FEC. Continuous electrolyte degradation inevitably results in the formation of a thicker SEI, contributing to a reduction in the discharge capacity due to the increased anion transport pathways and the depletion of Li\(^+\) and PF\(_6\). 

Through the application of ex-situ XPS Wu et al. confirmed that the increased presence of electrolyte decomposition products (Li\(_x\)PO\(_y\)F\(_z\) species) on the graphite surface correlated with a reduced discharge capacity, suggesting that the deposition of these species may block anion migration pathways at the graphite cathode surface. In comparison, graphite cathodes with stable SEI layers displayed significantly greater capacities and the SEI contained less electrolyte decompositions products, with the concentration of these species not increasing from cycle to cycle. It was therefore concluded that a reduced Li\(_x\)PO\(_y\)F\(_z\) content within the SEI correlates with the successful intercalation and deintercalation processes of PF\(_6\) anions, as opposed to decomposition of electrolyte at the electrode surface, improving the overall reversible capacity of a cell with a stable SEI\(^{113,114}\).

Table 8 – A table displaying the polarisation values for Li-KS4 and Li-SP1 cells at cycles 60 and 150, as seen in the CD profiles in Fig.32. Where the polarisation is calculated as the difference between the average voltage of the charge curve and discharge curve.

<table>
<thead>
<tr>
<th></th>
<th>Polarisation Value</th>
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<th>Polarisation Value</th>
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<tbody>
<tr>
<td></td>
<td>Cycle 60</td>
<td>Cycle 150</td>
<td>Cycle 60</td>
</tr>
<tr>
<td><strong>No Add</strong></td>
<td>4.773 – 4.400 = <strong>0.373 V</strong></td>
<td>4.782 – 4.342 = <strong>0.440 V</strong></td>
<td>4.573 – 4.707 = <strong>0.134 V</strong></td>
</tr>
<tr>
<td><strong>KS4</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3 % VC</strong></td>
<td>Cycle 60</td>
<td>Cycle 150</td>
<td>Cycle 60</td>
</tr>
<tr>
<td></td>
<td>4.781 – 4.332 = <strong>0.449 V</strong></td>
<td>4.774 – 4.333 = <strong>0.441 V</strong></td>
<td>4.745 – 4.621 = <strong>0.124 V</strong></td>
</tr>
<tr>
<td><strong>3 % FEC</strong></td>
<td>Cycle 60</td>
<td>Cycle 150</td>
<td>Cycle 60</td>
</tr>
<tr>
<td></td>
<td>4.713 – 4.407 = <strong>0.306 V</strong></td>
<td>4.764 – 4.397 = <strong>0.367 V</strong></td>
<td>4.738 – 4.607 = <strong>0.131 V</strong></td>
</tr>
<tr>
<td><strong>SP1</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3 % VC</strong></td>
<td>Cycle 60</td>
<td>Cycle 150</td>
<td>Cycle 60</td>
</tr>
<tr>
<td></td>
<td>4.741 – 4.528 = <strong>0.213 V</strong></td>
<td>4.733 – 4.609 = <strong>0.124 V</strong></td>
<td>4.721 – 4.612 = <strong>0.109 V</strong></td>
</tr>
</tbody>
</table>
**Fig. 34A** and **Fig. 34B** display the CVs for the Li-KS4 and Li-SP1 half cells respectively, where distinct pairs of redox peaks are visible. These peaks correspond to the staging of anion intercalation and correspond with the staging potentials discussed previously from the CD profiles. The peaks present in the anodic sweep (2.5 – 5.2 V direction), ~ 4.5 V, ~ 4.6 V, ~ 4.8 V and ~ 5.0 V, can be paired with the corresponding cathodic redox peaks (5.2 – 2.5 V direction), ~ 4.2 V, ~ 4.4 V, ~ 4.6V and ~ 4.8 V. It is noted that the redox peaks present in cells without VC or FEC are shifted to more positive voltage values, with this being more prominent in Li-SP1 cells. The initial redox peaks at ~ 4.4 V in the VC and FEC Li-SP1 CVs, **Fig. 34B**, are shifted to ~ 4.6 V for the no additive electrolyte cells. Suggesting that the anion intercalation into SP1 graphite is less favourable without the presence of VC or FEC additives given the greater effort (voltage) required for the onset of intercalation to occur. Likewise, the stage I peak for the Li-SP1 cell without additive is at a more positive voltage value (5.036 V) compared to VC and FEC (5.018 V and 5.02 V). Again, suggesting that the formation of a stage I GIC is less favourable without the presence of VC or FEC.
To gain an insight into the kinetics of anion transport one can determine the peak-to-peak separation from the stage I redox peak pair voltage values, seen in Table 9. A smaller separation value indicates that the anion intercalation and deintercalation process occurs at a faster rate. Cells without the presence of VC or FEC have larger peak separation values, suggesting that anions experience greater resistance during charging and discharging. The addition of FEC significantly reduces the barrier to intercalation, which is again consistent with
the SEI formation arguments given above. Furthermore, it is noted that for both the KS4 and SP1 Li half-cells the CE values for the FEC electrolyte are superior of the 3 electrolytes trialled, confirming the formation of a more stable and efficient SEI layer at the cathode/electrolyte interface.

Table 9 - A table displaying the peak-to-peak separation values and coulombic efficiency values calculated from the CVs of Li-KS4 and Li-SP1 cells in Fig.33, when the scan rate is 1 mV s⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>Peak-to-Peak Separation</th>
<th>Coulombic Efficiency</th>
<th>Peak-to-Peak Separation</th>
<th>Coulombic Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>KS4</td>
<td>No Add</td>
<td>5.036 V – 4.688 V, 0.348 V</td>
<td>86 %</td>
<td>No Add</td>
</tr>
<tr>
<td></td>
<td>3 % VC</td>
<td>5.018 V – 4.698 V, 0.320 V</td>
<td>91 %</td>
<td>3 % VC</td>
</tr>
<tr>
<td></td>
<td>3 % FEC</td>
<td>5.020 V – 4.724 V, 0.296 V</td>
<td>96 %</td>
<td>3 % FEC</td>
</tr>
</tbody>
</table>

4.5.2 GDIB Performance

Given the impressive performance of the vinylene carbonate and fluoroethylene carbonate additives in Li half-cells the electrolytes were implemented into dual graphite cells with KS4 anode and varied cathode materials as in previous tests. Initially the EMC 2 M LiPF₆ + 3 % VC electrolyte was trialled in a GDIB configuration, with the discharge capacity and coulombic efficiency of these cells reported in Fig.35A and Fig.35B. The discharge capacity performance closely reflected the trend observed for the Li-half cells, with KS4 graphite and SP1 graphite cathodes outperforming natural graphite and EEG cathodes significantly. However, over the initial 150 cycles the KS4 GDIB displayed a higher discharge capacity than the SP1 GDIB (65 mAh g⁻¹ vs 61 mAh g⁻¹ at 100 mA g⁻¹ after 150 cycles). In comparison to the Li-half cells, the capacities reported for the GDIBs with EMC 2 M LiPF₆ + 3 % VC electrolyte are significantly lower (reduced by ~ 15 – 20 mAh g⁻¹). This reduction in discharge capacity when moving from Li-half cell configuration to a full dual graphite cell is likely a result of the formation of the SEI at both the graphite anode and graphite cathode. It is reported for LIBs that during initial cycling a typical capacity decrease of 10-20 % is observed due to the significant consumption of electrolyte during the SEI formation process at the anode. In future, to combat this capacity drop when transitioning to a full cell the addition of a greater % wt. of additive should
be trialled given that the initial 3% of additive trialled in this report was based on the optimum % wt. for an Al-DIB configuration where only one electrode was graphite. SP1 GDIB displayed a CE of 95% at cycle 150 along with a capacity retention of 100% after 150 cycles, whilst the KS4 GDIB displayed a lower CE of 90% at cycle 150 and a capacity retention of 97%. These findings are also a reflection of the Li-half cell performance, with KS4 experiencing a greater capacity fade as a result of its increased defect content. Fig.36A and Fig.36B display the cycling performance of KS4 and SP1 GDIBs over 250 and 350 cycles respectively. It can be seen that the cycling performance of the KS4 GDIB decreases rapidly after 220 cycles with the capacity retention falling to 78% after 250 cycles. Whereas SP1 GDIB maintained an impressive capacity retention of 100% after 350 cycles at a current density of 0.1 A g⁻¹.

When decreasing the current density decreasing CEs are typically observed, with this trend being consistently observed in the cell performance of DIBs throughout this report. Fig.35B displays the CE performance of the GDIBs with the EMC 2 M LiPF₆ + 3% VC electrolyte over 150 cycles, where all 4 sets of results display a decrease in their CE when the current density is subsequently decreased. The exact values of the CEs at 2, 1, 0.5, 0.3, 0.2 and 0.1 A g⁻¹ can be seen in Table 10. Numerous studies by Placke et al. have discussed the effect of current density on the CE of GDIBs with TFSI⁻ based electrolytes, where increasing the current density from 10 mA g⁻¹ to 50 mA g⁻¹ increased the CE at the 50th cycle from 96.6% to 98.9% when the upper cut-off voltage was 5.2 V. These results were accentuated by the impressive CE performance of the same GDIB system at a current density of 500 mA g⁻¹, where a coulombic efficiency of 99.8% was reported along with a significantly reduced discharge capacity < 50 mAh g⁻¹ after 500 cycles (vs. 121 mAh g⁻¹ @ 10 mA g⁻¹). The lower CEs observed at lower current densities are a direct result of the “dwell-time” of the intercalated anions at high cathode potentials, thus leading to a rise in the degree of parasitic reactions (electrolyte oxidation) that occur. Whilst these findings indicate that greater current densities improve the CEs of DIBs, the same improvements are not reflected in the discharge capacities of DIBs – where discharge capacity decreases as current density increases. Therefore, for the future development of DIBs it is important to consider the influence of the current density on the discharge capacity and CE, identifying an optimum balance between the two performance parameters.
Figure 35 – A) Discharge capacities and B) coulombic efficiencies of dual graphite cells with EMC 2 M LiPF₆ 3% VC electrolyte. Cycles 1-35: 2.5 – 5.0 V. Where the first 20 cycles are at a rate of 2 A g⁻¹, followed by 3 cycles each at 1.0, 0.5, 0.3, 0.2 and 0.1 A g⁻¹. Cycles 36 – 150: 2.5 – 5.2 V. Where 3 cycles at each of the rates 2, 1, 0.5, 0.3 and 0.2 A g⁻¹, followed by the remaining cycles at a constant rate of 0.1 A g⁻¹.

The electrochemical performance of the FEC containing electrolyte and no additive electrolyte in KS4 and SP1 GDIBs is presented in Fig.36A and Fig.36B. Both KS4 and SP1 GDIBs containing FEC and those with no additive display significantly lower discharge capacities in
comparison to cells with the VC additive (ie. SP1 GDIBs with the FEC electrolyte displayed a discharge capacity of 23 mAh g\(^{-1}\) after 50 cycles at a current density of 0.1 A g\(^{-1}\), whereas SP1 GDIBs with the VC electrolyte displayed a discharge capacity of 60 mAh g\(^{-1}\)). Whilst this was expected from the electrolyte without additives given the poorer performance of Li half-cells without additives, such performance was not expected in cells with the FEC additive. The electrolyte with 3 % FEC outperformed its VC counterpart, displaying impressive anion intercalation capacities and CE values that suggested the stabilisation of the cathode/electrolyte interface. As a result, the reduction in the full cell performance (discharge capacity and coulombic efficiency) seen in **Fig.36A** and **Fig.36B** indicates that the anode stability during Li\(^+\) intercalation is the limiting factor. The performance of VC containing GDIBs suggests that VC stabilises the anode/electrolyte interface as well as the cathode/electrolyte interface, as suggested from the Li half-cell performance – whereas FEC appears to only effectively stabilises the cathode/electrolyte interface.

Whilst VC is a commonly used SEI forming additive in LIBs with graphite anodes, FEC is typically used in cells with silicon electrodes.\(^{117}\) As a result reports comparing the two additives in similar systems with graphite anodes are limited. Gasteiger et al. studied the differences in SEI composition at the surface of graphite anodes in LIBs with lithium iron phosphate (LFP) cathodes when 2 % VC and 2 % FEC were used. Whilst differences in the SEI composition were identified, cell performance was not significantly discussed, and the quantities of the additives were not optimised beyond 2 %.\(^{118}\) Further to this point, Wang et al. studied the electrochemical performance of LIBs consisting of graphite anodes and LiCoO\(_2\) cathodes with a 1 M LiPF\(_6\) EC/EMC (3:7) electrolyte with varying concentrations of VC and FEC additives. The findings of which indicated that both VC and FEC are effective SEI forming anode additives that improved overall cell performance – with improvements in the CE values reported and a reduced voltage drop during storage, resulting in improved cycling lifetimes compared to cells with control electrolytes containing no additives. Of the additive concentrations investigated (0, 0.5, 1, 2, 4 or 6 %) 2 % VC outperformed all other concentrations of VC and FEC, yielding a greater CE than the best performing FEC concentration (4 %) and a lower change in charge-discharge polarisation (<0.3 mV per cycle). However, increasing the VC concentration beyond 2 % increased charge transfer resistance
at the anode in this system, whereas increasing the FEC concentration from 2 % to 6 % did not significantly alter charge transfer resistance at the anode.\textsuperscript{108}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure36.png}
\caption{Discharge capacities (dots, left axis) and coulombic efficiencies (crosses, right axis) of A) KS4 and B) SP1 GDBs with EMC 2 M LiPF\textsubscript{6} electrolyte, with 3 % VC/3 % FEC/no additive. Cycles 1–35: 2.5 – 5.0 V. Where the first 20 cycles are at a rate of 2 A g\textsuperscript{-1}, followed by 3 cycles each at 1.0, 0.5, 0.3, 0.2 and 0.1 A g\textsuperscript{-1}. Cycles 36 – 350: 2.5 – 5.2 V. Where 3 cycles at each of the rates 2, 1, 0.5, 0.3 and 0.2 A g\textsuperscript{-1}, followed by the remaining cycles (48 – 350) at a constant rate of 0.1 A g\textsuperscript{-1}.}
\end{figure}
<table>
<thead>
<tr>
<th>Cycle #</th>
<th>Current density</th>
<th>KS4 Graphite</th>
<th>SP1 Graphite</th>
<th>Natural Graphite</th>
<th>EEG</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle 10</td>
<td>2 A g⁻¹</td>
<td>98.2 %</td>
<td>99.1 %</td>
<td>98.7 %</td>
<td>83.9 %</td>
</tr>
<tr>
<td>Cycle 20</td>
<td>2 A g⁻¹</td>
<td>98.9 %</td>
<td>99.3 %</td>
<td>98.9 %</td>
<td>94.5 %</td>
</tr>
<tr>
<td>Cycle 23</td>
<td>1 A g⁻¹</td>
<td>98.3 %</td>
<td>98.9 %</td>
<td>98.3 %</td>
<td>87.0 %</td>
</tr>
<tr>
<td>Cycle 26</td>
<td>0.5 A g⁻¹</td>
<td>97.2 %</td>
<td>98.0 %</td>
<td>97.1 %</td>
<td>79.8 %</td>
</tr>
<tr>
<td>Cycle 29</td>
<td>0.3 A g⁻¹</td>
<td>96.2 %</td>
<td>96.3 %</td>
<td>95.9 %</td>
<td>79.7 %</td>
</tr>
<tr>
<td>Cycle 32</td>
<td>0.2 A g⁻¹</td>
<td>95.4 %</td>
<td>95.6 %</td>
<td>94.9 %</td>
<td>63.1 %</td>
</tr>
<tr>
<td>Cycle 35</td>
<td>0.1 A g⁻¹</td>
<td>92.8 %</td>
<td>93.5 %</td>
<td>91.9 %</td>
<td>63.9 %</td>
</tr>
<tr>
<td>Cycle 38</td>
<td>1 A g⁻¹</td>
<td>98.2 %</td>
<td>98.9 %</td>
<td>98.4 %</td>
<td>94.5 %</td>
</tr>
<tr>
<td>Cycle 41</td>
<td>0.5 A g⁻¹</td>
<td>97.3 %</td>
<td>98.3 %</td>
<td>97.4 %</td>
<td>87.8 %</td>
</tr>
<tr>
<td>Cycle 44</td>
<td>0.3 A g⁻¹</td>
<td>96.1 %</td>
<td>97.4 %</td>
<td>96.0 %</td>
<td>88.2 %</td>
</tr>
<tr>
<td>Cycle 47</td>
<td>0.2 A g⁻¹</td>
<td>94.5 %</td>
<td>96.5 %</td>
<td>83.5 %</td>
<td>79.2 %</td>
</tr>
<tr>
<td>Cycle 50</td>
<td>0.1 A g⁻¹</td>
<td>91.3 %</td>
<td>94.2 %</td>
<td>73.6 %</td>
<td>77.1 %</td>
</tr>
<tr>
<td>Cycle 100</td>
<td>0.1 A g⁻¹</td>
<td>90.9 %</td>
<td>95.8 %</td>
<td>88.5 %</td>
<td>85.4 %</td>
</tr>
<tr>
<td>Cycle 150</td>
<td>0.1 A g⁻¹</td>
<td>90.5 %</td>
<td>95.2 %</td>
<td>89.0 %</td>
<td>64.6 %</td>
</tr>
</tbody>
</table>

\textbf{Table 10} – A table displaying the coulombic efficiency values for the GDIBs with the EMC 2 M LiPF6 + 3\% VC electrolyte, where the cathode material of the GDIB is listed as a column header.

\textbf{Fig. 37} displays the CVs for the GDIBs with the no additive electrolyte (A & B) and the FEC additive electrolyte (C & D). The CV for the KS4 GDIB without the presence of additive (\textbf{Fig. 37A}) displays a reduction in the intercalation peak at 4.7 V from cycle 1 to 2, followed by a disappearance of this peak during cycle 3. A similar observation is made for the corresponding deintercalation peak at 4.5 V on the reverse scan where the peak significantly decreases after 2 cycles, suggesting that the lack of additive has prevented the reversible intercalation and deintercalation of PF₆⁻. On the other hand, the CV for the SP1 GDIB with the no additive electrolyte (\textbf{Fig. 37B}) displays more reversible behaviour given that the intercalation (4.8 V) and deintercalation (4.5 V) peaks do not diminish significantly after 3
cycles. The single redox peak pair present in the CVs for both KS4 and SP1 GDIBs with the no additive electrolyte suggests only a single stage of anion intercalation is achieved in these cells, given the potential of these peaks (~ 4.7/8 V and ~ 4.5 V) one would assume this to be a stage I intercalation phase. However, given the reduced capacity performance of the cells this would appear unlikely, these peaks may correspond to a lower staging phase of anion intercalation (potentially stage II or III or IV) where the onset potential for this stage has been shifted to a more positive value. The peaks displayed at ~ 4.3 V in the first cycle of both Fig.37A and Fig.37B can be attributed to the initial wetting and anion intercalation into the graphite cathode, this is typical of the formation process that occurs during the first cycle, generally this peak would still be present in subsequent cycles if the anion intercalation/deintercalation process was reversible. The lack of a deintercalation redox peak in the reverse scan of cycle 1 suggests that the anions intercalated at ~ 4.3 V in the initial half of the scan have not been extracted from the graphite cathode. Blocking of the anion transport pathways as a result of excessive electrolyte degradation may prevent the reversible deintercalation of these anions.

Similar observations can be determined from the CVs of the GDIBs with the FEC electrolyte in Fig.37C and Fig.37D, where the lack of multiple redox peak pairs corresponds to a reduced anion intercalation/deintercalation density, supporting the reduction in discharge capacity that is observed in the electrochemical performance figures discussed previously (Fig.36).
Figure 37 – Cyclic voltammograms of A) KS4 GDIB w/ EMC 2 M LiPF₆ (no additive), B) SP1 GDIB w/ EMC 2 M LiPF₆ (no additive), C) KS4 GDIB w/ EMC 2 M LiPF₆ + 3 % FEC, D) SP1 GDIB w/ EMC 2 M LiPF₆ + 3 % FEC. At a scan rate of 1 mV/s within the voltage range 2.5 – 5.2 V vs. Li/Li⁺.

The CVs for GDIBs with EMC 2 M LiPF₆ + 3 % VC electrolyte are seen in Fig.38A and Fig.38B. Like CVs of the Li half-cells, clear redox peak pairs corresponding to the staging of anion intercalation are visible. One significant difference arising during cycling of full cells is the presence of a split peak at 4.8 – 5.0 V, corresponding to the transition from a stage II to stage I GIC. As the number of cycles increases from 0 to 250 the intensity of the first peak, ~ 4.8V, decreases and the intensity of the second peak, ~ 5.0 V, increases. With this splitting behaviour being more evident when the cathode is KS4 graphite, with only a small shoulder peak visible in SP1 GDIBs at cycle 0 and cycle 50. The splitting of these peaks indicates that as the number of cycles increases it becomes increasingly more difficult to achieve a stage I intercalation phase. The coulombic efficiency values calculated from the CVs peak at 150 cycles for both KS4 and SP1 GDIBs, 85.57 % and 91.33 % respectively, with these values significantly lower than those observed in the GCD results in Fig.36A and Fig.36B (90.5 % and 95.0 % for KS4 and SP1 GDIBs at cycle 150). The difference in CE values can be attributed to the measuring technique of the CVs, where the GCD tests were stopped at cycles 50, 150 and 250 in order to record the CV of these cells before resuming the GCD test afterwards. Also, a
single cycle at 1 mV s\(^{-1}\) during CV testing was longer than a single cycle at 0.1 A g\(^{-1}\) during GCD testing. As discussed previously the time of a single cycle is the dominant contributor to reduced CE values, increasing the number of irreversible charge consuming parasitic reactions that occur at the electrodes.\(^{119}\)

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**Figure 38** - Cyclic voltammograms of A) KS4 and B) SP1 GDIBs with EMC 2 M LiPF\(_6\) + 3 % VC electrolyte at a scan rate of 1 mV/s within the voltage range 2.5 – 5.2 V vs. Li/Li\(^+\).
The CD profiles for the KS4 (cycles 100 and 250) and SP1 (cycles 100 and 350) GDIBs with the EMC 2 M LiPF$_6$ + 3 % VC electrolyte are displayed in Fig.39A and Fig.39B. Generally, the profiles display similar shapes when the number of cycles is increased. In the case of the KS4 GDIB (Fig.39A) the shape of the CD profile at cycle 250 is like that at cycle 100, however the profile is shifted and reduced in size (due to the reduced charge/discharge capacities) with this being more prominent in the charging half of the profile. It is seen that at cycle 250 the onset potential for anion uptake is increased, taking on a value closer to 4. as the SEI layer grows from cycle 100 to cycle 250. This has behaviour has been discussed in previous examples as being a result of a thicker SEI resulting in increased anion transport pathways, and due to the decreasing number of available anion intercalation sites.92 Alternatively, the CD profile for the SP1 GDIB (Fig.39B) displays a good overlap between cycle 100 and cycle 350 with no reduction in discharge capacity. A significant difference between the two profiles is the increase in capacity at an earlier voltage (ie. At 4.0 V cycle 100 displays a capacity of 0.5 mAh g$^{-1}$, cycle 350 displays a capacity of 4 mAh g$^{-1}$) suggesting that anion uptake occurs faster after 350 cycles as a result of well-established anion transport pathways.

Table 11 displays the specific energy values for the KS4 and SP1 GDIBs with the EMC 2 M LiPF$_6$ + 3 % VC electrolyte based on both the electrode mass and full cell mass. The specific energy is calculated by multiplying the average discharge voltage (V) by the maximum discharge capacity (mAh g$^{-1}$). As expected, the specific energy of the KS4 GDIB decreases from cycle 100 to cycle 250 given that this cell experienced a reduction in its discharge capacity. The specific energy of the SP1 GDIB is more stable, with only a slight decrease of 2.007 Wh kg$^{-1}$ from cycle 150 to cycle 350. The specific energy values based on the total electrode mass are impressive and outperform values reported for DIBs in literature, however in comparison, the specific energy values when considering the mass of a full cell are significantly lower highlighting the importance of optimising cell components as well as the electrode composition.
Table 11 – Table displaying the discharge capacities and calculated specific energy values for KS4 and SP1 GDIBs after 100 and 250 cycles, based on electrode mass (3.2 mg) and the total cell mass (5.0 g). Specific energy values are calculated from the average operating voltage during discharging and the discharge capacities seen in Fig.39.²

<table>
<thead>
<tr>
<th></th>
<th>Average Operating Voltage (V)</th>
<th>Discharge Capacity³ (mAh g⁻¹)</th>
<th>Calculated Specific Energy³ (Wh kg⁻¹)</th>
<th>Discharge Capacity⁴ (mAh g⁻¹)</th>
<th>Calculated Specific Energy⁴ (Wh kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>KS4 GDIB</strong> Cycle 100</td>
<td>4.422 V</td>
<td>64.912</td>
<td>287.041</td>
<td>0.042</td>
<td>0.186</td>
</tr>
<tr>
<td></td>
<td>4.469 V</td>
<td>52.230</td>
<td>233.416</td>
<td>0.033</td>
<td>0.147</td>
</tr>
<tr>
<td><strong>SP1 GDIB</strong> Cycle 100</td>
<td>4.531 V</td>
<td>60.551</td>
<td>274.357</td>
<td>0.039</td>
<td>0.177</td>
</tr>
<tr>
<td></td>
<td>4.463 V</td>
<td>61.024</td>
<td>272.350</td>
<td>0.039</td>
<td>0.174</td>
</tr>
</tbody>
</table>

² Values for the average operating voltage and discharge capacities were obtained from the Autolab potentiostat with a potential accuracy of +/- 0.2 % and a current accuracy of +/- 0.2 %.
³ Discharge capacity and calculated specific energy based on total electrode mass (3.2 mg).
⁴ Discharge capacity and calculated specific energy based on total cell mass (5.0 g).
Figure 39 – Charge discharge profiles for A) KS4 and B) SP1 GDIBs with EMC 2 M LiPF$_6$ + 3 % VC electrolyte at a current density of 0.1 A g$^{-1}$ at an upper cut off voltage of 5.2 V.

When accounting for the full cell mass, the specific energy values reported in this research fall below the lower region of the specific energy band for DIBs, as seen in Fig. 40. However, it is important to note that the specific energy values reported in literature do not always report the specific energy based on the total mass of the cell (electrodes and cell components), in many cases values are based only on the total electrode mass. The examples
highlighted in the upper regions of the DIB band correspond to theoretical calculations of GDIBs with highly concentrated electrolyte compositions (HCE), when a discharge capacity of $\sim 90 \text{ mAh g}^{-1}$ is achieved along with an average discharge voltage of 5.0 V. The energy densities of DIBs remain relatively low in comparison to the excellent energy densities of LIBs, with such low energy densities not optimal for handheld or portable devices. However, the low-cost and environmental benefits associated with DIBs and GDIBs increases their potential application as future stationary energy storage solutions where reduced energy densities are less of a hindrance.

*Figure 40 - Energy density (Wh L$^{-1}$) vs. specific energy (Wh Kg$^{-1}$) diagram displaying a comparison between different battery chemistries. The estimated values are based on the performance of these systems at the cell level. Energy density and specific energy values for DGB C/C KPF6, DGB C/C LiPF6 and DIB Li/C are theoretical calculations based on the use of HCEs.*
4.6 3-Electrode Studies of EMC 2 M LiPF$_6$ 3 % VC

To investigate the effect of VC on the electrochemical stability of the electrolyte CVs were obtained using a 3-electrode system consisting of a glassy carbon working electrode, lithium reference electrode and lithium counter electrode. The redox behaviour of VC has been investigated at length in literature given its application in LIBs as an anode SEI additive.$^{107,108,118,120–122}$ It is reported that VC is oxidised between 4.5 – 5.0 V vs. Li/Li$^+$, with the intercalation of PF$_6$ anions into graphite occurring also in this potential range. For this reason, a glassy carbon working electrode was used, preventing the intercalation of anions at the working electrode and allowing the CV current response to be a response based purely on the oxidation/reduction of the electrolyte and additives.

**Fig. 41A** displays the cathodic CV scan in the potential range 2.6 – 0.1 V vs. Li/Li$^+$ for both the EMC 2 M LiPF$_6$ + 3 % VC (black) and EMC 2 M LiPF$_6$ (red) electrolytes. The peak at ~ 1.4 V present in cycle 1 of the VC containing electrolyte CV corresponds to the reduction of VC, contributing to the formation of the SEI at the electrode surface.$^{121}$ This peak decreases in subsequent cycles and is almost completely diminished by cycle 3 as the VC is consumed. The greater current observed in the VC CVs compared to the no-VC CVs indicates that a greater degree of electrolyte reduction takes place in these early cycles, promoting the quick formation of the SEI through the reduction of VC. Whilst the initial reduction of the electrolyte is catalysed in the presence of VC, the decrease in current observed at ~ 0.5 V (corresponding to EMC reduction) from cycle 1 to cycle 3 suggests that the reduction of EMC is minimised in subsequent cycles after the initial VC reduction process.

The anodic CV scans in the potential range 2.6 – 5.2 V vs. Li/Li$^+$ for the VC (black) and no-VC (red) electrolytes are presented in **Fig. 41B.** A distinct difference between the VC and no-VC CVs is the significantly greater current present in cycle 1 of the VC CV, suggesting that the initial oxidation of the electrolyte to form the SEI is catalysed in the presence of VC.$^{121}$ Furthermore, the addition of VC is seen to shift the electrochemical window of stability of the electrolyte to more positive potentials, meaning that the VC is preferentially oxidised before EMC to form the SEI. This is highlighted by the EMC oxidation peak at ~ 4.7 V in no-VC CVs being shifted to potentials > 5.2 V in the CVs with VC. An extended anodic CV (2.6 – 6.2 V vs.
Li/Li\textsuperscript{+}) for the VC containing electrolyte can be seen in Appendix 4, clearly displaying the shift of the oxidation peaks to more positive potentials beyond 5.2 V.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure41}
\caption{CVs obtained from 3-electrode experiment with glassy carbon working electrode. A) reductive scan, 2.7 – 0.1 – 2.7 V. B) oxidative scan, 2.7 – 5.2 – 2.7 V (inset: zoomed fig.41B).}
\end{figure}

Fig.42 displays the full scan CV for VC and no-VC electrolytes in the potential range 0.1 – 5.2 V vs. Li/Li\textsuperscript{+}. The shapes of the CV curves for both electrolytes are similar to the respective half scan CVs discussed previously from which many of the same conclusions can be deduced, with an increased electrochemical window of stability observed in the VC containing CVs as
seen in Fig. 41B. However, the lack of a VC reduction peak is noted at ~ 1.4 V in cycle 1 of the VC electrolyte CV. Instead, a peak is present at ~ 1.7 V in cycle 1 for both the VC and no-VC electrolyte CVs, with this peak decreasing on the second cycle. This peak is unlikely to correspond to the reduction of vinylene carbonate given the different nature of the two CV’s. The CVs for the VC electrolyte display an increase in current from cycle 1 to cycle 2 at ~ 0.8 V and ~ 5.0 V indicating the occurrence of a parasitic reaction at the working electrode surface. Such behaviour is not expected from the VC electrolyte based on the previous half scan CVs and the knowledge that VC stabilises the electrode/electrolyte interface. As stated, parasitic reactions may be responsible for the increasing current from cycle 1 to cycle 2 – with one possible explanation being the presence of surface impurities/contaminants on the glassy carbon electrode from previous tests. Whilst the glassy carbon electrode was removed and washed with EMC after every use to minimise contamination, the electrode surface was not mechanically polished between tests – suggesting that some contaminants remained deposited on the surface between tests.\textsuperscript{123}

Time limitations of the research project prevented further 3-electrode experiments from being conducted and future work should aim to include more detailed 3-electrode experiments, focusing on the oxidative and reductive behaviour of VC and FEC additives in EMC 2 M LiPF\textsubscript{6} electrolytes.
Studies by Gasteiger and Pritzl employed a combination of on-line electrochemical mass spectrometry and impedance analysis with a micro-reference electrode to investigate the oxidative stability of VC and the impact it has on the interfacial resistance of electrodes in graphite/LNMO LiBs. It was concluded that when small quantities of VC (0.09 wt.%) are added to a graphite/LNMO cell the VC is preferentially reduced at the anode before it is able to be subsequently oxidised at the cathode. Alternatively, when excess VC (0.17 – 2 wt.%) is added some residual VC remains that is then oxidised at the cathode surface at high potentials (4.8 V), increasing the interfacial resistance at the cathode as a result of the formation of a poly(VC) layer.\textsuperscript{118, 120, 122}

4.7 Ex-situ XPS Analysis of Electrode Surfaces

XPS analysis of the SP1 GDIB with the EMC 2 M LiPF\textsubscript{6} + 3 % VC electrolyte (the best performing GDIB reported in the previous sections) was conducted in an attempt to further understand the SEI composition and its growth at both electrodes as cycling progressed.

It is to be noted that the initial GDIB tests contained glass microfiber separating membranes, widely used in DIBs to contain the excess electrolyte typically used in these systems. These
membranes proved problematic when deconstructing the cells to retrieve the electrodes for XPS analysis, with large patches of the membrane remaining on the electrode surface after washing with DMC and drying under vacuum. Removal of the membrane with tweezers was attempted however it was deemed that this could potentially damage the SEI layer on the surface of the electrodes. As a result, the glass microfiber separators were replaced with polymer separating membranes. Images of the electrodes after cycling with both separators can be seen in Fig.43.

![Figure 43 – A) Electrodes after cycling with glass microfiber separator. B) Electrodes after cycling with polymer separator.](image)

The change in separators resulted in a decrease in the cell performance of the SP1 GDIB (Fig.44) with significant capacity fade being observed after 150 cycles and a discharge capacity of 50 mAh g\(^{-1}\) after 250 cycles (vs. 61 mAh g\(^{-1}\) after 350 cycles when using the glass microfiber separator reported previously). This decrease in discharge capacity may be a result of electrolyte depletion given that during cell construction the polymer membrane did not fully absorb the electrolyte, resulting in leakage of the electrolyte during crimping. Regardless of this, ex-situ XPS analysis was conducted on the electrodes of the polymer separator containing-GDIBs.
XPS peak position values and group composition percentages are displayed in Appendix 5.

The composition of the KS4 anode surface at 0, 150 and 250 cycles can be seen in Fig.45. Fig.45A and Fig.45B display the composition of the uncycled KS4 anode from the C1s and F1s spectra respectively, with the C1s spectra displaying a strong C-C peak (~ 284 eV) corresponding to the graphite surface. The presence of oxygenated carbon groups (C-O, C=O & CO3) indicates surface oxidation due to contact with atmospheric oxygen when transferring the samples. The F1s spectra of the uncycled anode displays a single peak corresponding to the presence of PVDF, the binder used for the KS4 anode, at ~ 688 eV. The percentage of PVDF decreases at 150 cycles (5.26 %) as the SEI forms, increasing its thickness and reducing the amount of PVDF “visible” through XPS. Subsequently after 250 cycles this peak increases (16 %), corresponding to the presence of LiPF6 and its decomposition products.107 Also visible in the F1s spectra after 150 and 250 cycles (Fig.45D and Fig.45F) are the peaks corresponding to LiF, ~ 684 eV, and Li3PF6O4 species, ~ 686 eV. LiF content increases from 18 % to 33 % from cycle 150 to cycle 250, whereas Li3PF6O4 increases to 67 % at cycle 150 and then decreases to
50 % at cycle 250 given the increase in LiF content on the anode surface. The significant growth in LiF content between cycle 150 and cycle 250 points to the poor stabilisation of the anode/electrolyte interface, with this continual growth occurring as a result of excessive electrolyte and salt decomposition.\textsuperscript{124}

Continuing the discussion of the C1s spectra, the C-C peak seen in the uncycled anode spectra, Fig.\textsuperscript{45A}, decreases as the number of cycles increases and the SEI layer grows. As mentioned previously, the initial C-O, C=O and CO\textsubscript{3} peaks correspond to the oxidation of the graphite with atmospheric oxygen – however, the increased content of these species seen in Fig.\textsuperscript{45C} and Fig.\textsuperscript{45D} arises due to the reduction of VC and the electrolyte to form lithium alkyl carbonates. These lithium alkyl carbonates form the basis of the poly(VC) SEI layer.\textsuperscript{107,125}

XPS spectra of the SP1 graphite cathode after 0, 150 and 250 cycles can be seen in Fig.\textsuperscript{46}. As expected, no signal was recorded in the F1s spectra for the uncycled cathode in Fig.\textsuperscript{46B}, this is attributed to the use of a NaAlg binder as opposed to the F-containing PVDF binder. After 150 cycles, Fig.\textsuperscript{46D}, the appearance of strong Li\textsubscript{x}PF\textsubscript{y}O\textsubscript{z} and LiF peaks is seen due to electrolyte degradation and SEI formation. Whilst the LiF content increases from 27 % at cycle 150 to 36 % at cycle 250, Fig.\textsuperscript{46F}, this increase is not as substantial as what is observed in the F1s spectra of the KS4 anode where LiF content almost doubles. In addition, the increase in PF\textsubscript{6} content can be attributed to the presence of PF\textsubscript{6}– anions trapped/remaining in the SEI layer from the charging/discharging process.

Looking at the C1s spectra of the uncycled cathode, Fig.\textsuperscript{46A}, the presence of oxygenated species arises, again, as a result of the cathode coming into contact with atmospheric oxygen during sample transfer. The dominant C-C peak at \sim 284 eV remains relatively constant between cycle 150, Fig.\textsuperscript{46C}, and cycle 250, Fig.\textsuperscript{46E}, with the content reducing from 47 % to 45 %. Similar results are seen for the remaining C-O, C=O and O-C=O groups, with the content of these species remaining relatively constant from cycle 150 to cycle 250 – with increases of 1.45 % and 2.26 % for C-O and C=O respectively. Along with a decrease in O-C=O content of 1.58 %. These small changes in the content of oxygenated organic species indicate a stable SEI at the graphite cathode/electrolyte interface, with electrolyte degradation and oxidation of the graphite cathode being suppressed presumably through the earlier oxidation of the VC additive.\textsuperscript{109,126}
The XPS results discussed indicate that the graphite anode experiences a greater degree of electrolyte degradation and, in this case, fails to form a stable SEI layer – whereas the graphite cathode surface is stabilised after 150 cycles. Furthermore, the C-C peak intensity in the C1s spectra for the SP1 cathode does not diminish significantly after 250 cycles unlike the C-C peak in the C1s spectra for the KS4 anode. Suggesting that a thinner SEI layer is formed at the cathode than at the anode, given that the graphite surface is still detectable with such intensity despite the formation of the SEI on the surface.
Figure 45 – XPS spectra (C1s: left) (F1s: right) of KS4 graphite anodes after 0 cycles, 150 cycles and 250 cycles.
Figure 46 – XPS spectra (C1s: left) (F1s: right) of SP1 graphite cathodes after (A & B) 0 cycles, (C & D) 150 cycles and (E & F) 250 cycles.
5 Conclusions & Future Work

This research aimed to explore and identify highly effective electrolyte and additive combinations in order to maximise the performance of PF$_6^-$-based dual ion batteries (DIBs). Of the many variations of DIBs that have been reported in literature, graphite dual ion batteries (GDIBs) are an attractive option given their intrinsically environmentally friendly nature and low-cost as a result of both electrodes consisting of graphite-based materials. The capacities of GDIBs are limited by the theoretical capacity of anion intercalation into graphite cathodes (up to 140 mAh g$^{-1}$ based on a stoichiometry of C$_{16}$PF$_6$), although to attain these capacities high operating potentials are required (> 5.0 V) generally exceeding the working potentials of many traditional organic electrolytes. Therefore, identifying suitable high-voltage electrolytes that are compatible with graphite electrodes is crucial when developing DIBs. Whilst an increased operating potential can increase the energy density of a system, maintaining the electrochemical stability of the cell through reducing excessive electrolyte degradation during prolonged cycling is imperative. The inclusion of electrolyte additives can provide an economical route to tackling the issue of electrolyte degradation through improving the oxidative stability of the electrolyte, at the same time as offering a myriad of electrochemical and physical property enhancements.

Few studies have successfully achieved discharge capacities close to the theoretical value for PF$_6^-$ intercalation, with values in the range of 40 – 70 mAh g$^{-1}$ typically reported in GDIB literature, highlighting the potential for significant developments in this area of battery chemistry.

Ethyl methyl carbonate (EMC) based electrolytes have been highlighted as key components of PF$_6^-$-based DIBs in the attempts to optimise their performance. In this work two EMC electrolytes previously reported in GDIB literature have been investigated and adapted. Initial tests featured the application of these electrolytes in aluminium DIBs (Al-DIBs) alongside GDIBs. The EMC/fluoroethylene carbonate (FEC) (6:4) 2 M LiPF$_6$ + 5 mM tris(hexafluoro-isopropyl)phosphate (HFIP) electrolyte displayed low discharge capacities in Al-DIBs and GDIBs (35 mAh g$^{-1}$ and 41 mAh g$^{-1}$ respectively), with this being attributed to the reduced content of EMC in the electrolyte due to the large FEC content (40 %). Furthermore, the cycling
performance of the Al-DIB was substandard, with poor rate capabilities and capacity fade experienced as a result of continuous electrolyte degradation at the aluminium anode in these cells. With these effects being intensified when the operating voltage increased from 5.0 V to 5.2 V. To combat the aluminium anode stability issue pre-treatment methods and the implementation of Al-protecting additives (such as AlF₃) have been reported. The electrolyte EMC 2 M LiPF₆ + 3 %vinylene carbonate (VC) & 2 % AlF₃ displayed a discharge capacity of 86 mAh g⁻¹ after 50 cycles, an improvement on the previously reported values for the HFiP Al-DIB. Despite the addition of AlF₃ to Al-DIBs the cell performance was difficult to reproduce, with many cells experiencing short-circuiting due to dendrite formation at the Al-anode when high current densities are applied. As a result, further work focused on the application of an EMC based electrolyte in GDIBs.

The addition of 3 % VC and 3 % FEC, individually, to EMC 2 M LiPF₆ improved the electrochemical performance of Li-half cells with low-defect content graphite cathodes (SP1 and KS4 graphite), with anion intercalation capacities of ~ 80 mAh g⁻¹ reported after 150 cycles. Graphite quality was consistently a determining factor in the overall cell performance of each system trialled, with low I₀/I₇ ratio graphite cathodes (ie. SP1 and KS4 graphite) producing greater discharge capacities and coulombic efficiencies. For the best performing Li-half cell (SP1 graphite cathode) the addition of 3 % FEC increased the coulombic efficiency to 96 % after 150 cycles, compared to 85 % when the control electrolyte without additives was used. The performance difference between the two additives, VC and FEC, was marginal in the discharge capacity values (82.5 mAh g⁻¹ vs. 83.8 mAh g⁻¹) and more significant in the coulombic efficiency values (90.6 % vs. 94.6 %) after 150 cycles. Concluding that FEC forms a more compact SEI at the graphite cathode than VC, increasing the efficiency of anion transport. This is further supported by the low electrochemical polarisation and peak-to-peak separation values obtained from Li-half cells with the 3 % FEC electrolyte. Transitioning this electrolyte into a GDIB configuration did not reproduce similar results with the cells displaying a discharge capacity of < 35 mAh g⁻¹ after 50 cycles. These values are greater than the discharge capacity of cells without additives (~ 10 mAh g⁻¹), although significantly less than the discharge capacities seen when the 3 % VC electrolyte is used (~ 60 mAh g⁻¹ after 350 cycles). The differing behaviour of the FEC electrolyte in Li-half cells and GDIBs is likely attributed to the introduction of a graphite anode in a full cell configuration, where the 3 %
additive may be insufficient for the simultaneous formation of two graphite SEI layers. Indicating that whilst the FEC additive stabilises the cathode in Li-half cells, the performance at the graphite anode is reduced. Given that the additive concentration was not varied in this work, and that FEC has previously been reported as an effective SEI forming additive, future work should investigate the effect of increasing the FEC content on the electrochemical performance of GDIBs. Further to this point, with the knowledge that FEC improves the cathode stability in Li-half cells, the performance at the graphite anode is reduced. Given that the additive concentration was not varied in this work, and that FEC has previously been reported as an effective SEI forming additive, future work should investigate the effect of increasing the FEC content on the electrochemical performance of GDIBs. Further to this point, with the knowledge that FEC improves the cathode stability in Li-half cells, and VC improves the anode stability, a combination of VC and FEC additives may be worth consideration in the pursuit of optimising GDIB performance in the future.

In addition, XPS results indicated that the cathode/electrolyte interface appeared to stabilise and form a thin SEI layer in the presence of VC, whereas anode SEI growth was detrimental to cell performance, resulting in capacity fade after 150 cycles. Whilst this analysis was conducted on an un-optimised cell (due to the use of a polymer separator as opposed to the typical glass microfiber separator), the results highlight the importance of tuning the electrolyte additive content to the cell configuration in order to stabilise both electrodes.

Finally, the use of a low-defect SP1 graphite cathode and a highly effective electrolyte/additive combination (EMC 2 M LiPF$_6$ + 3 % VC) produced impressive cycling performance (> 60 mAh g$^{-1}$, > 96 % coulombic efficiency and 100% capacity retention after 350 cycles), on par with the best performance values reported in the limited studies on PF$_6^-$ based GDIBs. Despite this, achieving discharge capacities closer to the theoretical value of 140 mAh g$^{-1}$ remains a distant feat and may require the further developments of anion hosting cathode materials to achieve this goal and unlock the true potential of DIBs in the future.
6 References


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Appendix 1 — Comparisons of the cell performance of EEG and NBD cathodes with the EMC 2 M LiPF₆ + 3 % VC electrolyte. 
A) Coulombic efficiency of Li-half cells; B) Discharge capacities of Li-half cells; C) Discharge capacity and coulombic efficiency of GDIBs.
Appendix 2 – CVs of EEG and NBD GDIBs after 150 cycles, displaying similar intercalation and deintercalation current responses. 2.5 – 5.2 V vs. Li/Li⁺, scan rate 1 mV/s, EMC 2 M LiPF₆ + 3 % VC electrolyte.
Appendix 3 – CD profiles of A) KS4 and B) SP1 GDIBs with the EMC/FEC (4:6) 2 M LiPF$_6$ + 5 mM HFIP electrolyte. Displaying an initial increase in the discharge capacities as the current density decreases, followed by a decrease in discharge capacity at 0.1 A g$^{-1}$ (cyc 50) and 0.2 A g$^{-1}$ (cyc 47) in KS4 and SP1 GDIBs respectively.
Appendix 4 – CV obtained from 3-electrode experiment with glassy carbon working electrode between 3.0 – 6.3 V vs. Li/Li$^+$ highlighting the shift in electrochemical stability window due to the presence of VC. EMC 2 M LiPF$_6$ + 3 % VC electrolyte. (inset zoomed)
Appendix 5 – A table displaying the peak positions and areas for the XPS spectra seen in Fig. 34 and Fig. 35.

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