

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Highly Concentrated Electrolytes for Lithium Batteries

From fundamentals to cell tests

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CHALMERS

Department of Physics
CHALMERS UNIVERSITY OF TECHNOLOGY
Göteborg, Sweden 2018

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This thesis is for a double degree at Chalmers University of Technology and Uppsala University.

This work has been funded by ALISTORE – European Research Institute and by the Swedish Energy Agency through “Batterifonden” grant #39042-1.

Chalmers, Reproservice

Göteborg, Sweden 2018

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Licentiate Thesis

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Abstract

The electrolyte is a crucial part of any lithium battery, strongly affecting longevity and safety. It has to survive rather severe conditions, not the least at the electrode/electrolyte interfaces. Current commercial electrolytes based on 1 M LiPF₆ in a mixture of organic solvents balance the requirements on conductivity and electrochemical stability, but they are volatile and degrade when operated at temperatures above ca. 70 °C. The salt could potentially be replaced with e.g. LiTFSI, but corrosion of the aluminium current collector is an issue. Replacing the graphite negative electrode by Li metal for large gains in energy density challenges the electrolyte further by exposing it to freshly deposited Li, leading to poor coulombic efficiency (CE) and consumption of both Li and electrolyte. Highly concentrated electrolytes (up to >4 M) have emerged as a possible remedy, by a changed solvation structure such that all solvent molecules are coordinated to cations – leading to a lowered volatility and melting point, an increased charge carrier density and electrochemical stability, but a higher viscosity and a lower ionic conductivity.

Here two approaches to highly concentrated electrolytes are evaluated. First, LiTFSI and acetonitrile electrolytes with respect to increased electrochemical stability and in particular the passivating *solid electrolyte interphase* (SEI) on the anode is studied using electrochemical techniques and X-ray photoelectron spectroscopy. Second, lowering the liquidus temperature by high salt concentration is utilized to create an electrolyte solely of LiTFSI and ethylene carbonate, tested for application in Li metal batteries by characterizing the morphology of plated Li using scanning electron microscopy and the CE by galvanostatic polarization. While the first approach shows dramatic improvements, the inherent weaknesses cannot be completely avoided, the second approach provides some promising cycling results for Li metal based cells. This points towards further investigations of the SEI, and possibly long-term safe cycling of Li metal anodes.

Keywords: Li-ion battery, SEI, Highly concentrated electrolyte, Al corrosion, Li metal battery.

List of Papers

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

- I *Critical evaluation of the stability of highly concentrated LiTFSI - Acetonitrile electrolytes vs. graphite, lithium metal and LiFePO₄ electrodes*
V. Nilsson, R. Younesi, D. Brandell, K. Edström and P. Johansson
J. Power Sources 384 (2018) 334–341.

- II *Highly concentrated LiTFSI - EC electrolytes for Li metal batteries*
V. Nilsson, A. Kotronia, K. Edström and P. Johansson
Manuscript

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My contribution to the papers:

- I I planned the work together with the co-authors, performed all analysis and all experiments except for SEM, where I took part. I wrote the first draft of the manuscript, and with feedback from co-authors, finalized it and responded to reviewers. The sections on SEM and XPS were added during revision and are written solely by me.
- II I planned all the work, performed all analysis and experiments except for SEM, where I took part. I wrote the manuscript.

Contents

1	Introduction	11
2	Batteries	13
2.1	Battery working principles	13
2.2	Battery assembly	14
2.3	Electrode materials	15
2.4	Electrolytes	17
2.4.1	The solid electrolyte interphase (SEI)	17
2.4.2	Salts	18
2.4.3	Solvents	19
2.4.4	Highly concentrated electrolytes	19
3	Experimental	21
3.1	Materials preparation	21
3.2	Electrochemical methods	21
3.2.1	Reference electrodes	22
3.2.2	Galvanostatic cycling	22
3.2.3	Cyclic voltammetry (CV)	22
3.2.4	Electrochemical impedance spectroscopy (EIS)	23
3.3	X-ray photoelectron spectroscopy (XPS)	24
3.4	Scanning electron microscopy (SEM)	24
4	Results and discussion	27
4.1	LiTFSI – Acetonitrile electrolyte	27
4.2	LiTFSI – Ethylene carbonate for Li metal batteries	31
5	Concluding remarks	33
6	Sammanfattning på svenska	35
7	Acknowledgements	36
	References	37

1. Introduction

The mobile electronics industry was revolutionized by the introduction of the Li-ion battery in 1991, and with improvements to the chemistry, manufacturing and cell design over the years, the specific energy has since tripled to ca. 250 Wh/kg [1, 2]. We have indeed not seen a comparable development as Moore's law for semiconductors [3], as batteries have fundamentally different limitations imposed by the size, mass and electrochemical potential of the materials used. Improved batteries have nonetheless led to renewed hopes to reduce our oil dependency, especially in the transport sector, currently using ca. 50 % of all crude oil [4]. Finite oil reserves, local air pollution and global CO₂ emissions all make substitution of internal combustion engines very desirable.

More battery powered electric vehicles (EVs) are now appearing on the market, with sales significantly aided by governmental subsidies [5]. For the EV to be competitive against vehicles run on cheap oil, further improvements in battery energy density, charge rate, expected lifetime and a lower cost is required. In addition to automotive use, there are applications of batteries for load balancing and energy storage in the power grids with high amounts of fluctuating solar and wind power. To cater for this demand, alternatives to the state of the art Li-ion battery such as Li metal and Li-sulfur batteries are being researched.

Lithium batteries are complex systems, for which we do not yet have a full understanding of all reactions and processes at play, especially after modifications to the chemistry [6] or even to the usage pattern. Important factors are the transport properties and electrochemical stability of the electrolyte [7], the formation and stability of the passivation films on the electrodes [8], and the slow side-reactions ultimately leading to failure [9].

This thesis focuses on the electrolyte, more specifically *highly concentrated electrolytes* for Li-ion and Li metal batteries – a concept which may address some of the aforementioned issues by adding much more salt to the electrolyte, creating a very ion-dense liquid [10]. Both the fundamental physical and chemical properties, and practical aspects for application are treated: What is the feasibility of highly concentrated electrolytes for Li-ion batteries and how do we overcome the obstacles that exist? On the more fundamental level, how do the changed coordination structures and transport properties in the bulk relate to the processes at the electrode surfaces?

2. Batteries

In this thesis *battery* refers to the cell and not to the battery pack, which is an assembly of cells such as the huge battery powering an electric vehicle. Battery and cell are used interchangeably, but battery is exclusively the energy storage device, while cell may refer to other cells for electrochemical experiments.

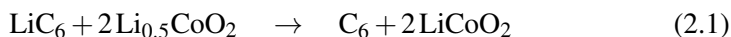
Battery: A container consisting of one or more cells, in which chemical energy is converted into electric energy and used as a source of power.

Oxford Dictionary of English [11]

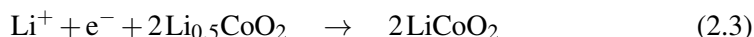
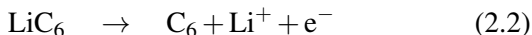
Although much of the following introduction is general, the Li-ion battery is used as an example, with emphasis on materials that have been studied in the appended papers.

2.1 Battery working principles

The principle of a battery is to convert chemical energy directly to electricity by separating the electron transfer from a redox reaction. For the example of a typical Li-ion battery, the total reaction of discharge can be written as



where Li in the lithiated graphite anode (LiC_6) is reduced by cobalt oxide cathode to form LiCoO_2 . This reaction can be separated into two half-reactions



where the first is the anodic and the second is the cathodic reaction. Now, by physically separating the anode and cathode but connecting them through an external electrical circuit, the electrons are transferred outside of the cell whereas the Li-ions (Li^+) move through the electronically insulating but ionically conducting electrolyte, as illustrated in Fig. 2.1. The anions should ideally not react with the electrodes, they are thus not carrying sustained current and stop moving shortly after the cell is turned on. If the reaction is reversible, as is the case with (2.1), the battery can generally be recharged. Li-ion cells use layered materials where the Li occupies the space between the layers, roughly maintaining

the structure upon *cycling* (charge and discharge). The insertion process is called *intercalation*.

The two half reactions (1.2) and (1.3) have corresponding electrochemical potentials E_{an} and E_{cat} respectively, often measured in V vs. Li^+/Li . The cell voltage is

$$E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}}$$

and the energy content of the cell

$$\int_{0\%}^{100\%} E_{\text{cell}}(Q) dQ,$$

where the integration is done over the usable capacity Q of the cell, typically determined by *cut-off voltages* for E_{cell} .

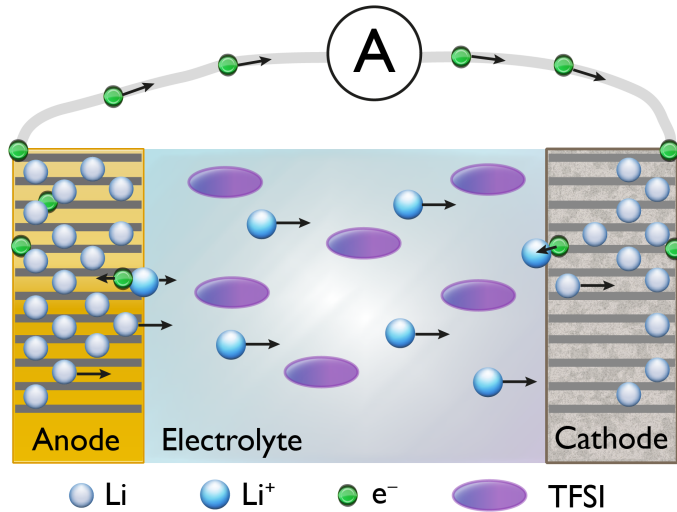


Figure 2.1. A discharging battery. TFSI is the anion of the Li salt.

Traditionally, *anode* is defined as the electrode where oxidation occurs, whereas the *cathode* is where reduction occurs. A discharging battery is a *galvanic cell* where the negative electrode is the anode and the positive electrode is the cathode. For the charging cell, the poles should technically switch names, but in battery literature the electrodes by convention keep their names: anode (–) and cathode (+).

2.2 Battery assembly

The electrode materials are mixed in a slurry with an electronically conductive carbon additive and a polymeric binder, and coated on thin metal foil current

collectors. For the cathode, Al foil is used, while the anode must be coated on more expensive and heavy Cu to avoid capacity loss through Al-Li alloying. The foils are coated and stacked or rolled with a ca. 25 μm thin polymeric separator between anode and cathode (Fig. 2.2). The cell layout may be described using the notation *graphite*|*LiCoO₂* or *graphite*|*electrolyte in separator*|*LiCoO₂*. The electrode assembly is placed in a flat or tubular casing, filled with a small amount of electrolyte to wet the electrodes and separator, and then sealed. Common cell formats in research are coin-cells, customised pipe-fittings from Swagelok and vacuum-sealed pouches.

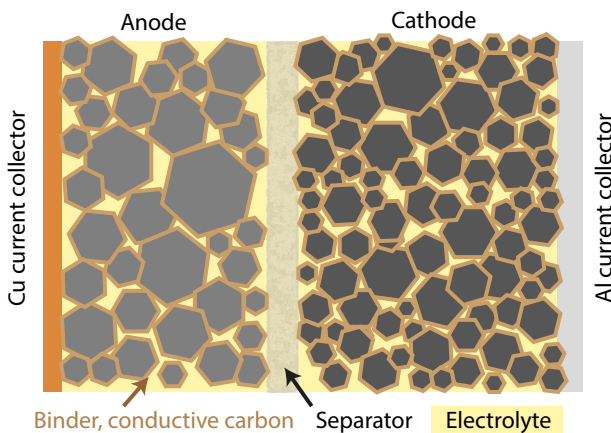


Figure 2.2. A slightly more realistic rendering of a small section of a Li-ion cell.

2.3 Electrode materials

Current Li-ion cells almost exclusively use graphite as the anode together with a lithium oxide cathode. The graphite has a theoretical capacity of 372 mAh/g, which is calculated directly from the mass of C_6 which hosts one Li. The potential of the electrode depends on the state of charge (SOC), where stages arise from different phases (Fig. 2.3a). Plateaus are observed in the equilibrium between two phases, e.g. $2 \text{LiC}_6 \rightleftharpoons \text{Li} + \text{LiC}_6 \cdot \text{C}_6$ at 85 mV for the almost full electrode [12].

There is a range of materials to choose from for the cathode, where LiCoO_2 was used in the original Li-ion cells and is still the cathode of choice for mobile electronics thanks to its high energy density. However, the cycle life and safety are insufficient for automotive applications, where $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$, (NMC) is most common,¹ often in a blend with LiMn_2O_4 (LMO) [13, 14]. A drawback for

¹Various formulations with $x + y + z = 1$ exist, with more Ni giving higher capacity but lower stability at high voltages and lowered thermal stability.

these materials are that they contain Co, which is toxic, insecure in supply and connected child labour [15]

Another cathode, popular for heavy duty applications such as buses, is LiFePO_4 (LFP) which has a lower energy density but compensates for this with a high rate (power) capability, long life and low cost [13]. LFP has a voltage plateau at 3.43 V vs. Li^+/Li that stretches across the whole capacity window, again a consequence of the equilibrium between two phases in the material (Fig. 2.3b). We exploit this when using LFP as a reference electrode (Paper I), but it makes monitoring the SOC of the electrode more difficult, as it cannot be determined from the electrode potential.

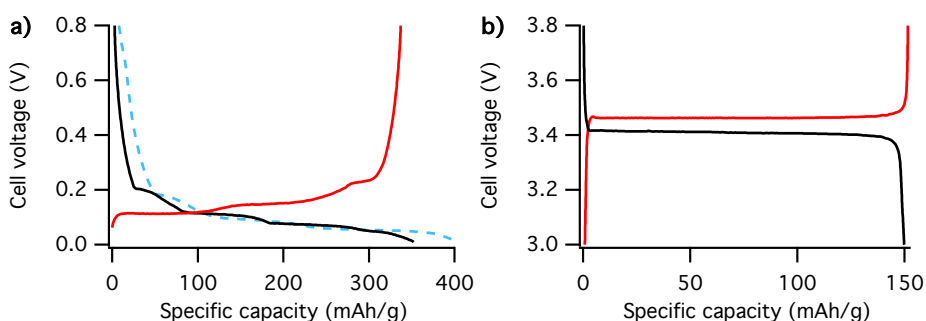


Figure 2.3. Voltage profiles for a) $\text{Li}|\text{graphite}$ and b) $\text{Li}|\text{LFP}$ cells. Lithiation is shown with black lines, delithiation with red, and the first graphite lithiation, including more side-reactions of electrode passivation, with dashed blue.

To raise the energy density of the cells, apart from finding higher capacity and voltage cathodes, there are options also on the anode side. One is to replace graphite with silicon which has a very high capacity but suffers from large volume expansion upon cycling [16]. Another option is to replace graphite with a Li metal foil, which gives a very high specific capacity of 3860 mAh/g – there is no inactive material (apart from eventual overcapacity). Li metal anodes are seen as the “holy grail” of Li batteries, and actually predates the Li-ion battery, but was withdrawn from market because of safety issues; dendrites can grow upon charging and penetrate the separator, short-circuiting the cell which then explodes [17].

Li metal anodes are commonly used as counter electrode in battery research cells because they have a constant potential which is used as a reference, and the Li foil is usually thick, $> 100 \mu\text{m}$, leading to an overcapacity. Together, this ensures that cell voltage and capacity are governed by the working electrode. Examples of such *half-cells* are shown in Fig. 2.3, where the discharged (low voltage) graphite cell has a graphite electrode in the same state as in a charged *full cell*.

Li has the lowest electrochemical potential of all elements at -3.04 V vs. SHE.² This is together with the low atomic weight the reason why Li is so attractive. Graphite has potentials for Li intercalation around 0.1 V vs. Li^+/Li and silicon between 0.1 and 0.4 V vs. Li^+/Li . A notable exception to these low potential anodes used in Paper I, is $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) with a potential of 1.55 V vs. Li^+/Li [18].

2.4 Electrolytes

Important properties of a good liquid electrolyte are high Li^+ conductivity, low viscosity to penetrate the pores of the electrode, ability to wet the separator, inertness towards cell components, a wide liquid temperature range and a wide electrochemical stability window. Apart from liquid electrolytes there are some other types, notably solid polymer electrolytes and ceramic ion conductors. The liquid electrolytes are typically salts in aprotic organic solvents, but research is also done on ionic liquid and aqueous electrolytes.

The state of the art electrolyte in commercial Li-ion cells is 1 M LiPF_6 in a mixture of the cyclic ethylene carbonate (EC) with a linear carbonate, usually diethyl carbonate (DEC), dimethyl carbonate (DMC) or ethyl methyl carbonate (EMC) [19]. This formulation balances various requirements in the cell well but has drawbacks such as limited stability at elevated temperatures [19] or when combined with high voltage cathodes [20]. In particular these electrolytes form good passivating films on the graphite anode and Al current collector.

2.4.1 The solid electrolyte interphase (SEI)

Since the electrochemical potentials of the anode materials are very low, they act as strong reducing agents which few solvents and salts could withstand. However, in the widely used electrolytes, a passivating film forms from the reduced electrolyte species, preventing further electrolyte reduction similar to how aluminium in air is protected by its surface oxide [8]. This passivating film, the solid electrolyte interphase (SEI) [21], is thus a crucial “component” in the Li-ion battery. The composition and morphology of it must be investigated to understand the effect of modifications to the electrode and electrolyte chemistry. Conditions for a good SEI is that it is: electronically insulating (or the reduction will continue on the surface of the film), ionically conducting (to let Li^+ through and not kill the cell), insoluble in the electrolyte, dense and flexible to follow volume changes in the electrode and thermally stable [22].

EC is included in the electrolyte since it was found to form a good SEI on graphite. The problem with many other solvents is that they *co-intercalate* with Li^+ without leaving the solvation shell, and cause graphite exfoliation. EC on

²Standard hydrogen electrode is the universal reference in electrochemistry.

the other hand, readily reduces on the anode at a higher potential than Li intercalation or decomposition of other components. In addition to this EC reduction, the salt will also decompose; in particular the very stable LiF is formed from electrochemical salt decomposition [7]. All together the SEI is a mix of polycrystalline, amorphous and polymeric phases that make up a 10–100 nm film covering the electrode [8]. Furthermore, additives such as vinylene carbonate are often included in the electrolyte to improve the SEI [7].

Apart from efforts to form an “artificial” SEI before cell assembly [8], the SEI is formed in the cell. Some reactions occur spontaneously but many take place during the first charge, in the *formation cycle* as illustrated in Fig. 2.3 by the higher capacity required for the first lithiation. Since the SEI is formed from electrolyte decomposition, it must indeed be analysed again for every change that is made to the electrolyte. This is why the SEI on graphite was analysed for multiple concentrations and more in depth in Paper I than what was done for the same electrolyte by Yamada *et al.* in [23].

The cathode may also have a passivating film, called the cathode electrolyte interphase (CEI), but it is thin in comparison to the SEI. Formation of both SEI and CEI can furthermore be affected by crosstalk between the electrodes where decomposition products from one deposit on the other [24].

2.4.2 Salts

Before the commercialization of Li-ion batteries using LiPF₆, the structurally similar LiAsF₆ and LiClO₄ were widely used in research but were discarded because of the toxicity and risk for explosions respectively. LiBF₄ was also used in early commercial cells, but ultimately LiPF₆ turned out to best meet the requirements, especially with higher conductivity of the electrolyte. LiPF₆ is however a compromise, especially limited by the thermal stability [25] and sensitivity to hydrolysis [26].

Many new salts have been developed in attempts to replace LiPF₆ [7, 27], e.g. the sulfonimides LiFSI, LiTFSI and LiBETI (Fig. 2.4), with especially the former two being amongst the most researched salts for new electrolytes. The big and flexible anions do not tend to form crystalline complexes with solvents as easily as PF₆ does, and the salts dissociate easily, allowing a much higher concentration [28, 29]. They also significantly improve the thermal stability and lower the sensitivity to moisture [30, 31, 32]. A drawback of these salts is corrosion of the Al current collector generally observed for cathode potentials above 3.7 V vs. Li⁺/Li for LiTFSI and 4.6 V vs. Li⁺/Li for LiBETI [33]. Furthermore, in combination with nitrile solvents the Al corrosion potential is raised [33], which is also seen in Paper I. LiFSI gives a higher electrolyte conductivity and may even avoid the Al corrosion, but availability of highly pure salt has been an issue [31, 34].

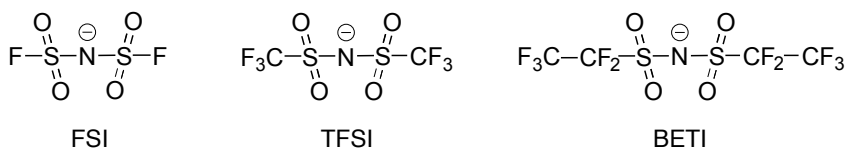


Figure 2.4. Sulfonimide anions.

2.4.3 Solvents

In order to avoid hydrogen evolution, the solvents for Li battery electrolytes are aprotic, and to dissolve the salt they must be polar, excluding many common organic solvents. Most common in early research was propylene carbonate (PC) which however never allowed lithiation of graphite because of severe graphite exfoliation. The very similar EC has a high melting point at 36 °C vs. -49 °C for PC. However, when mixed with the linear carbonates (DMC/DEC/EMC) it gets a liquid range to well below room temperature [19].

Acetonitrile (ACN) is widely used in supercapacitors thanks to its low viscosity and high permittivity (polarity) [35] and is also a common solvent for general non-aqueous electrochemistry. Drawbacks of ACN are that it suffers from a narrow electrochemical stability window, especially poor reductive stability and inability to form a good SEI as we see in Paper I. Furthermore, it forms toxic cyanides when degraded, and ACN supercapacitors are even forbidden in Japan [35].

Some other important types of solvents are ethers which have been mostly applied to Li metal anodes but suffer from low oxidation potentials, and glymes which act as multidentate ligands to form chelate Li^+ -complexes. LiTFSI in a mix of the cyclic ether dioxolane (DOL) and dimethoxyethane (DME) is the by far most common used electrolyte for Li-S [36] where one of the major problems is the Li metal stability. Such an electrolyte is used as a reference in Paper II.

2.4.4 Highly concentrated electrolytes

Highly concentrated or “solvent-in-salt” electrolytes have a significantly higher salt concentration than 1 M – already a rather high concentration. They are also known as *superconcentrated* which suggests supersaturation – dissolving more salt than thermodynamically allowed.

Some key points make these electrolytes special [10]:

- A low amount of solvent, especially in free, non-solvating form.
- An extremely high ion density which makes it similar to an ionic liquid.
- Higher density, viscosity and a lower conductivity.

This leads to some interesting benefits, such as lower solubility of other species such as transition metals dissolving from cathodes, higher rate capabilities and a

widened electrochemical window. The main drawbacks are costs from increased salt use and poor wetting of electrodes and separator.

Research on highly concentrated electrolytes traces back to 1985, when a saturated LiAsF_6 -PC electrolyte was shown to inhibit solvent co-intercalation in the layered compound ZrS_2 [37]. Then in 2002 successful Li^+ intercalation in graphite was demonstrated by Jeong *et al.* using a 1:2 LiBETI-PC electrolyte where the corresponding dilute electrolyte (1:8) causes graphite exfoliation [38]. This was attributed to the changed solvation structure of Li^+ , where all solvent is coordinated to the ions. Since 2010, similar experiments were done by Yamada *et al.* for LiTFSI and LiFSI in various solvents [23, 39, 40, 41, 42]. One finding was that the cells can operate at a higher or equal rate to a normal 1 M LiPF_6 electrolyte despite a lower conductivity. Another conclusion is that the SEI is formed mainly by anions in these electrolytes. It is notable that these electrolytes are EC-free but still allow reversible intercalation of Li^+ into graphite, which is desirable because of the negative impact EC has on the low-temperature performance and oxidation stability [43]. The increased rate capability could arguably be due to other transport mechanisms [44], or due to an increased Li^+ transference number [45].

Li metal anodes, have also been studied with highly concentrated electrolytes. Suppressed dendrite growth and improved cycling efficiency was shown with highly concentrated LiBETI-PC [46]. LiTFSI in DOL:DME (1:1 by vol.) in addition showed a significantly raised transference number and lower solubility of polysulfides with a higher salt concentration in Li-S cells [47].

Another property that greatly improves with highly concentrated electrolytes is prevention of corrosion of the Al current collector when using LiTFSI at high electrode potentials, which is something we revisit in Paper I. There is no consensus on the mechanisms for this [48], some options are: lack of solvent to solvate Al^{3+} and blocking of solvent access to the surface [49], a shift of the reaction equilibrium when the vicinity of the electrode gets saturated with Al^{3+} [50], and formation of a LiF film on the Al, like when using 1 M LiPF_6 [51].

Finally, the work on LiTFSI- H_2O “water-in-salt” electrolytes by Xu and co-workers claim expansion of the electrochemical stability window of aqueous electrolytes from 1.2 V to > 3 V [52, 53]. This has spurred derivative work finding aqueous highly concentrated electrolytes to be viable alternatives for supercapacitors, although the usable stability window seems smaller than previously claimed [54, 55].

Herein two approaches to highly concentrated electrolytes are tested. The LiTFSI-ACN electrolytes introduced in [23] are evaluated for their use in Li-ion batteries, focusing on the anode passivation (Paper I), and the LiTFSI-EC electrolytes introduced in [49] are tested for use with Li metal anodes (Paper II).

3. Experimental

The nature of batteries makes electrochemical analysis an obvious part of determining the properties of a novel electrolyte. For a fundamental understanding we also need to determine physical properties of the electrolyte, as well as investigate components *post mortem*. Here follows a brief introduction to the used methods and techniques.

3.1 Materials preparation

Electrolytes and cells were prepared in an Ar-filled glovebox to avoid trace moisture and, especially for Li metal, reaction with N₂. Mixing of electrolytes is straightforward, but highly concentrated electrolytes often have a salt volume higher than the final volume, and so both salts and solvents were weighed. Only commercial materials were used, but some composite electrodes were prepared in the lab.

Slurries for electrode coating were done using the active materials graphite or LFP, carbon black, polyvinylidene difluoride (PVdF) binder and the solvent N-methyl-2-pyrrolidone (NMP). The ingredients were mixed thoroughly in a planetary ball-mill. The PVdF was typically added as a 5 wt.% solution in NMP, but mixing of all dry ingredients with subsequent NMP addition allows easy tuning of the viscosity without changing the composition. The slurries were coated on the current collectors using a roll-to-roll coater to achieve maximum homogeneity. The exception was the small batches made with ultra-thin graphite coatings, that were made with a bar coater.

3.2 Electrochemical methods

We will first look at the choice of reference electrode (RE), relevant to many techniques, then turn to galvanostatic cycling, which is often one of the firsts tests of an electrolyte, giving much information from a single experiment. Then follows how to determine the electrochemical stability windows (ESW) using cyclic voltammetry (CV), and how to measure conductivity with electrochemical impedance spectroscopy (EIS).

3.2.1 Reference electrodes

The electrochemical tests are usually done in two or three-electrode cells, where in the latter a separate RE is used to avoid the shift in electrode potential that arise when current is passed through the counter electrode (CE). It also allows separate recording of the CE potential (on certain instruments) which is useful both for full cell battery tests and to avoid side reactions on the CE when running CV. In Paper I the electrolyte was not stable vs. Li metal, and as an alternative, LFP was used. To ensure a stable potential, the electrodes were de-lithiated to the middle of the 3.43 V vs. Li^+/Li plateau in a separate cell.

3.2.2 Galvanostatic cycling

The first test of how an electrolyte performs is typically galvanostatic cycling of a two-electrode cell. This can give preliminary information on both electrode integrity and electrolyte stability, especially when the cells are disassembled and examined afterwards. In this way the compatibility with separators and the cell layout can be tested. Indications are seen in e.g. discolouration of the separators, reactions with the current collectors or deposits on electrodes.

Inspection of the voltage profiles clearly shows loss of capacity as in Paper I and growth of cell polarization as in Paper II. Differentiating the capacity–voltage (Q – V) curves, dQ/dV analysis, results in what resembles a CV with peaks at prominent reactions or plateaus of the electrode material. Differentiation using Savitzky–Golay filtering [56] handles noisy measurement data much better than simple numeric differentiation.

Coulombic efficiency is easily extracted as the ratio $Q_{\text{discharge}}/Q_{\text{charge}}$ when cycling full cells, but in a Li metal cell the anode is typically not exhausted, and so another method is often used to determine Li plating/stripping efficiency. Li is galvanostatically plated on e.g. Cu for a certain time (capacity) and then stripped until the Cu electrode is polarized to 1 V vs. Li^+/Li .

To test the SEI stability, 120 h pauses in the cycling scheme were used in Paper I [57]. Pausing at high SOC tests the self-discharge, which is either reversible or irreversible and observed as a capacity loss, implying that the electrode passivation was insufficient. A pause at low SOC probes the dissolution of the SEI through the need to re-passivate the electrode during the next charging step.

3.2.3 Cyclic voltammetry (CV)

When galvanostatic testing applies a current and records the voltage, CV sweeps the potential of the WE and records the resulting current. This reveals the potential at which electrode reactions occur. Also capacitance, reversibility of reactions, mass transfer limitation, kinetics and difference between surface-confined vs. solution reactions can be seen in CV.

To obtain a measure of the ESW, a common method is to only make a single *linear sweep* in each direction (ox/red) until the current dramatically increases. Instead of electrochemically active battery electrodes, blocking electrodes unable to sustain a Li^+ current are used. Since the useful ESW is determined not only by the electrolyte but also by the choice of electrodes, Cu and Al were selected in Paper I, since they are used for the battery electrodes. To see the effect of passivation or activation, multiple CV sweeps rather than a linear sweep were run.

When testing the reduction stability, only the reactions above Li plating were considered. The current was supported by oxidation and de-intercalation of Li from the LFP CE, and the potential of the CE was recorded to ensure electrolyte oxidation was not happening. If the capacity of the CE is too low, crosstalk may occur, where some species other than Li are oxidized at the CE and gets reduced at the WE. In a similar way, LTO was used as the CE when testing oxidation stability. The lower conductivity at higher electrolyte concentrations causes large *iR-drops* between WE and RE which alters the recorded potential. By measuring the resistance with EIS, this can be compensated for.

3.2.4 Electrochemical impedance spectroscopy (EIS)

In impedance spectroscopy, a sinusoidal voltage perturbation is applied to the cell, and the magnitude and phase of the current is recorded. The voltage must be small, typically < 10 mV, such that the current depends linearly on the voltage. The frequency f is stepped from ca. 0.1 Hz to 100 kHz or even 10 MHz in certain setups, giving the complex cell impedance $Z(f)$ as output. By fitting a circuit model to the data, parameters matching physical properties can be extracted, but the choice of circuit is not straightforward. A basic model that works reasonably for one electrode or a symmetric cell is the Randles circuit (Fig. 3.1). C_{DL} represents the double layer capacitance, R_S the solution resistance, R_{CT} the charge transfer resistance for faradic processes and W is the Warburg element representing diffusion to the electrode. Since different processes occur at different timescales, they can be separated from each other. In particular, R_S is given by $Z(f)$ at high f .

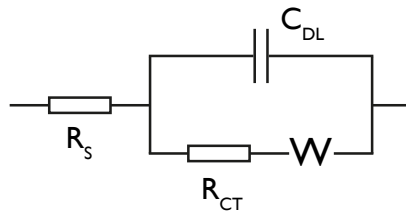


Figure 3.1. The Randles circuit model of an electrochemical cell.

For measuring electrolyte conductivity σ in Paper I, a broadband spectrometer connected to a programmable cryostat was used. The temperature was equilibrated at predetermined points before each measurement. Using blocking electrodes $R_{CT} = \infty$ and thus $R_S = Z(f)$ for high frequencies. The solution conductivity is then calculated from R_S .

3.3 X-ray photoelectron spectroscopy (XPS)

XPS probes the core electron binding energy E_b of atoms with a resolution < 0.3 eV. Since the E_b is affected by interactions with the valence electrons, a shift indicating the chemical environment and oxidation state can be detected. Hence, XPS is not only for composition analysis in terms of atomic species, but can be used to distinguish between different compounds. The operating principle is to focus X-rays on the sample and detect the kinetic energy E_{kin} of the emitted electrons. The process is described by

$$h\nu = E_b + E_{\text{kin}} + \Phi$$

where $h\nu$ is the incident photon energy and Φ is the work function of the analyser. By increasing $h\nu$, E_{kin} will increase and, for a given mean free path, also the probe depth. The X-ray source on in-house instruments is limited to one or two energies, and typically the Al K_α source is used ($h\nu = 1486.4$ eV), with a typical probe depth of a few nm [58]. To probe deeper or shallower, a tunable synchrotron X-ray source can be used. Sputtering with Ar ions can also reveal deeper layers, however with a risk for preferential sputtering of certain species.

XPS is one of the most important tools for investigation of electrode surfaces and the SEI in particular. Two important conditions for the experiment is a conductive sample and ultrahigh vacuum in the sample chamber which poses some restrictions on the sample. To study a cycled electrode, residual electrolyte must be removed since the vacuum removes all solvent. However, since washing may partially dissolve the SEI, multiple measurements with more or less washing can be used.

To analyse the obtained spectra, references are needed that can sometimes be found in literature but may also have to be measured. An example is to compare cycled and pristine electrodes as in Paper I, or electrodes at different SOC. For the latter case, additional energy shifts arise from new electrostatic interactions.

3.4 Scanning electron microscopy (SEM)

SEM is a versatile microscopy technique based on scanning a beam of electrons across the sample rather than illuminating the whole sample with photons to form an image. The $0.2 \mu\text{m}$ diffraction limitation of resolution is avoided and the

resolution is instead determined by the beam spot size and interaction volume with the sample, typically a few nm. Another benefit is the depth of field for simultaneous focus on objects near and far.

The SEM is well suited for morphology studies of Li metal plating (Paper II), easily spanning a magnification range from $< 100 \text{ X}$ for overview, to $> 100\,000 \text{ X}$ revealing details on the surface of single Li features (Fig. 3.2). A low acceleration voltage and beam current (e.g. 3 kV, 100 pA) must be used to avoid melting Li when using high magnifications (localized beam).

A good and thin SEI can not be easily observed with SEM, but on the graphite electrodes in Paper I, surface films were seen even with the naked eye, so some cycled graphite electrodes with different degree of solvent washing were studied. The cells were disassembled in a glove box and the electrodes were transferred inertly to the microscope with a commercial transfer-box.

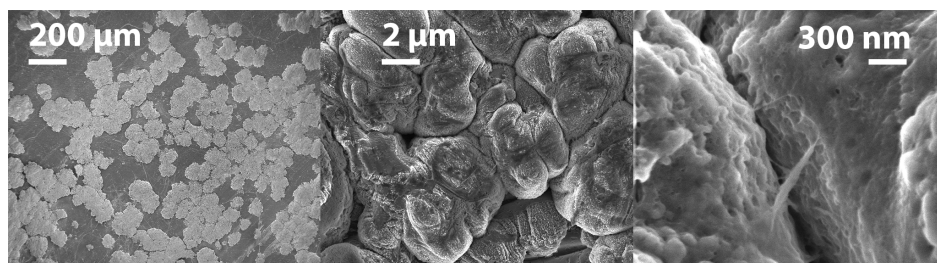


Figure 3.2. Li plated on Li foil studied in the SEM, with three magnifications as indicated by the scale bars.

4. Results and discussion

In the following two chapters, the results from Paper I and Paper II are summarized, including some more detailed explanations for crucial parts.

4.1 LiTFSI – Acetonitrile electrolyte

LiTFSI–ACN electrolytes of varying concentrations were tested for Li-ion batteries.

Galvanostatic cycling of a 1:1.9 LiTFSI:ACN electrolyte in a Li|graphite cell results in fast capacity fading (Fig. 4.1a), which is attributed to instability at the Li metal surface. The separator was attached to the Li electrode, full of yellow and black electrolyte decomposition products and dendritic Li (Fig. 4.1b). This severe instability was unexpected since Yamada *et al.* reported stability of Li metal immersed in the electrolyte, and cycling a Li|graphite cell without significant capacity loss, whereas yellow ACN reduction products formed at 1 M LiTFSI concentration [23].

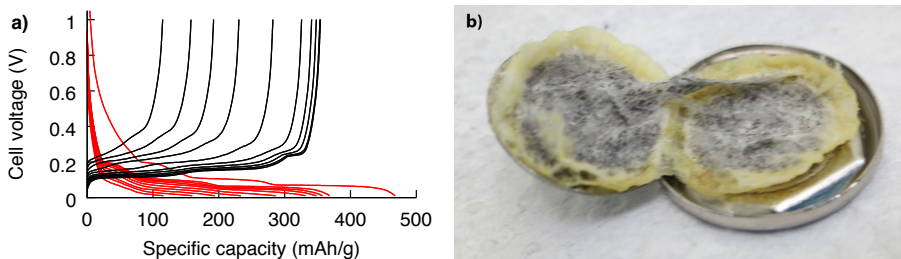


Figure 4.1. a) 10 cycles of a Li|1:1.9 LiTFSI:ACN|graphite cell. b) Glass-fibre separator from the cycled cell.

Attempting to reproduce the stable cycling by Yamada *et al.*, the graphite mass loading was lowered from 1.9 mg/cm^2 to 0.3 mg/cm^2 , a coating so thin that the current collector shines through (Fig. 4.2a). When the specific current of the graphite is maintained at $C/10$ this leads to a lower areal current density, which significantly improves the stability (Fig. 4.2b). Furthermore, the maintained voltage profile suggests that the graphite is stable during intercalation.

The Li counter electrode was replaced with LFP in order to study graphite electrodes of relevant capacity. An LFP|LFP cell was used to show that this does

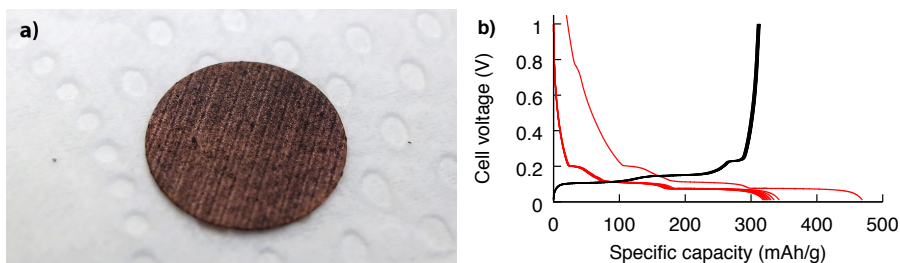


Figure 4.2. a) Coating with 0.3 mg/cm^2 graphite mass loading on Cu foil. b) 10 cycles of a Li|1:1.9 LiTFSI:ACN|graphite cell with 0.3 mg/cm^2 graphite loading.

not impact cycling stability. 50 galvanostatic charge/discharge cycles were performed with electrolyte concentrations ranging from 1:16 to 1:1.67 LiTFSI:ACN. With the lowest salt concentrations, 1:16 and 1:9, the graphite can not be fully lithiated, limited by electrolyte decomposition at ca. 1.2 V vs. Li^+/Li . Higher salt content leads to CEs and capacity retentions improving up to the solubility limit (Fig. 4.3). The highest concentration 1:1:67 LiTFSI:ACN reaches a CE of 97% CE and a capacity retention of 78% which is far from a reference cell using 1 M LiPF_6 in EC:DEC electrolyte, reaching >99%. For the 1:1.9 LiTFSI:ACN electrolyte, the capacity loss during the first 10 cycles is much higher than for the thin coating (Fig. 4.3b), even without Li metal present, again indicating that the current density is more important than the charging rate of the graphite particles.

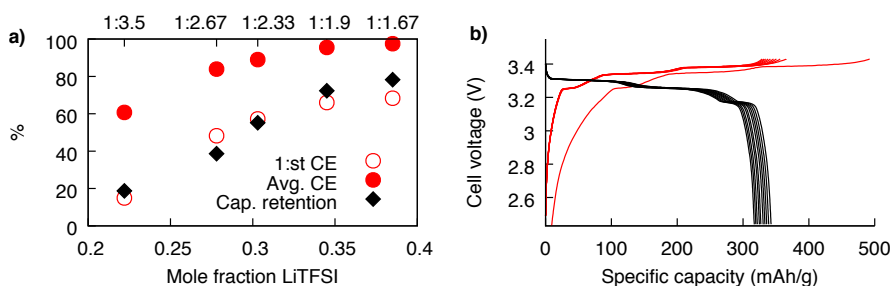


Figure 4.3. a) First cycle CE, average CE, and capacity retention of LiTFSI:ACN electrolytes in graphite|LFP cells. b) 10 cycles of a graphite|LFP cell with a 1.9 mg/cm^2 graphite mass loading.

By introduction of 120 h pauses to the cycling, the stability of the SEI was probed. When the pauses are done at a high SOC, the cell self-discharges followed by a permanent capacity loss indicating that an irreversible side-reaction is responsible. Pauses at a low SOC are not coupled to an immediate capacity loss, but in the following cycle a large overcapacity is required – the SEI has to reform, suggesting that it has dissolved in the electrolyte.

To shine more light on the SEI properties, cycled graphite electrodes were analysed using XPS, after either a gentle or a thorough wash in DMC (Fig. 4.4). The signal of graphite is observed through the SEI to a larger extent for the electrodes cycled in lower concentration electrolytes – the SEI is less dense or dissolves easily. The higher concentration leads to the deposition of Li_3N and a higher quantity of insoluble fluoro-organic compounds on the electrode. Finally, more oxidized S, in the form of SO_4^{2-} or from the SO_2 -group in TFSI is present on the electrode cycled in highly concentrated electrolyte.

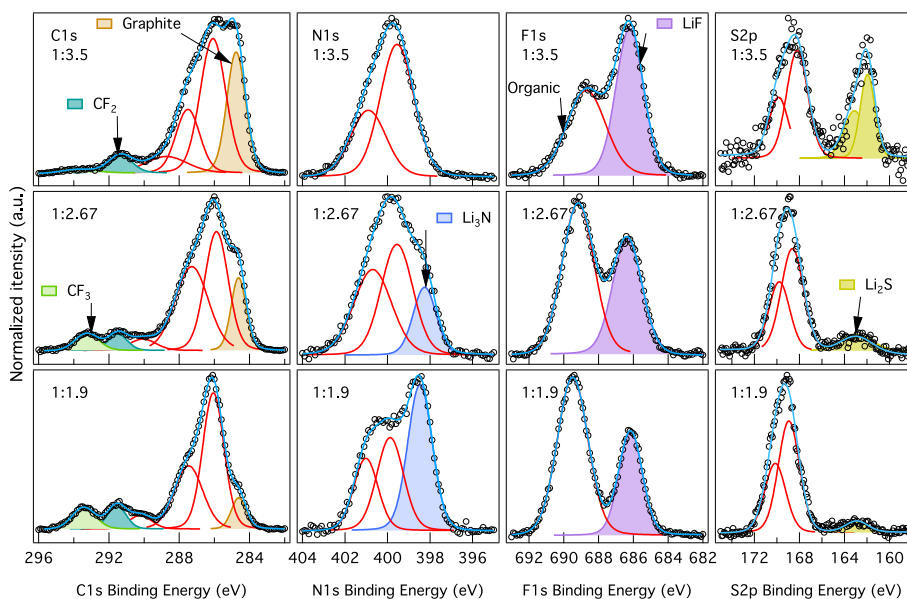


Figure 4.4. XPS spectra for thoroughly washed graphite electrodes after one lithiation-delithiation cycle. Each spectrum is normalized to the frame height. Reproduced from Paper I with permission from Elsevier.

Finally, the electrochemical stability vs. Cu and Al respectively was examined using CV. The most important observation is that the potential for electrolyte reduction does not shift, so the electrochemical stability window has not widened towards lower potentials. Instead, the current is lowered, likely caused by a mass transport limitation with no available solvent to reduce. The reduction onset is ca. 1.2 V vs. Li^+/Li , which is where ACN reduction happens.

Oxidation stability vs. Al is increased from ca. 3 V vs. Li^+/Li to 4.2 V vs. Li^+/Li in 1:1.9 LiTFSI:ACN compared to the 1:16 electrolyte, but not higher, as previously claimed [23]. After repeated cycles up to 5 V vs. Li^+/Li , an oxidation peak appears at 4.2 V vs. Li^+/Li , the same potential as where corrosion turns severe in the 1:16 LiTFSI:ACN electrolyte.

In all, the electrolyte has shown some dramatic improvements when going to higher concentrations, but the instabilities observed nonetheless render this system uninteresting for practical purposes.

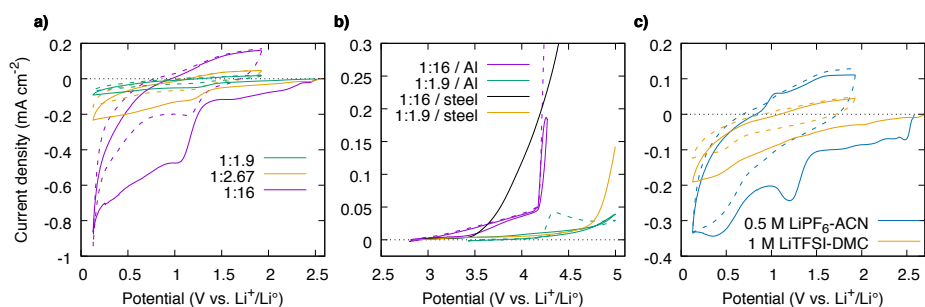


Figure 4.5. Cyclic voltammograms, cycles 1 (solid) and 2 (dashed). a) Reduction test on Cu. b) Oxidation test on Al and steel, for 1:1.9 dashed shows cycle 100. c) Reduction test on Cu. Reproduced from Paper I with permission from Elsevier.

4.2 LiTFSI – Ethylene carbonate for Li metal batteries

EC has a melting point of ca. 36°C , which makes it unsuitable as the sole electrolyte solvent for batteries operating at ambient temperatures. However, when mixing EC with LiTFSI in ratios 1:6 or 1:2 LiTFSI:EC, the resulting electrolyte melts at ca. 0°C or -50°C respectively [49]. In Paper II these two electrolytes were evaluated for their use with Li metal batteries. 1 M LiTFSI + 0.25 M LiNO₃ in DOL:DME is known to work well with Li metal and was used as a reference.

Long term Li plating/stripping was tested in Li|Li cells with glass-fibre separators for the two EC-based electrolytes. Current densities 0.5 mA/cm^2 and 0.05 mA/cm^2 were applied, with a duration per cycle of 2 h and 20 h respectively for a cycle capacity of 0.5 mAh. The cell with 1:2 LiTFSI:EC and 0.5 mA/cm^2 only sustained a few cycles before reaching $>1\text{ V}$ polarization, whereas the 1:6 LiTFSI:EC cell cycled at 0.05 mA/cm^2 short-circuited. The test of 1:2 LiTFSI:EC at 0.05 mA/cm^2 was aborted after 96 cycles or 80 days with almost no polarization increase (Fig. 4.6a). 1:6 LiTFSI:EC at 0.5 mA/cm^2 was stable for ca. 250 cycles or 20 days (Fig. 4.6b).

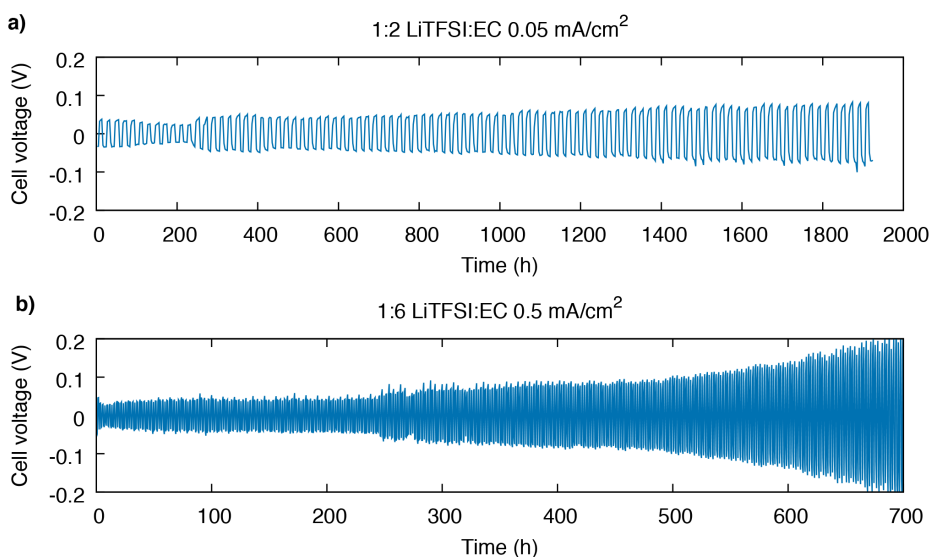


Figure 4.6. Galvanostatic cycling of Li|Li cells with 0.5 mAh/cm^2 capacity per cycle.

Since glass-fibre separators are bad at confining the deposited Li, the electrolyte decomposition is faster and the risk of dendrites causing short-circuit higher. The increased electrode distance leads to a larger resistive contribution to cell impedance and overpotential. To avoid these issues and allow electrode surface analysis with SEM or XPS, alternative separators were evaluated. It was found that Solupor gives sufficient wetting and confinement of Li growth.

The deposition morphology was studied with SEM after plating 1 mAh/cm^2 on Li foil. The Li foil was in all cases full of *mossy Li*, but the surface of the freshly deposited Li in the two EC-based electrolytes was smooth, while it was flaky when using the reference electrolyte (Fig. 4.7).

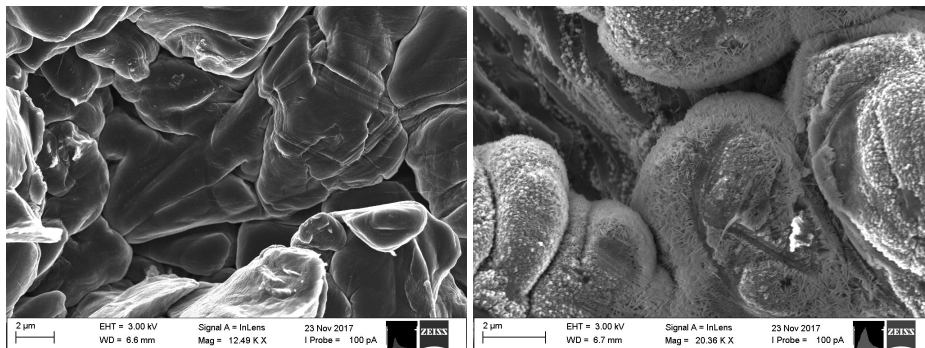


Figure 4.7. Left: Li surface deposited in the 1:6 LiTFSI:EC electrolyte. Right: Li surface deposited in the LiTFSI/LiNO₃ – DOL:DME reference electrolyte.

The CE of Li plating/stripping on a clean Cu surface was found to be relatively high at 94.5 %, but still lower than than for the ref. electrolyte with a CE > 97% (Table 4.1). The improvement from the first to the second cycle is much larger for the EC:LiTFSI electrolyte suggesting that surface passivation is responsible for the rise in CE, whereas the ref. electrolyte has a higher inherent electrochemical stability. Since the LiNO₃ is included to increase the CE, the EC-electrolyte should be compared to another reference further on.

Table 4.1. Coulombic efficiencies for Li plating/stripping.

Cycle	1	2	3	4	5
6:1 EC:LiTFSI	0.804	0.926	0.945	0.945	0.945
Ref. electrolyte	0.934	0.969	0.974	0.971	0.973

Overall, the 2:1 EC:LiTFSI electrolyte has a very high viscosity which makes separator and cathode wetting difficult. Furthermore, the overvoltage is high, indicative of the low electrolyte conductivity. The somewhat lower CE is an obvious drawback of the 6:1 electrolyte. However, the benefits of an extremely low vapour pressure could still make it interesting. Furthermore, the morphology of deposited Li is smoother as compared to the ref. electrolyte, and without flakes.

5. Concluding remarks

The change in current density has a high impact on the stability of the super-concentrated LiTFSI–ACN electrolytes. In general, the approach to use a highly unstable electrolyte and alter it by increasing the salt concentration may be impressive, but it seems like ultimately some of the drawbacks will persist. For instance, the presence of uncoordinated solvent molecules in the highly concentrated electrolytes could react with the electrodes and affect the stability [49].

The LiTFSI–EC electrolyte shows promise for Li metal electrodes, why some further experiments are planned, in particular to remove the LiNO_3 from the reference electrolyte, and to investigate the SEI composition using XPS.

Another way forward is the concept of diluting a highly concentrated electrolyte with an inert solvent to form a ternary electrolyte which still maintains a unique solvation structure. This lowers the cost and improves the viscosity and separator/electrode wettability [59].

6. Sammanfattning på svenska

Elektrolyten är en fundamental del av ett litiumbatteri som starkt påverkar livslängden och säkerheten. Den måste utstå svåra förhållanden, inte minst vid gränzytan mot elektroderna. Dagens kommersiella elektrolyter är baserade på 1 M LiPF₆ i en blandning av organiska lösningsmedel. De balanserar kraven på elektrokemisk stabilitet och jonledningsförmåga, men de är lättflyktiga och bryts ned när de används vid temperaturer över ca. 70 °C. Saltet skulle kunna bytas ut mot t.ex. LiTFSI, vilket ökar värmetåligheten avsevärt, men istället uppstår problem med korrosion på den strömsamlare av aluminium som används för katoden.

Genom att byta ut grafitanoden i ett Li-jonbatteri mot en folie av litiummetall kan man öka energitätheten, men då litium pläteras bildas ständigt nya Li-tytor som kan reagera med elektrolyten. Detta leder till en låg *coulombisk effektivitet* genom nedbrytning av både Li och elektrolyt.

Högek koncentrerade elektrolyter har en mycket hög saltkoncentration, ofta över 4 M, och har lags fram som en möjlig lösning på många av de problem som plågar denna och nästa generations batterier. Dessa elektrolyter har en annorlunda lösningsstruktur, sådan att alla lösningsmedelsmolekyler koordinerar till katjoner – vilket leder till att de blir mindre lättflyktiga, får en ökad täthet av laddningsbärare, och en ökad elektrokemisk stabilitet. Samtidigt får de en högre viskositet och lägre jonledningsförmåga.

Här har två angreppssätt för högek koncentrerade elektrolyter utvärderats. I det första har acetonitril, som har begränsad elektrokemisk stabilitet och ett högt ångtryck, blandats med LiTFSI för en uppsättning av elektrolyter med varierande koncentration. Dessa har testats i Li-jonbatterier och i synnerhet den passiverande ytan på grafitelektroder har undersökts med både röntgen-fotoelektron-spektroskopi (XPS) och elektrokemiska metoder. En markant förbättring av den elektrokemiska stabiliteten observeras, men de inneboende bristerna hos elektrolyten kan inte kompenseras fullständigt, vilket skapar tvivel på hur väl detta kan fungera i en kommersiell cell.

Med det andra angreppssättet har hög saltkoncentration nyttjats för sänka smältpunkten för en elektrolyt baserad på etylenkarbonat, som annars inte kan användas som enda lösningsmedel. Dessa elektrolyter har testats för användning i Li-metall-batterier genom långtidstest, mätning av den coulombiska effektiviteten och analys av deponerade Li-tytor med svepelektronmikroskop. Resultaten är lovande, med över 250 cykler på 0.5 mAh/cm² och en effektivitet på över 94 %, men framförallt observeras en mycket jämnare deponerad Li-tyta, vilket kan möjliggöra säker cykling av Li-metall-batterier. Ett logiskt nästa steg är studier av Li-tytan med t.ex. XPS för att utröna vad som skiljer den från ytan som bildats i en 1 M referenselektrolyt.

7. Acknowledgements

First of all, I would like to thank my main supervisors Patrik and Kristina for making this complicated double-degree possible. For setting the bar high and forcing me to work independently, and for hosting me in two different but equally creative environments.

Thanks to Daniel for being such a great facilitator, Reza for your suggestions on experiments, Matt L for plenty of discussions, and Torbjörn for being supportive and such a great source of practical knowledge. Thanks Mario W for your interest in my project and help with the reviewer comments.

Huge thanks to Chao who provided me with shelter for a large share of my time Uppsala, and to Carmen who I provided with shelter in Gothenburg, for all discussions and company.

Thanks to administrators Ewa Larsson and Anna Lindqvist who are really helpful with the paperwork, and thanks to Henrik and Ezio who kept the labs running and always are open for discussion.

Thanks to all my other current and former colleagues in Uppsala: Anders, Andoria, Andreas, Andy, Burak, Charlotte, Chenjuan, Christofer, David, Dennis, Erik, Fabian, Fredrik B, Fredrik L, Guiomar, Hanna, Johan C, Johan G, Jonas H, Jonas M, Julia M, Julia M, Kristina, Le Anh, Leif, Linus, Mahsa, Marco, Mario, Markus, Ocean, Rasmus, Ronnie, Ruijun, Sara, Sebastian, Solveig, Stefan, Steven, Therese, Tim N, Victor, Viktor, Will, Yu-Chien and all I may have forgotten.

To my officemates at KMF: Du-Hyun, Rasmus, Fabian, Christoffer, Khalid. Thanks to Muhammad, Marco, Adriana and Roza for electrochemistry talks, to former KMF colleagues Andrea, Anke, Bee, Damien, Florian, Fredrik, Jan, Johan Scheers, Karin, Laura, Luis, Manfred, Martin, Steffen, Tuan, Yajing.

Thanks Piotr, Wladek and Marek for good times at Alistore meetings.

And thanks to you who were at KMF more recently: Aleksandar, Alice, Athmane, Ellen, Filippa, Gustav, Joachim, Joakim, Juan, Laura, Linnéa, Marianne, Niklas, Rafael, and Simon for nice vacations and mountain biking the last days before printing.

I finally want to thank Henning and Johan for welcoming me to Uppsala, and all my teaching colleagues, with special mentions to Lars H, Patric and Ingrid.

References

- [1] Nishi Yoshio, "The development of lithium ion secondary batteries," *The Chemical Record*, vol. 1, pp. 406–413, Sept. 2001.
- [2] A. Manthiram, "An Outlook on Lithium Ion Battery Technology," *ACS Cent. Sci.*, vol. 3, pp. 1063–1069, Oct. 2017.
- [3] M. M. Waldrop, "The chips are down for Moore's law," *Nature News*, vol. 530, p. 144, Feb. 2016.
- [4] *2017 OPEC World Oil Outlook*. Organization of the Petroleum Exporting Countries, Oct. 2017.
- [5] "Global EV Outlook 2017," tech. rep., International Energy Agency, 2017.
- [6] E. S. Takeuchi and M. M. Doeff, "An Argument for Basic Battery Science: Each Time an Application Demands a New Battery Chemistry To Achieve Previously Unrealized Functionality, a New Fundamental Understanding Is Required," *Acc. Chem. Res.*, vol. 51, pp. 573–574, Mar. 2018.
- [7] K. Xu, "Electrolytes and Interphases in Li-Ion Batteries and Beyond," *Chem. Rev.*, vol. 114, pp. 11503–11618, Dec. 2014.
- [8] E. Peled and S. Menkin, "Review—SEI: Past, Present and Future," *J. Electrochem. Soc.*, vol. 164, pp. A1703–A1719, Jan. 2017.
- [9] M. R. Palacín and A. de Guibert, "Why do batteries fail?," *Science*, vol. 351, p. 1253292, Feb. 2016.
- [10] Y. Yamada and A. Yamada, "Review—Superconcentrated Electrolytes for Lithium Batteries," *JES*, vol. 162, pp. A2406–A2423, Jan. 2015.
- [11] *Oxford Dictionary of English*. Oxford University Press, 2016.
- [12] T. Ohzuku, Y. Iwakoshi, and K. Sawai, "Formation of Lithium-Graphite Intercalation Compounds in Nonaqueous Electrolytes and Their Application as a Negative Electrode for a Lithium Ion (Shuttlecock) Cell," *J. Electrochem. Soc.*, vol. 140, pp. 2490–2498, Jan. 1993.
- [13] G. Zubi, R. Dufo-López, M. Carvalho, and G. Pasaoglu, "The lithium-ion battery: State of the art and future perspectives," *Renewable and Sustainable Energy Reviews*, vol. 89, pp. 292–308, June 2018.
- [14] R. Schmich, R. Wagner, G. Hörpel, T. Placke, and M. Winter, "Performance and cost of materials for lithium-based rechargeable automotive batteries," *Nature Energy*, vol. 3, pp. 267–278, Apr. 2018.
- [15] T. C. Frankel, "Cobalt mining for lithium ion batteries has a high human cost." *The Washington Post*, Sept. 2016, Accessed: 2018-05-15
<https://www.washingtonpost.com/graphics/business/batteries/congo-cobalt-mining-for-lithium-ion-battery/>.
- [16] H. Wu and Y. Cui, "Designing nanostructured Si anodes for high energy lithium ion batteries," *Nano Today*, vol. 7, pp. 414–429, Oct. 2012.
- [17] D. Lin, Y. Liu, and Y. Cui, "Reviving the lithium metal anode for high-energy batteries," *Nat Nano*, vol. 12, pp. 194–206, Mar. 2017.

- [18] X. Sun, P. V. Radovanovic, and B. Cui, "Advances in spinel Li₄Ti₅O₁₂ anode materials for lithium-ion batteries," *New J. Chem.*, vol. 39, pp. 38–63, Dec. 2014.
- [19] K. Xu, "Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries," *Chem. Rev.*, vol. 104, pp. 4303–4418, Oct. 2004.
- [20] R. Petibon, J. Xia, L. Ma, M. K. G. Bauer, K. J. Nelson, and J. R. Dahn, "Electrolyte System for High Voltage Li-Ion Cells," *J. Electrochem. Soc.*, vol. 163, pp. A2571–A2578, Jan. 2016.
- [21] E. Peled, "The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems—The Solid Electrolyte Interphase Model," *J. Electrochem. Soc.*, vol. 126, pp. 2047–2051, Jan. 1979.
- [22] P. Verma, P. Maire, and P. Novák, "A review of the features and analyses of the solid electrolyte interphase in Li-ion batteries," *Electrochimica Acta*, vol. 55, pp. 6332–6341, Sept. 2010.
- [23] Y. Yamada, K. Furukawa, K. Sodeyama, K. Kikuchi, M. Yaegashi, Y. Tateyama, and A. Yamada, "Unusual Stability of Acetonitrile-Based Superconcentrated Electrolytes for Fast-Charging Lithium-Ion Batteries," *JACS*, vol. 136, pp. 5039–5046, Apr. 2014.
- [24] J.-N. Zhang, Q. Li, Y. Wang, J. Zheng, X. Yu, and H. Li, "Dynamic evolution of cathode electrolyte interphase (CEI) on high voltage LiCoO₂ cathode and its interaction with Li anode," *Energy Storage Materials*, vol. 14, pp. 1–7, Sept. 2018.
- [25] S. E. Sloop, J. K. Pugh, S. Wang, J. B. Kerr, and K. Kinoshita, "Chemical Reactivity of PF₅ and LiPF₆ in Ethylene Carbonate/Dimethyl Carbonate Solutions," *Electrochem. Solid-State Lett.*, vol. 4, pp. A42–A44, Jan. 2001.
- [26] M. Stich, M. Göttlinger, M. Kurniawan, U. Schmidt, and A. Bund, "Hydrolysis of LiPF₆ in Carbonate-Based Electrolytes for Lithium-Ion Batteries and in Aqueous Media," *J. Phys. Chem. C*, vol. 122, pp. 8836–8842, Apr. 2018.
- [27] R. Younesi, G. M. Veith, P. Johansson, K. Edström, and T. Vegge, "Lithium salts for advanced lithium batteries: Li–metal, Li–O₂, and Li–S," *Energy Environ. Sci.*, vol. 8, pp. 1905–1922, July 2015.
- [28] D. M. Seo, O. Borodin, S.-D. Han, P. D. Boyle, and W. A. Henderson, "Electrolyte Solvation and Ionic Association II. Acetonitrile-Lithium Salt Mixtures: Highly Dissociated Salts," *J. Electrochem. Soc.*, vol. 159, pp. A1489–A1500, Jan. 2012.
- [29] S.-D. Han, O. Borodin, D. M. Seo, Z.-B. Zhou, and W. A. Henderson, "Electrolyte Solvation and Ionic Association V. Acetonitrile-Lithium Bis(fluorosulfonyl)imide (LiFSI) Mixtures," *J. Electrochem. Soc.*, vol. 161, pp. A2042–A2053, Jan. 2014.
- [30] C. G. Barlowz, "Reaction of Water with Hexafluorophosphates and with Li Bis(perfluoroethylsulfonyl)imide Salt," *Electrochem. Solid-State Lett.*, vol. 2, pp. 362–364, Jan. 1999.
- [31] M. Kerner, N. Pylahan, J. Scheers, and P. Johansson, "Thermal stability and decomposition of lithium bis(fluorosulfonyl)imide (LiFSI) salts," *RSC Advances*, vol. 6, no. 28, pp. 23327–23334, 2016.
- [32] M. Kerner, N. Pylahan, J. Scheers, and P. Johansson, "Ionic liquid based lithium battery electrolytes: Fundamental benefits of utilising both TFSI and FSI anions?," *Physical Chemistry Chemical Physics*, vol. 17, no. 29, pp. 19569–19581, 2015.
- [33] D. Di Censo, I. Exnar, and M. Graetzel, "Non-corrosive electrolyte compositions containing perfluoroalkylsulfonyl imides for high power Li-ion batteries," *Electrochemistry Communications*, vol. 7, pp. 1000–1006, Oct. 2005.

- [34] H.-B. Han, S.-S. Zhou, D.-J. Zhang, S.-W. Feng, L.-F. Li, K. Liu, W.-F. Feng, J. Nie, H. Li, X.-J. Huang, M. Armand, and Z.-B. Zhou, "Lithium bis(fluorosulfonyl)imide (LiFSI) as conducting salt for nonaqueous liquid electrolytes for lithium-ion batteries: Physicochemical and electrochemical properties," *Journal of Power Sources*, vol. 196, pp. 3623–3632, Apr. 2011.
- [35] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, and J. Zhang, "A review of electrolyte materials and compositions for electrochemical supercapacitors," *Chemical Society Reviews*, vol. 44, no. 21, pp. 7484–7539, 2015.
- [36] M. Hagen, D. Hanselmann, K. Ahlbrecht, R. Maça, D. Gerber, and J. Tübke, "Lithium–Sulfur Cells: The Gap between the State-of-the-Art and the Requirements for High Energy Battery Cells," *Adv. Energy Mater.*, vol. 5, p. 1401986, Aug. 2015.
- [37] W. R. McKinnon and J. R. Dahn, "How to Reduce the Cointercalation of Propylene Carbonate in Li_xZrS_2 and Other Layered Compounds," *J. Electrochem. Soc.*, vol. 132, pp. 364–366, Jan. 1985.
- [38] S.-K. Jeong, M. Inaba, Y. Iriyama, T. Abe, and Z. Ogumi, "Electrochemical Intercalation of Lithium Ion within Graphite from Propylene Carbonate Solutions," *Electrochem. Solid-State Lett.*, vol. 6, pp. A13–A15, Jan. 2003.
- [39] Y. Yamada, Y. Takazawa, K. Miyazaki, and T. Abe, "Electrochemical Lithium Intercalation into Graphite in Dimethyl Sulfoxide-Based Electrolytes: Effect of Solvation Structure of Lithium Ion," *J. Phys. Chem. C*, vol. 114, pp. 11680–11685, July 2010.
- [40] Y. Yamada, M. Yaegashi, T. Abe, and A. Yamada, "A superconcentrated ether electrolyte for fast-charging Li-ion batteries," *Chem. Commun.*, vol. 49, pp. 11194–11196, Nov. 2013.
- [41] Y. Yamada, K. Usui, C. H. Chiang, K. Kikuchi, K. Furukawa, and A. Yamada, "General Observation of Lithium Intercalation into Graphite in Ethylene-Carbonate-Free Superconcentrated Electrolytes," *ACS Appl. Mater. Interfaces*, vol. 6, pp. 10892–10899, July 2014.
- [42] J. Wang, Y. Yamada, K. Sodeyama, C. H. Chiang, Y. Tateyama, and A. Yamada, "Superconcentrated electrolytes for a high-voltage lithium-ion battery," *Nat Commun*, vol. 7, p. 12032, June 2016.
- [43] L. Ma, S. L. Glazier, R. Petibon, J. Xia, J. M. Peters, Q. Liu, J. Allen, R. N. C. Doig, and J. R. Dahn, "A Guide to Ethylene Carbonate-Free Electrolyte Making for Li-Ion Cells," *J. Electrochem. Soc.*, vol. 164, pp. A5008–A5018, Jan. 2017.
- [44] D. M. Seo, O. Borodin, D. Balogh, M. O'Connell, Q. Ly, S.-D. Han, S. Passerini, and W. A. Henderson, "Electrolyte Solvation and Ionic Association III. Acetonitrile-Lithium Salt Mixtures–Transport Properties," *J. Electrochem. Soc.*, vol. 160, pp. A1061–A1070, Jan. 2013.
- [45] M. Doyle, T. F. Fuller, and J. Newman, "The importance of the lithium ion transference number in lithium/polymer cells," *Electrochimica Acta*, vol. 39, pp. 2073–2081, Sept. 1994.
- [46] S.-K. Jeong, H.-Y. Seo, D.-H. Kim, H.-K. Han, J.-G. Kim, Y. B. Lee, Y. Iriyama, T. Abe, and Z. Ogumi, "Suppression of dendritic lithium formation by using concentrated electrolyte solutions," *Electrochemistry Communications*, vol. 10, pp. 635–638, Apr. 2008.
- [47] L. Suo, Y.-S. Hu, H. Li, M. Armand, and L. Chen, "A new class of Solvent-in-Salt

- electrolyte for high-energy rechargeable metallic lithium batteries,” *Nature Communications*, vol. 4, p. ncomms2513, Feb. 2013.
- [48] T. Ma, G.-L. Xu, Y. Li, L. Wang, X. He, J. Zheng, J. Liu, M. H. Engelhard, P. Zapol, L. A. Curtiss, J. Jorne, K. Amine, and Z. Chen, “Revisiting the Corrosion of the Aluminum Current Collector in Lithium-Ion Batteries,” *J. Phys. Chem. Lett.*, vol. 8, pp. 1072–1077, Mar. 2017.
- [49] D. W. McOwen, D. M. Seo, O. Borodin, J. Vatamanu, P. D. Boyle, and W. A. Henderson, “Concentrated electrolytes: Decrypting electrolyte properties and reassessing Al corrosion mechanisms,” *Energy Environ. Sci.*, vol. 7, pp. 416–426, Dec. 2013.
- [50] Y. Yamada, C. H. Chiang, K. Sodeyama, J. Wang, Y. Tateyama, and A. Yamada, “Corrosion Prevention Mechanism of Aluminum Metal in Superconcentrated Electrolytes,” *ChemElectroChem*, vol. 2, pp. 1687–1694, Nov. 2015.
- [51] K. Matsumoto, K. Inoue, K. Nakahara, R. Yuge, T. Noguchi, and K. Utsugi, “Suppression of aluminum corrosion by using high concentration LiTFSI electrolyte,” *Journal of Power Sources*, vol. 231, pp. 234–238, June 2013.
- [52] L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, and K. Xu, ““Water-in-salt” electrolyte enables high-voltage aqueous lithium-ion chemistries,” *Science*, vol. 350, pp. 938–943, Nov. 2015.
- [53] C. Yang, J. Chen, T. Qing, X. Fan, W. Sun, A. von Cresce, M. S. Ding, O. Borodin, J. Vatamanu, M. A. Schroeder, N. Eidson, C. Wang, and K. Xu, “4.0 V Aqueous Li-Ion Batteries,” *Joule*, vol. 1, pp. 122–132, Sept. 2017.
- [54] D. Reber, R.-S. Kühnel, and C. Battaglia, “High-voltage aqueous supercapacitors based on NaTFSI,” *Sustainable Energy & Fuels*, vol. 1, no. 10, pp. 2155–2161, 2017.
- [55] P. Lannelongue, R. Bouchal, E. Mourad, C. Bodin, M. Olarte, S. le Vot, F. Favier, and O. Fontaine, ““Water-in-Salt” for Supercapacitors: A Compromise between Voltage, Power Density, Energy Density and Stability,” *J. Electrochem. Soc.*, vol. 165, pp. A657–A663, Jan. 2018.
- [56] A. Savitzky and M. J. E. Golay, “Smoothing and Differentiation of Data by Simplified Least Squares Procedures,” *Anal. Chem.*, vol. 36, pp. 1627–1639, July 1964.
- [57] R. Yazami and Y. F. Reynier, “Mechanism of self-discharge in graphite–lithium anode,” *Electrochimica Acta*, vol. 47, pp. 1217–1223, Feb. 2002.
- [58] A. Klein, T. Mayer, A. Thissen, and W. Jaegermann, “Photoelectron Spectroscopy in Materials Science and Physical Chemistry,” *Bunsen-Magazin*, no. 10, 2008.
- [59] Chen Shuru, Zheng Jianming, Mei Donghai, Han Kee Sung, Engelhard Mark H., Zhao Wengao, Xu Wu, Liu Jun, and Zhang Ji-Guang, “High-Voltage Lithium-Metal Batteries Enabled by Localized High-Concentration Electrolytes,” *Advanced Materials*, vol. 0, p. 1706102, Mar. 2018.