The multifunctional role of carbon in electrochemical energy storage

Graphitic foams for 3D microbatteries and dual-ion batteries

by Antonia Kotronia

Licentiate thesis
Abstract

The lithium-ion battery concept has, since its birth in 1991, matured into one of the most widely used electrochemical energy storage technologies. A vital breakthrough for its commercialization was the introduction of graphite as a negative electrode in 1983. Nearly 40 years after that, carbon (graphite in particular) remains an essential component in every lithium-ion battery, but also constitutes an active research topic within the field of electrochemical energy storage. This licentiate thesis deals with (i) the catalytic graphitization of emulsion-templated carbon foams and their potential use as negative electrodes in 3D lithium-ion microbatteries, and (ii) a study on the electrode-electrolyte interphase in graphite positive electrodes in dual-ion batteries. The latter will serve as a basis for an ongoing study in which anion intercalation into graphitized carbon foams is being pursued.

The thesis initially explores the graphitization of emulsion-templated carbon foams and their application as the negative electrode in 3D lithium-ion microbatteries. The impact of heat treatments and the incorporation of graphitizing agents is studied with respect to both the structure of the carbon foams and their electrochemical performance. Raman spectroscopy, X-ray diffraction and transmission electron microscopy reveal that the structure of the carbon foams evolves from an amorphous state to turbostratically-disordered graphite when increasing the temperature from 1000 °C to 2200 °C. Alongside the structural changes, the electrochemistry improves considerably, with the initial coulombic efficiency increasing from 40 % to 70 % and the reversible lithiation capacity reaching 100 mAh g−1. The enhanced performance is attributed to an overall reduction in the surface area of the carbon foam, elimination of surface functional groups and appearance of more ordered graphitic domains. As a next step, Ca- and Mg-containing salts that were initially added to stabilize the emulsion precursors were utilized to further catalyze the graphitization. In consequence, the growth of larger graphitic domains was achieved that in turn resulted in an enhanced electrochemical performance. The reversible capacity increased up to 140 mAh g−1 in this case and the staging mechanism for the lithium-ion intercalation became discernible. Most importantly, the hierarchically porous structure and monolithic nature of the foam were retained even after the graphitization. This enables decent rate capabilities and makes the foam attractive for use in 3D microbatteries.

In addition, this thesis introduces a study on the intercalation chemistry of anions into graphitic carbon materials and the concomitant surface-bulk processes occurring as a result. The ultimate aim of this project is to utilize the carbon foams in the so-called dual-ion batteries wherein simultaneous anion/ cation intercalation occurs in the positive/ negative electrode, respectively. The investigation of this system begins, however, with an attempt to stabilize the electrochemical performance of commercial KS6 graphite, using
different electrolyte compositions. First off, the impact of the chosen anion and the salt concentration on the electrochemical reversibility of this system is evaluated. This entailed studying the electrolyte stability at critical interfaces (mainly on the positive electrode and Al current collector) through SEM and XPS and monitoring the structural changes of the KS6 graphite during cycling through Raman. Specifically, the studied anions included PF$_6^-$, FSI and TFSI, at concentrations ranging from 1 M to 4 M in 1:1 (v/v) EC:DEC solvent mixtures. The 4 M LiTFSI in EC:DEC stood out as a particularly suitable electrolyte, delivering stable, reversible capacities of 100 mAh g$^{-1}$ and an average operating voltage of 4.6 V. Spectroscopic and microscopic evidence indicated that this electrolyte composition suppresses graphite exfoliation and solvent decomposition, while it also prevents the corrosion of the Al current collector. All in all, the 4 M LiTFSI in EC:DEC system appears to be a promising starting point for future studies on carbon foams as positive electrodes.
Στον Αθανάσιο Κοτρωνιά (1931-2019)
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.


III Kotronia, A., Asfaw, H. D., Hahlin, M., Brandell, D. & Edström, K. The Cathode Electrolyte Interphase on Graphite Positive Electrode in Dual-ion Batteries Probed Using X-ray Photoelectron Spectroscopy. (In manuscript)

Reprints were made with permission from the respective publishers.

Comments on my contributions to the papers:

I  I performed part of the experimental work (mainly concerned with the electrochemical characterization), took part in the scientific discussions and participated in the proofreading of the manuscript.

II I contributed to the design of the project, planned the study and performed all of the experiments with the exception of the TEM characterization, where I took part. Performed the data analysis and wrote the manuscript with input from the co-authors. I was involved in all discussions.

III I participated in the planning of the project and performed all of the experiments. Performed the data analysis and wrote the manuscript with input from the co-authors. I was involved in all discussions.
Contents

Abstract .......................................................................................................................... ii

1. Introduction .................................................................................................................. 10
   1.1 Lithium-ion batteries: history and current efforts ................................................. 10
   1.2 Microbatteries and 3D carbon foams ................................................................. 12
   1.3 All-carbon dual-ion batteries .............................................................................. 14

2. Thesis scope .................................................................................................................. 17

3. Materials and synthesis .............................................................................................. 18

4. Characterization techniques ....................................................................................... 19
   4.1 Electron microscopy ............................................................................................. 19
       4.1.1 Scanning electron microscopy .................................................................... 19
       4.1.2 Transmission electron microscopy .............................................................. 19
   4.2 Spectroscopy .......................................................................................................... 20
       4.2.1 Raman spectroscopy .................................................................................. 20
       4.2.2 X-ray photoelectron spectroscopy ............................................................... 21
   4.3 X-ray diffraction .................................................................................................... 21
   4.4 Specific surface area and porosity analysis using nitrogen-gas physisorption .... 22
   4.5 Thermogravimetric analysis ................................................................................ 22
   4.6 Electrochemical characterization ......................................................................... 23
       4.6.1 Chronopotentiometry .................................................................................. 23
       4.6.2 Cyclic voltammetry ..................................................................................... 23
   4.7 Electrode and cell preparation ............................................................................. 24
       4.7.1 Carbon foams for 3D microbatteries .............................................................. 24
       4.7.2 Carbon cathodes for dual-ion batteries ......................................................... 24

5. Results and discussion ............................................................................................... 25
   5.1 Graphitic carbon foams in 3D microbatteries ....................................................... 25
       5.1.1 Graphitization through heat-treatment ......................................................... 25
       5.1.2 Catalytic graphitization ............................................................................... 27
   5.2 Graphite positive electrodes for dual-ion batteries .............................................. 31
       5.2.1 Impact of electrolyte composition on the cycling efficiency of the graphite cathode ........................................................................................................ 31
       5.2.2 Surface studies on cathodes and current collectors ....................................... 34
       5.2.3 Following the exfoliation of graphite through Raman .................................. 40

6. Concluding remarks and outlook .............................................................................. 44

7. Populärvetenskaplig sammanfattning ..................................................................... 46
8. Acknowledgements ................................................................................. 48
9. References ............................................................................................... 49
**Abbreviations**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>BF</td>
<td>Bright field</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered electron</td>
</tr>
<tr>
<td>CEI</td>
<td>Cathode electrolyte interphase</td>
</tr>
<tr>
<td>CMC</td>
<td>Sodium carboxymethyl cellulose</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>DF</td>
<td>Dark field</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DIB</td>
<td>Dual-ion battery</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>EC</td>
<td>Ethyl carbonate</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectroscopy</td>
</tr>
<tr>
<td>FSI</td>
<td>Bis(fluorosulfonyl)imide</td>
</tr>
<tr>
<td>GCPL</td>
<td>Galvanostatic cycling with potential limitation</td>
</tr>
<tr>
<td>HIPE</td>
<td>High internal phase emulsion</td>
</tr>
<tr>
<td>HOPG</td>
<td>Highly oriented pyrolytic graphite</td>
</tr>
<tr>
<td>LIB</td>
<td>Lithium-ion battery</td>
</tr>
<tr>
<td>NIR</td>
<td>Near infrared</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electron</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TFSI</td>
<td>Bis(trifluoromethane)sulfonimide</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
1. Introduction

An electrochemical cell is a device that allows the storage of chemical energy and enables its conversion into electrical energy. The basic components that constitute an electrochemical cell are the positive and negative electrodes and the electrolyte. Typically, the electrodes are where the energy storage and conversion takes place, while the electrolyte acts as a pathway for ion conduction and compensates for the electronic current flowing in the external circuit. The extent to which the interconversion of energy between the chemical and electrical forms is reversible leads to the classification of cell chemistries as rechargeable or non-rechargeable [1]. Concerning rechargeable electrochemical cells, a popular and technologically mature chemistry is that of the lithium-ion battery (LIB). This chapter aims to give a brief overview of LIBs, their applications and potential technological extensions. Additionally, a short background on systems of interest for this work is provided, herein including 3D microbatteries and dual-ion batteries (DIBs).

1.1 Lithium-ion batteries: history and current efforts

The debut of LIBs can be traced back to the 1970s, along with the flourishing of works examining candidates for the intercalation of the lithium ion. The possibility of reversibly inserting/removing lithium ions from a host structure was initially tied to the exploration of layered compounds, mostly involving transition metal dichalcogenides. At early developmental stages, a Li-metal negative electrode was paired with a positive electrode commonly consisting of TiS_2 [2], MoS_2 [3] or Li_xMnO_2 [4]. Nonetheless, the unsafe nature of Li-metal limited the use of these battery chemistries, up until Yoshino constructed a full cell employing a conducting polymer as a lithium host and a LiCoO_2 positive electrode. This was the foundation for Sony’s commercialization where the polymer was replaced with coke. Graphite was introduced as a negative electrode in the mid 1990s when better electrolytes, preventing graphite exfoliation were discovered. Graphite enabled high lithiation capacities (372 mAh g^{-1}) at low potentials (between 0-0.2 V vs. Li^+/Li), while it eluded the issues related to dendritic Li growth. Combined with appropriate cathodes, graphite gave rise to the “rocking-chair” battery, where Li-ions shuttled between the negative and positive electrodes upon charge and discharge, respectively (see Figure 1).
Since then, a plethora of battery materials and chemistries for Li-ion batteries has been tested with a handful of them standing out. Intercalation compounds for the negative side, apart from graphite, are basically limited to Li$_4$Ti$_5$O$_{12}$, which offers the benefit of long cycle life due to its “zero-strain” property, but which is unfortunately limited due to its capacity (175 mAh g$^{-1}$) and rather high Li$^+$-intercalation potential (1.55 V vs Li$^+$/Li$^0$)\cite{5}. Further alternatives for negative electrodes are found amongst the p-block elements (M = Al, Si, Sb, Sn) which can be lithiated to form alloys with the general formula Li$_x$M \cite{6}. Despite the fact that these materials exhibit capacities up to an order of magnitude higher than graphite, they suffer from rapid capacity fading. The extensive volumetric changes that they undergo during cycling lead to particle cracking upon delithiation, loss of active material and continuous reformation of the solid electrolyte interphase (SEI) layer \cite{7}. A third category of materials considered for the negative electrode operate on conversion reactions; meaning that a solid-state redox reaction occurs, which encompasses the breaking/forming of bonds and the alteration of the crystal structure. Typical conversion materials on the negative side include transition metal oxides (such as Fe$_2$O$_3$, Fe$_3$O$_4$, Co$_3$O$_4$, Cu$_2$O), phosphides, sulfides and nitrides. These materials are nevertheless nowhere near commercial implementation as they exhibit high voltage hysteresis and poor cyclability \cite{7,8}. Lastly, it should be mentioned that apart from graphite there are other types of carbonaceous negative electrode materials, operating on different principles. These include mainly hard carbons exhibiting a “house-of-cards” configuration. The main energy storage mechanism of these carbons is not intercalation, but rather surface-confined reactions and adsorption. Consequently, hard carbons may exhibit
initial capacities far higher than graphite but will on the contrary suffer from low capacity retention (since most of the surface-based chemistry is irreversible) [9, 10].

The existing alternatives for the positive electrode material in Li-ion batteries are equally numerous. Many of these materials fall however under the broad umbrella of transition metal oxides. The closest successors to Goodenough's suggestion of using LiCoO$_2$ in 1980 [11] include similar layered LiMO$_2$ structures (M = Ni, Mn) [12, 13]. Another material thoroughly studied as the positive electrode is LiFePO$_4$, exhibiting an olivine structure and one-dimensional pathways for the diffusion of Li$^+$ [14]. LiFePO$_4$ offers stable cycling, decent gravimetric capacities (170 mAh g$^{-1}$) and a redox potential of 3.45 V vs Li$^+/Li^0$ which makes it commercially attractive. Be as may be, the use of LiFePO$_4$ requires optimal nanostructuring (due to the 1D nature of its diffusional channels) and is even so restricted to applications that do not require high rate capabilities. Lastly, another class of highly promising positive electrode materials is based on the structure of the high-voltage spinel LiMn$_2$O$_4$ [15]. Contemporary research efforts are also focusing on morphological aspects and cation mixing to achieve superior properties, with an example being the material known as NMC 111, LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ [16].

The broad spectrum of active materials available for LIBs is but a mere reflection of the diverse nature of their corresponding applications. With the latter ranging from portable electronics, to transportation, to grid energy storage, it is easy to understand that the demands on the battery will differ greatly from case to case. Metrics of relevance may be expressed in terms of gravimetric and volumetric energy densities, rate capability, cycle life, self-discharge, operating temperature range, cost and carbon footprint [17]. It is practically impossible for a single battery chemistry to meet all these criteria and excel. Hence, one of the biggest future challenges in order to create an energy-efficient society based on renewable resources will be to identify and assign suitable battery chemistries to the vast pool of applications.

1.2 Microbatteries and 3D carbon foams

The driving force behind research in 3D microbatteries is the steadfast miniaturization occurring in the electronics industry. The success in developing devices where processors, sensors and communicators are confined in volumes below 1 mm$^3$ needs to be followed by an equivalent reduction in the size of the power source [18]. In the course of the past years, several designs for microbatteries have been proposed, including both “thin-film” and “thick-film” microbatteries. Thin-film microbatteries are capable of delivering high rate capabilities but experience limitations in terms of the maximum energy den-
sities that they can store. The thick-film design solves the problem of insufficient energy density, as a larger quantity of active material is present. However, this is a clear disadvantage in applications where this energy needs to be accessed promptly. A long-known strategy that could achieve the best of both worlds would be to use a three-dimensional design for the microbattery [19].

The electrode architecture is of primary significance in order to fulfill the purpose of the 3D microbattery. The design should pay attention to (a) enabling the incorporation of high amounts of active materials (b) ensuring that the active materials possess a large surface area and (c) minimizing the ion transport distance between the positive and negative electrodes. If these prerequisites are met, a decent compromise between the available energy and power density should be possible. Thus far, electrode architectures that have been considered encompass interdigitated microrods [20], microchannel plates [21] and trenches [22], self-supported nanotubes [23] and reticulated foam structures [24]. Apart from the electrode design in itself, in order to produce a functional 3D microbattery, it is important to consider how to incorporate the electrolyte in the structure. Due to the complicated geometries of these systems, it is often desirable to use thin, solid polymer electrolytes that can act as separators and as ion conductors at the same time [25]. In practice, it is still difficult to deposit such polymer layers in a homogenous, pinhole-free manner and without exerting a negative influence over the initial electrode porosity.

In this context, carbon-based electrode materials have received plenty of attention. The underlying reason behind this is not merely the decent electrochemical performance of carbon-based electrodes, but also their extreme tailorability. Monolithic, carbon-based 3D electrodes have been produced in a variety of ways so far, with literature examples including arrays of carbon microrods fabricated by means of photolithography and etching [20], interconnected graphene sheets [26], graphene aerogels [27] and carbon foams prepared via either hard [28] or soft templating [29]. The soft templating technique shows high promise in terms of production upscaling. Previous studies have shown that water-in-oil emulsion-templating allows for the synthesis of large batches of monolithic carbon foams with high surface areas and controlled porosities. Nevertheless, although these foams possessed ideal characteristics from a theoretical perspective, they exhibited large irreversible capacities upon the first discharge. This troublesome performance was directly linked to the “house-of-cards” carbon foam structure and to its high surface area; and the graphitization of the 3D electrodes was identified as a possible remedy [30, 31].

As previously mentioned, graphitic samples demonstrate reversible capacities of 372 mAh g\(^{-1}\) at low lithiation potentials. However, the synthesis of microporous, highly graphitized carbons is a challenge in practice, as these two attributes counteract one another. The extensive porosity creates structural defects, whose nature hampers graphitization. These defects were initially ascribed to the existence of sp\(^3\)-crosslinks [32] and more recently to ribbon- or fullerene-like structures [33-35]. Such defects inhibit the creation of long-
ranged graphitic domains, thereby resulting in “turbostratically disordered” carbons. The turbostratic disorder reduces the lithiation capacity of the carbon, since it induces a “pinning effect” preventing the configurational change of the graphitic sheets from ABA- to AAA-stacking upon lithiation. An illustration of the structures of soft carbons (easily graphitizing) and hard carbons (non-graphitizing) is presented in Figure 2.

![Figure 2: Schematic illustration of the structures and main energy storage mechanisms in graphitizing and non-graphitizing carbons.](image)

The first part of this thesis deals with strategies to increase the graphitic content of carbons that exhibit extensive microporosity, which are normally classified as non-graphitizing carbons.

1.3 All-carbon dual-ion batteries

Despite the indisputable dominance of LIBs within consumer electronics and fair share of the market for electric vehicles and grid energy storage, alternative cell chemistries are being intensively studied. Lowering the cost and increasing the specific capacity, energy density, cycle life and environmental friendliness are some of the driving forces for that. A promising system, where porous, graphite-based electrodes are also of interest is that of DIBs [36].

The working principle of DIBs would be identical to that of LIBs, were it not for two important differences: in DIBs, (i) the positive electrode becomes a host for anionic intercalation and (ii) the electrolyte salt is the sole provider of ions for the purpose of intercalation [37]. Figure 3 depicts the charge and discharge mechanisms of an all-carbon DIB using graphite on both sides. The half- and net reactions for the charging process can be summarized as follows:

Negative electrode: \[ C + xLi^+ + xe^- \rightarrow Li_xC \]
Positive electrode: \[ C + xA^- \rightarrow A_xC + xe^- \]
Total reaction: \[ 2C + xLi^+ + xA^- \rightarrow Li_xC + A_xC \]
Here, Li⁺ is being used as the cation, but it could easily be replaced by either Na⁺ [38] or K⁺ [39], which are interesting from the perspective of availability and cost. The term “A” stands for the anion. A handful of the anions that have been tested as intercalant species so far include PF₆⁻ [40] BF₄⁻ [41], FSI [39], TFSI [42], FTFSI [43] and BETI [44]. The reaction potentials, capacity and reversibility of the intercalation appear to be heavily dependent on the type of anion used, but also on the type of solvent and salt concentration [45]. The latter is of paramount importance since a large amount of non-coordinated solvent may result in severe degradation of the carbon cathode through solvent co-intercalation, which causes exfoliation and loss of active material [39].

Figure 3: In a) charging (intercalation) and discharging (de-intercalation) mechanism in an all-carbon DIB. Note the distinct differences to LIBs. In b) molecular structures of some typical anions used in DIBs and in this work. These include the hexafluorophosphate (PF₆⁻), bis(fluorosulfonyl)imide (FSI) and bis(trifluoromethane)sulfonimide (TFSI) anions.

The structure and morphology of the carbon cathode itself are also of great significance, as these will influence the amount of anions that can be intercalated [46, 47]. Previous studies suggest that highly oriented pyrolytic graphite (HOPG) is a most promising material for carbon-based cathodes as it exhibits reasonable capacities and intercalation kinetics [48]. Furthermore, an estimate regarding the optimal size for the graphite particles puts them in the range between 4-6 µm [49, 50]. The small particle size is necessary in order to fully anionate the graphite host; as the anions themselves are normally large (often much larger than the graphite interlayer distance) and have hence low mobility values once intercalated. Nanostructuring the graphite and modifying its surface characteristics is another way to enhance its performance. Graphitic materials possessing a higher surface area showed higher initial capacities in comparison to low surface area counterparts. Regrettably, these materials have
so far also exhibited fast capacity fading, which could possibly be attributed to increased electrolyte degradation [49].

Lastly, another major culprit for the degradation of DIBs is the corrosion of the current collector at the high operational voltages. Even aluminium, with its high oxidative stability, tends to corrode under these conditions [51]. To tackle this problem, a combination of strategies may be needed, such as: (i) coating the aluminium current collector with corrosion-resistant layers such as TiN [39, 52], and/or (ii) making use of electrolyte compositions/additives that can efficiently passivate both the electrode and Al current collector surface [53-55].

Hence, in order to construct DIBs that will be of commercial value, it is necessary to consider the complex interplay between the specific carbon host used and the electrolyte. At the same time, it is critical to evaluate the compatibility of the system with other components such as the current collector and the separator. The second part of this thesis is devoted to the investigation of suitable electrolyte systems, which will support reversible anionic intercalation in the graphite positive electrode and which will prevent the corrosion of the Al current collector. The aim is that this research will eventually enable the use of the graphitic carbon foam in DIBs.
2. Thesis scope

The works presented in this thesis aim at developing carbon materials that are of interest for use in 3D-microstructured batteries. The first part explores strategies to increase the degree of graphitization in emulsion-derived carbon foams, while maintaining their monolithic and bi-continuous microstructures. Two methods have been employed thus far to graphitize the carbon foams: firstly, heat-treatments to temperatures from 1000 to 2200 °C and secondly, the use of Ca- and Mg-based salts, which are known to promote graphitization. As the intended use for the carbon foams is as negative electrodes in 3D microbatteries, in-depth understanding of the electrode microstructures and surface morphology are of paramount importance. Therefore, extensive characterizations using N$_2$-gas physisorption analysis, electron microscopy, Raman spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) are performed. Following that, the electrochemical performance of the carbon foams is studied, and their potential benefits in lithium-ion microbatteries are compared to literature examples.

The second part of the thesis focuses on exploring the use of carbon foams as the positive electrode in DIBs. In this preliminary study, the search for electrolyte systems that will enable reversible and stable intercalation of anionic species in graphite is of primary focus. Thus far, the majority of this work has been performed on graphite foil (Goodfellow) and Timcal KS6 graphite (Imerys). The main aspects studied have included the following:

(i) Which electrolyte compositions will enable the most stable cycling for the graphitic positive electrode by minimizing structural changes and what are their common characteristics?

(ii) Which combinations of electrolyte compositions and current collectors will be able to ensure the formation of a passivating layer inhibiting corrosion at the high operational potentials of DIBs?

In order to gain insight regarding these questions, electrolytes with different anions and with varying salt concentrations have been tested. Their interaction with the positive graphite electrode and current collector has been probed by the means of electrochemical cycling, Raman and XPS.
3. Materials and synthesis

The precursor for the graphitic foam was synthesized from a water-in-oil high internal phase emulsion (HIPE). An HIPE is formed when an organic phase is mixed with an aqueous phase of much larger volume (>80%) to produce an emulsion. Successful emulsification procedures exploit suitable surfactants to stabilize the boundary between the two phases. Here, the organic phase consisted of styrene monomer (3 mL, Aldrich®, ≥ 99%), divinylbenzene (1.5 mL, Aldrich®, 80%), 4-vinyl-benzyl chloride (0.5 mL, Fluka®, ≥ 90%) and Span 80 (1.5 g, Aldrich®). The aqueous phase consisted of 30 mL of de-ionized water, the K₂S₂O₈ initiator (0.075 g, Merck 99%) and the stabilizing salt, which was either CaCl₂·6H₂O (0.825 g, Aldrich®, ≥ 99%) or its molar equivalent of MgCl₂·6H₂O. The aqueous phase was transferred dropwise to the organic, which was constantly stirred with a rotor-stator mixer. The stirring increased progressively from 200-2000 rpm during 30 minutes. The emulsion was then heated to 65 °C and left to polymerize for 48 h. In continuation, the stabilizing salt present in the polyHIPE was either leached out by Soxhlet extraction (24 h in distilled water at 100 °C and 24 h in ethanol at 85 °C) or left inside the polyHIPE for all further functionalization steps. Subsequently, the polyHIPEs were immersed in concentrated H₂SO₄ (95-97%, Emsure®, Merck) and heated at 100 °C for 24 h. The sulfonated polyHIPEs were washed with deionized water and dried under vacuum (100 °C, 24 h) to remove excess H₂SO₄. This was followed by a carbonization step through the slow ramping of temperature up to 1000 °C in Ar atmosphere. Finally, a graphitization step took place, during which the carboHIPEs were heat-treated at a temperature of 2200 °C for 1 h in N₂ atmosphere. The most important steps of the synthesis are summarized schematically in Figure 4.

Figure 4: Schematic summary of the synthesis procedure from the formation of the HIPE to the graphitized carbon foam.
4. Characterization techniques

This chapter aims to provide a synopsis of the techniques employed to study the relevant materials properties and electrochemical performance of the carbon-based electrodes.

4.1 Electron microscopy

4.1.1 Scanning electron microscopy

Scanning electron microscopy (SEM) is an imaging technique that can achieve a higher spatial resolution than traditional optical microscopy, by making use of a focused electron beam instead of white light. The electron beam is scanned across the sample, which causes the incoming electrons to interact with the specimen either in an elastic or inelastic manner. These scattering processes result in backscattered electrons (BSE), secondary electrons (SE) and X-rays. The detected signal from the BSEs and X-rays provides valuable insights regarding the elemental composition of the specimen, while the signal from the SEs carries topographical information.

SEM analysis is a tool employed regularly throughout this entire work. In Papers I and II, SEM is mainly used to study the morphology of the as-synthesized carbon foams. The instrument used for that purpose was a Zeiss Merlin SEM, where surface-sensitive imaging took place at an acceleration voltage of 3.0 keV, a current of 100 pA, a working distance of 6.7 mm and with the in-lens detector. In Paper III, SEM was employed as a method for studying the exfoliation of graphite particles upon anionic intercalation and the corrosion of the Al current collector. Electrodes cycled in different electrodes and for varying amounts of time were firstly washed with dimethyl carbonate (DMC) and then mounted on the SEM holders inside an Ar-filled glovebox (O₂ < 1 ppm, H₂O < 1 ppm). The samples were afterwards brought to the microscope with the aid of an inert transfer shuttle. The analysis consisted mostly of surface imaging through the in-lens and SE detectors in a way similar to what previously described.

4.1.2 Transmission electron microscopy

In a similar way to SEM, transmission electron microscopy (TEM) exploits highly energetic electrons to resolve features on the atomic scale. As the name
suggests, the electrons are transmitted through the sample, which is the reason why the requirement of electron transparency must be met. TEM imaging can be performed in one of two different modes; either in bright field (BF) or in dark field (DF) mode. The principal difference between the two is that BF imaging utilizes the information coming from the direct, while the DF mode uses information from the diffracted part of the beam for the image reconstruction.

TEM is used in Papers I and II, in order to probe the nanostructure of the as-synthesized graphitic foams. Prior to the analysis, the foams were ground to a fine powder, dispersed in ethanol and deposited on holey carbon tape. For the measurement itself, a JEOL JEM-2100F microscope was used, which was equipped with a Gatan Ultrascan 1000 CCD camera and a JEOL annular dark field detector.

4.2 Spectroscopy

4.2.1 Raman spectroscopy

Raman scattering analysis is a spectroscopic technique that relies on the inelastic scattering of optical light to retrieve information regarding the vibrational and rotational modes in certain molecules. During a measurement, the sample of interest is illuminated with light from a monochromatic source, normally a laser operated in the ultraviolet (UV), visible (Vis) or near infrared (NIR) regime. The majority of photons (approximately 99.999 %) are scattered elastically, this meaning that no change in frequency is observed. This is the so-called Rayleigh scattering, which is usually filtered out and removed from the Raman spectra. The remaining 0.001 % of the photons are scattered inelastically, meaning that these return with an either higher or lower frequency than their original one.

The high sensitivity of Raman spectroscopy towards symmetric covalent bonds renders it ideal for the study of carbon. Qualitative information regarding the structure, bonding and defects can be easily obtained. For partially graphitic carbon materials, the ratio between two particularly distinct Raman bands (the D band at around 1350 cm⁻¹ and the G band at 1580 cm⁻¹) can provide valuable insights regarding the degree of graphitic ordering and graphitic crystallite size. Thus, an extensive use of Raman spectroscopy is made in Papers I and II. The instrument used was a Renishaw inVia Raman spectrometer equipped with a Leica LM optical microscope and a CCD camera. A green laser (λ = 532 nm) was used and the samples were measured in static mode (20 accumulations, 20 s exposure time at 0.5% intensity and with
the 50X magnification lens). Additionally, a few operando-Raman experiments were performed, where a pouch cell with an optically transparent window was used (see Figure 5).

![Figure 5: a) The configuration used for enabling operando Raman during electrochemical cycling b) photograph of a pouch cell with an optically transparent window.](image)

4.2.2 X-ray photoelectron spectroscopy

The surface chemistry of the pristine samples and the nature of the interphases formed during the cycling of the electrochemical cells have been probed through XPS in Papers I and II. The underlying operational principle of XPS takes advantage of the photoelectric effect to obtain not only the sample’s elemental composition but also information regarding oxidation states and local chemical environments. During the measurement, the sample is exposed to monochromatic X-rays of a known wavelength, which leads to the ejection of photoelectrons from the elements’ inner core levels. The short mean free path of the generated photoelectron assures that the information reaching the detector emanates exclusively from the substrate’s surface.

The XPS measurements demonstrated in this work were performed with the aid of a PHI-5500 spectrometer, using monochromatic Al Kα radiation (1487 eV) and an electron emission angle of 45°. The cycled electrodes were washed with DMC inside an Ar-filled glovebox (O₂ < 1 ppm, H₂O < 1 ppm), mounted on the XPS holder and taken to the instrument in an inert transfer shuttle. As regards the data analysis, all of the obtained spectra were calibrated with respect to the hydrocarbon peak, which was fixed to 284.8 eV.

4.3 X-ray diffraction

X-ray diffraction (XRD) utilizes elastically scattered X-rays as a means for probing the crystal structure of materials. Materials that exhibit periodic ordering with interatomic spacing features in the same order of magnitude as the
wavelength of the incoming radiation will generate distinct diffraction patterns. The diffraction pattern is the result of coherently scattered X-rays interfering in a constructive manner, in accordance with Bragg’s law:

\[ n\lambda = 2dsin\theta \]

**In Papers I and II**, XRD serves as a tool for the qualitative study of the structure of the as-synthesized graphitic foam. More specifically, XRD is used as a tool to track the evolution of the 002 diffraction peak after graphitizing the carbon foams. The diffractometer used for the XRD measurements was a Bruker D8 Advance using a Cu Kα radiation source. Prior to the measurement, the carbon foams were crushed to a powder form, dispersed in ethanol and drop-casted on the Si-substrate holder.

### 4.4 Specific surface area and porosity analysis using nitrogen-gas physisorption

Nitrogen-gas physisorption has evolved into a highly standardized technique for the evaluation of sample surface area and sample porosity. In this work, nitrogen gas sorption was used to monitor the porosities and BET surface areas of the synthesized carbon foams. The instrument with which all measurements were performed was a Micromeritics ASAP 2020 analyzer. The sample mass was kept between 0.1-0.3 g and all samples were degassed prior to analysis by heating under vacuum (250 ℃, 4 h). The analysis itself took place at 77 K.

### 4.5 Thermogravimetric analysis

In a thermogravimetric analysis (TGA) measurement, a sample is heated (often at a constant rate) in a chosen atmosphere and its mass loss is recorded as a function of temperature. TGA is hence a useful technique when it comes to deducing the kinetics of pyrolysis, the thermal stability of a sample in different types of atmosphere and can even be used to get insights regarding the degree of sample purity.

The instrument used in this work was a DQ500 apparatus. Prior to the analysis, all samples were pulverized and between 2-3 mg of each sample were evenly distributed in an alumina crucible. The sample was then loaded in the instrument and let to equilibrate for 10-15 minutes, until a steady value of its mass would be recorded. The measurements themselves took place in an air atmosphere, at a heating ramp of 5 ℃ min⁻¹ and had 800 ℃ as their maximum target temperature.
4.6 Electrochemical characterization

4.6.1 Chronopotentiometry
A commonly used technique to study an electrochemical cell is to apply a controlled current between the working and counter/auxiliary electrodes and track the potential between the working and reference electrodes. This is normally done within a determined potential window. Several important system parameters can be deduced from chronopotentiometric measurements including the reaction potentials, active material capacities, rate capability and cyclability.

The electrode capacity can be theoretically calculated, or experimentally obtained by making use of Faraday’s law:

$$Q_{\text{grav}} = \frac{It}{m} = \frac{nF}{M}$$

Here, $I$ stands for the applied current, $t$ for the time passed, $m$ for the mass of the active material, $M$ for its molar mass, $n$ for the number of moles of charge carriers passed and $F$ is the Faraday constant.

Another useful concept is that of the Coulombic efficiency of cycling. The Coulombic efficiency (for a negative electrode) is given by the following relationship:

$$\text{Coulombic efficiency} = \frac{Q_{\text{charge}}}{Q_{\text{discharge}}} \times 100$$

Deviations from a Coulombic efficiency of 100% are indicators of parasitic reactions and/or irreversibility of the electrochemical reactions.

4.6.2 Cyclic voltammetry
In cyclic voltammetry (CV), the potential of the working electrode is swept at a given scan rate up to the first cut-off value; the direction of the scan is then reversed and continued until the final cutoff value is reached. The parameter being recorded is the system’s current response.

Following the current response enables the determination of reaction potentials and reaction reversibility and at the same time provides valuable information regarding electron transfer and mass transfer kinetics. That said, measuring the CV of an electrochemical system is probably one of the best ways to identify its mechanistic aspects.

In this study, the cycling equipment used in order to perform CV was a Biologic MPG2 and a Biologic VMP2. After the identification of appropriate
cut-off potentials for the systems considered had taken place, the cells were cycled between these at the low scan rates of 0.050 mV s⁻¹.

4.7 Electrode and cell preparation

4.7.1 Carbon foams for 3D microbatteries
Monolithic pieces of the graphitic carbon foams were cut down to suitable dimensions and polished to a thickness between 200-300 µm. The foams were sonicated in water and ethanol in order to remove any debris from the inside of their structure. That was followed by a drying step (120 °C, overnight) in a Büchi oven inside an Ar-filled glove box. The carbon foams were tested in half-cell format, using glassfiber as the separator, 1 M LiPF6 in a 1:1 (v/v) solution of EC:DEC as the electrolyte and metallic Li as both the reference and counter electrode. Cu-based current collectors were used on both sides and all of the electrochemical cell components were vacuum-sealed in a pouch cell.

4.7.2 Carbon cathodes for dual-ion batteries
Electrode coatings were prepared by mixing 1.2 g of KS6 graphite (90 %) with Super P carbon additive (6 %) and sodium carboxymethyl cellulose (CMC) binder (4 %). 3 mL of a 10:1 (v/v) water: ethanol solution were added and the mixture was transferred to a vortex. The rotational speed was gradually increased to 4000 rpm over 30 min. The resulting slurry was applied on a carbon-coated Al-foil with a 100 µm applicator. Once dry, electrodes with a 13 mm diameter were punched out and transferred to an Ar-filled glove box, where they were dried overnight at 120 °C.

Most of the electrochemical testing took place in half-cells with a glassfiber separator, Li counter electrode, Cu (negative) and Al (positive) current collectors. The tested electrolyte compositions are summarized in Table 1.

<table>
<thead>
<tr>
<th>Salt</th>
<th>Concentration</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiPF6</td>
<td>1 M</td>
<td>1:1 (v/v) EC:DEC</td>
</tr>
<tr>
<td>LiPF6</td>
<td>4 M</td>
<td>1:1 (v/v) EC:DEC</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>1 M</td>
<td>1:1 (v/v) EC:DEC</td>
</tr>
<tr>
<td>LiTFSI</td>
<td>4 M</td>
<td>1:1 (v/v) EC:DEC</td>
</tr>
<tr>
<td>LiFSI</td>
<td>1 M</td>
<td>1:1 (v/v) EC:DEC</td>
</tr>
<tr>
<td>LiFSI</td>
<td>4 M</td>
<td>1:1 (v/v) EC:DEC</td>
</tr>
</tbody>
</table>
5. Results and discussion

5.1 Graphitic carbon foams in 3D microbatteries

This section summarizes the results concerned with the degree of graphitization and electrochemical performance of the emulsion-derived carbon foams. More specifically, the effects of heat treatment and catalytic graphitization are discussed.

5.1.1 Graphitization through heat-treatment

The first attempts to graphitize the emulsion-templated carbon foams involved several heat-treatments. Three temperatures were tested: 1000 °C, 1500 °C and 2200 °C [56]. The heat-treatment was found to have a profound impact on the structural evolution and electrochemical performance of the carbon foam.

The carbon foams became increasingly more graphitic as a function of the temperature. The sample heat-treated at 2200 °C exhibited a sharp diffraction peak (at 26.0°), indicative of the formation of turbostratically-disordered graphitic domains. The Raman spectra of this sample exhibited a well-defined defect mode (D) at 1344 cm\(^{-1}\) and a graphitic mode (G) at 1587 cm\(^{-1}\). Additionally, the second order scattering bands were visible for the 2200 °C sample. The intensity ratio between the D and G bands kept on decreasing as a function of temperature, which implies that the amount of sp\(^2\)-bonded carbon increased. A visual confirmation was provided through TEM imaging of the heat-treated samples. In contrast to the samples heated to lower temperatures, the 2200°C sample exhibited proper fringes, reflecting the existence of consecutive graphitic layers.

The enhancement of the electrochemical performance after extensive heat-treatment could be observed through cyclic voltammetry. The carbon foams heat-treated to 1000 °C and 1500 °C exhibited broad peaks upon the first reduction, indicative of surface-confined reactions (Figure 6a). Most of these peaks lacked an equivalent upon oxidation, which further supports the theory of these representing irreversible surface reactions. On the other hand, the carbon foam graphitized at 2200 °C exhibited significantly more well-defined redox peaks and an improved initial coulombic efficiency (75 % instead of the previously observed 40 %, see Figure 6b and 6c). In addition, the graphitized foams delivered decent capacities even at higher rate capabilities (Figure 6d). Overall, these results suggest that the carbon foam heated to 2200 °C is better suited as a negative electrode for 3D microbatteries than its less graphitized counterparts are.
Nevertheless, even the carbon foam heat-treated at 2200 °C exhibited much lower specific capacities than commercial graphite (350-370 mAh g⁻¹), as seen in Figure 6c. The fact that the capacity was lower than expected was attributed to the turbostratic nature of the formed graphite. Efforts to further graphitize the carbon foams through other strategies are described in the upcoming section.
5.1.2 Catalytic graphitization

Catalytic graphitization was subsequently attempted, in order to enhance the graphitic content of the carbon foams. In this case, the CaCl₂ and MgCl₂ salts which were initially added to stabilize the HIPE were kept inside the carbon foam structure throughout the entire synthesis. The catalytically graphitized foams (henceforth referred to as carboHIPE-Mg, carboHIPE-Ca and carboHIPE) were probed using XPS, Raman spectroscopy and XRD. The physicochemical characterization revealed an increased degree of crystallinity and long-range order for carboHIPE-Mg and carboHIPE-Ca.

Conclusive evidence for the increase in graphitization is provided by XRD (Figure 7c). The broad peak located between 20-30° (denoted as A-component) decreases in intensity for the catalytically graphitized samples. This implies a decreased content of amorphous carbon and nanocrystalline graphite. Furthermore, the growth of the G-component of the 002 peak (at 26.6°) is observed, which occurs at the expense of the T-component (at 26.0°). The T-component corresponds to turbostratically-disordered graphite, while the G-component indicates long-range graphitic stacking. The Raman spectra of the foams (Figure 7b) suggest that carboHIPE-Ca is the most graphitized, since it exhibits the lowest Ip/Ig ratio. The extracted Ip/Ig ratios are 1.53, 1.22 and 1.52 for carboHIPE-Mg, carboHIPE-Ca and carboHIPE, respectively. Surface characterization using XPS (Figure 7a) reveals that the catalytically graphitized foams are more oxidized than the carboHIPE sample. This is evidenced in the form of an increased amount of -C-OH/-C-O- and -O-CO₂/-OOCO₂- surface functionalities. An explanation to this phenomenon is that more extensive sulfonation has occurred for these samples. This was indeed observed after the sulfonation step, as carboHIPE-Ca and carboHIPE-Mg turned into a darker brown nuance than carboHIPE.

![Figure 7](image_url)

Figure 7: In (a), the C 1s photoelectron spectra of carboHIPE (bottom), carboHIPE-Ca (middle) and carboHIPE-Mg (top). The corresponding Raman spectra and X-ray diffractograms are shown in (b) and (c), respectively.
The XRD patterns and Raman spectra received further support from TEM imaging. In the micrographs of carboHIPE (Figure 8a), only amorphous and turbostratically-disordered regions are present. The turbostratically-disordered domains do not exceed more than 5-10 consecutive graphene layers, which exhibit extensive curvature and structural defects. The case of carboHIPE-Mg (Figure 8b) and carboHIPE-Ca (Figure 8c) differs, as ribbons or shells of well-ordered graphitic layers (G-component) can be discerned in these micrographs. The G-component appears to have evolved around the salt seed particle, which can be seen in some of the transmission electron micrographs and which was further confirmed with the aid of electron energy loss spectroscopy (EELS).

Figure 8: In (a), scanning (top) and transmission (bottom) electron micrographs for carboHIPE. The corresponding micrographs for carboHIPE-Mg and carboHIPE-Ca are provided in (b) and (c).
The graphitization mechanism most likely proceeds through the intermediary carbide species CaC$_2$, which reacts with the N$_2$ atmosphere to form gaseous cyanamide and free carbon (reaction formulas 1-5).

$$\text{CaCl}_2\text{(aq)} + \text{H}_2\text{SO}_4\text{(aq)} \rightarrow \text{CaSO}_4\text{(s)} + 2\text{HCl\text{(aq)}}$$ \hspace{1cm} (1)

$$\text{CaSO}_4\text{(s)} + 2\text{C\text{(s)}} \leftrightarrow \text{CaS\text{(s)}} + 2\text{CO}_2\text{(g)}$$ \hspace{1cm} (2)

$$2\text{CaS\text{(s)}} + 5\text{C\text{(s)}} \leftrightarrow 2\text{CaC}_2\text{(s)} + \text{CS}_2\text{(g)}$$ \hspace{1cm} (3)

$$\text{CaC}_2\text{(s)} + \text{N}_2\text{(g)} \rightarrow \text{Ca(\text{CN})}_2\text{(s)}$$ \hspace{1cm} (4)

$$\text{Ca(\text{CN})}_2\text{(s)} \rightarrow \text{CaCN}_2\text{(g)} + \text{C\text{(s)}}$$ \hspace{1cm} (5)

Since the aim of this study was not merely graphitizing the foams, but also ensuring the preservation of their porosity, morphological studies were required. SEM revealed that carboHIPE-Mg and carboHIPE-Ca maintained a hierarchical porous structure with open voids in the microscale range (Figure 8). This design enables good electrolyte infiltration in the electrode and thereby accessibility to the active material. N$_2$ gas-sorption measurements resulted in BET specific surface areas of 9.5, 7.6 and 11.9 m$^2$g$^{-1}$ for carboHIPE, carboHIPE-Ca and carboHIPE-Mg, respectively. In conclusion, the catalysts did not significantly alter the foam morphology and porosity.

The electrochemical properties of the foams were probed through cyclic voltammetry and galvanostatic cycling (Figure 9).

![Figure 9](image-url)

Figure 9: In (a), first CV cycle for all carboHIPEs, acquired at a scan rate of 0.050 mV s$^{-1}$. In (b), potential-capacity curves for the first (solid) and fifteenth cycle (dashed) and in (c) galvanostatic cycling at a current density of 10 mA g$^{-1}$. A comparison of the electrochemical performance in this work to other literature examples is provided in (d).
The increase in graphitic content for the catalytically graphitized foams is confirmed by the appearance of separate redox peaks in the CVs (Figure 10a). This is especially true for carboHIPE-Ca, for which a staging behavior is observed during Li\(^+\) intercalation. Initial coulombic efficiencies amount to 67\% for carboHIPE-Mg and carboHIPE-Ca and to 77\% for carboHIPE (Figure 10b). The explanation behind this goes back to the XPS analysis of these samples and the increased amount of surface termination groups for carboHIPE-Mg and carboHIPE-Ca. These groups tend to react irreversibly upon the first formation cycle to give rise to the solid electrolyte interphase (SEI) layer; hence the lower coulombic efficiency. The more extensive formation of the SEI layer for carboHIPE-Mg and carboHIPE-Ca is also observed in the CV, where it is represented by the reduction peak at 0.6-1.0 V vs Li\(^+\)/Li\(^0\). The formed SEI appears to be nonetheless stable and the coulombic efficiency increases to 100\% upon subsequent cycling.

During galvanostatic cycling at a current density of 10 mA g\(^{-1}\) (Figure 10b-c), carboHIPE displays a reversible gravimetric capacity of 105 mAh g\(^{-1}\), whereas carboHIPE-Ca and carboHIPE-Mg reach 140 and 130 mAh g\(^{-1}\), respectively. This amounts to a ca. 33\% increase of the reversible gravimetric capacity. Still, it is noteworthy that the obtained capacities in this work are much lower than for commercial graphite electrodes. The underlying reason behind this is likely that part of the bulk of the carbon foams is not accessible to the electrolyte. Similar reports have been made in the literature. Nevertheless, the graphitic 3D foams perform well both in terms of capacity and rate capability when compared to similar alternatives from the literature (Figure 10d). Figure 9d highlights the difficulties associated with devising 3D carbonaceous electrodes with the full lithiation capacity of graphite and underlines the importance of developing new strategies to achieve this.
5.2 Graphite positive electrodes for dual-ion batteries

This chapter summarizes the efforts conducted in order to stabilize the interphase between the electrolyte and the graphite cathode for DIBs. This has so far included the identification of suitable electrolytes, investigations related to the exfoliation of the graphitic cathode upon cycling and studies of the surface films formed on the positive electrode. The ultimate goal is that this study will be extended to the testing of the graphitic carbon foams as potential positive electrodes for DIBs.

5.2.1 Impact of electrolyte composition on the cycling efficiency of the graphite cathode

The influence of the electrolyte composition upon the cycling performance of the KS6 graphite positive electrode was investigated, to establish a functional system. The chosen solvent in this case is a 1:1 (v/v) mixture of EC:DEC, which is already a well established alternative for the negative electrode. The anion type and concentration was however varied; and systems including the PF₆⁻, FSI and TFSI anions at concentrations of 1 M, 2 M and 4 M were investigated.

An overview of the electrochemical behavior in these systems is provided in Figure 10. The obtained results indicate that all three anions can be intercalated in the KS6 cathode; the intercalation of the FSI and TFSI anions nevertheless seems to be reversible to a larger extent than that of PF₆⁻. By looking at the CVs related to LiFSI and LiTFSI, it may be deduced that the higher the concentration of these anions, the more stable and reversible the electrochemical performance of the KS6 graphite. While intercalation from 1 M solutions of LiFSI and LiTFSI results in high, oxidative currents with no corresponding reduction reaction, the 2 M and 4 M solutions exhibit well defined, reversible redox peaks. The large oxidative currents produced in the electrolytes with low salt concentrations may originate from a combination of the following processes: oxidative electrolyte decomposition, graphite exfoliation and/or corrosion of the Al current collector [57-60]. All of these phenomena could be caused by an excessive amount of uncoordinated solvent [61-63]. It could be speculated that uncoordinated solvent molecules can co-intercalate in the positive electrode and also facilitate the dissolution of Al³⁺ from the Al current collector [64].
Figure 10: CVs recorded at a scan rate of 0.050 mV s\(^{-1}\) showing the performance of a KS6 graphite cathode in LiPF\(_6\) (a), LiFSI (b) and LiTFSI based electrolytes (c). In (d), galvanostatic cycling (at 10 mA g\(^{-1}\)) in half-cells with 1 M LiPF\(_6\) in EC:DEC (LP40) reference electrolyte and 4 M LiFSI/4 M LiTFSI based electrolytes. The solid line represents the 1\(^{st}\) cycle and the dotted the 10\(^{th}\). In (e), extended galvanostatic cycling of the very same systems and in (f) initial trials on cycling full cells with LTO as the negative electrode.

Increasing the electrolyte concentration from 2 M to 4 M leads to distinct features for the LiFSI and LiTFSI based electrolytes. The potential stability window appears to have increased for the Al current collector and possibly for other electrolyte components as well, since the high oxidative current observed for the 1 M concentrations has now given way to well-defined redox peaks. At the same time, reaction overpotentials for what seems to be a staging
mechanism for anionic intercalation are decreased. Interestingly, cycling the graphite with the TFSI anion gives better reversibility and an overall more stable electrochemical performance than FSI, despite its larger size. This is further confirmed by galvanostatic cycling of the samples, where cycling in the LiTFSI-based electrolyte results in a stable gravimetric capacity of approximately 100 mAh g⁻¹. While the LiFSI analogue displays initial capacities of similar magnitude, it suffers from larger polarization and irreversibility.

Stability tests performed on the pure Al current collectors (Figure 11a-c) confirm the benefit of using highly concentrated electrolytes for the targeted application. The only electrolytes with the ability to passivate the Al surface within a potential window of 3.0-5.2 V vs Li⁺/ Li⁰ were the ones based on LiPF₆ or the sufficiently concentrated ones (4 M LiFSI/ LiTFSI).

![Graph showing CV test results](image)

**Figure 11:** CV test of the oxidative stability of the Al current collector in EC:DEC based electrolytes containing different salts (a: LiPF₆, b: LiFSI and c: LiTFSI) and varying salt concentrations (1-4 M). The solid and dotted lines correspond to the first and third oxidation, respectively. Note the difference in the scale of the y-axis. In (d), photograph of Al current collectors cycled in 1 M LiFSI/ LiTFSI and 4 M LiFSI/LiTFSI, showing the occurrence of extensive corrosion in the electrolytes with low salt concentration.
5.2.2 Surface studies on cathodes and current collectors

Morphological study
The surface study of the graphitic cathode and Al current collectors commenced by a morphological investigation, aided by SEM (see Figure 12).

Figure 12: On the two upper rows, SEMs revealing the Al current collector morphology after 4 cycles in LP40, 1 and 4 M LiFSI in EC:DEC, as well as 1 and 4 M LiTFSI in EC:DEC. An image of the pristine current collector is provided for comparison. In the third row, micrographs of KS6 cycled in LP40, 4 M LiFSI in EC:DEC and 4 M LiTFSI in EC:DEC are supplied for the 1st and 10th charge (5.1 V vs Li+/Li0).

The main finding is that the Al current collectors cycled in LP40, as well as those cycled in the concentrated, 4 M LiFSI or LiTFSI based electrolytes exhibit a smooth surface morphology, similar to that of the pristine Al foil after disassembly. On the contrary, cycling in the 1 M LiFSI/ LiTFSI based electrolytes results in the formation of corrosion pits. It can therefore be speculated that electrolytes with a high fluorine content and with a small amount of uncoordinated molecules can stabilize the Al current collector. This could be achieved by surface passivation or by suppression of Al3+ dissolution thanks to the high viscosity of the concentrated electrolytes and scarcity of uncoordinated EC and DEC molecules. The surface of the cycled KS6 graphite exhibits additional differences depending on the choice of electrolyte. SEM micrographs of electrodes cycled in the more stable systems (4 M LiFSI in EC: DEC and 4 M LiTFSI in EC:DEC as well as in LP40) are presented in the last row of Figure 12 for the 1st and 10th charge (5.1 V vs Li+/Li0). The most striking difference is that a dense layer of decomposition products covers the surface of the electrodes cycled in LP40. This could correspond to LiF, along with
polymerized solvent products. Cycling in the 4 M LiFSI/LiTFSI electrolytes does not drastically alter the graphite surface, which remains similar to the pristine particles. This indicates a decrease in electrolyte decomposition and/or the formation of soluble decomposition products. The graphite electrodes cycled in these electrolytes appear to be partially exfoliated; it is however difficult to say how much the cycling has contributed to this, since also the pristine KS6 particles exhibit a similar morphology.

**XPS on cycled KS6 electrodes**
An understanding of the chemical composition of the cathode electrolyte interphase (CEI) was achieved through XPS measurements on the cycled electrodes. Through initial comparison of the C 1s spectra, it becomes evident that the surface of the electrodes cycled in LP40 is covered with a dense layer of decomposition products. The CEI formed in this case appears to be dominated by -C-H (284.8 eV), -C-O- (286.0 eV) and -O-C-O- / >C=O functionalities (287.0-288.0 eV), while a broad peak close to the -CO2-/O-CO2- binding energy (289.0-290.0 eV) is also visible. The -O-C-O- / >C=O signals are believed to originate mainly from adsorbed EC and DEC molecules as well as from their decomposition products. EC is inherently unstable at these high potentials [64] and prone to ring opening and dimerization resulting in the formation of various alkyl carbonates, e.g. (CH2OCO2Li)2 [65, 66]. In combination with the PF6- anion, the oxidative stability of EC is predicted to decrease further [67]. The low intensity peak at 289.0-290.0 eV is partly due to the carboxymethyl moiety from the CMC binder. However, CMC accounts only for 4 wt % of the electrode, so the buildup of additional decomposition products containing -CO2-/O-CO2- is likely.

![C 1s spectra of the KS6 electrodes cycled in half-cells with the LP40 reference electrolyte, 4 M LiFSI in EC:DEC and 4 M LiTFSI in EC:DEC.](image)

Figure 13: C 1s spectra of the KS6 electrodes cycled in half-cells with the LP40 reference electrolyte, 4 M LiFSI in EC:DEC and 4 M LiTFSI in EC:DEC.
The C 1s spectra of the electrodes cycled in the 4 M LiFSI and 4 M LiTFSI in EC:DEC show far less decomposition products in comparison to the reference electrolyte. Two exceptions to this are the spectra of the first discharge for the 4 M LiFSI and the second charge for the 4 M LiFSI system; however, these are considered outliers originating from faulty cell design. The existing decomposition products for these two systems are principally of the same nature as for LP40. The additional peak appearing at approximately 292.0 eV for the 4 M LiTFSI system is attributed to the -CF₃ moiety belonging to the TFSI anion. Since this appears at a bit lower binding energy than expected, it is possible that partial decomposition to -(CF₂)- has occurred for this functional group.

Further insights into the nature of the CEI for the different systems were provided by the Li 1s and F 1s spectra. A most interesting finding was that Li could be observed on the electrodes cycled in LP40 (around 56.8 eV), indicating the presence of LiF. The beneficial impact of LiF on the stabilization of the negative electrode interphase is well known, which renders LiPF₆ at least interesting as an additive for all-carbon DIBs. No corresponding component was present in the samples cycled in 4 M LiFSI and 4 M LiTFSI in EC:DEC, as may be seen in Figure 14.

![Li 1s spectra of the KS6 electrodes cycled in half-cells with the LP40 reference electrolyte, 4 M LiFSI in EC:DEC and 4 M LiTFSI in EC:DEC.](image-url)

Figure 14: Li 1s spectra of the KS6 electrodes cycled in half-cells with the LP40 reference electrolyte, 4 M LiFSI in EC:DEC and 4 M LiTFSI in EC:DEC.
The absence of the inorganic LiF layer does not imply that the salt does not partially decompose in the cases of the LiFSI and LiTFSI systems. Initial fitting of the F 1s, N 1s and S 2p spectra indicate that other decomposition mechanisms may be at play. The broad F 1s spectra of the LP40 electrolyte suggests the presence of PF$_6^-$ along with LiF and possibly other salt decomposition products denoted with the general formula Li$_x$PF$_y$O$_z$. The F 1s spectra of the 4 M LiTFSI system can be fitted with a single (although somewhat broad) peak indicating that the -CF$_3$ functionality remains intact for the most part. In contrast, the F 1s spectra for the 4 M LiFSI system present significant chemical shifts for fluorine. This is a strong indication of a partial breakdown of the S-F bond during cycling. The exact nature of the products formed is not known and further investigations are necessary to shed light upon it. Nevertheless, the relative intensities between the F 1s components stay constant upon continued cycling. This could mean that the decomposition stops after the initial formation cycles, but it is difficult to draw definite conclusions as the decomposition product could very well solubilize.

Figure 15: F 1s spectra of the KS6 electrodes cycled in half-cells with the LP40 reference electrolyte, 4 M LiFSI in EC:DEC and 4 M LiTFSI in EC:DEC.
Finally, another interesting phenomenon is observed for the N 1s and S 2p peaks of the 4 M LiFSI and 4 M LiTFSI systems in EC:DEC (Figures 16 and 17). Unlike what could be expected from the molecular structure of FSI and TFSI, it appears that there are at least two distinct chemical environments for both N (at 398.0 and 400.5 eV) and S (at 166.8 and 168.2 eV). This could be indicative of the N-S bond breakdown in both FSI and TFSI. Another notable point is that the relative intensity of the N 1s components varies depending on state-of-charge of the electrodes. A similar trend is observed for S 2p, which components seem to be broader upon charge. While this could mean that the decomposition takes place mainly at a certain potential with the reaction product solubilizing and diffusing away in the subsequent steps, it is also possible that these distinct peaks represent the surface and bulk anion species (intercalated). More studies of both experimental and theoretical character are currently ongoing in order to understand this phenomenon.

Figure 16: N 1s spectra of the KS6 electrodes cycled in half-cells with 4 M LiFSI in EC:DEC and 4 M LiTFSI in EC:DEC electrolytes.
Figure 17: S 2p spectra of the KS6 electrodes cycled in half-cells with 4 M LiFSI in EC:DEC and 4 M LiTFSI in EC:DEC electrolytes.

In summary, the XPS studies showed that the 4 M LiTFSI in EC:DEC is a most promising electrolyte composition for the potential window of interest. This is motivated by the occurrence of minimal solvent degradation and the fact that the TFSI anion appeared to stay intact, apart from the possible breakdown of the -CF$_3$ group. Moreover, the XPS underlines the importance of using highly concentrated electrolytes in order to avoid solvent degradation. Finally, the LiPF$_6$ salt was identified as a former of a LiF-rich CEI layer. This could lead to efficient interphase passivation and positively influence the cycling performance, which makes LiPF$_6$ at least interesting as an additive in future studies.
5.2.3 Following the exfoliation of graphite through Raman

Lastly, some preliminary results regarding the changes in the Raman spectra of KS6 graphite during cycling are discussed. As previously mentioned, Raman is a powerful tool for probing changes in important properties of the graphite such as the defect density, degree of graphitization and exfoliation. In this case, graphitic electrodes were studied both ex-situ (on cycled KS6 electrodes) and in-operando (using a freestanding graphite foil from Goodfellow). Nevertheless, in order to establish a baseline, measurements on the pristine EC:DEC solvent are presented firstly, followed by measurements on the ready-mixed electrolytes with the different salt concentrations (see Figure 18).

![Figure 18: Raman spectra of the pure EC:DEC (black) and of the PF$_6^-$ (green), FSI (orange) and TFSI-based (blue) electrolytes at varying molarities.](image.png)

These measurements indicate that several of the Raman active modes in the pure EC:DEC solvent are affected by the increasing salt content. Specifically, the band at 711 cm$^{-1}$ splits, with a new band becoming visible at 740 cm$^{-1}$. A similar phenomenon is observed for the band at 893 cm$^{-1}$, with a new mode showing up at 903 cm$^{-1}$. This effect could potentially be ascribed to the coordination of the solvent molecules around Li$^+$ [68].

In continuation, Raman spectra of the cycled KS6 electrodes were collected ex-situ (Figure 19).
Figure 19: From left to right, ex-situ Raman spectra of KS6 electrodes cycled against Li in LP40, in 4 M LiFSI in EC:DEC and in 4 M LiTFSI in EC:DEC. The charged state corresponds to 5.1 V vs Li⁺/Li⁰ and the discharged to 3.0 V vs Li⁺/Li⁰. Four spectra were collected at different points on every electrode.

Since these electrodes were composite, including a carbon black additive and a CMC binder, care was taken during the measurements so that the spectral acquisitions were performed on the KS6 particles. Even so, variations could be observed depending on the acquisition spot, indicating that the anionation was not completely homogeneous throughout the electrode. To have some statistics, four spectra were collected per electrode.

A general trend observed was that the D-band of graphite increased upon anionation, as well as the D’-band. This was noticeable for all samples and is most likely due to the stress that the large-sized anions induce in the graphitic structure upon intercalation. Even though it may be difficult to say something conclusive due to the nature of these measurements, it appears that (i) this structural change is partially irreversible and (ii) that not all anions are causing exfoliation and structural disorder to the same extent. Regarding the latter statement, it appears that the FSI anion causes the least significant alterations to the graphitic structure. This could be explained be its small size and nearly linear shape. The most substantial changes are observed in the case of the TFSI anion, which can in the same way be explained by the large anionic size and complex geometry.

Preliminary operando Raman measurements have been performed so far on a graphitic carbon foil from Goodfellow. Here, two extreme cases are supplied for comparison, the first being 1 M LiTFSI in EC:DEC and the second 4 M LiFSI in EC:DEC (Figure 20).
Figure 20: Operando Raman spectra from a Goodfellow graphite cathode cycled with potential step in 1 M LiTFSI in EC: DEC (a) and in 4 M LiFSI in EC:DEC (b). In (c), photograph of the pristine and anionated graphite foil is presented, where the blue-shift of graphite can be seen.

By looking at the measurements on the 1 M LiTFSI in EC:DEC, a significant increase in the D and D’ bands can be observed. At the same time, the shape of the 2D band is altered. A change of similar magnitude is not observed for the 4 M LiFSI in EC:DEC electrolyte. The underlying reasons behind that could be many. Firstly, it is possible that the 1 M LiTFSI in EC:DEC electrolyte leads to more extensive exfoliation of the graphitic electrode, due to both solvent co-intercalation [69] and the larger anion size [70, 71]. Secondly, since Raman spectroscopy is surface sensitive, the shifts observed in the 1 M LiTFSI could have their origin in the formation of carbon-containing decomposition products on top of the positive electrode. The breakdown of EC could potentially lead to decomposition products rich in double-bonded carbon, which would, in its turn make the interpretation of the Raman spectra challenging. Another possibility is that the wettability of the graphitic foil is poor in the concentrated electrolyte. The foil consists of flat, compact flakes, which could prevent the efficient impregnation of the electrode with the viscous electrolyte. Ideally, these measurements should be performed with the KS6 graphite, which has already exhibited a well-defined electrochemical behavior together with the investigated electrolytes. Nevertheless, all attempts to do so failed so far due to electrode swelling [72] and due to the detection of a strong fluorescent signal at higher potentials. Lastly, it is also possible that this is a matter of the chosen acquisition spot on the sample. As already observed from
the ex-situ measurements, uniform anionation is not guaranteed across the electrode.

Despite the difficult nature of the operando measurements, getting a grasp of the graphite’s behavior in real time could offer useful insights and facilitate the selection of suitable electrolyte systems for all-carbon DIBs. For that reason, the work on operando Raman will continue, after re-considering suitable graphitic substrate materials.
6. Concluding remarks and outlook

In this thesis, it is demonstrated that heat-treatment at 2200 °C can be employed to effectively graphitize emulsion–derived carbon foams for applications within 3D microbatteries. Increasing the temperature from 1000-2200 °C altered the structure of the carbon foam from an amorphous state to turbostratically-disordered graphite. The appearance of these nanographic domains, in combination with the significant decrease in surface area and the elimination of surface terminations, resulted in the enhancement of the reversible capacity. The initially achieved Coulombic efficiency amounted to 75 % for the carbon foam heat-treated at the highest temperature (2200 °C), which is a clear improvement compared to the 40 % obtained for the carbon foam heated to 1000 °C.

In order to further graphitize the carbon foams, catalytic amounts of Ca- and Mg-based salts were used. The reason why this method was chosen is that these salts (CaCl₂ and MgCl₂) were anyway present in the carbon foams since the initial synthesis steps, where they acted as emulsion stabilizers. The graphitizing salts, combined with heat-treatment at 2200 °C resulted in the growth of substantially larger, ordered graphitic domains. This was confirmed through an increased I₆/I₅ intensity ratio in Raman spectroscopy, the growth of an extra 002 component in the XRD pattern and through TEM imaging. The more graphitic nature of these samples is attributed to a reaction mechanism which results in the formation of free carbon, with the possibility to form the most thermodynamically stable and stress-free structure. Even though the degree of graphitization could not be established in a reliable way in this study, the impact of the catalytic graphitization was clearly manifested in the electrochemistry as in increase in gravimetric capacity (reaching a new maximum of 140 mAh g⁻¹) and through the appearance of a staging behavior for the Li⁺-intercalation. Considering that the capacity of commercial graphite reaches 350-372 mAh g⁻¹, there is still plenty of room for improving the electrochemical performance.

In the latter part of this thesis, the use of graphite as the positive electrode in dual-ion batteries was explored, with the ultimate goal being to use the carbon foams for that purpose. Preliminary results on model systems (KS6 graphite from Imerys and graphitic foil from Goodfellow) highlighted the usefulness of concentrated electrolytes in order to achieve a stable electrochemical performance. The 4 M LiTFSI in EC:DEC outperformed other electrolyte compositions tested in terms of the stability window (~5.2 V vs Li/Li⁺), gravimetric capacity (100 mAh g⁻¹) and Coulombic efficiency (~92 %). Electrochemical and spectroscopic evidence indicates that concentrated electrolytes improve the cell performance by suppressing the exfoliation of the positive
graphite electrode and the corrosion of the Al current collector. The mechanisms by which this is achieved, as well as the reasons why the larger TFSI performs better than other anions (FSI, PF$_6^-$) are not worked out in detail and will be the subject of future research. Further insights into this will require the combined use of experimental and theoretical structural studies.

Apart from figuring out the mechanistic aspects of this result, the work ahead will naturally encompass the testing of the graphitized carbon foams as the positive electrode. Since the carbon foam is not fully graphitized, it will be interesting to see whether it will still be capable of reversible anionic intercalation. Lastly, future studies will focus on evaluating the electrochemical performance in full cells, using graphitic electrodes as both the positive and negative electrodes.


En tillämpning där kolbaserade elektrodmaterial har blivit synnerligt uppskattade är inom tredimensionella (3D) mikrobatterier. Mikrobatterier är, som namnet antyder, väldigt små batterier vars volym varierar mellan 1 och 5 mm³. Denna typ av batterier används för att energiförsörja miniatyriserade enheter som exempelvis sensorer, pacemakers och hörapparater. I detta fall är det volymrestriktionerna som ställer hårdar krav på framtagandet av elektrodarkitekturer som ska möjliggöra både hög energi- och effekttäthet. Optimala 3D-arkitekturer kan erbjuda just detta genom nanostrukturerade material.
med stora ytareor och betydande porositet som minimerar jontransportsträckan mellan den negativa och positiva elektroden.

I denna licentiatavhandling nyttjas först porösa, kolbaserade material som negativa elektroder för energilagring i 3D-mikrobatterier. Det porösa koler har framställts från en styrenbaserad emulsion. Denna framställningsmetod är attraktiv ur ett uppskalningsperspektiv och ger även god kontroll över yta- rean och porositeten. En mindre önskvärd effekt som blir tydlig efter pyrolys är att de resulterande kolmaterialen har svårt att anta en grafitisk struktur. Som diskuterat ovan behövs den grafitiska strukturen för att reversibla kapaciteter ska uppnås. Första delen av licentiatavhandlingen undersöker därför strategier för att höja den grafitiska halten hos dessa porösa kol och därmed öka deras potentiella värde som elektroder för 3D-mikrobatterier. Som ett första alternativ för att grafitisera de porösa kolen användes värmebehandling. Värmebehandling resulterade i avsevärt mer grafitiska kolmaterial och i samband med detta en förbättrad elektrokemisk prestanda (en reversibel kapacitet på 100 mAh g⁻¹ kunde uppnås). Försök till att vidare utöka den grafitiska halten genomfördes med hjälp av Ca- och Mg-baserade salter, vilka är kända för att gynna grafitisk tillväxt. Även denna strategi hade ett positivt utfall, då större och mer välordnade grafitiska domäner kunde observeras. Den elektrokemiska responsen innebar ytterligare en ökning i kolets reversibla kapacitet, vilken nådde 140 mAh g⁻¹. Framtida försök att öka den elektrokemiska pre- standan kommer istället fokusera på en ändring av syntesen i tidigare skeden, så att prekur sor användes i detta sammanhang utforskar möjligheten att istället använda de porösa grafitiska kolen som den positiva elektroden. Då den sotens system är förhållandevis nya utfördes en förstudie på mer ideala, välgra- fitiserade elektroder för att välja ut en kompatibel elektrolyt och strömsamlare. Detta är ingen försumbar uppgift i sig, då anjonisk interkalation i grafit sker vid väldigt höga potentialer (4.6 V vs Li⁺/Li⁰), där många material inte längre är kemiskt stabila. Till exempel är det vanligt att strömsamlaren korroderer vid dessa potentialer, samt att elektrolyten bryts ner. Denna förstudie identifi- erade en elektrolytsammansättning (4 M LiTFSI i EC:DEC) som verkar kunna leverera reversibla, stabila kapaciteter på 100 mAh g⁻¹. Preliminära resultat indikerar att denna elektrolyt förbättrar den elektrokemiska prestandan då den är mindre aggressiv mot strömsamlaren, samt att den inte leder till exfoliering av den grafitiska elektroden i lika stor utsträckning som andra sammansätt- ningar. Kommande studier i detta sammanhang kommer att (1) undersöka de bakomliggande mekanismerna för detta beteende i detalj, samt (2) involvera tester med de porösa grafitiska kolen. Avslutningsvis är det önskvärt att också (3) utvärdera den elektrokemiska prestandan i helceller, med kol som elektrodmateria- ler på båda sidor av batteriet.
8. Acknowledgements

First, I would like to thank my main supervisor, Kristina Edström for giving me the opportunity to work in an inspiring research environment. Your continual encouragement and guidance has helped me a long way. To my second supervisor, Daniel Brandell, I am thankful for all the discussions, meetings and feedback regarding the manuscripts. I would also like to express my gratitude for all conferences, summer schools and courses that I had the chance to participate in so far. Last but not least, I would like to thank the technically newest addition to my supervisor team, Habtom Asfaw. I am really grateful for all scientific discussions, patient explanations and all help in the lab!

I would also like to thank all the people who helped me overcome technical obstacles and who have during my time kept the labs running, here including Henrik, Pedro, Håkan, Long and Leif. Thanks to Victoria for the introduction to SEM and to Ashok for help with XRD. Thanks to Peter and Patrik for all help related to IT-related issues.

Thanks to Le Anh for the nice and productive atmosphere in our office. I cannot imagine having finished the writing of this licentiate thesis without your “emergency box”.


I also like to take this opportunity to thank my family in Greece, Sweden and France, especially my sister and brother. Finally I would like to thank my partner Antoine for all support and for making our days together most joyful!

Sincerely,

Andoria
9. References


[55] L. Zhang et al., "Synergistic effect between lithium bis(fluorosulfonyl)imide (LiFSI) and lithium bis-oxalato borate (LiBOB) salts in LiPF6-based electrolyte for high-performance Li-ion batteries," *Electrochimica Acta*, vol. 127, pp. 39-44, 2014/05/01/ 2014, doi: https://doi.org/10.1016/j.electacta.2014.02.008.


T. Ma et al., "Revisiting the corrosion of the aluminum current collector in lithium-ion batteries," *The journal of physical chemistry letters*, vol. 8, no. 5, pp. 1072-1077, 2017.

L. Yang, B. Ravdel, and B. L. Lucht, "Electrolyte reactions with the surface of high voltage LiNi0.5Mn1.5O4 cathodes for lithium-ion batteries," *Electrochemical and Solid-State Letters*, vol. 13, no. 8, pp. A95-A97, 2010.


M. Balabajew et al., "In-Situ Raman Study of the Intercalation of Bis(trifluoromethylsulfonyl)imid Ions into Graphite inside a Dual-Ion
