Building Sustainable Batteries

Organic electrodes based on Li- and Na-benzenediacylate

ALINA OLTEAN
Abstract

As possible alternatives to the conventional inorganic Li- or Na-ion battery electrode materials, organic compounds have recently drawn considerable attention. However, major challenges such as poor electronic conductivity, solubility in battery electrolyte or fast capacity decay of the resulting electrochemical cells are some of the reasons that hold these compounds back from becoming commercial solutions in the energy system.

The goal of this thesis work was to investigate the background to these phenomena and find strategies for improvements. Two different compounds were studied: dilithium and disodium benzenediacylate, in their respective cells. First, improving the performance of the dilithium compound was performed by applying different electrode fabrication strategies. A freeze-drying technique was combined with carbon coating in the liquid state, which rendered an improved electrode morphology. Moreover, when using the compound in pouch cell format instead of Swagelok® cells, a different technique was applied: calendaring. Successful results were obtained both in half-cells and in full-cells when the compound was cycled versus LiFePO$_4$-based cathodes. Second, the sodium analogue was investigated, and while the synthesis of this compound is straightforward, the electrochemical performance in Na-ion battery cells displays an unexpected degree of complexity. The compound displays a considerably faster capacity decrease in comparison to the Li compound, and generally a poor chemical stability in the applied system. When cycled at higher currents (C-rates of C/4 or C/10, in comparison to C/40), the compound presents an capacity increase while the Li decreases, likely due to a chemical process more dependent on time than on the number of cycles for the Na compound.

The fast capacity decay in the first cycles of these types of compounds is often considered to be related to the Solid Electrolyte Interphase (SEI) layer formation. Its study was also performed and it was concluded that the Na compound has a thicker SEI layer in comparison to the Li counterpart, and mostly consisted of inorganic species such as the electrolyte salt and its decomposition products. Finally, a concept for a sustainable manufacturing and recycling process of a hybrid full cell is also performed with positive results.

Although the organic compounds cannot yet outperform the inorganic compounds used commercially in Li-ion batteries, important steps towards their employment in the energy system have been taken in this thesis work.

Keywords: Organic Electrode Materials, Li-ion Batteries, Na-ion Batteries, Calendaring, Recycling Process

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To my family
List of Papers

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


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**Disclaimer:** Part of this thesis are based on my licentiate thesis entitled: *Organic negative electrode materials for Li-ion and Na-ion batteries* (Uppsala University, 2015)
Author contribution to the papers

Paper I. I performed the development of the electrode formulation, roughly half of the electrochemical characterizations and was involved in the discussions of the results.

Paper II. I performed all the experiments, wrote the manuscript and was involved in all discussions.

Paper III. I performed the preparation of the samples and assisted at the collection of XPS data. I was involved in discussions and wrote parts of the manuscript.

Paper IV. I performed all the experiments, wrote the manuscript and was involved in all discussions.


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Abbreviations

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<th>Full Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiBs</td>
<td>Lithium-ion Batteries</td>
</tr>
<tr>
<td>TEMPO</td>
<td>2,2,6,6-tetramethyl-1-piperidinyloxyl</td>
</tr>
<tr>
<td>PTCDA</td>
<td>3,4,9,10-perylene-tetracarboxylic-dianhydride</td>
</tr>
<tr>
<td>PMDA</td>
<td>pyromellitic dianhydride</td>
</tr>
<tr>
<td>PID</td>
<td>pyrido[3,4-g]isoquinoline-5,10-dione</td>
</tr>
<tr>
<td>PAn</td>
<td>polyacrylonitrile</td>
</tr>
<tr>
<td>PDMcT</td>
<td>poly[dithio-2,5-(1,3,4-thiadiazole)]</td>
</tr>
<tr>
<td>BDA</td>
<td>benzenediacrylate</td>
</tr>
<tr>
<td>ATR</td>
<td>Attenuated total reflectance</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
</tr>
<tr>
<td>CMC</td>
<td>Sodium carboxymethyl cellulose</td>
</tr>
<tr>
<td>LFP</td>
<td>LiFePO₄</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DMC</td>
<td>Dimethyl carbonate</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulfoxide</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
</tr>
<tr>
<td>FEC</td>
<td>Fluoroethylene carbonate</td>
</tr>
<tr>
<td>FSI</td>
<td>Bis(fluorosulfonyl)imide</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared spectroscopy</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltammetry</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
</tr>
<tr>
<td>PC</td>
<td>Propylene carbonate</td>
</tr>
<tr>
<td>PVdF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
</tr>
<tr>
<td>TFSI</td>
<td>Bis-trifluoromethanesulfonimide</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrroldione</td>
</tr>
</tbody>
</table>
1. Introduction

1.1 Lithium-ion batteries

The explosive increase in small gadgets and energy based technology over the last years has been associated with a similar increase in energy consumption. The global energy consumption increased by 1% in 2016, following a 0.9% growth in 2015 and 1% in 2014, and is expected to grow by another 28% by the year 2040, with an average growth of 1.1% per year. Fuels provided from non-renewable resources such as oil, natural gas or coal account for 86% of the total world energy consumption, and for which nature has needed millions of years to produce. The rate of consumption being higher than the rate of production will most probably lead to a depletion of these resources. Moreover, the environmental impact that comes from the production and consumption of fossil fuels is also a matter of consideration. Ocean acidification, smog, ozone depletion and an increasing greenhouse effect result from the release of high amounts of carbon dioxide plus many other combustion compounds.

Taking all these issues into perspective and wanting to address a better future for the next generations, efforts have been made for quite some time to diminish the usage of such fossil resources and favor the usage of energy from other sources such as wind, solar or wave power. The energy generated from these sources is, however, intermittent and also problematic as it is highly dependent on geographical position. Being able to accumulate and store this energy when the conditions are favorable is one of the key solutions for the usage of renewable energy resources. Energy storage can be achieved in many ways, for example by storing fuels for combustion (chemical storage), pump-stored hydroelectricity (mechanical storage), and electrochemically in the form of rechargeable batteries, fuel cells or supercapacitors. One of the most widespread electrochemical energy storage devices are lithium-ion batteries (LiBs), although there are still more lead-acid batteries in circulation. The popularity of LiBs has increased since the early 1990s with the commercial success of portable electronics, and later with the hybridization and electrification of vehicles. By 2020, ~140 GWh of Li-ion batteries are expected to be required to meet the needs of consumer use; ~100 GWh being taken by electric-powered vehicles.

The first commercial Li-ion batteries were set on the market by Sony and Asahi Kasei in 1991. Ten years later they became dominant for specific ap-
plications in portable electronics, by offering the highest gravimetric and volumetric energy densities of all available rechargeable battery systems.⁶

A schematic representation of a Li-ion battery is shown in Figure 1. A Li-ion cell is composed of two electrodes: a negative electrode (anode) and a positive electrode (cathode) which are separated by a conductive medium (electrolyte) impregnated in a separator. During the discharge process, Li⁺ ions are transferred from the negative electrode through the electrolyte to the positive electrode, while the flow of electrons generated in the external circuit will create an electrical current. The charging process of the battery is based on the opposite reactions, i.e. by a flow of lithium ions from the positive electrode towards and into the structure of the negative electrode. The principal participants in the electrochemical redox processes are the negative and positive electrodes, while the electrolyte provides the medium for the lithium ions to move between them. Generally in today’s LiBs, the negative electrode is made of graphite, the positive electrode is a metal oxide or phosphate, while the electrolyte is a lithium salt dissolved in a liquid organic solvent.

Figure 1. Schematic representation of a Li-ion battery operating a car during discharge.

Already in 1979, Goodenough and co-workers⁷ reported the use of LiCoO₂ as a positive electrode material, and in 1982 Yazami and Touzain reported the first experiment demonstrating intercalation and release of lithium into and from graphite.⁸ These major discoveries were the foundation for the lithium-ion batteries as we know today.

The first cell of this type, i.e. containing transition metal oxides such as LiCoO₂ as positive electrode and polyacetylene as negative electrode was presented in a patent by Akira Yoshino in 1985. Due to their low density, stability issues of polyacetylene and limited capacity, carbonaceous materials such as graphite were investigated instead. Later, Yoshino presented such
graphite-based cells and demonstrated that they could overcome several of the problems present in the lithium-metal battery, which constituted the state-of-the-art battery chemistry at the time.9

The first commercial LiB thus contained LiCoO₂ as positive electrode, graphite as negative electrode and LP40 (LiPF₆ dissolved in a mixture of ethylene carbonate and diethyl carbonate) as electrolyte.10 Although much research had been conducted on similar chemistries before, it was – as mentioned above – Sony and Asahi Kasei that commercialized the first LiBs.

Since then, many materials have been investigated and tested in cells, either as anodes or cathodes. Also the formulation of the electrolyte has been intensively investigated. Nevertheless, today’s batteries, which are used to power portable electronics, still generally contain similar materials as in the 1990s. There is, however, extensive research going on in the development of next-generation LiB electrode materials.

On the anode side three different classes of materials have been investigated in recent years, encompassing both insertion, conversion, and alloying compounds (Table 1).11 Graphite is still one of the most used materials, exhibiting a capacity of 372 mAh g⁻¹ and a lithiation potential close to 0 V vs. Li⁺/Li. Two of the other most investigated insertion materials are TiO₂ and Li₄Ti₅O₁₂, which have good rate capabilities but are feasible only when high voltage cathodes are used due to their relatively high potential: ca. 1.55 V vs. Li⁺/Li.12 Some compounds that alloy with Li have also been investigated as anodes: Al, Sb, Si, Sn, etc. Si is by far the most investigated Li-alloy material in this context and shows good specific energy density, but the processes of alloying and dealloying is associated with large volume changes which lead to cracking and loss of electrical contact within the electrode.13

Table 1. Common anode materials, corresponding theoretical capacity and the potential at which the lithiation is performed.

<table>
<thead>
<tr>
<th>Anode materials</th>
<th>Theoretical capacity (mAh g⁻¹)</th>
<th>Lithiation potential (V vs. Li⁺/Li)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>372</td>
<td>0.125</td>
</tr>
<tr>
<td>LTO (Li₄Ti₅O₁₂)</td>
<td>175</td>
<td>1.55</td>
</tr>
<tr>
<td>Si</td>
<td>3600</td>
<td>~0.1</td>
</tr>
<tr>
<td>Sn</td>
<td>994</td>
<td>0.6</td>
</tr>
<tr>
<td>Sb</td>
<td>660</td>
<td>0.9</td>
</tr>
<tr>
<td>Al</td>
<td>993</td>
<td>0.3</td>
</tr>
</tbody>
</table>

On the cathode side (some of the compounds are presented in Table 2), similar layered oxides comparable to LiCoO₂ have been investigated as positive electrodes materials. One of them is LiNiO₂ which is isostructural with LiCoO₂, and would be beneficial in terms of cost, but its commercial use has been prevented by its intrinsic structural instability due to the presence of nickel ions in the lithium layers.14 One of the most used materials today is
LiFePO₄, which presents good rate capabilities and is comparatively inexpensive. The higher stability of phosphates as compared to oxides gives an increased safety during battery operation, which has lead to research on similar polyanionic materials such as LiFeSO₄F. Spinel materials (e.g. LiMn₂O₄) have also been investigated, but are associated with some major challenges such as dissolution of manganese in the electrolyte and subsequent reduction on the negative electrode.

Table 2. Common cathode materials, corresponding experimental capacity and their average potential.

<table>
<thead>
<tr>
<th>Cathode materials</th>
<th>Experimental capacity (mAh g⁻¹)</th>
<th>Average potential (V vs. Li⁺/Li)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCoO₂</td>
<td>148</td>
<td>3.8</td>
</tr>
<tr>
<td>LiNiO₂</td>
<td>150</td>
<td>3.8</td>
</tr>
<tr>
<td>LiMnO₂</td>
<td>140</td>
<td>3.3</td>
</tr>
<tr>
<td>LiNi₀.₃₃Mn₀.₃₃Co₀.₃₃O₂</td>
<td>160</td>
<td>3.7</td>
</tr>
<tr>
<td>Li₂MnO₃</td>
<td>180</td>
<td>3.8</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>120</td>
<td>4.1</td>
</tr>
<tr>
<td>LiFePO₄</td>
<td>160</td>
<td>3.4</td>
</tr>
<tr>
<td>LiMnPO₄</td>
<td>168</td>
<td>3.8</td>
</tr>
<tr>
<td>LiFeSO₄F</td>
<td>130</td>
<td>3.7</td>
</tr>
<tr>
<td>LiNi₀.₅Mn₁.₅O₄</td>
<td>~148</td>
<td>4.7</td>
</tr>
</tbody>
</table>

1.2 Sodium-ion batteries

The need for lithium metal in different fields of industry has increased tremendously in recent years. Some of the fields that consume the highest amount of lithium are ceramics and glasses (27%) and batteries (46%). Lithium as an element is widely distributed in the Earth’s crust, but is not considered an abundant element and has certain geographical constraints. The price of the lithium has subsequently increased steeply during the past years; for example, only from the year 2016 to 2017 it increased with more than 50 %.

Due to the strain on the lithium world resources, alternative solutions have been researched and possible replacements investigated. One of the most considered metal-ion alternatives for batteries is sodium. This element is one of the most abundant in the Earth’s crust and sodium resources are present in high concentrations in oceans. Moreover, sodium is the second lightest and smallest alkali metal after lithium, exhibiting relatively homologous behavior and similar properties. Due to its vast abundance in comparison with lithium, which has its commercial viable resources located primarily in Bolivia, Chile and Argentina, sodium is less sensitive to price variations or geopolitical issues.
Sodium battery systems are not younger than Li systems. Sodium-ion batteries were researched almost in parallel with lithium chemistries until the LiBs were commercialized. After this, the Li-based systems developed at a faster pace partly due to their higher energy density. Moreover, finding a suitable negative electrode material has shown to be a difficult issue to overcome for Na-ion batteries.

Over the past decade, Na-systems have been put under the spotlight again and started to be increasingly investigated. One of the major leaps in the development of Na-ion batteries was taken in the year 2000 when the group of Dahn reported a cell with a high reversible capacity of 300 mAh g⁻¹, using hard carbon as negative electrode material. Hard carbon has since then been used as the standard negative electrode for sodium ion batteries; this anode having a very low potential of insertion (vs. Na⁺/Na), and thus being able to achieve high energy densities. A second important step was reported by Osaka and co-workers based on the discovery of NaFeO₂ being electrochemically active in sodium cells utilizing the Fe³⁺/Fe⁴⁺ redox couple. This material is nowadays often used as a standard positive electrode.

Throughout the recent years, several compounds have been investigated either as positive or as negative Na-ion battery electrodes. On the negative side, the materials have primarily been different carbons, Ti-based compounds or Na alloys with Sn or Sb. In contrast, a variety of layered oxides, iron, manganese and vanadium-based oxides, polyanionic compounds and some miscellaneous sodium insertion materials have been studied as possible candidates for Na-ion battery positive electrode materials. Nevertheless, although the Na-chemistries have experienced large improvements in the last couple of years, they still fall short and cannot yet reach the performance of Li cells. The similarities and differences between Na and Li systems still need to be further investigated and the Na chemistries present several challenges which must be overcome. One of the problems is that the Na⁺ ionic radius is larger than that of the Li⁺ ion, and therefore requires more space in the structure in order to complete the insertion/deinsertion process. Still, these systems are certainly considered as possible complementary systems to the higher energy density lithium systems.

1.3 Organic compounds as electrode materials

It is apparent from the text above that the best performing Li-ion batteries as well as Na-ion batteries are based on inorganic compounds as electrodes. The environmental impact of especially LiB materials has been thoroughly investigated and the production of lithium-ion batteries corresponds to 150-200 kg CO₂-eq/kWh battery depending on design, inventory data, modelling and manufacturing. While production steps such as mining and refining have a limited contribution to the environmental impact during the life cycle
of the battery, emissions from cell and battery manufacturing is often around 50%, from the total. When studying the different battery components, the electrodes are the main contributors to emissions, especially the cathodes. Also the associated electronics have a high impact. The metals that can be recovered from the batteries are cobalt, nickel and copper using pyrometallurgy\textsuperscript{35}. Due to these issues, and considering the rapid depletion of metals extracted from ores, scientists have begun to search for alternative and more sustainable materials.

From a perspective of sustainability, organic redox compounds containing abundant elements (C, H, O, N, etc.) with resource renewability can be ideal battery electrode materials\textsuperscript{36}. These materials can be obtained from low-energy synthetic routes with very little waste, low cost and are potentially environmentally non-harmful. Organic electrode materials can also be used either as cathodes or as anodes by tuning their voltages through molecular design. In agreement with all the above merits, various organic compounds have been proposed as electrode materials, classified in certain groups such as conducting polymers\textsuperscript{37-40}, organosulfur compounds\textsuperscript{41-43}, organic free radical compounds\textsuperscript{44-46}, organic carbonyl compounds\textsuperscript{47-49} and even ‘superlithiated’ materials\textsuperscript{50-51}. Among all this diversity of organic electrode materials, the perhaps most promising type are conjugated carboxylates due to their high theoretical capacity (illustrated in Figure 2), fast reaction kinetics and structural diversity\textsuperscript{52}. Although they are very good candidates for replacing inorganic compounds from an environmental point of view, organic materials have not yet been broadly employed due to issues such as dissolution in the electrolyte, generally followed by capacity fading, and an inherent poor electronic conductivity. In order to overcome these problems, several methods have been adopted. Examples include nanosizing, electrolyte optimization or different molecular design methods.
Figure 2. Specific redox potential and specific capacity of some of the most used inorganic and organic electrode materials for Li-ion batteries (such as carbonyl based materials Li$_2$C$_6$O$_6$, nitroxide TEMPO, conductive polymer PAN, organodisulfur PDMcT). Reprinted from reference 52 with permission from The Royal Society of Chemistry.

One of the molecular engineering methods adopted in order to increase the available capacity of such compounds is to increase the number of carbonyl groups on a low molecular weight molecule. This should theoretically lead to an increase in capacity. However, if not all the carbonyl groups are electrochemically active, the compound can still not achieve its full capacity. This is clearly visible from the example of nonylbenzo-hexaquinone$^{53}$ (Figure 3) which could reach a theoretical capacity of 489 mAh g$^{-1}$, if all the twelve carbonyls would insert lithium reversibly. Practically half of the sites are however unavailable for lithiation because their redox reactions are taking place at very low potential. This in turn would instead lead to electrolyte decomposition, and the resulting practical capacity is only ca. 125 mAh g$^{-1}$ when cycling between 3.5-2.0 V vs. Li$^+$/Li. Several molecules have presented similar problems, and very few multi-carbonyl (more than 2 carbonyl groups) compounds are able to realize high active site utilization. Li rhodizionate, on the other hand, is one exception by achieving 85% of its theoretical capacity (Figure 4).

Figure 3. Schematic representation of nonylbenzo-hexaquinone
In contrast to inorganic materials, the carbonyl-based molecules rarely display average operating voltages higher than 3 V vs. Li⁺/Li. By tailoring their molecular structure, the operating voltage will also change and several compounds have been investigated in this context. An example is based on the introduction of electron-withdrawing or electron-donating groups. Depending on which type of substituents are added to the structure, the voltage can be shifted upwards (electron-withdrawing) or downwards (electron-donating). One example is the introduction of electron-withdrawing or electron-donating groups (-NMe₂) to electron-withdrawing groups (-F, -CN), the discharge potentials shifts from 2.3 V to 2.9 V vs. Li⁺/Li, thereby demonstrating the ease in tuning these types of compounds. Another example is the electron-deficient benzoquinone with perfluoroalkyl groups (-CF₃) which can display reduction potentials higher than 3 V vs. Li⁺/Li. However, increasing the potential via the introduction of large substituents groups renders a decrease in the theoretical capacity due to the increase in molecular mass. Possible solutions in this case can be the introduction of electronegative atoms such as O, N, S that could facilitate the reduction with little change in the mass. One such example involves the introduction of two N atoms in the structure of antraquinone by the formation of pyrido[3,4-g]isoquinoline-5,10-dione (PID). The first discharge potential could then be raised by 0.44 V (to 2.71 V vs. Li⁺/Li), and simultaneously its theoretical capacity merely dropped from 257 to 255 mAh g⁻¹.

A second method that can be applied for increasing the voltage of these compounds is by switching between different positions of the substituents on an aromatic ring. From the examples of dilithium (2,3-dilithium-oxy)terephthalate (Li₄-o-DHT) and its para-regioisomer (Li₄-p-DHT) it was found that the former molecule exhibited a higher average operating potential (2.85 V vs. Li⁺/Li) than the latter (2.55 V vs. Li⁺/Li). Taking advantage of the positive potential shift when switching from para to ortho-position in the quinone/hydroquinone moiety, is a well-known phenomenon in molecular electrochemistry.

One of the major problems in the case of carbonyl compounds is the dissolution of the often small molecules in traditional aprotic electrolytes. This problem is a huge impediment in the applications of the materials in batteries. Moreover, the dissolution products can be shuttled to the other battery electrode and create side reactions which lead to relatively fast capacity decay. Over the years, scientists have tried to solve this problem in several different ways: increasing the molecular mass by polymerization, using organic salts, grafting the active species on insoluble particles or using solid-state electrolytes. Several types of redox-active polymers have been considered as possible candidates: oligomeric polyketones, carbonyl-based polymers linked by thioether groups (R-S-R'), and the widely investigated polyimides, are just some examples. For instance, the capacity of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) was im-
proved by introducing sulfur bridge bonds to create a polymer structure. Stable values for the sulfur containing polymers of 150 mAh g\(^{-1}\) for P450 (polymer obtained at 450 °C), and 180 mAh g\(^{-1}\) for P500 (polymer obtained at 500 °C) could be obtained, while the PTCDA capacity on the other hand decreased constantly. A series of polyimides have also been investigated as cathode materials for Li-ion batteries,\(^{58}\) displaying practical capacities between 180 and 200 mAh g\(^{-1}\) and an average discharge voltage of 2.0-2.5 V. They also display a very good coulombic efficiency, insolubility and good cyclability.

At the same time, many organic salts have been investigated either as a positive or as negative electrode materials. For positive electrodes, molecules such as indigo dye\(^{60}\) and anthraquinone\(^{61}\) based compounds have been explored. On the anode side, the usage of carboxylates started with dilithium trans-trans-muconate and dilithium terephthalate\(^{74}\), where the former can insert only one Li\(^+\) ion, while the latter can undergo the full reaction and insert two Li\(^+\) ions in its structure. The muconate structure has a voltage plateau situated at 1.4 V with a reversible capacity of 170 mAh g\(^{-1}\) which slowly decreases to 125 mAh g\(^{-1}\) after 80 cycles, while the terephthalate has a voltage discharge plateau situated at 0.8 V, with a reversible capacity of 300 mAh g\(^{-1}\) which decreases to 234 mAh g\(^{-1}\) after 50 cycles. Due to their general good performance and comparatively high capacity retention, carboxylates gained interest and became more and more investigated, including a series of changes such as modifying the aromatic core, nanosizing, changing the metal ion, carbon coating and constructing metal-organic frameworks.\(^{75-85}\)

The majority of the published studies on these compounds involves investigating the compounds against lithium metal, but more recently studies including organic \textit{vs.} organic material or sometimes \textit{vs.} inorganic have gained interest. For example, organic dilithium (2,3-dilithium-oxy)-terephthalate (Li\(_4\)-p-DHT)\(^{62}\) was investigated both as a cathode material and anode (the material can undergo either lithiation or delithiation), thereby being able to realize an all-organic LiB cell. Another example with the same concept of an all-organic cell is tetralithium salt of tetrahydroxybenzoquinone which can be both reduced to Li\(_2\)C\(_6\)O\(_6\) and oxidized to Li\(_6\)C\(_6\)O\(_6\).\(^{63}\)

Many of the organic compounds that have been investigated for Li-ion batteries have also been explored for Na-ion batteries. One of the most studied conjugated carboxylate salts is dilithium/disodium terephthalate (Figure 4 left), that has been used both for Li\(^{74}\) and in Na\(^{86-88}\) batteries as a negative electrode material. In the case of Li cells (and as mentioned before), the compounds presents a voltage discharge plateau at 0.8 V \textit{vs.} Li\(^+\)/Li and a reversible capacity of 300 mAh g\(^{-1}\), while its Na analogue displays a discharge plateau at 0.4 V \textit{vs.} Na\(^+\)/Na and a reversible capacity of 250 mAh g\(^{-1}\). Both compounds present good cyclability and capacity retention, irrespectively of the cation type.
Another compound that has displayed reasonable results in both Li and Na batteries is dilithium\textsuperscript{49}/disodium\textsuperscript{89-90} rhodizonate (Figure 4 right). As an organic material for Li cells, the compound presents a stable reversible capacity of 300 mAh g\textsuperscript{-1}, in comparison to its Na homologue which displays a stable reversible capacity of only 170 mAh g\textsuperscript{-1}. Even though many of the organic compounds used for Na batteries have previously been investigated for Li batteries, similar electrochemical behavior at device level for the analogue compounds does not constitute a general rule. The mechanism of de/insertion is often similar, but most of these electrode materials will not behave in the same way in the respective systems. Generally, the Na systems present extended challenges, one being the poor kinetics of the Na systems which result from relatively larger ionic radius of the Na\textsuperscript{+} cation (102 pm) as compared to Li\textsuperscript{+} (76 pm). Inorganic materials have rigid crystal structures, and it is generally harder to de/insert larger sized ions such as Na. On the other hand, it has recently been discovered that some organic materials present a certain structural flexibility compared to inorganic materials, providing higher mobility for the Na\textsuperscript{+} ions\textsuperscript{87}. However, the large size of this ion can still induce large energy barriers to overcome, together with a larger irreversible capacity due to SEI layer formation. The Na chemistry therefore still presents severe challenges that need to be overcome. To further accentuate the high diversity and strong flexibility of organic materials, they have also started to be used in several chemistries besides Li and Na-ion batteries, for example K-ion\textsuperscript{91-92} or Mg-ion\textsuperscript{93-94} batteries.

When studying the often limited performance of the organic electrode materials in published literature, it should be kept in mind that inorganic materials used as electrodes in either Li or Na batteries have been investigated for decades, in contrast to organic materials that have raised an interest only in the past few years. The problems that the inorganic materials have exhibited have therefore been thoroughly investigated and solutions have been employed so that the compounds have become commercially viable. For exam-
ple, electrode calendaring is a very common technique used regularly in the case of inorganic materials such as LFP (LiFePO$_4$), and has been applied since the commercialization of batteries. For the organic materials, similar methods are rarely implemented. Moreover, the investigation of the SEI layer has been thoroughly performed and its influence and consistency is well known for inorganic materials. The investigation of this layer can be done using several methods; the most used and conclusive being XPS (X-ray Photoelectron Spectroscopy). In the case of organic materials, several of the problems encountered – such as fast capacity decay and loss of material – are usually assigned to the formation of an SEI layer. However, the investigation of the SEI layer has obviously not been a priority in the research community, perhaps due to the fact that this layer usually consists of species and elements very similar to the organic material itself, thereby making the processing of data challenging. Therefore, very little tailoring of the surface electrochemistry has been performed for the organic electrode materials in comparison to the inorganic counterparts. It is in this context – the current lack of tailoring the organic active materials for practical use in battery cells – that this thesis work has an important role to play.

1.4 Scope of this thesis

Having in mind all the problems discussed above, not least the poor sustainability of the inorganic battery materials, the main scope of this thesis is to investigate how to better realize organic electrode materials. The thesis work starts from the materials level, and evolve to cell construction and cell operation. The work focus is on making use of techniques and scientific insights from the broader battery research field, but here applied to organic electrode materials. The used methods, such as calendaring or SEI characterization, which are regularly used for inorganic battery materials, have rarely been applied for studies of organic electrode materials. The materials used as templates are dilithium benzenediacylate (Li$_2$BDA) and disodium benzenediacylate (Na$_2$BDA) (Figure 5), belonging to the class of carboxylates, which have been applied in their respective Li- and Na-cells.

![Figure 5. Schematic representation of dilithium (left) and disodium (right) benzene diacrylate.](image-url)
In **Paper I**, Li$_2$BDA and its behavior in Li-ion cells is investigated. Following a previous study on processing of composite electrodes of this compound, this paper discusses its improved performance by using a freeze-drying method in the preparation of the electrode.

In **Paper II**, a comparative study of Na and Li BDA battery chemistries and their electrochemical performances is made. The Na analogue Na$_2$BDA is synthesized and its chemistry is investigated in Na-ion batteries. The surface chemistry of both these materials is then investigated in **Paper III**, but then using the same cell format (pouch cells), where their respective SEI layers are characterized.

Thereafter, the comparatively poor electrochemical performance of Li$_2$BDA in pouch cells seen in previous studies led to the studies summarized in **Paper IV**. Here, the performance of electrodes containing Li$_2$BDA as active material is improved using calendaring techniques, a method widely used for the inorganic systems but relatively unexplored for the organic electrode materials.
2. Methods

2.1 Materials characterization

The structural and morphological features of the studied compounds were analyzed using a wide range of methodologies. This chapter contains a short description of each of the methods used. The materials characterization was performed by nuclear magnetic resonance, infrared spectroscopy, etc., while the electrochemical characterization of the compounds was done by galvanostatic cycling and cyclic voltammetry. Finally, this chapter also contains a discussion of the electrode fabrication techniques used.

2.1.1 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) is an important and largely used method for chemical structure determination, interaction of molecules and detailed molecular conformational and configurational information.\textsuperscript{96}

NMR measurements can generally be performed on two different types of samples: in solution (typically in deuterated solvents) or in solid-state. The measurements of samples in solution are more common due to that solid-state measurements are less sensitive (and hence require a larger amount of sample). The solid-state method gives also broader peaks and weaker signal to noise ratio. The principle on which NMR functions is that the nuclei of certain isotopes possess spin angular momentum characterized by the nuclear spin number (I). If a nucleus that possess I ≠ 0 is placed in a strong magnetic field, the nuclear magnetic dipole assumes quantized sets of orientations, depending on the nuclear spin number.\textsuperscript{97} By radiofrequency pulses of short duration, transitions between the spin states are induced. The return of the spin system back to the equilibrium gives rise to a free induction decay signal, which is transmitted to the detector. This signal is then transformed to a spectrum consisting of signal intensity vs. frequency with the help of computational methods. This spectrum is further analyzed and interpreted to obtain information on chemical shift, intensities, spin-spin coupling, etc.

The information obtained from a NMR analysis consists of molecular motion and dynamics, determination of the purity and quantity in mixtures, determination of chemical structure, conformation and stereochemistry of structures, etc. The NMR technique can be considered somewhat restricted if it is compared to other techniques due to the fact that it is limited to the ob-
ervation of nuclei that present magnetic moment. The solubility limitations of some of the compounds may also present difficulties. Nevertheless, due to that there exists naturally occurring magnetic spin isotopes of carbon \(^{13}\text{C}\) and hydrogen \(^{1}\text{H}\), it is widely used for characterization of organic materials, where the technique can be used to distinguish straightforwardly between different atoms in the same molecular structure. In this thesis, proton and carbon spectra were recorded at room temperature on a JEOL ECP-400 spectrometer at 400 MHz and 100 MHz, respectively. This method has been used in this thesis to confirm the structure of the organic materials used as electrodes.

2.1.2 Infrared spectroscopy

Infrared (IR) spectroscopy is used to identify which type of functional groups are present in the structure that is investigated, and relies on the fact that many functional groups have characteristic vibrations that correspond to absorption bands in certain regions of the infrared spectrum. The materials studied with this technique can be in the solid, liquid or gaseous state, and the amount of material needed can be as low as 50 picograms.

IR measurements are based on the fact that molecules have specific frequencies associated with internal vibrations of groups of atoms. When a sample is submitted to a beam of infrared radiation, it absorbs the radiation at frequencies corresponding to molecular vibrational frequencies. The spectrometer measures the frequencies of transmitted radiation, and the results are then given in the form of plots of the absorbed energy vs. frequency.

While the identification of a substance is possible due to the unique frequencies of absorption for every functional group, the magnitude of the absorption of a given species is related to the concentration of that specie.

IR spectroscopy is useful in the identification of functional groups of one specific structure but needs to be coupled with other techniques in order to render a complete picture of the chemical structures in a system. The method also presents some limitations; for example, some materials do not absorb IR radiation and therefore do not possess any useful spectrum. Moreover, some inorganic materials such as metal oxides cannot be measured in the normal frequency range.

The IR method was employed in this thesis as a complementary method to NMR, primarily to confirm the presence of different functional groups. Infrared spectra were recorded in the 650–4000 cm\(^{-1}\) range on a Perkin Elmer Spectrum One FT-IR spectrometer equipped with an attenuated total reflectance (ATR) probe.
2.1.3 Thermogravimetric analysis

Thermal analysis can be defined as a range of methodologies for characterization of a material by measuring its physico-chemical properties over a temperature range as a function of increasing or decreasing temperature. In thermogravimetric analysis (TGA), the change in weight of a sample is measured as a function of temperature. This method can give information about certain physical and chemical phenomena such as decomposition, oxidative degradation, sublimation, absorption, desorption, etc.

The method can be conducted in various atmospheres (vacuum, flowing air, inert atmosphere, etc.) and the mass of the sample is generally in the range of 2 to 25 mg. The samples can be studied in the solid or liquid state.

The typical operational procedure is that the sample is heated from room temperature to a specific desired temperature with a rate typically between 5 and 10 °C/min. Another alternative is to heat the sample quickly to a specific temperature and then follow the loss of weight as a function of time. TGA has here been employed to confirm the stability of the studied compounds at higher temperatures and to study the decomposition materials. Thermogravimetric analysis was performed using a TGA Q500 apparatus.

2.1.4 X-ray diffraction

Each crystalline material has its unique diffraction pattern. X-ray powder diffraction is often used to investigate the structure, degree of crystallinity and composition of materials. An unknown compound can be identified by comparing its diffraction pattern with those of already established structures. From XRD measurements, an electron density map can also be calculated, and the crystal structure can be refined.

A diffraction pattern is obtained when a beam of monochromatic X-rays is directed through a crystalline material and reflections of the X-rays at various angles with respect to the primary beam are obtained. Samples are generally measured in the solid state, and the quantity of material required is a few milligrams. In this thesis, the X-ray powder diffraction patterns were recorded with a Siemens D 5000 diffractometer using Cu Kα radiation.

2.1.5 Scanning electron microscopy

In scanning electron microscopy (SEM) an electron beam passes through a scan coil and an objective lens and scans the surface of a sample. During operation, a source of electrons is focused in vacuum into a fine probe that is sent over the surface of the specimen. As the electrons hit and penetrate the sample, a number of interactions occur that result in the emission of electrons or photons from or through the surface. Those interacting particles are
collected by a detector, and with the help of a cathode ray tube, the image of
the sample surface is obtained.
One major advantage of this method is that the materials characterization
can be done on nanometer to micrometer scale, and it is therefore one of the
most frequently used methods to study the morphology of different
samples. In this thesis, the SEM technique was employed to investigate
the electrode morphologies. SEM micrographs were recorded using a Zeiss
1550 instrument.

2.1.6 Photoelectron spectroscopy
Photoelectron spectroscopy is based on the external photoelectric effect,
where illumination of a sample with photons of defined energy larger than
the ionization energy cause electrons to be emitted from the sample together
with the absorption of the photon. When X-rays are used as excitation
source, the technique is called X-ray photoelectron spectroscopy (XPS). The
X-ray tubes typically utilize Mg or Al anodes which provide photons of
1253.6 eV and 1486.6 eV energy. The kinetic energy of the emitted pho-
toelectron (KE) is measured by an analyzer and the binding energy of the
electrons (BE) vs. the Fermi level is calculated from:

\[ \text{BE} = h\nu - KE - \phi \]  

(2.1)

where \(\phi\) is a spectrometer work function.
Variations in the binding energy of a specific core level are often referred
to as ‘chemical shift’. The chemical shift provides information about the
chemical state of the element in question. This way, XPS is a powerful tool
for identifying compounds with different chemical environments.
In this thesis, the evolution of the organic electrode SEI layer during cy-
cling is analyzed by synchrotron-based hard X-ray photoelectron spec-
troscopy (HAXPES). Compared to classical XPS (\(h\nu = 1486.6\) eV), HAXPES is
less surface sensitive technique and allows depth profiling of (thin) surface
layers and access to the electrode-electrolyte interface. Due to the high
brightness of the radiation source, it is possible to do fast measurements and
thus reducing the time of exposure for the sample and the impact of beam
damage that might occur during prolonged measurement times. The measure-
ments were carried out at the High Kinetic Energy photoelectron spectrometer (HIKE) end-station located at the BESSY II KMC-1 beamline at
Helmholtz-Zentrum Berlin (HZB). The excitation energies used were
2005 and 6015 eV by selecting first- and third-order light from a Si (111)
crystal of a double-crystal monochromator (Oxford-Danfysik). These ener-
gies correspond to probing depths of approximately 15 and 37 nm, respec-
tively.
2.2 Electrochemical characterization

2.2.1 Cyclic voltammetry

Cyclic voltammetry (CV) is one of the most widely used methods in electrochemistry. This method is based on recording the current while the potential of the working electrode is scanned between two limiting values at a certain scan rate. The representation of current vs. the applied potential constitutes the voltammogram, which can be used to extract useful information about the properties of the active electrode materials such as oxidation and reduction potentials, reversibility of the electrochemical reaction involved or kinetic properties.

CV is also a reasonably fast technique (depending on the scan rate), and it can be used for battery cells to get an overview of the electrochemistry in the system, to study the potential limits and to enhance the understanding of the different processes. It also constitutes an important complementary technique to interpret results obtained with controlled current technique. In this thesis, CV has been applied in the investigation of the electrochemical processes in the battery cells.

2.2.2 Galvanostatic cycling

Galvanostatic cycling is a controlled current technique and is used extensively for the investigation of battery cells. A fixed current is extracted or enforced between the two battery electrodes, thereby discharging or charging them, while the voltage response between the electrodes is monitored. This is normally done for a fixed potential window. The current is usually expressed as C rate (a terminology that signifies a charge or discharge rate equal to the capacity of the battery in one hour), where the magnitude of the current determines the rate of the charge and discharge processes. The technique is often applied for several charge-discharge cycles of the batteries, i.e. cycling. In this thesis work, galvanostatic cycling has been performed on different battery testing systems for both Li and Na systems at different C rates.

2.3 Fabrication of electrodes

2.3.1 Freeze drying technique

Freeze drying is a dehydration process that extracts most of the water from a sample in order to make the material more convenient to transport or to preserve perishable materials. It is a widely used method in pharmaceutical and biotechnological fields to increase the shelf life of products such as vaccines. The food industry also uses this process to preserve the food; a lot of freeze
dried products can be bought in the supermarket. Another example is food production for astronauts.106

The process works by freezing the material and then reducing the surrounding pressure to allow the water in the material to sublime directly from the solid phase to the gas phase (see Figure 6). The freezing step is usually performed at the laboratory scale by placing the material in a freeze drying bath which is cooled by mechanical refrigeration, such as dry ice and methanol or liquid nitrogen. At the industrial level, this step is performed in a machine. During the drying step the pressure is lowered and enough heat is delivered to sublimate water.106

This method has been used in this thesis work to increase the surface area of the electrochemically active materials by decreasing the average particle size while preserving the advantages of carbon coating in liquid state (explained in detail in Paper I).

![Figure 6. Phase diagram for water illustrating three different types of drying.](image)

2.3.2 Calendaring technique

Calendaring is a common compaction process for lithium-ion battery electrodes and has a great impact on the pore structure, and therefore the electrochemical performance, of Li-ion cells.95 Mainly uniaxial hydraulic presses have been used in laboratory work; roll presses or calendars of technical scale are rarely utilized in academic research. The compaction between two rolls working in opposite directions is, however, the established method in industrial fabrication. The electrode, a current collector foil with its specific electrode coating, gets pulled into a gap between the rolls. For process control, either the gap size is set significantly smaller than the electrode thickness or the rolling force is adjusted, ensuring the desired compaction of the electrode coatings.107 In this thesis, the calendaring was performed at room
temperature on a Roll Press HT-200 with a variation of pressure by changing the distance between the rolls.
3. Results and discussions

3.1 Materials synthesis and characterization

3.1.1 Synthesis of Li and Na benzenediacrylate

Dilithium benzenediacrylate was synthesized after the method described by Renault et al.,\textsuperscript{108} a quite straightforward method implying stirring benzenediacrylic acid with a stoichiometric equivalent of lithium carbonate at 50 °C for two days in a solution of water and ethanol (1:1, v/v) (as seen in the schematic diagram below). An immediate bubbling is observed corresponding to CO\textsubscript{2} evolution and reaction progress. An extended reaction time insures the complete conversion of the reaction. After drying the compound overnight in an oven at 100 °C, a white powder is obtained with a high yield of 98%. The success of the synthesis and purity of the sample was demonstrated by different methods such as IR and NMR (\textsuperscript{13}C and \textsuperscript{1}H).

\begin{center}
\textit{Scheme 1.} Schematic diagram for the synthesis of dilithium benzenediacrylate.
\end{center}

A similar synthetic route (denoted method A) was applied in the case of the sodium analogue, which resulted in a two-phase mixture of the monosodiated and disodiated compounds. The pure disodiated compound was later obtained after recrystallization in water:ethanol (1:1) with a 76 % yield. An alternative route (method B) was proposed for this compound involving a modified procedure of the synthesis of sodium terephthalate by Park \textit{et al.}\textsuperscript{87}(as seen in the schematic diagram below). The compound was prepared via the addition of benzenediacrylic acid to an aqueous solution of NaOH at 50-60 °C. Ethanol was thereafter added at 90 °C to precipitate disodium benzenediacrylate in a deionized water:ethanol mixture. After refluxing at 90 °C for 12 h, the compound was hot-filtered and dried overnight in an oven at 100 °C. A pure white compound was obtained with an 87 % yield. The characterization of the compound was performed in a similar fashion as for the Li analog, using all the necessary methods such as IR, NMR (\textsuperscript{13}C and \textsuperscript{1}H) and TGA. The yield for method A is significantly lower than the yield obtained using method B as synthesis route. These values, however, are rea-
reasonable considering that the first route has an extra step in the purification of the compound. All analyses were made on the compound obtained according to method B.

Scheme 2. Schematic diagram for the synthesis of disodium benzenediacrylate

3.1.2 Electrode fabrication

After synthesis, the materials were prepared for testing. For Paper I, a number of aqueous solutions with different concentrations of Li₂BDA were prepared: 2, 5, 6 and 7 wt. %. The 6 wt. % sample is just below the saturation limit, while the 7 wt. % corresponds to a sample with a fraction of the material in a suspension. The samples were thereafter submitted to a freeze drying process. The resulting powders were mixed with carbon SP (33 % or 50 % in total weight) either ex-situ or in-situ (in this case the carbon was mixed before the freeze drying step) and the mix were ball-milled during 1 h and subsequently dried. The obtained electrodes were characterized electrochemically in a Swagelok® cell format against metallic lithium using fiberglass separator soaked in 1 M LiTFSI in DMC as electrolyte.

Later, in Paper III and IV, the same compound was introduced in a different type of cell – a pouch cell – after preparing the electrode by making slurry containing active material, C65 carbon and PVdF binder. Prior to testing, the electrodes were submitted to calendaring. The electrodes were densified to different degrees by calendaring performed at room temperature with a variation of pressure by changing the distance between the rolls from 17 to 50 μm. The electrodes were then tested vs. Li metal or vs. LiFePO₄ electrodes. For disodium benzenediacrylate, Paper II and III, the electrode fabrication was performed by mixing Na₂BDA with carbon black and carboxymethylcellulose (CMC) as binder.

3.1.3 Electrochemical characterization

3.1.3.1 Dilithium benzenediacrylate

In order to benchmark these electrode materials for batteries, their electrochemical performance was investigated, primarily in Paper I. The samples prepared by freeze drying and mixed ex-situ with C were introduced in Li-ion batteries and tested between 0.9 and 3 V vs. Li⁺/Li at a rate of 1 Li⁺ per 10 h. From the galvanostatic cycling (Figure 7), it is noticeable that the 6 wt. % saturated solution gave the best results. The capacity for the 7 wt. % solution is lower than the 6 wt. %, which might be explained by a lower perfor-
mance of the particles in suspension during the freeze-drying step as compared to solubilized molecules. In suspension, only a fraction of the active material will generate a smaller particle size.

Figure 7. Capacity retention curves of Li half cells using dilithium benzenediacrylate prepared by freeze drying of an aqueous solution with different concentrations and cycled galvanostatically between 0.9 and 3 V at a rate of 1 Li⁺/10 h (C/20) in 1 M LiTFSI/DMC.

The analysis of the SEM micrographs reveals significantly smaller particles for the freeze-dried samples than the previously reported 2 to 25 μm, and a more complex surface morphology. The BET measurements show values around 12.5 and 18 m²/g surface area before and after ball-milling, respectively, for the 6 wt.% freeze dried sample, which is a clear improvement in comparison to 7.0 and 10.6 m²/g for the sample prepared in the liquid state. This proves the utility of the freeze drying technique in the preparation of water-soluble organic electrode material.

Combining carbon coating in the liquid state with freeze drying results in a relative high surface area, limited aggregation and homogeneous carbon repartition for the 6 wt.% sample (Figure 8). It could therefore be expected that the electrochemical characteristics of the material should be optimal. However, it can be observed that this is not the case from galvanostatic cycling tests. From the cycling data (Figure 9), the material shows poor performance with high capacity fading and high polarization. These results can be explained by an increase in the cell resistance due to a poorly connected particle matrix in the electrode, resulted from too small mass of conductive additive coated on a sample with a high surface area. By increasing the car-

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bon content to 50 % of the total weight, a clear improvement in the repartition of the additive can be observed. The same improvement is instantly reflected on the capacity values. Obviously, the electrochemical performance can be improved at the expense of energy density.

Figure 8. SEM micrograph of Li$_2$BDA prepared by freeze drying from a 6 wt. % aqueous solution and carbon SP (33 wt. %) added in situ.

Figure 9. Capacity retention curves of a Li/Li$_2$BDA half-cell prepared by freeze drying and liquid-state carbon-coating and cycled galvanostatically between 0.9 and 3 V at a rate of 1 Li$^+$/10 h (C/20) in 1 M LiTFSI/DMC. Inset: corresponding voltage profile.
When cycling at higher C rates, the compound can still present good capacity values and only moderate capacity fading at C/2 and 2C (rates corresponding to one Li every hour or 15 min per molecule; Figure 10). It is clear that by using a simple optimization method, such as freeze drying, a clear improvement and promising results can be obtained when considering the poor conductivity of these types of compounds as active materials. This method can be extended to any water-soluble material and constitutes a significant improvement for this class of materials. In this context, it can be applied not only for lithium carboxylates but also for sodium carboxylates used as anode materials in sodium-ion batteries.

![Figure 10. Capacity retention curve of a Li/Li₂BDA half-cell prepared by freeze drying of a 6 wt. % aqueous solution with in situ carbon coating (50 % in total weight) and cycled galvanostatically between 0.9 and 3 V at a rate of C/2 or 2C in 1 M LiTFSI in DMC.]

As mentioned, several of the initial electrochemical characterizations were performed in Swagelok® cells. When such type of cell is used, binders (such as CMC or PVdF) are not usually present. When changing the cell format to pouch cells, the binder becomes an important part of the electrode configuration. The major roles of the binder are to act as an effective dispersion agent, to connect the electrode species together and then steadily adhere to the current collector. PVdF is one of the most commonly used binders for both anode and cathode materials due to the excellent electrochemical and thermal stability and the good adhesion provided between the current collector and electrode films. This type of binder was used in the electrode formu-
tion in Paper IV, were the electrochemical performance of dilithium benzenediacylate was investigated in pouch cells.

The obtained electrodes were then submitted to a calendaring step under ambient conditions. The electrodes were densified to different degrees, and the porosity of the electrodes was estimated by measuring the electrodes thickness with a micrometer and calculated according to the formula:

$$\text{Electrode porosity (\%)} = \frac{V_{\text{matrix pores}} + V_{\text{AM pores}}}{V_{\text{total}}} = \frac{V_{\text{total}} - V_{\text{dense}}}{V_{\text{total}}}$$

The total volume was calculated by multiplying the thickness of the electrode with its geometrical area. The volume of the dense electrode was calculated by dividing the mass of the composite by its average density:

$$V_{\text{dense}} = \frac{m_{\text{cast}}}{\rho_{\text{cast}}}$$

with $\rho_{\text{cast}}$ being the sum of the different components densities multiplied by their weight fraction ($w_n$):

$$\rho_{\text{cast}} = w_1 \rho_{\text{Li}_2\text{BDA}} + w_2 \rho_{\text{binder}} + w_3 \rho_{\text{carbon black}}$$

This generated electrodes with porosities between 20 and 50 %, while the non-calendared electrode possessed a porosity of ca. 55 %. This difference can be clearly observed from the SEM micrographs (Figure 11) of the non-calendared electrode and the lower porosity electrodes. It is clear that the size of the active material particles is significantly smaller for calendared electrodes with porosities as low as 20 and 25 %. Furthermore, the connection between the particles is also more pronounced. The calendaring process thus disrupts the larger particles and agglomerates, while at the same time it improves the electronic wiring through the electrodes by increased carbon-carbon particle contacts. Moreover, the active material is better embedded in the carbon matrix. On the other hand, all of these benefits may lead to too compact electrodes which are likely to generate a limited wetting of the active material by the electrolyte and causing diffusion limitations within the electrodes.
The differently calendared electrodes were investigated electrochemically vs. Li metal; the capacity retention curves are presented in Figure 12. The non-calendared sample has a porosity of 55% and a poor average capacity of only \( \text{ca.} \ 50 \ \text{mAh g}^{-1} \). In comparison, all calendared electrodes display both lower porosities and higher capacities.
By slightly decreasing the porosity to 50%, a significant improvement of the capacity to ~75 mAh g⁻¹ was recorded. The best capacity retention was obtained for the sample with 30% porosity. With a capacity of ~200 mAh g⁻¹, this electrode achieved similar performance as the compound had formerly displayed in Swagelok® cells. However, decreasing the porosity below 30% did not render better performing electrodes in terms of capacity, at least not at the fast cycling rate used. Calendering at higher pressures resulted in porosities of 25 and 20%, but these samples possessed significantly lower capacities. This indicates mass transport limitations in the electrodes; i.e. that Li-ion diffusion in the electrolyte within the porous electrodes becomes limited in these compact systems. The same type of behavior has been reported previously for sub-micron sized LiFePO₄ particles, where similarly porosities of 30-35% were found to be optimal, however, the variety in capacity is significantly smaller for the inorganic material (140-160 mAh g⁻¹).

Figure 13. Electrochemical behavior of a Li half-cell using Li₂BDA electrode with 30% porosity cycled galvanostatically between 0.9 and 2.7 V at a rate of 1 Li⁺/0.5 h (1C) in 1 M LiTFSI in DMC/EC.

In Figure 13, the first three discharge/charge cycles are presented for Li₂BDA cycled at a rate of 1 Li⁺ every 0.5 h for the electrode with the best performance in terms of capacity. As can be observed, the first discharge presents a long voltage plateau with an average value of 1.2 V vs. Li⁺/Li and also displays significantly higher capacity in comparison to subsequent cycles. In the first cycles, the capacity is higher with approximately 70 mAh g⁻¹ than the theoretical capacity, which is often assigned to a combination of lithium adsorption on the conductive additive and solid electrolyte interphase (SEI) layer formation. The following decrease in capacity is commonly ob-
served for carboxylate materials and normally ascribed to structural changes causing inactive material and loss of material into the electrolyte.

After successful results in half-cells, full-cell experiments were performed for the best performing electrode (30 % porosity) against LiFePO₄. The cell was fabricated with an overcapacity on the cathode side to better reveal any short-comings of the organic anode. The resulting cell displayed promising capacity retention and cycled relatively stable for 200 cycles at a rate of 1 C. The resulting cell voltage is around 2.25 V which is clearly useful for many applications, and although the cathode is a conventional inorganic compound this concept has appealing properties in terms of potential sustainability.

3.1.3.2 Disodium benzenediacrylate

If the Na-analogue of this compound is considered instead of Li, a completely different behavior is observed; this compound was investigated in Paper II. The insertion mechanism proposed is similar to its Li compound counter-part (Scheme 3), however, the electrochemical results are quite different. The Na compound presents a more inconsistent behavior in the cyclic voltammetry, faster capacity decay and a different behavior at increasing C rates in comparison to the Li compound; see discussions below.

![Scheme 3. Expected mechanism for insertion/deinsertion of Na in Na₂BDA.](image)

First, since this compound was a novel electrode material, finding a good electrolyte and a functional potential window are imperative for the studies. The electrolyte plays an important role for battery life and performance, especially for organic materials where the dissolution of active material in the electrolyte is generally a major problem. A series of different electrolytes were tested, of which 1 M NaFSI in EC: DEC 1:1.5 gave the best capacity retention and cycling stability. Even though FEC has been used in other studies to improve the stability of the cells,¹⁰⁹ the addition of FEC in the electrolyte did here not improve the performance of the cell. The EC: DEC mixture is a commonly used combination, because EC has a broad electrochemical stability window and possess a high dielectric constant, while DEC has low viscosity and melting point.

Finding an appropriate cut-off voltage value also needs consideration when implementing a new active material. In CV tests, the upper cut-off voltage was set to 2 V, while the lower cut-off voltage investigated were 0.5, 0.3 and 0.1 V (vs. Na⁺/Na). Most satisfying results in terms of capacity and performance were observed for the 0.1 V cut-off. However, Na metal den-
drite formation could be expected at such low potentials. On the other hand, the CV data in Figure 14 show that a cut-off voltage of 0.5 V is too high to complete the insertion process of Na during discharge. From the reduction side, it can be noticed that the reduction starts at ~1.2 V and a clear reduction peak is observed at 0.5 V. The increase in current between 1.2 and 0.5 V can be ascribed to electrolyte reduction and SEI formation, while the large peak corresponding to 0.5 V can be ascribed to sodium insertion in the electrode. The chosen potential window was therefore 0.1-2 V, since it gave the highest values in capacity and a good distribution of the reduction and oxidation peaks, even though the risk of metal dendrites must be taken into account.

Figure 14. Cyclic voltammograms of Na₂BDA at 0.1 mV s⁻¹, first cycle for different cut-off potentials (left) and first 3 cycles (right) for 0.1-2 V cell. All cycles started at ≥2 V.

Once the optimal potential window was established as 0.1-2 V, CVs for this window were performed (Figure 14, right). A noticeable difference can be observed between the first cycle and the following ones. In the first cycle, during reduction, the first small peak can be assigned to the formation of the SEI layer, while the clear peak at ~0.4 V and the shoulder at 0.25 V are assigned to the reduction of the compound and the insertion of two Na ions into the electrode. The same features are visible for the subsequent cycles, but with less SEI layer formation. Corresponding features, with a peak and a shoulder are also visible during oxidation. The first cycle presents a peak at 0.9 V and a shoulder at 1.6 V, which evolves in the subsequent cycles. This peak can be assigned to the deinsertion of Na while the shoulder can perhaps be attributed to decomposition products formed during reduction. This shoulder decreases significantly during the next cycles. An important observation that needs to be highlighted is that the first cycle has a lower capacity in comparison to the next ones. This might be explained by an activation step which the compound undergoes in the first cycle; the full capacity being achieved in the next cycles after passing this barrier. This activation step might be related to loss of a passivating layer on the electrode through dissolution into the electrolyte.
A capacity of 177.7 mAh g\(^{-1}\) is obtained in the first cycle at a rate of 1 Na\(^+\)/20 h (C/40) (Figure 15), as observed from the galvanostatic cycling. The capacity does not decrease drastically in the second cycle; however, after approximately 10 cycles the capacity undergoes a drastic decrease to a value of only 50 mAh g\(^{-1}\) and remains constant during the following cycles (presenting a stable coulombic efficiency of ~95%). From the galvanostatic cycles for this compound, a plateau at 0.6 V \(\text{vs.} \ \text{Na}^+/\text{Na}\) is observed and attributed to the reduction of the carbonyl groups during Na insertion. As mentioned, a capacity decrease is often encountered for organic materials and is often attributed to the dissolution of the material into the electrolyte. Thus, this problem might be solved by tailoring the composition of the electrolyte. Moreover, it should not be forgotten that the larger ionic radius of Na ion in comparison to Li can play an important role. Sluggish kinetics and the sodiation process of the carbonyl group can lead to a destabilization of the organic molecule to a higher degree than the equivalent lithium mechanism.

Figure 15. Electrochemical behavior of a Na/Na\(_2\)BDA cell cycled galvanostatically between 0.1 and 2 V at a rate of 1 Na\(^+\)/20 h (C/40) in 1 M NaFSI in EC/DEC. Inset: corresponding capacity and coulombic efficiency curves.

Three different C rates were investigated for Na\(_2\)BDA (Figure 16). When cycled at C/10, the compound has a very similar behavior as compared to C/40, however, when the C rate is increased to an even higher value, such as
C/4, the compound displays a less pronounced capacity fading per cycle number. This similarity can likely be assigned to the operational time of the battery and an electrode decomposition reaction that is more dependent on the time than on cycle number. At a lower C rate (C/40 and C/10) the compound has more time to decompose or react chemically with the electrolyte, while at higher rate the compound has less time to engage in secondary reactions. The similar behavior at C/10 and C/40 might be due to the rate constant of this decomposition reaction.

![Graph](image_url)

*Figure 16. Electrochemical behavior of a Na/Na₂BDA cell cycled galvanostatically between 0.1 and 2 V at a rate of 1 Na⁺/20 h (C/40), 1 Na⁺/5 h (C/10) and 1 Na⁺/2 h (C/4) in 1 M NaFSI in EC/DEC.*

### 3.2 Na vs. Li

#### 3.2.1 Electrochemical behavior – advantages and disadvantages

As mentioned, there are advantages and disadvantages regarding the use of Na for electrochemical energy storage as compared to Li. A few advantages would be that Na is much cheaper than Li, and that compounds containing Na are equally simple to prepare using the same synthetic strategies as for the Li-based counterparts. However, as highlighted throughout this thesis, the electrochemistry of Na is generally more complicated than for Li compounds, just like for the rhodizonate example mentioned in the introduction. First of all, the electrolyte systems for Na-ion batteries are not that well developed, i.e., there is not a standard electrolyte that can be used in most situations, as in the case of LiBs. The insertions mechanisms also seem to be
more complicated for Na materials due to complicated kinetics and different crystallographic structures. Due to these issues, the Na compounds are often associated with faster capacity fading and cycling instabilities.

In terms of cycling at different C rates, there is a clear difference between the Li compound and the Na compound. As noticed from Figure 16, the Na material displays better capacity retention with increasing C rates, while the Li compound presents a decreasing capacity with higher C rates, similar to most inorganic materials. In Figure 17, the electrochemical characterization of Li$_2$BDA was performed at three different C rates: C/20, C/2 and 1 C. As can be seen, limited capacity fading is visible for this compound; more limited than for the case of the Na compound.

![Figure 17. Electrochemical behavior of a Li/Li$_2$BDA cell cycled galvanostatically between 0.9 and 3 V at a rate of 1 Li$^+/10$ h (C/20), 1 Li$^+/1$ h (C/2) and 1 Li$^+/0.5$ h (1C) in 1 M LiTFSI in DMC.](image)

If the cyclic voltammograms of bezenediacylates are compared, the Li compound presents a more consistent cyclic voltammogram (Figure 18). Even if the potential window used is larger, the compound displays completely reversible reactions at ~1 V. The reduction peak lies as high as at 1 V vs. Li$^+/Li$, in comparison to 0.25-0.4 vs. Na$^+/Na$ in the case of the Na compound, likely due to the smaller Li ion ionic radius which is therefore easier to insert and deinsert. At this potential, it is visible that the compound forms significantly less SEI layer in comparison to the Na compound, which probably would not be true if the compound would be cycled to lower potentials.
3.2.2 Interfacial chemistry of organic electrodes

The SEI layer formation is often used to explain the irreversible capacity observed in the first cycle for organic electrode materials. Therefore, it is striking that very few studies have been performed to properly investigate the formation of this layer and its influence in battery performance. One can perhaps explain this anomaly by the fact that the SEI layer components are made of elements and molecular species very similar to the organic electrodes materials themselves, thus making the analysis and interpretation of data difficult.

This problem was challenged in the case of the materials investigated in this thesis. The investigation of the SEI layer in Paper III followed naturally to get a better in-depth picture of how the surface chemistry affects the electrochemical performance. Both Li and Na systems were investigated, and clear differences could be seen. For both Li and Na systems, the samples were investigated at four different stages: the pristine composite electrode, the pristine electrode after contact with the electrolyte (OCV samples), and the electrodes after 1 and 15 charge/discharge cycles, respectively. The first sample (the pristine electrode) was used as a reference, while the second sample was used to investigate the reactivity between the electrode and the electrolyte before any electrochemical cycling. The last samples were used to investigate the SEI formation and its evolution.

If the OCV samples are investigated, it can be noticed that the effect of storage in the electrolyte does not have any major impact on the LiB ele-
trode; the main features being similar to the pristine sample. In the C 1s spectra (Figure 19), a small peak at high binding energy is observed and assigned to $-\text{CF}_3$ groups of the LiTFSI salt, this presence being confirmed also by the O 1s spectra (Figure 19). Apart from the presence of the salt, no passivation layer is observed, thus suggesting no preliminary degradation of the solvent by simple contact with the electrode surface. For the case of the Na-system, some changes can be seen in the OCV samples. The overall C 1s intensity decreases significantly and new signals appear or are increased in intensity ($-\text{C}-\text{C}$, $-\text{CO}$, $-\text{CO}_2$, $-\text{CO}_3$). The presence of new species is also confirmed by the O 1s spectrum, leading to the conclusion that a pre-deposit layer is formed in the Na system, while the LiB surface remains largely unchanged.

Figure 19. C 1s and O 1s core level peaks of the Li and Na samples for the pristine samples and their evolution after contact with the electrolyte, and after 1 and 15 cycles. The spectra were recorded with photon energy of 2005 eV.

If the cycled samples are studied, important changes can be noticed after just one cycle for the LiB system. The intensity of the peaks already present increases and new peaks related to $-\text{CO}$ and $-\text{CO}_3$ (Figure 19) environments appear at $\sim 286.5$ and $\sim 290.6$ eV, respectively. These evolutions are even more pronounced after 15 cycles. The presence of such modifications is directly related to SEI layer formation and deposition of byproducts of the solvents at the electrode surface. The corresponding O 1s spectra are in good agreement with the species already identified from the C 1s spectra. The intensities in both cases increases during prolonged cycling, which confirms the accumulation of solvent decomposition products while not much extra
salt is deposited. For the SiB system, on the other hand, it can be noticed after 1 and 15 cycles that the overall intensity of the C 1s spectra decreases and the intensities of the new species appearing at the OCV are increasing upon cycling, if compared to the signals of CMC and carbon additives. The species present in the SEI layer are similar to the ones in the LiB configuration, e.g., a -CO₃ peak can be assigned to Na₂CO₃ and/or alkylcarbonates ROCO₂Na.

From these investigations, it can be concluded that more carbonate species are formed on the LiB electrode. By observing the evolution of the carbon additive peak, the SEI layer in the Na system seems to be somewhat thicker than the one on Li system, similar to the differences observed for Fe₂O₃). In conclusion, the Na composite reacts with the electrolyte prior to cycling, forming a thin layer similar in composition to the SEI layer formed during cycling, while the Li composite is more unaffected by the contact with the electrolyte. Upon cycling, the passivation layer keeps growing for Na₂BDA, while for Li₂BDA, and increases in thickness for both materials while the number of cycles is increased.

From the investigation of the F 1s, S 2p, and N 1s core level spectra and their evolution, some insights can be done into the role of the electrolyte salt in the SEI layer formation. For the case of the Li system, the salt does not undergo any major decomposition; only traces of LiTFSI are found in the OCV sample, and even though more salt residuals are found upon cycling they do not correspond to any major degradation. On the other hand, the situation is different in the case of the Na system. NaFSI salt can be seen to start decomposing already in the OCV sample, forming mainly NaF. The content of this specie increases with cycling.

![Figure 20. Schematic drawing of the evolution of the electrode-electrolyte interface layer on composite electrodes cycled in Li or Na half-cells (on the left and right, respectively) after contact with the electrolyte and after 1 and 15 cycles.](image-url)
The major conclusions from this XPS study are summarized in Figure 20. It is clear that the SEI formed on the Li system is mainly based on organic species resulting from solvent degradation, and this occurs continuously during cycling. For the Na system, the SEI layer was found to be composed of mostly inorganic species resulting from the salt and its degradation products, and starts forming already from the OCV sample when the electrode is merely in contact with the electrolyte – i.e., no electrochemical processes going on – and grows continuously during cycling. This means that the SEI layer of the Na analogue is thicker than the Li analogue. This can perhaps contribute to explain the fast capacity fading and instability in case of the Na compound.

3.3 Full cell performance and recycling process

All the battery studies described above have been performed using half-cell configurations, where the compound is cycled against a Li or Na metal foil as counter electrode. As mentioned in section 3.1.3.1, Li$_2$BDA was also introduced in full-cells were the compound was cycled against a commercial LFP cathode (Figure 21).

As a consequence of the rapid depletion of metals and the large increase in price for some relevant LiB elements such as Li and Co, scientists are investigating strategies for more sustainable chemistries. In this context, there is also a focus being directed towards spent materials. Commonly, metals like Li are difficult to recycle from spent materials, and are often not done at all. The recycling method as well as the synthesis of inorganic active materials comprises harsh acid treatments and energy consuming techniques, which have great environmental impacts.\textsuperscript{111-114}
Figure 21. Capacity (per mass of Li$_2$BDA) retention curve of a Li$_2$BDA/LFP cell, cycled galvanostatically between 1.5-2.7 V at a rate of 1 C (1 Li$^+$/0.5 h) in 1M LiTFSI in DMC/EC.

Figure 22. Schematic representation of synthesis and potential recycling sequence for anode material (above) and cathode (below), respectively, in an organic-inorganic hybrid cell.

Within the scope of this thesis work, an effort has been made to produce a cell based on materials synthesized by employing environmentally friendly solvents such as water and ethanol. Moreover, a recycling process strategy
has been identified, also based on non-toxicity and low-temperature processing, whereby the spent materials have been introduced in a ‘second life’ cell in order to close the life cycle of these compounds. In Figure 22, a schematic representation of potential recycling processes for both anode and cathode based on water and ethanol as solvents is presented.

As seen, on the anode side the recycling process takes advantage of the water solubility property for dilithium benzenediacrylate in order to separate the active material from the binder and conductive additive. Washing with ethanol contributes to eliminate the electrolyte residue and with a final thermal destruction step, Li₂CO₃ ashes are obtained. They can be introduced in a second life synthesis with fresh benzenediacrylic acid to obtain the needed active material. The LiFePO₄ cathode, on the other hand, can also be synthesized using water-based processes. After battery usage, it can be washed with water to eliminate the surface residues of salt and electrolyte and thermally treated at high temperature. The obtained ashes can then be treated with nitric acid and introduced into a new synthesis step with fresh H₃PO₄ and LiOH•H₂O, to obtain LiFePO₄.

For the anode side, the recycling finishes with the obtained sample being submitted to a thermal treatment consisting of a ramp using a heating rate of 5 °C min⁻¹ up to 450 °C, followed by an isothermal step under air for 3 h. From the obtained TGA, it is clear that Li₂CO₃ is the main decomposition product, 34.6 % of the weight remains after combustion, a value close to the theoretical weight ratio (Li₂CO₃/Li₂C₁₂H₈O₄; 73.89:230.07= 32.1%). The IR measurement (Figure 23) of the obtained ash confirms this data, if compared to commercial Li₂CO₃, with only a very small contamination product visible at approx. 1200 cm⁻¹.

**Figure 23.** Infrared spectra recorded in transmission mode of commercial Li₂CO₃ and ash obtained after the thermal destruction of spent dilithium benzenediacrylate.
The synthesis of materials and the recycling process of such an organic-inorganic hybrid cell, utilizing environmentally friendly solvents, shows that it is possible to build more sustainable batteries.
4. Conclusions

Organic materials used as battery electrodes materials have been an important field of research that scientists have now investigated for several years. This work is based on investigating two compounds from this class, \textit{i.e.} dilithium/disodium benzenediacrylate. More precisely, they belong to the class of conjugated carboxylates.

In the first part of this thesis, the compounds were benchmarked in their respective cells, where different electrolytes and different carbon coatings were primarily investigated. Several steps were taken in order to increase the performance of these compounds. For the Li compound, when Swagelok-type cells were used, the freeze-drying technique was employed to obtain a good coated material. When the compound was used in pouch cells, on the other hand, calendaring was investigated as a technique that helps to improve the adhesion to the current collector, to provide better connection between the particles and disrupts the larger particles and agglomerates, while also improving the wiring through the electrodes. For the Na compound, a search for the best potential window and electrolyte system was in focus in this work, as well as cycling at different current rates. A comparison between these two different systems and the implications of the different ion sizes was also investigated.

A fast capacity fading in the first cycles has been a problem encountered for many organic electrode materials, and has often been associated to the SEI layer formation. However, very few actual measurements have been performed to prove this. In the second part of this thesis, one such study is undertaken, and based on XPS measurements it is shown that a clear difference in the formation and composition of SEI layers exists in these two different cationic systems. The major conclusion from this study is that the Li compound forms an SEI layer based mostly on organic species, resulting from solvent degradation. The Na compound, on the other hand, forms a thicker SEI layer based on inorganic species resulting from the degradation of salt. This might contribute to the poor stability of this compound observed in the cells and a much faster capacity fading in comparison to its Li analogue.

It should also be noted that much of the studies of organic electrode materials have been performed in so called ‘half-cells’, were the compounds are cycled against a Na or Li foil as counter electrode. Li$_2$BDA was here also used in full cells, were the compound was cycled against a LiFePO$_4$ cathode.
For this cell chemistry, recycling strategies have also been explored. The ambition has been to recycle both electrodes, by introducing the obtained spent materials in a second life synthesis, and generate a second life battery to complete the life cycle of both these compounds. Promising results have been achieved for the recycling of the anode, while the processing of the cathode needs further efforts. Since both electrodes are also fabricated by comparatively green methods, this would in the end render more sustainable batteries. Important steps towards the employment of organic materials in the next generation of Li- and Na-ion batteries have thus been taken in this thesis work.
Energilagring kan uppnås på många sätt, till exempel genom att lagra bränsle för förbränning (kemisk lagring), pumpkraftverk (mekanisk lagring), etc.-och elektrokemiskt i form av batterier, bränsleceller och superkondensatorer.

Litiumjonbatterier blev populära på 1990-talet på grund av den kraftiga expansionen av bärbar elektronisk utrustning. Idag används de i praktiskt taget alla mobiltelefoner och bärbara datorer samt i en stor del av vår övriga bärbara elektronik eftersom denna typ av batterier har den högsta energilagringskapaciteten av alla uppladdningsbara batterier som finns på marknaden.


De första litiumjonbatterierna innehöll oorganiska material som elektroder. Batterierna som används idag bygger fortfarande på samma typer av material. De oorganiska föreningarna har dock vissa nackdelar eftersom de måste utvinnas ur malmer (ändliga resurser), och deras ekologiska hållbarhet och fotavtryck är mindre imponerande där det behövs högtatursreaktioner för att framställa elektrodmaterialen. Därför har på senare år många inom vetenskapssamhället valt att arbeta med organiska material som alternativa elektroder. Dessa är ofta lätt att syntetisera, kan göras från billig material, och det behövs inte höga temperaturer för att syntetisera elektrodmaterialen. Organiska material har dock andra nackdelar, som dålig energitäthet, hög löslighet i elektrolyter och dålig elektrisk ledningsförmåga.

En annan stor fördel med de organiska materialen är att de ofta kan extraheras som naturliga föreningar vilka förekommer i jästa frukter, alfalfa, citroner, mera. Organiska material från biomassaderivat skulle också göra processerna enklare för återvinning av material som används i ett litiumjonbatteri, minska den totala miljöpåverkan för litiumjonbatterier och sänka deras CO2 fotavtryck.
Figur 1. Schematisk bild av ett ”grönare” Li-jonbatteri som driver en bil under urladdning.

På grund av den ökande användning av litium – inte bara för batteriindustrin, utan även inom andra branscher som keramik och glasframställning – har priset på litium ökat kraftigt under de första decennierna av detta århundrade. En lösning på detta problem skulle vara att ersätta litium i batterierna med en annan metall, som natrium. Natrium förekommer i stor utsträckning i jordskorpan och på grund av att resurserna finns nästan överallt är natrium inte så känsligt för prisvariationer eller geopolitiska begränsningar. Natrium uppvisar även låg toxicitet och syntesmetoderna liknar ofta de för litiumförbindelser. Men natrium har också vissa nackdelar, som större atomradie och högre redoxpotential (-2.71 V vs. vätgaselektroden; SHE) i jämförelse med litium (-3.04 V vs. SHE). Detta leder dels till att materialen utsätts för högre påfrestningar vid upp- och urladdning, dels till att den lagrade mängden energi blir något mindre.

I denna avhandling analyserades två analoga molekyler (bensendiaakrylat) med endast olika joner, det vill säga Li och Na, i sina respektive celler. Olika metoder har använts för att förbättra prestandan för elektroder baserade på sådana föreningar: frystorkning i fallet med Li-föreningen i Swagelok-celler eller kompaktering när föreningarna används som elektrodmaterial i påsceller. Eftersom kapacitetsförlusten för organiska molekyler i batterier ofta tillskrivs ytskiktbildningen (s k ”Solid Electrolyte Interphase”; SEI) på elektroderna utfördes dessutom studier av detta. Både Li och Na-föreningen undersöktes med fotoelektronspektroskopi, varifrån det var uppenbart att SEI-skiktet i fallet Li huvudsakligen är baserat på organiska föreningar som harrror från lösningsmedelsnedbrytning, och att detta sker kontinuerligt under cykling. För Na-systemet befanns SEI-skiktet bestå av oorganiska föreningar som harrror från saltet och dess nedbrytningsprodukter. Detta kan bidra till att
förklara den snabba kapacitetsförlusten och instabiliteten i fallet med Na-
föreningen.
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