

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

**Toward Safer Energy Storage Solutions by Development of Fluorine-Free
Battery Electrolytes**

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Göteborg, Sweden 2017

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Licentiatuppsatser vid Institutionen för kemi och kemiteknik
Chalmers tekniska högskola.
Serie Nr: 2017:06

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Cover:
Schematic of a rechargeable battery which contains Mickey-Mouse salt.

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Göteborg, Sweden 2017

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Abstract

Portable electronic devices such as mobile phones, laptops, cameras and electronic vehicles (EVs) which contain lithium-ion batteries (LIBs), are indispensable part of our modern society. The safety of conventional electrolytes of LIBs, composed of fluorinated lithium salts and organic solvents is the source of some concerns. While the former is meta-stable at room temperature, quite expensive to synthesis and unsafe in the presence of moisture, the latter have high vapor pressure and are also flammable. Therefore, development of more stable salts and electrolytes are highly desirable, especially in the light of increased use of battery technology in *e.g.* electric vehicles (EVs).

In order to mitigate the challenges with current fluorine containing electrolytes, we set out to develop a new class of safer, fluorine-free anions based on the concept of pseudo-delocalized Mickey Mouse™ anions. Their Lithium and sodium salts have been synthesized for the first time, and fully characterized by different analytical methods such as NMR, mass spectroscopy and elemental analysis. Thermogravimetry analysis and X-ray crystallography were conducted to reveal both basic properties in terms of thermal stability and solubility of the salts. To further assess their properties as electrolytes, ion conductivity and electrochemical stability windows (ESWs) were performed.

Keyword: lithium-ion batteries (LIBs), safer electrolyte, fluorine-free salt, sodium-ion batteries (SIBs), aqueous electrolyte.

List of Publications

This thesis based on the following publications:

Paper I. **Fluorine-free salts for aqueous lithium-ion and sodium-ion battery electrolytes**
Elham Hosseini-Bab-Anari, Andrea Boschin, Toshihiko Mandai, Hyuma Masu, Kasper Moth-Poulsen, and Patrik Johansson
RSC Advances 6 (2016), 85194-85201.

Paper II. **Comparison between two fluorine-free anions and their lithium and sodium salts as battery electrolyte**

Elham Hosseini-Bab-Anari, Yajing Yan, Kasper Moth-Poulsen, and Patrik Johansson
(*Manuscript*).

Contribution Report

Paper I. Responsible for synthesis of the salts and performing chemical characterization such as NMR, mass spectroscopy and also writing the first draft of manuscripts as the first author.

Paper II. Responsible for synthesis of the salts and performing chemical characterization such as NMR, mass spectroscopy and also writing the first draft of manuscripts as the main author.

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List of Acronyms:

^1H NMR	Proton Nuclear magnetic resonance
^{13}C NMR	Carbon Nuclear magnetic resonance
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
EVs	Electric vehicles
ESW	Electrochemical stability window
EC	Ethylene carbonate
FSI	Bis(fluorosulfonyl)imide
HC	Hard carbon
HMM3311	3-dimethyl(3-sulfopropyl)ammonio propane-1-sulfonic acid
IM	Imidazolium
ILs	Ionic liquids
LIBs	Lithium-ion batteries
MM3311	3,3'-(dimethylammonio)bis (propane-1-sulfonate)
MM4411	4,4'-(dimethylammonio)bis (butane-1-sulfonate)
NiMH	Nickel-metal-hydride
PC	Propylene carbonate
PCPI	Pentadicyanopropenide
PF_6^-	Hexafluorophosphate
Pyr	Pyrrolidinium
SIBs	Sodium-ion-batteries
TADC	4,5-dicyano-1,2,3 trizole
TDI	Trifluoromethyl-4,5-dicyanoimidazole
TFSI	Bis(trifluoromethanesulfonyl)imide
WCAs	Weakly base coordinating anions
Z311	Dimethylammonio-propane sulfonate
ZDMBS	Dimethylammonio-butane sulfonate

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1

Introduction

Today's rechargeable batteries have made a remarkable impact on our daily lives. From their application in portable electric devices such as laptops, cellphones, cameras to electric vehicles (EVs). In particular, since the early 1990's when the first rechargeable battery [1] was introduced, the dependence of modern society on this new technology has increased dramatically. As a consequence, every year a huge amount of used batteries that contain non-environmentally friendly materials are accumulated in the environment [2], which undoubtedly forces us to reconsider the necessity of developing safer and more environmentally friendly battery technology.

Among rechargeable batteries, lithium-ion batteries (LIBs) are the most popular commercial class of batteries with high specific energy [3]. Typically, LIBs are composed of a series of cells. Each cell contains three main components, cathode and anode which host the lithium during charge and discharge processes and the electrolyte. Despite the rapid advancement of applying eco-friendly electrode materials [4-7], the main composition of electrolyte, which is one of the problematic aspects of today's LIBs, has been unchanged over the past two decades [8].

Typically, fluorinated lithium salts based on PF_6^- anions, which are dissolved in highly flammable organic solvents, have some intrinsic safety problems [9]. Owing to the meta-stability of the PF_6^- anion, it reacts easily with moisture and releases toxic gases in runaway conditions or even abuses [8, 10-16]. Therefore, moisture-free production or use of additives is pivotal to avoid any unwanted reactions, which in turn causes an increase in battery price [17-19]. Furthermore, the costly synthesis of fluorine salts [20] and the high flammability of the used organic

solvents are another source of concern. To overcome safety and cost issues, development of battery concepts that are fluorine-free and/or applying non-flammable solvents seems to be a very attractive option.

Here, to improve the safety and also cost issues of fluorine salts, this thesis focuses on synthesis and characterization of a new class of fluorine-free Li- and Na-salts, based on recent US patent [21], which has designed anions in a way that two negative charges are covalently attached to a positive central charge. As the charge is not fully localized and neither delocalized to a single region, the term pseudo-delocalized or Mickey Mouse™ anions is used to describe them [22]. While chapter 1 gives a basic motivation about the thesis, chapter 2 introduces the battery concept and its working principle. Chapters 3 and 4 of this thesis, are devoted to fluorine-free salts, specifically chapter 4 concentrates on the synthesis and chemical characterization of novel fluorine-free pseudo-delocalized salts.

2

Batteries

Transforming electrical energy to chemical energy which can be stored and then converted back to electrical energy, is one of the key features of batteries. Batteries are categorized as primary or secondary/rechargeable ones, the former can be used just once before discarding while the latter can be charged and discharged several times.

Different types of batteries with different chemistries have been invented over the past two centuries. The invention of the first battery occurred over 200 years ago, when Volta used two different metals such as silver and zinc that were separated by a brine-soaked cloth [23]. Then, in 1859, the lead-acid rechargeable battery was introduced which, despite some safety and environmental concerns [24], is still used today due to its low cost and good power density. However, by some modifications in packaging materials, this battery is used as the main source of power supply in starting-lighting-ignition of cars [23]. Another type of battery which has a high power density, is the Nickel-metal hydride (NiMH). It can be found in many devices that need high power density, *e.g.* cameras. Moreover, this battery type is the pioneer one that has been used in the first modern generation of hybrid electric vehicles (HEVs) [25].

Today, LIBs are the most widely employed rechargeable battery type for portable devices, not only because of their light weight but also because of their high specific energy density. However, recently due to the increasing demand, some concerns about the abundance of lithium resources has been raised [26, 27].

2.1 Working Principle of Electrochemical Cell

Batteries are composed of one or a series of electrochemical cells with some additional components such as current collectors. Two electrodes and an electrolyte, which forms an electrochemical cell is depicted in figure 1.

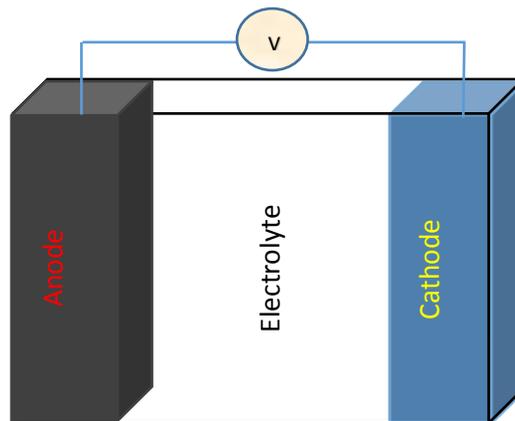


Figure 1. Main components of an electrochemical cell

During charge and discharging of cells, chemical reactions between electrodes and electrolyte takes place. Indeed, during the discharging process, oxidation at anode and reduction at cathode happen, while in charging process these reactions are reversed. To maintain the charge balance during redox reaction, ion transport via the electrolyte is occurring. If the used electrolyte is liquid, then a separator which is both an electronic isolator and ionic conductor, is used to prevent a physical contact between the two electrodes and consequently short circuiting the battery.

2.2 Lithium-Ion Batteries (LIBs)

The first rechargeable lithium battery was commercialized in the early 1980's. In fact the exploration of insertion or intercalation materials as cathodes, paved the way for commercialization of LIBs [23]. During charge and discharge, the lithium-ions are intercalated or de-intercalated from electrodes [28]. Cathodes in LIBs are normally a transition-metal oxides, which are usually layered in 2D or 3D structure to facilitate the intercalation. 3D-materials such as LiFePO_4 and LiMn_2O_4 are the most widely used materials in today's LIB [29]. Similar to cathodes, the anode material is also selected as a layered material, to ease the intercalation process. The most popular used anode material is graphite. The layered graphite, allows lithium-ions to be intercalated [30]. The formation of solid electrolyte interphase (SEI) is another important contributing factor to LIBs performance, within the initial cycle of

charging, reductive decomposition of electrolyte solution happens and forms a thin layer on the anode [31]. However, SEI layer is still permeable to lithium-ions, but can hamper further decomposition of electrolyte during battery operation [32]. The third main component of LIBs is the electrolyte that consists of a lithium salt, which in chapter 3 will be described in details.

2.3 Sodium-Ion Batteries (SIBs)

It is forecasted that the lithium resources in near future cannot satisfy market demand, hence a sudden jump in LIBs cost seems to be unavoidable [26, 27]. To overcome shortage of lithium, new battery concepts to replace LIBs is needed. Since 1980 onwards SIBs has attracted more attention, not only due to similar chemistry of sodium to lithium, but also because of its low cost and vast abundance [33-36]. However, to have an acceptable electrochemical cell in SIBs with good performance, some changes in electrodes and electrolyte should be exerted. For instance, while the SIB electrolyte is composed of a sodium salt solution to facilitate transferring of sodium-ion, hard carbon (HC) [37] as the anode and layered sodium metal oxide [38] as the cathode are used to provide intercalation/de-intercalation of sodium ion during charge and discharging process.

3

Electrolyte

As mentioned in chapter 2, the electrolyte is a medium which allows for transfer of ions between cathode and anode during charge and discharging process, inside the cell. The electrolyte should possess some specific properties to function well such as:

- Wide electrochemical stability window.
- High ion conductivity to secure a high mobility of ions.
- Stability toward unplanned electric, mechanical and thermal abuses such as overcharging or overheating.
- Be composed of non-toxic, eco-friendly and low cost materials.

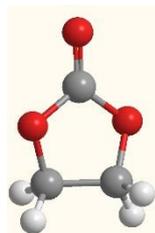
Based on the battery application, different electrolyte concepts such as liquid, gel, solid polymer or ionic liquids based has been used [38]. Liquid electrolytes among all has the highest ionic conductivity. Since the focus of this thesis is on liquid electrolyte, henceforth only liquid electrolytes for LIBs and SIBs will be discussed.

3.1 Liquid Electrolytes

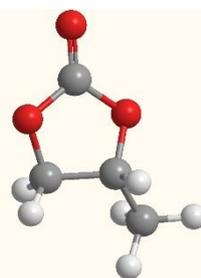
Typically, a liquid electrolyte contains a salt which is dissolved in aqueous or organic solvents. Depending on the solvents in the electrolyte, it can be categorized in 3 groups, organic electrolytes, ionic liquid electrolytes and aqueous electrolyte which will be introduced in the following paragraphs.

3.1.1 Organic Based Electrolyte

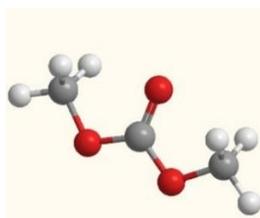
The conventional electrolyte for LIBs and SIBs is based on electrolyte salts dissolved in a combination of different linear and cyclic carbonate-based organic solvents [39]. Ethylene carbonate (EC), Dimethyl carbonate (DMC), Diethyl carbonate (DEC) and Propylene carbonate (PC) (Figure. 2) are the most used solvents in both LIBs and SIBs. Since none of these solvents have all the required physical properties, a combination is often used in order to meet the right electrolyte properties. For instance, EC has a high dielectric constant that can dissolve salts well, but since it has a high melting point, T_m , 36°C , it can be combined with other solvents *e.g.* DMC to decrease both melting point and viscosity [18]. These solvents have been used intensively since twenty years ago [40], but high flammability and other safety issues are still the problematic aspects.



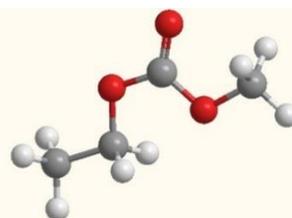
Ethylene Carbonate (EC)



Propylene Carbonate (PC)



Dimethyl Carbonate (DMC)



Diethyl Carbonate (DEC)

Figure 2. Chemical structure of conventional solvents for LIBs and SIBs electrolyte

3.1.2 Ionic Liquid Based Electrolyte

Ionic Liquids (ILs) are a group of liquid materials that are entirely made of ionic species. By definition ILs melt below 100°C [41]. Due to specific properties of ILs such as negligible vapor pressure, wide electrochemical window and high intrinsic conductivity, many different applications have been attributed to ILS. High ionic conductivity and also non-flammability of ILs, made them attractive as alternative solvents in battery electrolyte applications. Neat ILs cannot be used as electrolyte, due to lack of lithium- or sodium-ions, therefore lithium or sodium salt needs to be added to ILs to provide a source of mobile ions. However, this addition can cause increased viscosity of the electrolyte because of increasing ion-ion interactions [44]. Pyrrolidinium (Pyr) or imidazolium (IM) based cations and bis(trifluoromethanesulfonyl)imide (TFSI) or bis(fluorosulfonyl)imide (FSI) based anions are the most common ILs (Figure 3.), which is used as electrolyte in both LIBs [45-48] and SIBs [49, 50].

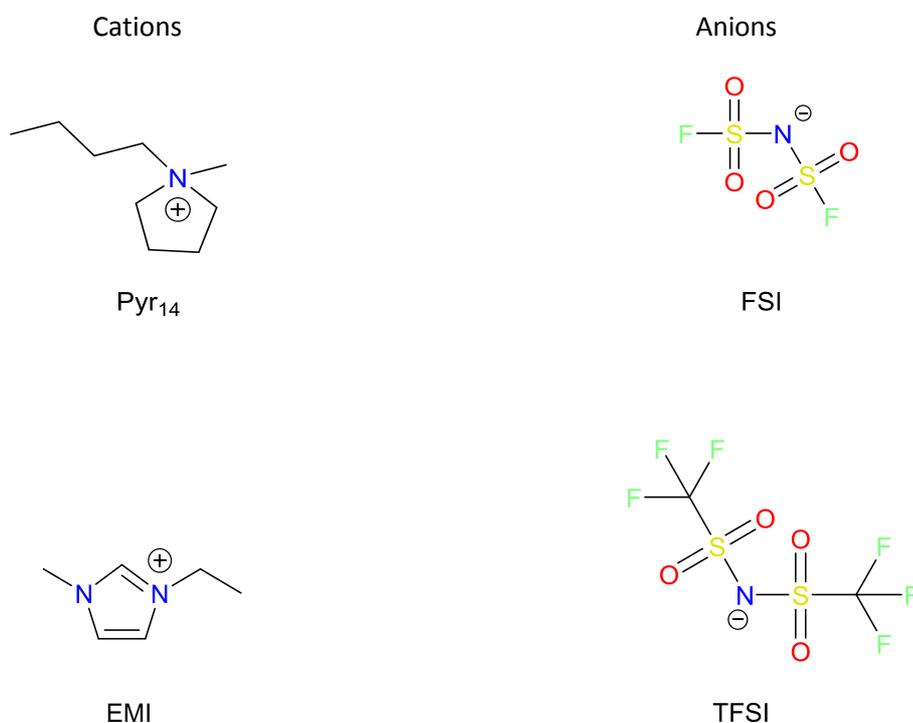


Figure 3. Chemical structure of cations and anions in ILS.

3.1.3 Aqueous Based Electrolyte

Water is one of the first solvents that has been used in battery [22]. Some specific properties such as low viscosity [51], high dielectric constant, low cost and its safety compared to organic solvents, makes water a very attractive solvent candidate in battery applications. However, the narrow electrochemical stability window (ESW) of 1.23 V [52] is the main challenge. Nevertheless, some aqueous electrolytes based on inorganic salts and organic salts has been reported [8, 53-55]. Recently, Sue *et.al* [56] reported a high concentration electrolyte (20 M) based on organic salts, which can be uses as high voltage LIBs aqueous electrolyte. Here, also in paper I, II, new organic pseudo-delocalized salts for aqueous based LIBs and SIBs is introduced.

3.2 Lithium and Sodium Salts

As it was mentioned at the beginning of this chapter, the electrolyte is one of the three main components of any electrochemical cell. But unfortunately, when comparing to recent development in the cathode and the anode, much less advancement has been seen in the development of the electrolytes. Some intrinsic issues such as low safety, high price and non-eco-friendly constituents have accompanied today's electrolytes [20, 57]. Indeed, not only because of flammability and toxicity of used organic solvents, but also because of the common fluorinated salts in dominant LIBs, from that perspective, the state of the art electrolytes is very far from ideal. The high influence of used salt in overall properties of electrolyte, is a key point to be taken into account. Some basic properties that an ideal electrolyte salt should possess, have been listed below [58]:

- High solubility in electrolyte solvents.
- Stability of anions against oxidative decomposition at cathode.
- The anion should be inert to electrolyte solvents.
- The anion should remain stable against thermally induced reactions with electrolyte solvents and other cell components.
- Its components should be environmentally friendly and non-toxic.

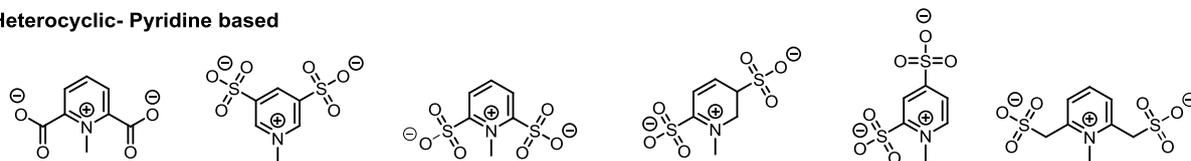
Dominant commercial electrolyte concepts are based on a fluorine containing salt such as LiPF_6 . Some features of fluorinated salts are very problematic for any battery, owing to meta-stability of its anions such as e.g. PF_6^- . In traces of water into the cell, PF_6^- will readily decompose and produce highly toxic gases such as HF and POF_3 [10-16]. Moreover, the use of fluorine chemistry is in general challenging and costly [20, 57]. To overcome these problems,

moisture-free cell preparation or the use of additives is indispensable strategies that causes increase in LIBs price [17, 18, 59].

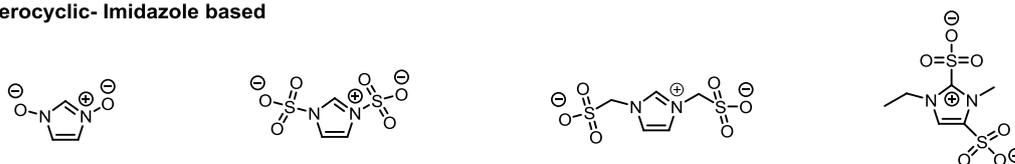
Over the past decade, many different salts have been tested for application in LIBs [60]. Amongst them “weakly based coordinating anions” (WCAs), such as TFSI ($\text{CF}_3\text{SO}_2\text{NSO}_2\text{CF}_3$), FSI ($\text{FSO}_2\text{NSO}_2\text{F}$) and also “Hückel-anions” like 2-trifluoromethyl-4,5-dicyanoimidazole (TDI), were safer compared to other more classical choices, but because of fluorine [61, 62], price issues and safety concerns still remain. Some other attractive alternative are based on fluorine-free WCAs [63, 64] such as 4,5-dicyano-1,2,3-triazole (TADC) [65, 66] and Pentadicyanopropenide (PCPI) [8, 67] has also been investigated.

Jónsson *et al.* have proposed a series of WCAs based on molecular design and DFT modelling (Figure 4.). The WCA's fall in 4 different categories of chemical structures, which are heterocyclic compounds such as pyridinium- and imidazolium-based. While the rest were aliphatic- and spiro-based anions. All were completely fluorine-free, because of their specific chemical structures, they coined them pseudo-delocalized or “Mickey MouseTM” anions (Figure 5.).

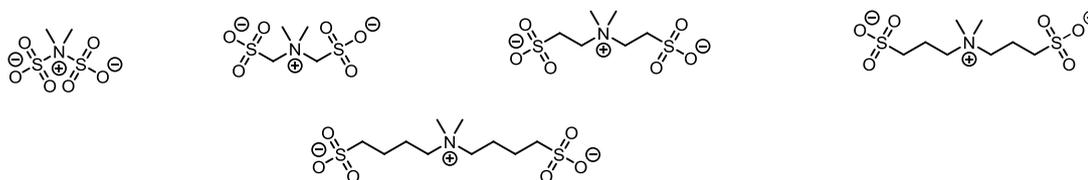
Heterocyclic- Pyridine based



Heterocyclic- Imidazole based



Aliphatic



Spiros

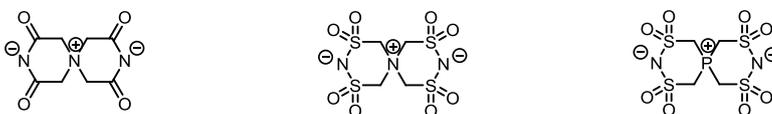


Figure 4. Chemical structure of Mickey Mouse™ anions. (Reproduced with permission from [68] from the PCCP Owner Societies).

As it can be seen in figure 5. the chemical design includes a positively charged unit which is covalently attached to two negatively charged groups. The charge in the anions is neither completely localized to a specific region nor delocalized, hence the term pseudo-delocalized has been used to describe them.

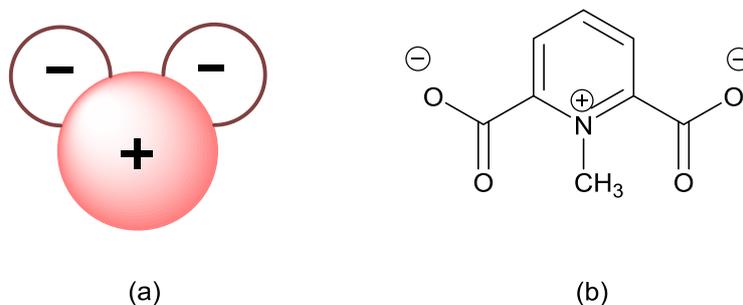
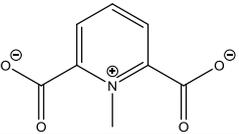
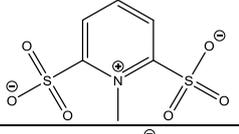
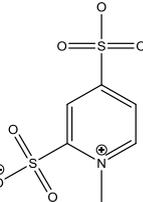
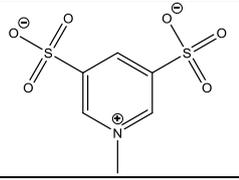
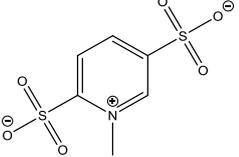
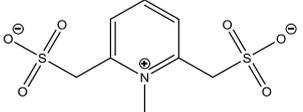
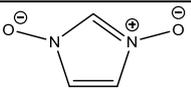
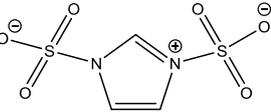
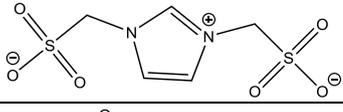
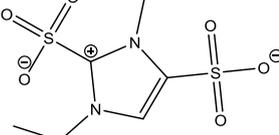
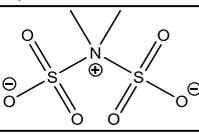


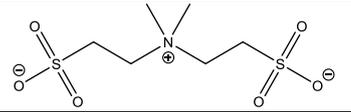
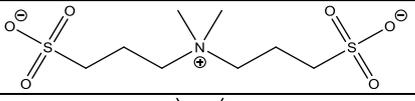
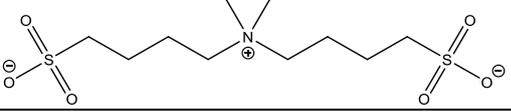
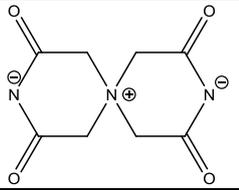
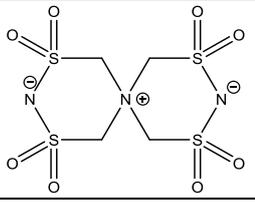
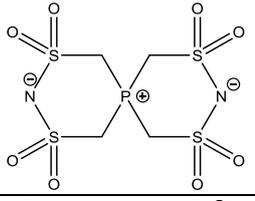
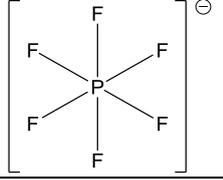
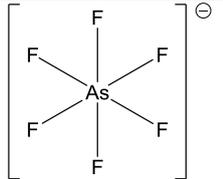
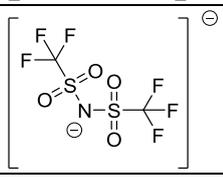
Figure 5. a) The pseudo-delocalized concept and “Mickey Mouse™” anions. b) 1-methylpyridin-2,6-dicarboxylate

Jónsson and co-workers investigated two factors about these anions, by the use of DFT calculations. First, they evaluated the cation-anion interaction through the salt dissociation reaction (ΔE_d) $\text{Li}^+ \text{A}^- \rightleftharpoons \text{Li}^+ + \text{A}^-$ and then stability of anion against oxidation (ΔE_v) via oxidation of anion to the radical state. They also made a quantitative comparison of their results (Table 1.) with the most common anions such as PF_6^- , AsF_6^- and TFSI [69, 70]. As the dissociation energy ΔE_d , estimates the ease of formation of ions, therefore lower dissociation energy means, it can provide charge carrier species at low energy, which is one of the most important properties that ideal salts for battery application should have. On the other hand, anion oxidation potential ΔE_v , also provides information about the stability of the anion against oxidation. Hence, higher oxidation potential, shows the oxidative resistance of anions at anode during battery performance, which is again another key point for an ideal electrolyte salt.

However Jónsson *et.al.* performed DFT calculation to investigate the salts dissociation reactions energy and oxidation potentials, but the focus of this licentiate thesis is the practical realisation of these proposed structures. Hence, the focuses of this thesis, will be on the synthesis and characterisation of these novel pseudo-delocalized anions and their lithium and sodium salts.

Table 1. The dissociation energy and anion oxidation potentials of the Mickey Mouse™ anions by DFT calculations. (Reproduce with permission from [68] from the PCCP Owner Societies).

Anions	ΔE_d (KJ mol ⁻¹)	ΔE_v (V vs. Li ⁺ /Li ⁰)
	597.5	2.9
	567.4	3.65
	580.7	3.47
	596.7	3.27
	542.0	3.57
	704.8	3.29
	598.4	0.74
	546.6	4.12
	662.9	3.39
	558.6	3.57
	635.8	3.82

	661.0	3.28
	659.5	3.13
	788.7	2.63
	604.9	3.32
	546.9	4.27
	562.9	4.45
	567	5.65
	558	6.05
	592	4.52

4

Experimental Methods

In this chapter the applied synthetic and characterisation methods are presented. According to figure 4. and table 1 in chapter 3 it seems that there were several anions that could be synthesized without any difficulties, apart from spiro-based. But when it comes to practical lab experiments, several challenges and difficulties appeared. Some restrictions such as availability of starting materials with reasonable price and also accessible literature procedures for needed synthetic transformations were sometimes scarce or not available at all. Known methods towards somehow similar compounds have confined our options. Nevertheless, we attempted to synthesis also anions from pyridinium and imidazolium sub group, but at this stage of the project we have not been able to isolate the desired lithium or sodium salts in reasonable yield or purity. In contrast, we were successful in synthesizing two anions and also both Li and Na salts from aliphatic subset. Therefore in the following experimental part, our focus will be on synthesis of the aliphatic anions.

4.1 Synthesis of LiMM4411 and NaMM4411

The synthesis of lithium and sodium salt based on (di-methyl ammonio)bis(butane-1-sulfonate), MM4411 (the abbreviation invented here refers to the counterion (Li or Na) the substituents on the ammonium moiety and the length of the alkyl spacer group) anions was conducted via two synthetic steps (Figure 6.) in aqueous medium. In the first step, the monomeric zwitterion, di-methyl ammonio-butanefulfonate (ZDMBS) precursor, was

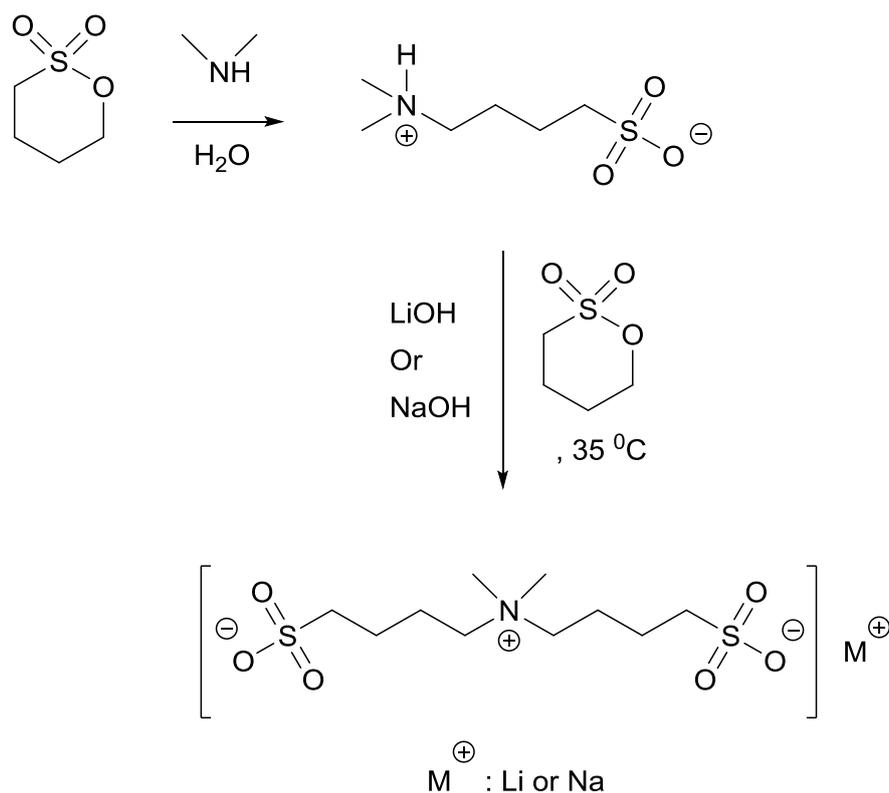


Figure 6. Synthesis path of fluorine-free LiMM4411 and NaMM4411 salts (Reproduce from Paper I with permission from Royal Society of Chemistry).

achieved by nucleophilic substitution reaction, which was previously reported [71] and here used with minor modification. Using di-methylamine as a nucleophile which attack to 1,4-butane sultone, leads to ring opening of butane sultone. This type of reaction, is quite common in preparation of sulfobetain compounds [72, 73], however to avoid unwanted reaction of butane sultone with water, we saw that low temperature should be exerted. In the second step of the synthetic procedure a nucleophilic substitution reaction between ZDMBS from first step and 1,4-butane sultone as the electrophile was employed. This step required a base such as lithium hydroxide or sodium hydroxide in stoichiometric amounts in order to activate the zwitterion for nucleophilic attack on butane sultone. The desired lithium and sodium salts were thus directly formed in the final step.

4.2 Synthesis of LiMM3311 and NaMM3311

The shorter variations of MM4411 with 3 carbons spacers, MM3311 was an interesting alternative. In fact, by applying a modified version of synthesis method that has been conducted for MM4411 (paper I), the anion 3,3'-(di methyl ammonio) bis(propane-1-sulfonate), MM3311 and its salts (Figure 7.) were synthesized in three consecutive synthesis steps (paper II).

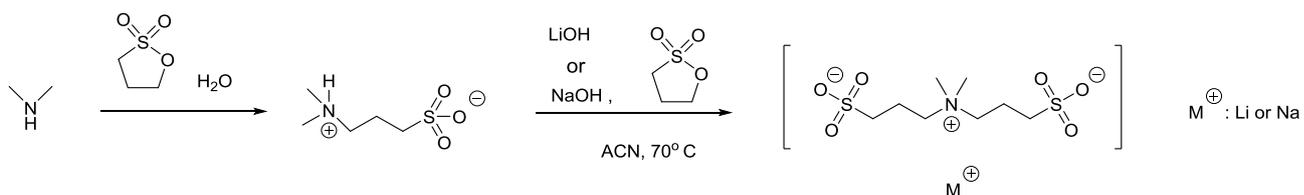


Figure 7. Synthesis route of LiMM3311 and NaMM3311 (Paper II).

The first step of the synthesis route employs a nucleophilic substitution of dimethyl amine and propane sultone in water. Ring opening of 1,3-propane sultone by nucleophilic attack of dimethylamine, causes formation of the zwitterion di-methyl ammonio-propane sulfonate (Z311) precursor. In the second step, nucleophilic substitution reaction took place by stirring a slurry of stoichiometric amount of Z311 from the first step with lithium hydroxide or sodium hydroxide as base and 1,3-propane sultone in anhydrous acetonitrile in contrast to the butane sultone used in synthesis of the Na/LiMM4411 salts, the propane sultone was much more reactive and water could therefore not be used as the solvent. "3- (dimethyl (3-sulfopropyl) ammonio) propane-1-sulfonate" HMM3311 was isolated as white crystals after removal of the solvent. Similar to MM4411, the need of using base in second step for activation of zwitterion, was crucial. The desired lithium and sodium salts, were achieved by neutralization of HMM3311 with a 1 molar solution of lithium hydroxide or sodium hydroxide respectively.

5

Results and Discussion

This chapter provides a summary of the results presented in the publication and manuscript appended at the end of this thesis.

5.1 LiMM4411 and NaMM4411

As mentioned in previous chapters, today's state-of-the art of LIBs electrolytes is far from ideal, mainly due to safety concerns and costly synthesis of fluorinated salts. In paper I, the first generation of fluorine-free salts based on pseudo-delocalized concept (Figure 8.a) were synthesized in high purity and yield in aqueous media.

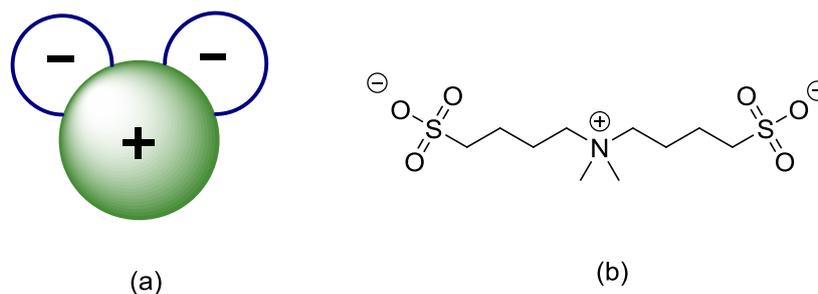


Figure 8. a) The concept of pseudo-delocalized “Mickey Mouse™” anions and **b)** (di-methyl ammonio)bis(butane-1-sulfonate), MM4411 (Reproduced from paper I with permission from the Royal Society of Chemistry).

The commercially available dimethylamine and 1,4-butane sultone were used as starting material for nucleophilic substitution reaction in first step, figure 6. and resulted in colorless product ZDMBS in high yield (96%). Synthesizing desired salts via nucleophilic substitution in second step were performed and yielded two highly pure LiMM4411 and NaMM4411 salts. However, second step was temperature dependence as it was monitored by NMR. Indeed increasing the temperature leading to faster completion but by expenditure of reaction conversion (table 2). Due to high reactivity of 1,4-butane sultone with water as solvent at higher temperature, lower yield would be achieved. Therefore, in order to get the optimum product with high yield and purity, 35°C was selected as the reaction temperature. By this optimized synthetic route the analytically pure target salts were isolated in excellent yield (LiMM4411: 92% and NaMM4411: 90%) on multi gram scale. From the chemistry point of view, both lithium, LiMM4411 and sodium, NaMM4411 were synthesized from readily available starting material with low cost and high yield and purity. The synthesis route was done entirely in water as solvent, and purification was done without any chromatography. From physical properties side, both of the salts showed high thermal stability compared to popular fluorine contains salts. However their poor solubility in organic based solvent and quite good solubility in aqueous solvent, pave the way of their application in low voltage aqueous battery.

Table 2. Optimization of reaction conditions. (Reproduced from paper I with permission from the Royal Society of Chemistry).

T (°C)	20	35	50	75	100
Conversion (%)	99	98	91	87	83
Reaction Time	21 days	72 h	48 h	36 h	24 h

5.2 LiMM3311 and NaMM3311

In paper II, two new fluorine-free aliphatic salts LiMM3311 and NaMM3311 based on the pseudo-delocalized concept with 3 carbons spacers were synthesized in 3 steps (Figure 7.). Since previously synthesized salts LiMM4411 and NaMM4411 showed low solubility in conventional electrolyte solvents, hence synthesizing of aliphatic salts with shorter alkyl chain was of interest. Then both anions and their salts were compared from chemistry view and also thermophysical properties. LiMM3311 and NaMM3311 salts were synthesized in 3 consecutive steps. Firstly, Z311 monomeric zwitterion Z311 was achieved in high purity and yield (96%) by the commercially available dimethylamine and 1,3-propane sultone as starting material via nucleophilic substitution reaction. Then it was followed in a second step by stirring a slurry of stoichiometric amounts of Z311 in hand from last step, LiOH or NaOH and propane sultone in anhydrous acetonitrile at 70 °C. it can be compared with the second step of LiMM4411 and NaMM4411 which was done in water. Albeit, changing solvent in second step, resulted some remarkable changes on the synthesis routes. Initially, the reaction temperature was raised to 70 °C compared to 35 °C in water, however by exerting lower temperature the completion of reaction would take longer (10 to 14 days). On the other hand, as it was showed before (paper I), by the end of second step, two desired lithium and sodium salts were afforded, but here instead, we obtained in the acidic form of anions, HMM3311 in high yield (94%). Furthermore, a white byproduct that was insoluble in most of the conventional polar and non-polar solvents, was also precipitated out with HMM3311, which was isolated by filtration after dissolving the mixture in water. In a final step, the neutralization of HMM3311 by an aqueous solution of lithium hydroxide or sodium hydroxide resulted in final products LiMM3311 (83%) and NaMM3311 (82%) in high purity. Then thermophysical properties of LiMM3311 and NaMM3311, were investigated more and also compared with the pervious salts (paper I). However, the solubility of the salts (table 3) in typical battery solvents are still quite low, because of strong interaction between lithium-/sodium-ions and the anion, but in contrast to the MM4411 salts, the solubility of new MM3311 salts in DMSO was about 10 times higher, indicating that these salts might be used as new fluorine-free salts in lithium air or sodium air batteries in the future.

Table 3. Solubility comparison for Li and Na salts based on MM3311 and MM4411 anions, in g/L.

Solvents Salts	Aprotic			
	ACN	PC	EC:DMC	DMSO
LiMM3311	< 0.01	< 0.01	< 0.01	≤ 0.1
NaMM3311	< 0.01	< 0.01	< 0.01	≤ 0.1
LiMM4411	< 0.01	< 0.01	< 0.01	< 0.01
NaMM4411	< 0.01	< 0.01	< 0.01	< 0.01

6

Conclusion and Outlook

This thesis has covered the synthesis of a first generation of fluorine-free Mickey Mouse™ anions based on the pseudo-delocalized concept. According to theoretical calculation and combination with experimental results, it seems that all the salts, are good candidates for low voltage aqueous batteries. However lithium and sodium salts, based on MM3311 anions had lower dissociation energy compare to LiMM4411 and NaMM4411, but it was still too high to hinder low solubility in conventional electrolyte solvents. To improve the performance of salts based on pseudo-delocalized concept, as promising electrolyte for both LIBs and SIBs some suggestion are mentioned here:

- One possible route could be to modify the sulfonate group in the synthesized anions to “soften” the sulfonate center and in consequence increasing the salts solubility in common battery solvents.
- Synthesis of second generation of MM salts, might be conducted on the aliphatic-based anions with shorter alkyl chains in order to overcome the solubility challenges.
- Other options could be synthesizing of asymmetrical MM anions to improve salts solubility's in common electrolyte solvents.

- Alternative could be trying to synthesis some other salts based on pseudo-delocalized concept, which showed more promising properties somehow the same as common fluorinated salt. They can be from any other subsets of MM anions like pyridine-, imidazole- or even spiro-based.

Acknowledgment

My deepest gratitude goes to my supervisor Kasper and also my co-supervisor Patrik, giving me opportunity to work on this intersecting project and of course for their continues support and guidance.

I would also thanks all my friends, present and former colleagues in Kasper Moth-Poulsen (KMP) group, everyone in KMF and also all the people from Floor 8th for very nice environment.

Special thanks to Lotta and Frida for their patience and continuous support since the first day of my Swedish journey.

I greatly appreciate my family, specially my parents and brothers for all their encouragement and unconditional support during all my studying time.

At last but not the least, Saeed and Avin, I am incredibly happy to have you and your lovely support! I am sure without your support and patience, this project would not be proceed.

Thank you all!

Elham

31 January 2017

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