

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Synthesis of Novel Fluorine-Free Salts for Battery Electrolytes

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Cover:

Schematic of a LIB battery, in which the electrolyte contains pseudo-delocalized anion. Four different anions based on this concept have been depicted. From top left MM26py (1-methylpyridinium-2,6-dicarboxylate) & MM3411 (4-(dimethyl(3-sulfonatopropyl) ammonio)butane-1-sulfonate) and bottom row from left MM3311 (3,3'-(dimethylammonio) bis(propane-1-sulfonate)) & MM4411 4,4'-(dimethylammonio)bis(butane-1-sulfonate).

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Abstract

Nowadays lithium-ion batteries (LIBs) are the dominant power sources of portable electronic devices such as mobile phones, laptops and cameras. Although recently their applications have extended to areas of electromobility and hybridization of vehicle, cost and safety issues remain as big obstacles for a smoother implementation. One particularly problematic aspect of conventional LIBs is the electrolytes which typically composed of fluorinated lithium salts (*e.g.* LiPF₆) and organic solvents. 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, design and 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 the current fluorine containing electrolytes, a concerted effort was set out on the synthesis and evaluation of a new class of fluorine-free lithium and sodium salts based on pseudo-delocalized concept. Four different electrolyte concepts include: aqueous, solid state, water-in-bisalt (WiBS) and ionic liquid based, containing these anions were proposed for lithium-ion and sodium-ion batteries for the first time.

In this thesis, ten novel non-fluorinated lithium and sodium electrolyte salts based on pyridinium and ammonium pseudo-delocalized concept were synthesized and fully characterized by analytical methods such as NMR, mass spectroscopy and elemental analysis. Further, it was also attempted to present the applied synthetic methods for other pseudo-delocalized anions based on imidazolium and ammonium salts and highlight the challenges and limitations which persist during the synthesis processes of these salts.

Keyword: lithium-ion batteries (LIBs), safer electrolyte, fluorine-free salt, sodium-ion batteries (SIBs), aqueous electrolyte, ionic liquid based electrolyte, solid state electrolyte, water-in-bisalt (WiBS) electrolyte.

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Elham

List of Publications

This thesis is based on the work contained in the following papers, referred to by Roman numerals in the text:

- Paper I **Fluorine-free salts for aqueous lithium-ion and sodium-ion battery Electrolytes**, Elham Hosseini-Bab-Anari, Andrea Boschini, Toshihiko Mandai, Hyuma Masu, Kasper Moth-Poulsen, and Patrik Johansson., *RSC Advances.*, 2016, **6**, 85194-85201.
- Paper II **Solvent-free lithium and sodium containing electrolytes based on pseudo-delocalized Anions**. Juan Forero-Saboya, Elham Hosseini-Bab-Anari, Muhammad Abdelhamid, Kasper Moth-Poulsen and Patrik Johansson., *Chem. Commun.*, 2019, **55**, 632–635.
- Paper III **Water-in-Bi-Salt electrolyte with record salt concentration and widened electrochemical stability window**. Juan Forero-Saboya, Elham Hosseini-Bab-Anari, Muhammad Abdelhamid, Kasper Moth-Poulsen and Patrik Johansson., *J. Phys. Chem. Lett.*, 2019, **10**, 17, 4942-4946.
- Paper IV **Ionic liquid based battery electrolytes by lithium and sodium pseudo-Delocalized pyridinium anion salts**. Elham Hosseini-Bab-Anari, Adriana M. Navarro-Suárez, Kasper Moth-Poulsen and Patrik Johansson., *Phys. Chem. Chem. Phys.*, 2019, **21**, 18393-18399.

This author has published the following paper which is not included in this thesis:

Substituted ferrocenes and iodine as synergistic thermoelectrochemical heat harvesting redox couples in ionic liquids. Elham Hosseini-Bab-Anari, Mark Romano, Wuan Xin Teh, Jeffry James Black, Edward Jiang, Jun Chen, Trang Quynh To, Janjira Panchompoo and Leigh. Aldous., *Chem. Commun.*, 2016, **52**, 745-748.

Contribution Report

- Paper I** Performed the synthesis and chemical characterization of the compounds except the elemental analysis and X-ray crystallography. Wrote the paper with the other co-authors and shared the first co-authorship together with Andrea Boschini.
- Paper II** Performed the synthesis and chemical characterization of the compounds except the elemental analysis. Wrote the paper with the other co-authors and shared the first co-authorship together with Juan Forero-Saboya.
- Paper III** Designed the anion and performed the synthesis and full chemical characterization of the salts, except the elemental analysis.
- Paper IV** Performed the synthesis and chemical characterization of the compounds except the elemental analysis. Wrote the paper with the other co-authors and shared the first co-authorship together with Adriana M. Navarro-Suárez.

List of Acronyms:

¹ HNMR	Proton nuclear magnetic resonance
¹³ CNMR	Carbon nuclear magnetic resonance
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DCM	Dichloromethane
DCTA	4,5-dicyano-1,2,3 trizole
DFT	Density functional theory
DSImCl	1,3-disulfonic acid imidazolium chloride
EC	Ethylene carbonate
EMC	Ethyl methyl carbonate
ESW	Electrochemical stability window
EVs	Electric vehicles
FSI	Bis(fluorosulfonyl)imide
HC	Hard carbon
HEVs	Hybrid electric vehicle
HMM1341py	3-(4-carboxypyridinium)propane-1-sulfonic acid
HMM2233	3,3'-(diethylammonio)bis(propene-1-sulfonic acid
HMM3311	3-(dimethyl(3-sulfopropyl)ammonio)propane-1-sulfonic acid
HMM3411	3-(dimethyl(4-sulfobutyl)ammonio)propane-1-sulfonic acid
HOMO	Highest occupied molecular orbital
HT-LIB	High temperature lithium ion battery
Im	Imidazolium
ILs	Ionic liquids
LC-MS	Liquid chromatography–mass spectrometry
LCO	Lithium cobalt oxide
LiAsF ₆	Lithium hexafluoroarsenate
LiBF ₄	Lithium tetrafluoroborate
LiBOB	Lithium bis(oxalato)borate
LIBs	Lithium-ion batteries
LiClO ₄	Lithium perchlorate

Li ₃ PO ₄	Lithium phosphate
LUMO	Lowest unoccupied molecular orbital
MeOTf	Methyl trifluoromethanesulfonate
MW	Microwave
MM13Im	Imidazolium-1,3-disulfonate
MM14py	1-(3-sulfonatopropyl)pyridinium-4-carboxylate
MM2234	4-(diethyl(3-sulfonatopropyl)ammonio)butane-1-sulfonate
MM26py	1-methylpyridinium-2,6-dicarboxylate
MM3311	3,3'-(dimethylammonio)bis (propane-1-sulfonate)
MM3333	3,3'-(diisopropylammonio)bis(propane-1-sulfonate)
MM33pyr	3,3'-(pyrrolidinium-1,1-diyl)bis(propane-1-sulfonate)
MM3411	4-(dimethyl(3-sulfonatopropyl) ammonio)butane-1-sulfonate
MM4411	4,4'-(dimethylammonio)bis(buatne-1-sulfonate)
NiMH	Nickel-metal-hydride
PC	Propylene carbonate
PF ₆ ⁻	Hexafluorophosphate
Pyr	Pyrrolidin
Pyr ₁₄	N-butyl-N-methyl pyrrolidinum
RTIL	Room temperature ionic liquid
SEI	Solid electrolyte interphase
SHE	Standard hydrogen electrode
SIBs	Sodium-ion-batteries
SPI	Solid permeable interface
SSE	Solid state electrolyte
TDI	Trifluoromethyl-4,5-dicyanoimidazole
TFSI	Bis(trifluoromethanesulfonyl)imide
TGA	Thermogravimetric analysis
T _m	Melting temperature
TMPA	Trimethylpropylamonium
WCA	Weakly coordinating anion
WiBS	Water-in-bisalt
WiSEs	Water-in-salt electrolytes
Z223	3-(diethylammonio)propane-1-sulfonate

Z311	Dimethylammonio-propane sulfonate
ZDMBS	Dimethylammonio-butane sulfonate
ΔE_d	Dissociation energy
ΔE_v	Oxidation potential

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Chapter 1

Introduction

Human greed in consuming more and more fossil fuel energy sources since the mid-20th century, has dramatically and uninterruptedly increased greenhouse gas emissions. Climate change and global warming are two major threats to humanity caused by man-made improper activity. But, rising global awareness about the consequences of the environmental changes led to the signing of the Paris Agreement in 2015 [1]. However, the success of this agreement, entirely depended on all countries world-wide efforts. Reducing greenhouse gasses emission and tackling the global warming, have spurred alternative energy sources such as rechargeable/secondary batteries. Nowadays rechargeable batteries have surrounded dominantly human's modern lives from their application in portable electric devices such as laptops, cellphones, cameras to even electric vehicles (EVs). Although, this technology has made our lives easier with more entertainments but still some failures are accompanying it, which can be a new threat for our environment in near future. According to wide range usage of this technology every year considerable amount of used batteries contain non-environmentally friendly materials are accumulated in the environment [1]. This concern persuades us to reconsider the battery technology for improving its safety and using more environmentally friendly materials.

Among all the available commercial rechargeable batteries such as Pb-acid, Ni-MH and Ni-Cd which based on different chemistries, lithium-ion battery (LIB) duo to its high energy capacity and lightweight [2] is the most promising and efficient class of battery. Although this battery technology firstly was commercialized in 1990 by Sony company [3], but after thirty years, three famous scientists John B. Goodenough, M. Stanley Whittingham and Akira Yoshino earned the chemistry Nobel prize 2019, for their efforts towards "The developments of lithium-ion batteries".

In general, LIBs have composed of a series of electrochemical cells. Each cell possesses three main components as cathode, anode and electrolyte which are considered as the common parts in all batteries technology. Despite the remarkable advancement of utilizing eco-friendly electrode materials [4-9], LIB electrolyte state of the art has not been changed significantly. Big concerns about the electrolyte safety is the most problematic aspect of today's LIBs technology, which unfortunately has not been touched over past two decades [10].

Typically, LIB electrolyte consists of a fluorinated lithium salt based on PF_6^- anion dissolved in organic solvents e.g. EC/DEC (1:1) – often at 1M concentration, has a combination of excellent properties: a high oxidation potential (>5.1 V vs. Li^+/Li), good solubility of the salt in the organic solvents and an excellent conductivity (≈ 11 mS cm^{-1} @ 20 °C) [11]. Despite having these good features, it has many intrinsic problems [12]. Leaving the costly synthesis of fluorinated salts [13] behind, meta-stability and moisture sensitivity of PF_6^- anion, which may lead to release of toxic gases in runaway conditions or even abuses, high flammability and leakage of organic solvents are the main safety issues of LIBs electrolyte [10, 14-20]. Therefore, moisture-free production or use of additives is pivotal to avoid any unwanted reactions, which in turn causes an increase in battery price [21-23]. To overcome safety and cost issues, development of battery concepts that are fluorine-free and/or applying non-flammable solvents seems to be very attractive options.

This thesis focuses on the synthesis and characterization of a new class of fluorine-free anions and their corresponding lithium and sodium salts, which have been designed and studied previously by a computer-aided assessment using DFT calculations [24, 25]. While chapter 1 gives some motivations about the thesis, chapter 2 provides a short introduction to the basic operation principles of batteries with the focus on LIB and SIB in general. Various electrolyte concepts and its components are described in chapter 3. A particular emphasis in chapter 4, is given to the experimental part which covers attempts to synthesis and characterization of novel fluorine-free pseudo-delocalized salts. An overview of the observations and concluding remarks is provided in chapter 5 and then the thesis will close with providing conclusions and outlook in chapter 6.

Chapter 2

This chapter provides a brief introduction to the basic concept of batteries and particularly focuses on Li- and Na-ion rechargeable batteries.

Batteries

Batteries are the most efficient and salient electrochemical devices that store energy chemically and liberate it to electrical energy via electrochemical reactions. Depending on the number of charge and discharge cycles, batteries can be sorted out as secondary/rechargeable or primary. While, the later should be discarded after single use, the former can be charged and discharged several times [26].

The first invention of batteries occurred over 200 years ago, by Alessandro Volta. Using alternating metal discs (zinc and copper), separated by pieces of brine-soaked cardboard [27]. Indeed, Volta's discovery had massive impact on the progress, advancement and invention of several important electrochemical concepts, which are still in use. Nowadays, industries can opt for a wide range of batteries as power sources for various applications. Every battery technology has its own unique properties such as specific energy, voltage and operating temperature which make them convenient for diverse use. While the battery *specific energy* is the energy (charge) amount that can be extracted per mass of battery materials, the cell voltage defines as the differences in potential between the anode and cathode. By combining different electrodes and electrolyte materials, various rechargeable batteries have been discovered which in table 1, some properties of a few selected ones are presented. The lead-acid battery introduced firstly in 1859 by Gaston Planté, is one of the oldest battery technologies still in use despite some safety and environmental concerns. Today by some modification in packaging materials, this battery is very well established as the main power source supply in vehicle, due to its low cost and wide

Table 1. Selected properties of some rechargeable batteries [26, 28].

Battery	Specific energy (Wh/Kg)	Cell voltage (V)	Temperature ranges (°C)	Invention year
Lead-acid	30	2.0	-40 to 60	1859
NiMH	90-110	1.2	-20 to 65	1970
LIB	200	4	-20 to 65	1990

operating temperature [27]. Nickel-metal hydride (NiMH) battery can be found in many devices that need high power density, *e.g.* cameras, EVs. Moreover, this battery technology is the pioneer one that has been used in the first modern generation of hybrid electric vehicles (HEVs) [29]. However, it was soon manifested that conventional rechargeable batteries cannot fulfill all the requirements for new evolving technology, due to having heavy weight and large size. Hence the breakthrough was emerged when lithium was firstly introduced in battery technology as electrode material [27, 30].

2.1. Working principle of the electrochemical cell

Batteries are composed of one or a series of electrochemical cells with some additional components such as current collectors and separator. Two electrodes and an electrolyte, which form an electrochemical cell is depicted in figure 1. When the battery is operating, the redox reactions take place. During the discharge process, oxidation at anode and reduction at cathode happen, while in charging process these reactions are reversed.

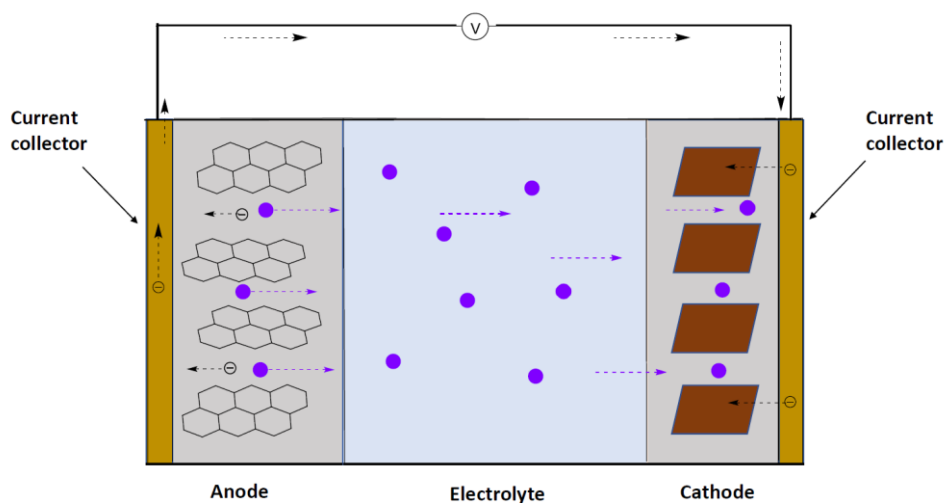


Figure 1. Schematic of LIB containing a graphite anode and a layered cathode (for more clarity in the electrolyte, anions were eliminated).

To maintain the charge balance during redox reactions, ion transport via the electrolyte is occurring. In order to prevent the direct contact between the two electrodes and short-circuits in the liquid electrolyte, an electronically insulating separator (membrane) is imperative [31]. Albeit, the separator can be avoided if the battery technologies use solid polymer electrolytes or apply a large distance between electrodes in case of the liquid electrolytes [22, 32]. The current collector, generally made of copper or aluminum with high electrical conductivity, can enable the electronic transport between electrodes. In continue, the most widely used rechargeable battery LIBs and another attractive alternative, SIBs will be in focused.

2.2. Lithium-ion batteries (LIBs)

The initial primary battery comprising lithium was introduced in 1970 as lithium-iodine battery for medical applications [27, 30]. Indeed, the propensity to use lithium as an electrode material due to its inherent properties such as low atomic weight, small ions ($r_{\text{ion}}=0.76 \text{ \AA}$) and low standard electrode potentials (-3.04 V vs hydrogen electrode (SHE)), provided low weight battery with reasonable energy density [27, 33].

The exploration of insertion or intercalation materials as cathodes paved the way for commercialization of the first rechargeable lithium batteries in the early 1980s [27]. These batteries were based on intercalation cathode materials (TiS_2) vs. lithium as anode and a non-aqueous electrolyte. During the charge-discharge cycle, unwanted deposition of lithium on the surface of metal lithium caused dendrite formation, which could create short-circuit in the cell and even cause fires and explosions [34]. To avoid plating lithium due to safety reasons, carbon-based anode with the ability to intercalate Li, was used instead [35, 36].

The first LIB based on lithium cobalt oxide LiCoO_2 (LCO) vs. carbon was commercialized in 1991 [37], and even today, most used batteries in electronic devices are based on this concept. The working mechanism of all LIBs is based on the shuttling of lithium ions between two electrodes which are different in intrinsic redox potential. During discharge, lithium is oxidized ($\text{Li} \rightarrow \text{Li}^+ + e^-$) and the anode slightly contracted [36], that leads to lithium ion transfer from anode to a moderately expanded cathode [36], while the released electron is collected by the current collector made of copper (Cu). During charging, lithium ions and electrons are forced back to the anode by an externally applied current, where reduction of Li-ion happens ($\text{Li}^+ + e^- \rightarrow \text{Li}$). Upon charge/discharge the term anode and cathode are interchangeable, but for simplicity, the discharge always determines the

electrodes in the battery field. Today, LIBs are the dominant rechargeable batteries for many electronic devices, not only because of their lightweight and high specific energy density but also due to their high cell voltage ($\approx 4V$) [28, 38]. However, recently due to the increasing demand for LIBs, some concerns about the abundance of lithium resources have been raised [39, 40]. Therefore, developing new battery chemistries to complement LIB is a must for the sustainability of battery technology.

2.2.1. Anode

Today's carbon-based material, e.g. graphite is the most inexpensive, safe and dominant anode material [41, 42]. The layered graphite, allows lithium-ions to be intercalated [41]. Graphite has a low reduction potential, therefore reacts easily with electrolyte components and results in the formation of a protective layer at the electrolyte/graphite interface. The formation of this thin layer, called solid electrolyte interphase (SEI), is another important contributing factor to LIBs performance [43]. In fact, SEI is an electronically insulating layer that can hamper the reaction between graphite and electrolyte, while it is still permeable to lithium-ions [44].

2.2.2 Cathode

Just as for the anode, cathode materials must be environmentally friendly, low cost with ability to intercalate lithium ion. Many different materials have been evaluated as cathodes [45, 46], but the most promising ones which can fulfill the LIB requirements [47, 48] are; layered transition-metal oxides with formula of $LiMO_2$ (M: Co, Ni, Mn), transition metal phosphate materials of the form $LiMPO_4$ (M: Fe, Mn, Ni, Co) [47, 49] and 3D spinel materials as LiM_2O_4 (M: Mn, Co, Ni). Similarly, to the SEI formation on anode surface, solid permeable interface (SPI) is also formed on the cathode surface when the electrolyte is oxidized by cathode materials [50]. In contrast to SEI, the thickness of the protective film on the cathode is thinner [51] and at elevated temperature, inconsistency in SPI composition has been observed [52].

2.2.3 Electrolyte

The LIB electrolyte is an inert media, that allows transporting of lithium ions between two electrodes and also maintain cell charge balance via internal ion transfer during the charge and discharge processes. Designing the perfect electrolyte, which fulfill all the cell requirements is very complicated. Because it must possess many properties to be matched

with the other cell components. As an example, active chemistry on electrode surfaces demands an optimized electrolyte to be decomposed selectively and forms stable protective layers on anode and cathode surfaces. Electrolyte can be found in different form according to the cell design and purpose: liquid, solid, gel or ionic liquid based electrolyte. In next chapter LIB electrolyte will be discussed exclusively.

2.3. Sodium-ion batteries (SIBs)

Today LIBs are the most popular energy sources for portable electronic devices and even EVs. However, due to growing demand of lithium consumption and its restricted resources in nature, some concerns about the price and long-term sustainability of this technology have been raised. It is predicted that, lithium production in future cannot satisfy market demand, hence an increase in LIBs cost seems to be unavoidable [39, 40]. Therefore, the quest for novel battery technology to complement LIBs is desirable. Since 1980 onwards sodium-ion batteries (SIBs) have attracted increasing attention, due to similar chemical and electrochemical properties of sodium and lithium, low cost production and vast abundance [48, 53-55].

By replacing lithium with sodium in SIB, some modifications in electrode materials, electrolyte and other cell components should be exerted to have an acceptable electrochemical cell with good performance. For instance, the copper current collector which is heavy and costly in commercial LIBs can be replaced with aluminum (low cost) in SIBs.

2.3.1. Anode

Using sodium as anode material in SIBs can be challenging, due to low melting point (97 °C) of sodium [56]. Therefore, applying intercalating materials such as graphite was another alternative that has been tried since early SIBs study [57-59]. However very soon it was revealed that graphite cannot intercalate sodium effectively [60], hence it was replaced by hard carbon (HC). These days HC is the most promising material for SIB, which can be achieved from various organic precursors such as saccharose-cookes and pyrolyzed cellulose [61, 62]. In fact, the disordered structure of HC allows sodium insertion while exhibits good reversibility. Similar to graphite expand/contract because of lithium insertion/deintercalation, small expansion in volume of HC has been also observed while SIB operates. The protective layer formation (SEI) on anode surface [44, 63-65] is one of the key factors for operating of SIB, however yet there is no clear trend to prove how to

the key factors for operating of SIB, however yet there is no clear trend to prove how to create stable SEI.

2.3.2. Cathode

The SIBs cathode materials usually contain Na in its structure. In parallel to different SIB anode materials, many investigations have been performed on cathode materials as well [54, 56, 66-68]. Layered sodium metal oxides with chemical formula Na_xMO_2 (M is transition metal) [69, 70] and 3D polyanionic are two main types of SIBs cathode materials that have been studied extensively [71]. Active chemistry on SIBs cathode surfaces, introduces the need for appropriate surface film. This protecting layer (SPI), that can be formed by oxidative decomposition of electrolyte, has a vital role to stabilize cell when operating, however less attention paid to SPI in comparison to SEI [72]. In totality the performance of SIB anode and cathode materials are still far behind LIBs, but since in this thesis sodium salts have been also synthesized, therefore brief introduction about SIB components was provided to give clear perspective to the readers.

2.3.3. Electrolyte

SIBs electrolyte is a medium that contains sodium salt and a solvent which can facilitate transferring of Na^+ between negative and positive electrodes while battery operating. The same as LIB electrolyte, liquid, solid, gel or ionic liquid based electrolyte are various forms of SIB electrolytes. It must meet some requirements to be applicable with electrode materials for long term. As an example, ability to form protective films on electrode surfaces is important factors which have direct impact on cell performance.

(In chapter 3 electrolyte will be in focused exclusively and SEI and SPI will be explained and illustrated in detail)

Chapter 3

This chapter is entirely focused on electrolyte components and also introduces various types of electrolytes that are used in today's LIBs and SIBs.

Electrolyte

The electrolyte is one of the main cell components which is composed of salt(s) and solvent(s), *ca.* 5-10% of the total cell weight has been attributed to it. Despite many developments in electrode materials, the main components of commercial electrolytes have not been modified much over the past two decades [10]. Some important reasons for this unequal advancement are firstly that the capacity of electrodes is quite insensitive toward electrolyte components which allows present electrolytes utilized continuously. The Second reason might be due to a better understanding of the cell operation mechanism and its failure in different conditions which enable using additives for compensating conventional electrolytes shortcoming. Thirdly, the battery industry has not been convinced to alter their available resources [23]. The electrolyte must meet some requirements to operate optimally, some of these characteristics are as below:

- ❖ Having high ionic conductivity (at least $10^{-3} \text{ S cm}^{-1}$) at room temperature (20 °C).
- ❖ Wide electrochemical stability window.
- ❖ High chemical stability.
- ❖ Passivate current collectors.
- ❖ Stability toward unplanned electric, mechanical and thermal abuses such as overcharging or overheating.
- ❖ Be composed of non-toxic, environmentally-friendly and inexpensive materials.

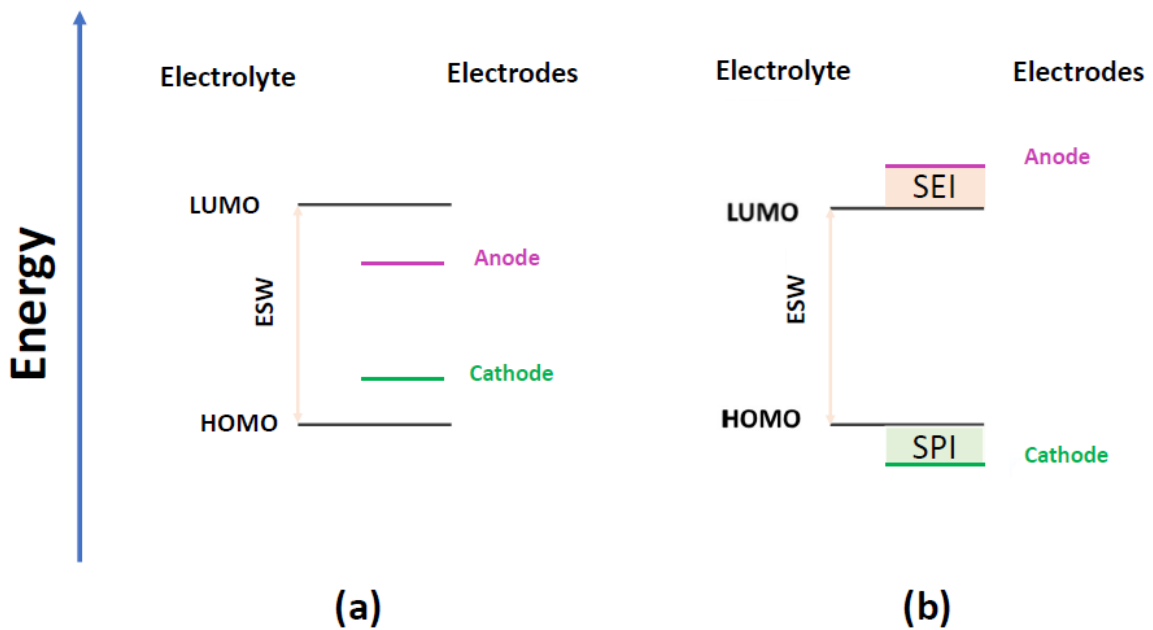


Figure 2. Electrolyte/electrode energy diagram: **a)** thermodynamically stable electrolyte and **b)** formation of SEI/SPI on electrode surfaces to stabilize electrolyte kinetically (inspired from[21]).

Among aforementioned electrolyte characteristics, the electrochemical stability window (ESW) is a key factor in determining which electrolyte can be used for a given combination of electrodes. The wider ESW, means electrodes with more potential difference can be selected and in consequence higher energy density can be extracted from the battery. In general, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the electrolyte, specify the theoretical limits of the ESW. If the electrolyte ESW is far beyond of electrodes potential, the electrolyte components are thermodynamically stable (figure 2a). In contrast, when anode and cathode energy is higher and lower than LUMO and HOMO of electrolyte respectively, decomposition of electrolyte happens and produces solid electrolyte interphase (SEI) on anode and solid permeable interphase (SPI) on cathode surfaces to kinetically stabilize the electrolyte (figure 2b).

Various electrolyte concepts according to the used solvents have been defined yet [33], in the following these electrolytes will be introduced shortly.

3.1. Organic solvent based electrolytes

While in aqueous electrolytes, water plays the solvent role [10], in conventional organic based LIBs and SIBs electrolytes, different linear and cyclic organic carbonate-based solvents (figure 3) have taken this role [73]. Polarity of organic solvent is one of the main factors that defines the solvent ability to salt dissolution [74], which is related to its dielectric constant (ϵ). Among organic solvents, cyclic-based such as ethylene carbonate (EC) and propylene carbonate (PC), possess higher dielectric constant, viscosity and boiling temperature.

Ethylene carbonate (EC)			 C O H
Propylene carbonate (PC)			
Dimethyl carbonate (DMC)			
Ethyl methyl carbonate (EMC)			
Diethyl carbonate (DEC)			

Figure 3. Sketch of conventional solvents for LIBs and SIBs electrolyte [74].

Table 2: Specific properties of linear and cyclic organic solvents used in LIBs and SIBs [75, 76].

	Organic solvents	Dielectric constant ϵ	Viscosity at 25 °C η (mPa s)	Melting point T_m (°C)
Linear	Diethyl carbonate (DEC)	2.8	0.75	-74
	Dimethyl carbonate (DMC)	3.1	0.59	4.6
	Ethyl methyl carbonate (EMC)	3.0	0.65	-53
Cyclic	Ethylene carbonate (EC)	89.8	1.9 (40 °C)	36
	Propylene carbonate (PC)	64.	2.5	-49

In contrast, linear carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC) have lower viscosity and dielectric constant (table 2). Indeed, their low viscosity provide excellent transport properties. Therefore, to have a well-functioning electrolyte, a combination of cyclic and linear carbonates is needed. The most used organic electrolyte for LIBs is based on the LiPF_6 salt dissolved in a combination of various cyclic and linear organic solvents, e.g. EC and DMC [77], which was firstly proposed by Tarascon *et al.* over twenty years ago [11]. The EC/DMC combination provides several important properties. For instance, EC has a high dielectric constant that can dissolve salts well, but because of its high melting point (T_m : 36 °C), it must be combined with other solvents e.g. DMC to decrease both melting point and viscosity [11]. There is a wide range of solvent mixtures for LIB and SIB electrolytes such as: EC/DMC, EC/DEC and DMC/EC/PC. However these solvent mixtures have been in used since last two decades [22], but their high flammability and low flash point are still the main problematic aspects which accompany them [78, 79].

In this thesis, we did not propose any new organic solvent electrolytes based on our synthesized lithium and sodium salts, because of their low solubility (< 0.01 M) in conventional organic solvents (EC/DMC, PC were tested in the **paper I**).

3.2. Aqueous based electrolytes

Water is the most inexpensive and common solvent for aqueous LIBs and SIBs electrolytes, that has been in use since the first battery invention [27]. Low viscosity that facilitates ion transport [80], high dielectric constant (ϵ ca. 80) which provides good salt dissolution and its safety (non-toxic, environmentally harmless) are specific features of water. In contrast, its narrow ESW (~1.23 V) [81] is considered as its main drawback. Because of this, it has restricted the selection of electrode materials [82]. Nevertheless, many aqueous electrolytes for LIBs and SIBs based on inorganic and organic salts have been reported yet (**paper I**) [10, 83-86]. Significant efforts have been paid to prevail narrow ESW limitation through different approaches such as using organic additives to protect electrode surfaces [87-90] or applying a highly concentrated aqueous electrolyte (20 M) so-called “water-in-salt” electrolytes (WiSEs) which lead to output voltage up to 2.0 V [91]. Indeed, the latter has opened new windows toward further explorations of aqueous electrolyte with more stable electrochemical windows. By introducing “water-in-bi-salt” (WiBS) electrolytes that contain two salts with different anions, electrochemical stability window was even further widened (**paper III**) & [92, 93]. In **paper III**, a new WiBS electrolyte with extended ESW and record salt concentration based on novel fluorine-free lithium salt was reported.

3.3. Ionic liquid based electrolytes

Ionic Liquids (ILs) are a group of materials that made entirely of ionic species. By definition ILs melt below 100°C [94], but when melting point is below room temperature, they are called room temperature ionic liquids (RTILs). Typically, ILs are composed of cations and anions that can be organic or inorganic in nature [95] (figure 4). By various combination of anions and cations according to their applications, potentially a huge number of ILs (10^{18}) can be designed and tailored [96, 97]. Indeed, distinctive properties of ILs such as negligible vapor pressure, wide ESW, low-flammability and high intrinsic conductivity, spread out their applications in various research areas from biomass processing [98], over pharmaceuticals synthesis [99, 100] to even energy application [101, 102].

In battery technology, ILs are considered as promising electrolyte solvents for LIBs and SIBs because of their high ionic conductivity and low vapor pressures [103-105]. Although neat ILs cannot be used solely as electrolyte, due to lack of lithium- or sodium-ions. Therefore, salt addition to ILs for providing a source of mobile ions is a must. However, this addition can increase electrolyte viscosity and in consequence increase ion-ion interactions [106]. Pyrrolidinium (Pyr), imidazolium (Im) or trimethylpropylammonium (TMPA) are organic

cations that accompany anions such as bis(trifluoromethanesulfonyl)-imide (TFSI) or bis(fluorosulfonyl)imide (FSI) to form ILs (figure 4). To prepare the LIBs [107-110] and SIBs [111, 112] electrolyte, usually the lithium (or sodium) salt is dissolved in IL matrix which has the same anion as salt. But, recently the propensity to add salt with different anion has been emerged, because ion conductivity [113] and battery performance [114] were improved. In (**paper IV**), by using the fluorine-free salts and 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr₁₄TFSI) as solvent, new ionic liquid based electrolytes for application in LIB and SIB were introduced and examined.

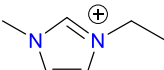
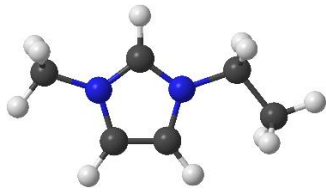
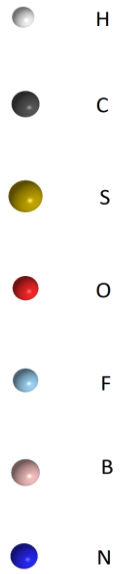
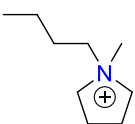
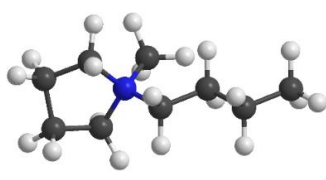
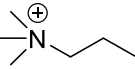
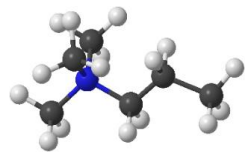
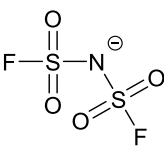
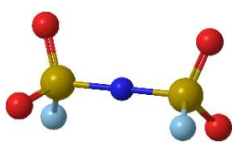
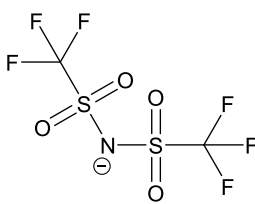
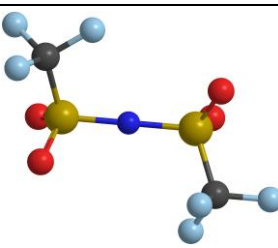
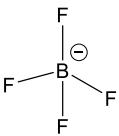
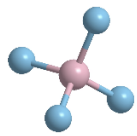
Cations	EMI			
	(Pyr ₁₄)			
	TMPA)			
Anions	FSI			
	TFSI			
	BF ₄			

Figure 4. Chemical structure of cations and anions in ILs [95].

3.4. Solid state electrolytes (SSE)

Solid state or solvent-free electrolytes have drawn increasing attention due to their remarkable safety, which stems from the elimination of liquid organic solvents [115]. The main drawback of most SSEs is their lower ionic conductivities compared to liquid electrolytes at room temperature. Hence, to have an acceptable and sufficient conductivity for battery performance, generally SSE operate at elevated temperature (*ca.* 80 °C) [116-118]. As a result, the high temperature lithium ion battery (HT-LIB) concept has arisen [119]. Molten salt mixtures with operating temperature between 350 °C and 550 °C, are another alternative which is considered as liquid solvent-free electrolyte. Low flammability, high ionic conductivity and thermal stability are specific properties that have attributed to this sort of batteries which are also referred to as “thermal batteries” [120]. This concept is also applicable for LIBs but a significant decrease in melting temperature of salt mixtures is required. Therefore, eutectic mixtures are reliable approaches to reach this goal [121], which are defined as a mixture of components that melts at a temperature (T_E) that is lower than the melting point of either of the constituents (figure 5). Such eutectic mixtures for LIBs have been obtained by combining two or three alkali cation salts with a common weakly coordinating anion (WCA), such as triflate [122], bis(fluorosulfonyl)imide (FSI) [123] or bis(trifluorosulfonyl)imide (TFSI) [124, 125]. In **paper (II)**, by *i.e.*, mixing two Li salts with various anions, a new strategy toward solvent-free electrolyte using novel fluorine-free salts and LiTFSI was presented.

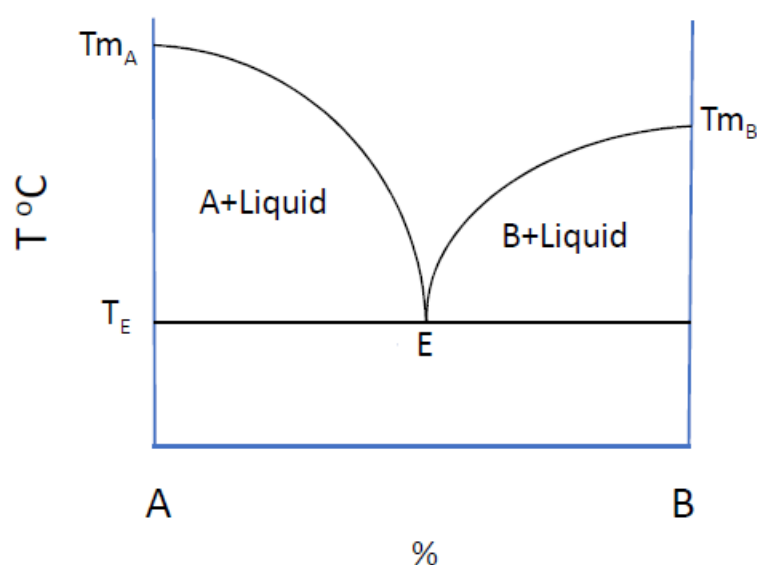


Figure 5. A phase diagram for a binary eutectic mixture.

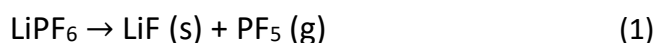
3.5. Electrolyte salts

As it was mentioned at the beginning of this chapter, salt is one of the electrolyte components with huge influences on the overall properties of the electrolyte. For example, salt concentration plays a key role in electrolyte performance and it is found that optimal conductivity can be obtained in the presence of 1 M salt [126]. Increasing salt concentration over 1 M, leads to a decrease in ion conductivity and an increase in viscosity, which deteriorates electrolyte performance [127].

Today's state-of-the-art electrolyte is very far from ideal, if leaving behind flammability and toxicity of used organic solvents still some of electrolyte drawbacks as low safety, high price and non-eco-friendly chemicals have been ascribed to the used salts [13, 128, 129]. Some basic properties that an ideal electrolyte salt should possess, are listed as below [130]:

- ❖ High solubility of salt in electrolyte solvent.
- ❖ Stability of anion(s) against oxidative decomposition at cathode.
- ❖ The anion should be inert towards cell packaging materials, electrolyte solvents and electrodes.
- ❖ The anion must remain stable against thermally induced reactions of electrolyte solvents and other cell components.
- ❖ If the anion decomposed, then decomposition products should be non-toxic.
- ❖ Over all the salts should be environmentally friendly and no-toxic with reasonable price.

The most widely used salt in commercial LIB is exclusively based on lithium hexafluorophosphate (LiPF_6) [21], owing to its good solubility in organic solvents, high ionic conductivity [131], wide ESW and ability to form protective layer on the anode [132] and Al current collector surfaces [132]. Despite these advantages, poor thermal stability and moisture sensitivity are the major problematic features of this salt. At elevated temperature (above 55 °C), LiPF_6 thermal stability is deteriorated and leads to auto-decomposition reaction (eq. 1) as:



While unwanted production of LiF is a favored product for SEI formation and also stabilization of Al current collector [133], in contrast PF₅ as a Lewis acid can further react with solvents (water trace) and produces highly toxic gases such as HF and POF₃ [14-20] which is a big concern for LIB safety [22, 134]. To overcome these problems, moisture-free cell preparation or the use of additives are essential strategies that increase LIBs price [21, 22, 135]. In addition, fluorine chemistry is also considered as very challenging and costly from chemistry perspective [13, 128].

The drawbacks and limitations of LiPF₆ have resulted in extensive efforts on finding other salts. Many different salts have been tested over the past decade, but due to various reasons, only a few of them have been established as electrolyte salts [136]. In the following, some of these salt properties are reviewed.

3.5.1. Fluorinated salts

Among salts containing fluorine, lithium hexafluoroarsenate (LiAsF₆) (figure 6a) was one of the widely used salt in research because of its long cycling life [137]. However very soon, it was realized that this salt is not practical, because of its reactivity toward electrolyte solvents [137] and high toxicity [130, 138].

Lithium tetrafluoroborate (LiBF₄) (figure 6b), was another candidate to replace LiPF₆, due to its lower toxicity compared to LiAsF₆ [139], promising electrochemical properties in certain solvent mixtures and thermal stability at temperature above 60 °C [140]. Despite these remarkable features, moderate ion conductivity of LiBF₄ has hindered its application in LIBs electrolyte salt [141].

The lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (figure 6c) is another member of the fluorinated salts family. It is considered as a salt with “weakly coordinating anion” (WCA), due to its weak anion interaction with cation (Li). This salt has been proposed as a promising alternative to LiPF₆, because of its safety, high thermal stability (no decomposition up to 360 °C), acceptable ionic conductivity and stability against water hydrolyzation [126, 142, 143]. Despite all these promising features, being corrosive to Al current collector [144] is the major drawback of this salt. In order to mitigate this challenge, an increase in the concentration of LiTFSI [145] or even the addition of other salts is needed to passivate the Al surface [146].

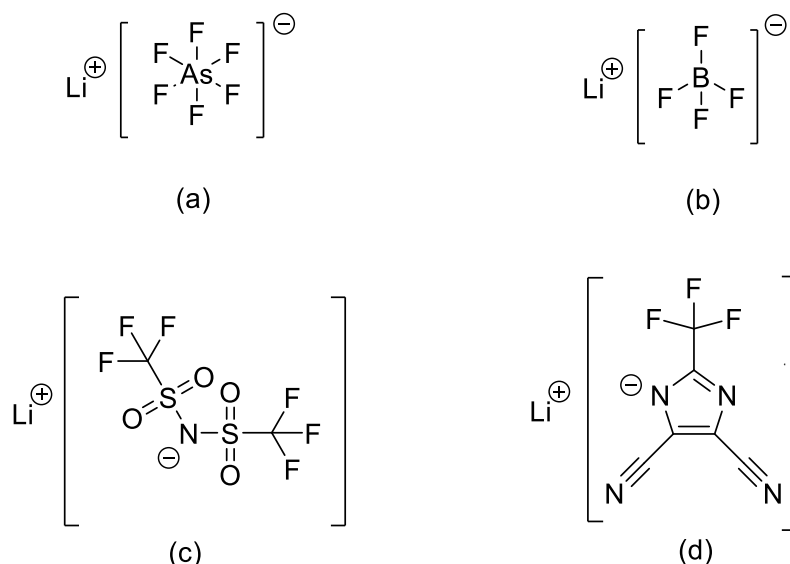


Figure 6. Chemical structure of common fluorinate anions; **a)** hexafluoroarsenate, **b)** tetrafluoroborate, **c)** Bis(trifluoromethanesulfonyl)imide and **d)** 4,5-dicyano-2-(trifluoromethyl)imidazole.

Other fluorinated salts such as lithium 4,5-dicyano-2-(trifluoromethyl)imidazole (LiTDI) (figure 6d), based on the heterocyclic ring (imidazole) has been evaluated as LIB electrolyte. In this salt, the anion is stabilized through conjugation with 5-membered ring (Hückel rule). Thermal stability at over 200 °C and good stability against Al corrosion are the notable properties of LiTDI. However, its lower conductivity compared to LiPF₆ in the same solvents, is the main restriction of this salt [147].

3.5.2. Fluorine-free salts

Lithium perchlorate (LiClO₄) (figure 7a) is one of the non-fluorinated inorganic salts, which has been considered as electrolyte salt due to its high ionic conductivity at room temperature, great oxidation resistance on cathode surface, good solubility and even less sensitivity to ambient moisture compare to LiPF₆ and LiBF₄ [11, 130]. However, strong oxidizing ability at elevated temperature, hampered its application as LIB electrolyte salt [130].

Another promising salt is lithium bis(oxalato)borate (LiBOB) (figure 7b) with many significant merits. High oxidation potential vs. Li⁺/Li⁰ (4.6 V), excellent thermal stability [148, 149], ability to form stable SEI on anodes [150] and passivation of Al current collector [151] made this salt not only as a good candidate for LIB electrolyte, but also as a co-salt to

compensate other salt limitations [152]. It has shown that LiBOB addition to LiTFSI can mitigate corrosion of the Al current collector and enabling high-temperature cycling in organic solvents electrolyte [153] or improving thermal stability of the electrolyte containing LiPF_6 which has good conductivity [129, 154]. Some LiBOB limitations include low solubility and ionic conductivity in organic solvents [155, 156], moisture sensitivity and as a consequence producing boric acid [152].

Another attractive alternative based on fluorine-free WCA is lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA) (figure 7c), which has been studied for application as LIB electrolyte salt more than 15 years [157, 158]. High thermal stability up to 300 °C, lowering cost in the manufacturing process and improved safety are the main LiDCTA advantages [159-161]. In contrast, moderate electrolyte ionic conductivities and low anion oxidation stability are the main limitations of this salt [159].

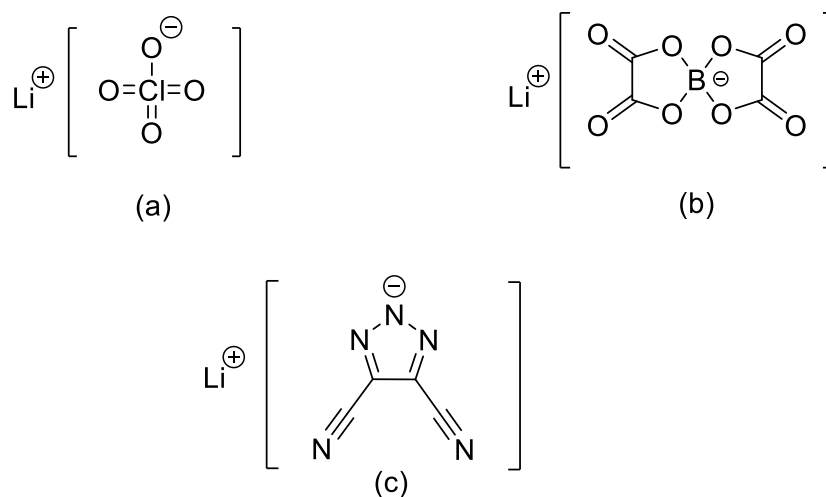


Figure 7. Chemical structure of non-fluorinate anions; **a)** perchlorate, **b)** bis(oxalato)borate and **c)** 4,5-dicyano-1,2,3-triazolate.

3.5.3. Non-fluorinated pseudo-delocalized anions

Pseudo-delocalized anions are a series of novel fluorine-free WCAs (figure 8), that were proposed firstly by Jónsson *et al.* [24, 25]. This new anion concept was studied and designed using computational DFT calculation to find promising lithium salts and enhance LIBs electrolyte performance. Based on the anions chemical structure, they were classified into four different categories: 1) heterocyclic-pyridinium, 2) heterocyclic-imidazolium, 3) aliphatic ammonium and 4) spiros. The anions were completely non-fluorinated containing electron withdrawing groups such as carbonate and sulfonate.

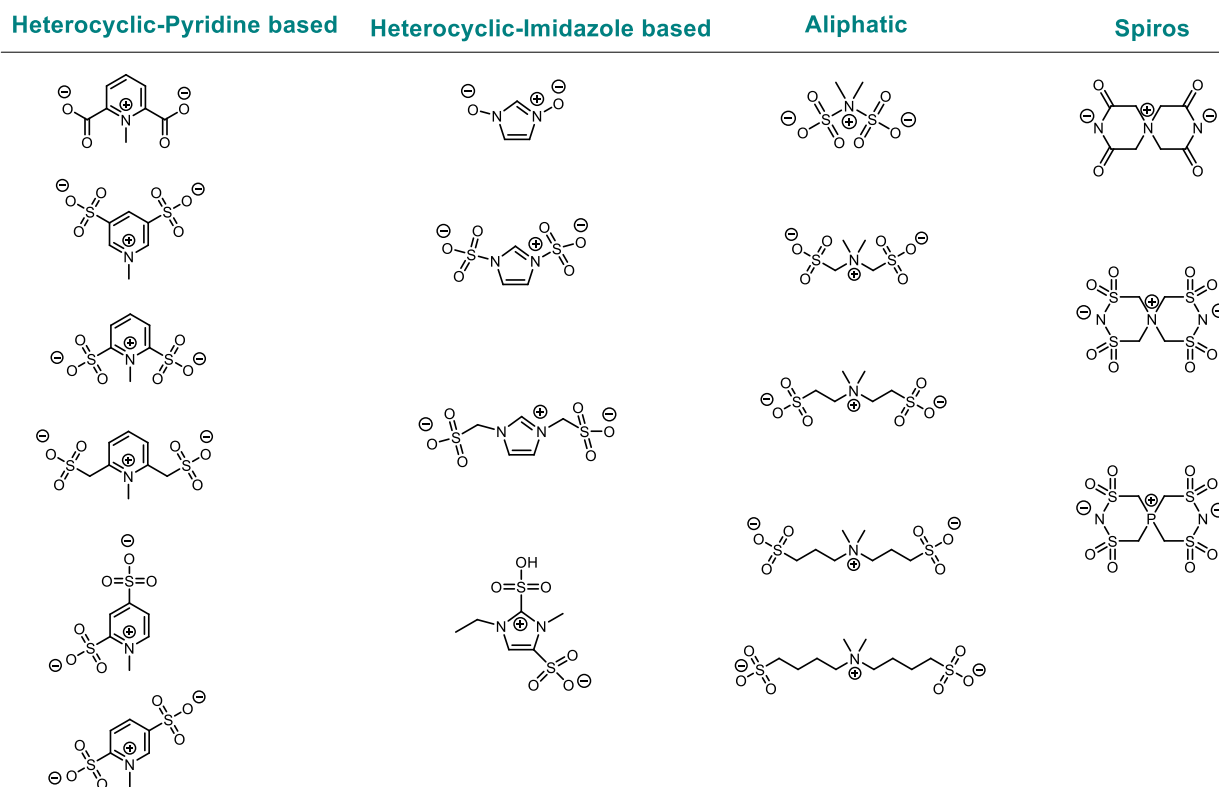


Figure 8. Chemical structure of pseudo-delocalized anions [25].

All the pseudo-delocalized anions had distinct negative and positive regions, that could be compared to the synthesized anion “bis(trifluoroborane)imidazolidium” (figure 9c), by Barbarich *et.al* [162], which does not have these distinct regions due to its anion charge delocalization over the aromatic ring and two boron centers.

According to figure 9, the pseudo-delocalized anions are composed of two negatively charged groups covalently connected to the positive central unit, thus they can also be considered as a special type of betaines. Since the charge is neither completely localized to a specific region nor delocalized, hence the term pseudo-delocalized anions have been used to describe them. However, due to the similarity of these anions to a famous cartoon character, also known as “Mickey Mouse™” anions (**paper I**).

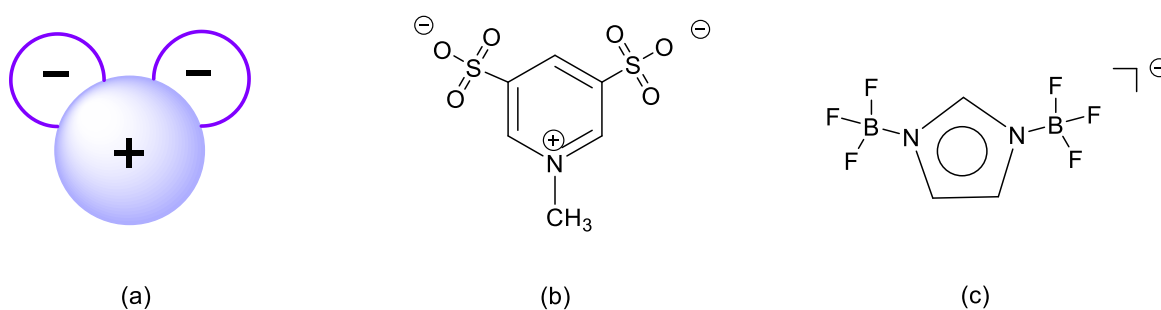
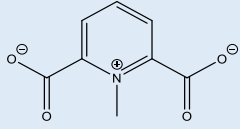
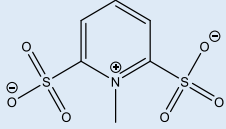
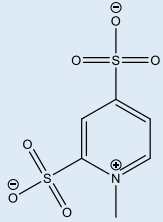
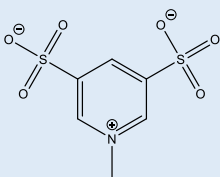
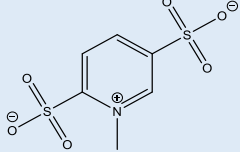
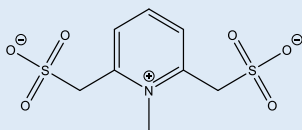
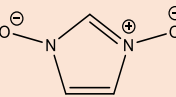
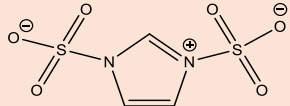
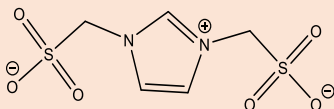
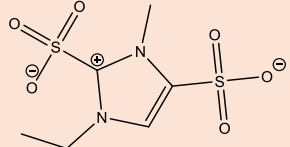


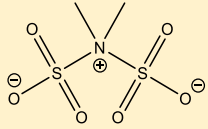
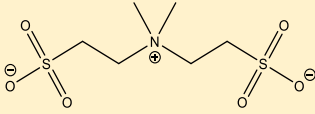
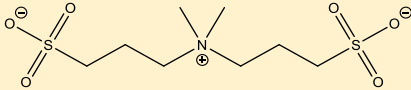
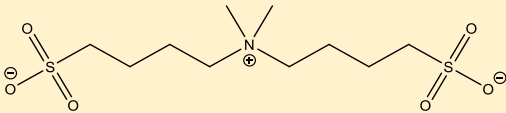
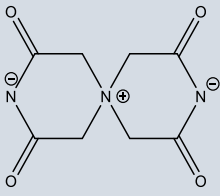
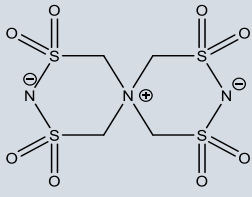
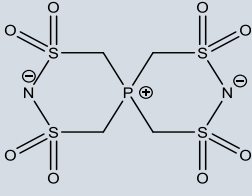
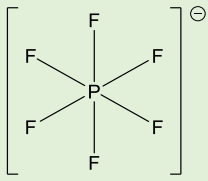
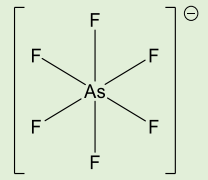
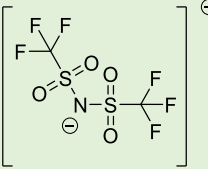
Figure 9. a) The pseudo-delocalized concept and “Mickey Mouse™” anions, **b)** 1-methylpyridin-3,5-disulfonate and **c)** bis(trifluoroborane)imidazolidium.

To evaluate the applicability of these anions and their salts as LIB electrolyte, Jónsson and co-workers investigated two main properties, cation-anion interaction through the salt dissociation reaction (ΔE_d) $\text{Li}^+ \text{A}^- \rightleftharpoons \text{Li}^+ + \text{A}^-$, and intrinsic anion oxidation stability (ΔE_v) via oxidation of anion to the radical state. Afterward, they made a quantitative comparison of their results (table 3) with the most common used anions such as PF_6^- , AsF_6^- and TFSI [163, 164].

Indeed, the dissociation energy ΔE_d , estimates the ease of ion formation in electrolyte and the anion oxidation potential ΔE_v , provides information about the anion stability against oxidation. Hence, an ideal salt has to have low dissociation energy to provide enough charged carriers, but in contrast, anion electrochemical stability vs. oxidation must be sufficiently high to be stable against oxidation when the battery is operating. By prediction of these two features the salt performance is determined for electrolyte purposes.

Table 3. The dissociation energy and anion oxidation potentials of the Mickey Mouse™ anions by DFT calculations (accepted from [25]).

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

Aliphatic-based		635.8	3.82
		661.0	3.28
		659.5	3.13
		788.7	2.63
Spiros-based		604.9	3.32
		546.9	4.27
		562.9	4.45
Conventional (fluorinated)		567	5.65
		558	6.05
		592	4.52

Jónsson *et.al.* [25] results implied that using sulfonate groups in general provide acceptable ΔE_v , although electrochemical stabilities of these anions are somewhat lower compared to PF_6^- . Furthermore, the ease of creating charge carriers, as computed by ΔE_d , and the lack of fluorine show the applicability of some of these anions as a promising anion concept for LIBs electrolyte purpose.

According to the possible advantages of these novel anions compared to the ubiquitous PF_6^- , some of them and their corresponding lithium and sodium salts have been synthesized and evaluated as LIBs and SIBs electrolytes for the first time. However, Jónsson *et.al.* [25] only focused on the properties of the lithium salts based on pseudo-delocalized anions, but we extended the synthesis to sodium salts, to have a better understanding of their performance as SIBs electrolyte salts. Furthermore, two new anions based on this concept, but with minor differences in chemical structure were designed and synthesized to evaluated and compared with the anions in figure 8. The following chapter is entirely devoted to the synthesis and chemical characterization of these anions.

Chapter 4

*In this chapter, the synthesis of pseudo-delocalized anions and their key chemical characterization will be presented. The work which is published in **papers I, II, III and IV** is discussed and put into context.*

Experimental Methods

As it was discussed in previous chapter the properties of pseudo-delocalized anions, were assessed by DFT modelling [25]. Therefore, the goal of this thesis was to experimentally realize as many of these structures as possible and to understand their chemical properties and limitations. Indeed, selection of suitable synthesis method has massive impact on the development of the final product. There is thus a need to identify a synthetic method which is not only simple and scalable but also highlight the use of inexpensive and readily available starting materials. Hence, here it has been tried to synthesis the salts by optimized practical synthetic route, that will be discussed in the following.

Considering the dissociation energy and oxidation potential of pseudo-delocalized anions (reported in table 3), there were several anions that could be synthesized without major difficulties, apart from spiro-based which were the most challenging ones [165]. However, when it came to practical lab work, different challenges and difficulties appeared hand in hand. Some restrictions such as availability of starting materials at a reasonable price, obtaining permission to purchase material which was unsafe to use and also unavailability of accessible literature procedures for needed synthetic transformations, have confined our options. Indeed, a great deal of effort has been on identifying simple and scalable ways (e.g. simple workup) to prepare high purity products. Because according to the electrochemistry point of view trace of impurity could disrupt the cell performance, therefore purification of the desired products was the most time consuming and

challenging part of this research study. Nevertheless, we attempted to synthesize some of the anions from pyridinium, ammonium (aliphatic based) and even imidazolium subgroups, but in spite of several efforts, we could not isolate the desired lithium or sodium salts with reasonable yield or purity (some of these approaches are presented at the end of this chapter). In contrast, we were successful in synthesizing three anions from aliphatic and two anions from pyridinium subsets. Totally ten lithium and sodium salts were synthesized and evaluated as LIB and SIB electrolytes. Therefore, in the following sections, the focus will be on the applied synthetic routes for selected pseudo-delocalized anion salts. However, the synthesis was done mostly in small scales for research purposes, but we believe that they even can be performed on larger scale with no difficulties.

4.1. Aliphatic based anions

The symmetrical aliphatic pseudo-delocalized anions contain a quaternary ammonium center, potentially has vast variations, due to the number of carbons that can be presented in aliphatic chains on ammonium center (figure 10a). However, it can be even more expanded if the asymmetric anions can also be designed (figure 10b). Here the synthesis of symmetrical and asymmetrical aliphatic anions and their corresponding salts have been presented briefly (more details can be found in the papers that have been appended at the end of this thesis). Since the anions have quite a long name, therefore abbreviation for each anion has been selected which composed of two capital letters and four digits. The capital letters in all pseudo-delocalized anions are “MM” which stands for “Micky Mouse” and the four digits refer to the number of alkyl chain carbons on ammonium moiety. In figure 10c, the anion “2,2'-(dimethylammonio)bis(ethanesulfonate) or MM2211 has been presented as an example. The red digits show the number of carbons in each alkyl chain.

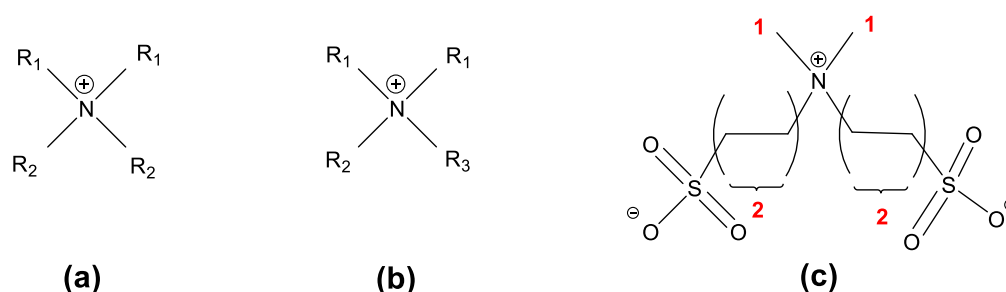
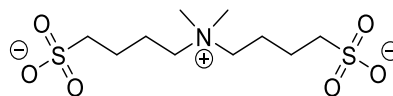


Figure 10. **a)** the symmetrical aliphatic anion, **b)** the asymmetrical aliphatic anion and **c)** 2,2'-(dimethylammonio)bis(ethanesulfonate) MM2211.

4.1.1. Synthesis of MM4411



The synthesis of lithium and sodium salts based on 4,4'-(dimethylammonio)bis(butane-1-sulfonate) pseudo-delocalized anion or MM4411 (**paper I**), were conducted via two synthetic steps (figure 11).

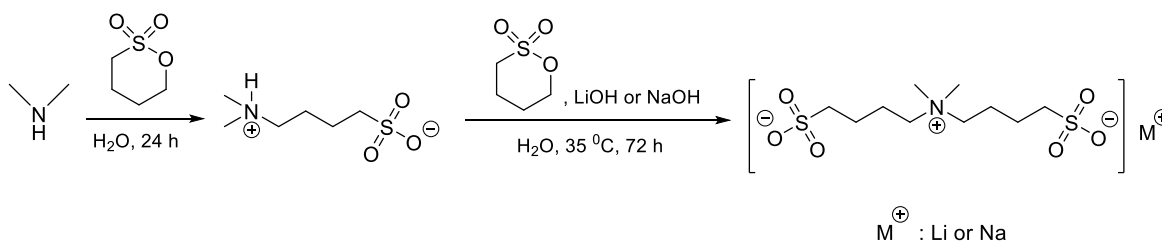


Figure 11. Synthesis path of fluorine-free LiMM4411 and NaMM4411 salts (Reproduce from **(paper I)** published by RSC advances © Royal Society of Chemistry).

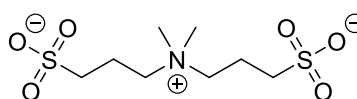
In the first step, the monomeric zwitterion, dimethyl ammonio-butanesulfonate or in brief ZDMBS intermediate, was achieved by nucleophilic substitution reaction, which was previously reported [166], albeit with minor modification. Using a cold ($\approx 0\text{ }^{\circ}\text{C}$) aqueous solution of primary amine (di-methylamine) as a nucleophile which attack to carbon in the C-O bond of 1,4-butane sultone, leads to ring opening of 1,4-butane sultone over 24 hours. This type of reaction is quite common in the preparation of sulfobetaine compounds [167, 168]. In the second step of the synthetic procedure, a nucleophilic substitution reaction between ZDMBS which was obtained as an intermediate and 1,4-butane sultone as the electrophile was employed in water at $35\text{ }^{\circ}\text{C}$ (more details about selected temperature, can be found in next chapter). This step also required a base such as lithium hydroxide or sodium hydroxide in stoichiometric amounts in order to treat and deprotonate the zwitterion for nucleophilic attack on 1,4-butane sultone. The desired lithium and sodium salts were thus directly formed in 92% and 90% yield after washing with chloroform and recrystallization from methanol.

ZDMBS: $^1\text{H-NMR}$ (400 MHz, D_2O): 3.05 (t, 2H, NCH_2); 2.83 (t, 2H, SCH_2); 2.75 (s, 6H, $2\times\text{CH}_3$); 1.62-1.80 (m, 4H, $-\text{CH}_2$ and $-\text{CH}_2-$). $^{13}\text{C-NMR}$ (100 MHz, D_2O): 57.1 (NCH_2); 49.9 (SCH_2); 42.6 ($2\times\text{CH}_3$); 22.8 (CH_2); 21.1 (CH_2). Elem. Anal. Calc. ($\text{C}_6\text{H}_{15}\text{NO}_3$): C, 39.76; H, 8.34; N, 7.73; S, 17.69; O, 26.5. Found: C, 40.02; H, 8.54; N, 7.97; S, 17.2; O, 25.9.

LiMM4411: $^1\text{H-NMR}$ (400 MHz, D_2O): 3.21 (t, 4H, NCH_2); 2.93 (s, 6H, $2\times\text{CH}_3$); 2.84 (t, 4H, SCH_2); 1.8 (m, 4H, $-\text{CH}_2$); 1.67 (m, 4H, $-\text{CH}_2-$). $^{13}\text{C-NMR}$ (100 MHz): 63.5 (NCH_2); 50.4 (SCH_2); 49.9 ($2\times\text{CH}_3$); 21 (CH_2); 20.7 (CH_2). Elem. Anal. Calc. ($\text{LiC}_{10}\text{H}_{22}\text{NO}_6\text{S}_2$): C, 37.15; H, 6.86; N, 4.33; S, 19.83; Li, 2.15. Found: C, 36.83; H, 6.69; N, 4.21; S, 18.93; Li, 2.07.

NaMM4411: $^1\text{H-NMR}$ (400 MHz, D_2O): 3.2 (t, 4H, NCH_2); 2.93 (s, 6H, $2\times\text{CH}_3$); 2.83 (t, 4H, SCH_2); 1.79 (m, 4H, $-\text{CH}_2$); 1.66 (m, 4H, $-\text{CH}_2-$). $^{13}\text{C-NMR}$ (100 MHz, D_2O): 63.5 (NCH_2); 50.4 (SCH_2); 49.9 ($2\times\text{CH}_3$); 21 (CH_2); 20.7 (CH_2). Elem. Anal. Calc. $\text{NaC}_{10}\text{H}_{22}\text{NO}_6\text{S}_2$: C, 35.39; H, 6.53; N, 4.13; S, 18.89; Na, 6.77. Found: C, 35.78; H, 6.76; N, 3.99; S, 18.00; Na, 6.47.

4.1.2. Synthesis of MM3311



The synthesis of shorter variations of MM4411 with three carbon spacers, MM3311 was an interesting alternative. According to DFT calculation results, MM3311 was a better candidate compared to MM4411 due to its lower ΔE_v (≈ 100 kJ/mol) and higher oxidation potential. In (**paper II**), by modification of synthesis method that has been conducted for MM4411 (**paper I**), the anion “3,3’-(dimethylammonio) bis(propane-1-sulfonate)”, MM3311 and its salts (figure 12) were synthesized in three consecutive synthesis steps [169].

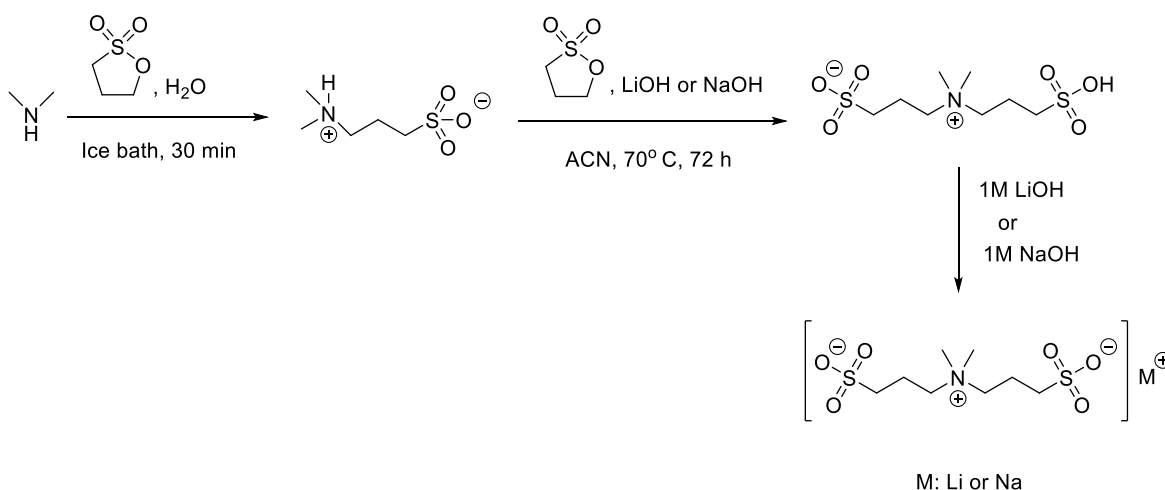


Figure 12. Synthesis route of LiMM3311 and NaMM3311 (Reproduced from (**paper II**) published by Chemical Communication (ChemComm) © Royal Society of Chemistry).

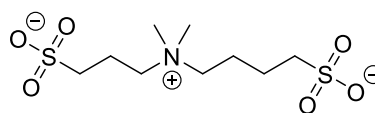
The first step of the synthesis route was initiated by bimolecular nucleophilic substitution (S_N2) reaction between dimethyl amine and propane sultone in water at low temperature (0 °C), which lead to ring opening of 1,3-propane sultone and formation of the zwitterion di-methyl ammonio-propane sulfonate (Z311) precursor. This reaction was quite fast and completed in 30 min due to the high reactivity of 1,3-propane sultone. In the second step of synthetic procedures, anhydrous acetonitrile was used as the solvent instead of water, because it was observed that even at room temperature the possibilities of reaction between 1,3-propane sultone with water is occurring. Therefore, nucleophilic substitution reaction between a slurry of Z311 in acetonitrile and 1,3-propane sultone in the presence of lithium hydroxide or sodium hydroxide as the base, was carried out. Similar to MM4411, the need of using base in second step for activation of the zwitterion was crucial, however instead of collecting final Li and Na salts, "3- (dimethyl (3-sulfopropyl) ammonio) propane-1-sulfonate" HMM3311 as the white crystalline product was obtained after recrystallization from methanol. By neutralization of HMM3311, the desired LiMM3311 (98%) and NaMM3311 (92%) were collected as colorless crystalline product.

Z311: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 3.18 (t, 2H, NCH_2); 2.87 (t, 2H, SCH_2); 2.79 (s, 6H, $2\times\text{CH}_3$); 2.05 (m, 2H, $-\text{CH}_2-$) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 56.15 (NCH_2); 47.45 (SCH_2); 42.65 ($2\times\text{CH}_3$); 19.81 (CH_2) ppm. Elem. Anal. Calc. ($\text{C}_5\text{H}_{13}\text{NO}_3\text{S}$): C, 35.9; H, 7.84; N, 8.38; S, 19.17. Found: C, 36.16; H, 7.96; N, 8.27; S, 18.78.

HMM3311: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 3.18 (t, 2H, NCH_2); 2.87 (t, 2H, SCH_2); 2.79 (s, 6H, $2\times\text{CH}_3$); 2.05 (m, 2H, $-\text{CH}_2-$) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 56.15 (NCH_2); 47.45 (SCH_2); 42.65 ($2\times\text{CH}_3$); 19.81 (CH_2) ppm. Elem. Anal. Calc. ($\text{C}_8\text{H}_{19}\text{NO}_6\text{S}_2 \cdot 1.0 \text{H}_2\text{O}$): C, 31.26; H, 6.89; N, 4.54; S, 20.86. Found: C, 31.15; H, 6.55; N, 4.56; S, 18.358.

LiMM3311: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 3.38 (t, 4H, NCH_2); 3.01 (s, 6H, $2\times\text{CH}_3$); 2.86 (t, 4H, SCH_2); 2.11 (m, 4H, $-\text{CH}_2-$) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 62.49 (NCH_2); 50.37 (SCH_2); 47.15 ($2\times\text{CH}_3$); 18.06 (CH_2) ppm. Elem. Anal. Calc. ($\text{LiC}_8\text{H}_{18}\text{NO}_6\text{S}_2 \cdot 1.0 \text{H}_2\text{O}$): C, 30.67; H, 6.43; N, 4.47; S, 20.47; Li, 2.22. Found: C, 30.33; H, 6.75; N, 4.09; S, 18.57; Li: 2.42.

NaMM3311: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 3.38 (t, 4H, NCH_2); 3.01 (s, 6H, $2\times\text{CH}_3$); 2.86 (t, 4H, SCH_2); 2.11 (m, 4H, $-\text{CH}_2-$) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 62.49 (NCH_2); 50.36 (SCH_2); 47.16 ($2\times\text{CH}_3$); 18.07 (CH_2) ppm. Elem. Anal. Calc. ($\text{NaC}_8\text{H}_{18}\text{NO}_6\text{S}_2$): C, 30.86; H, 5.83; N, 4.5; S, 20.59; Na, 7.38. Found: C, 31.03; H, 5.74; N, 4.73; S, 20.43; Na: 7.33.



4.1.3. Synthesis of MM3411

Molecular symmetry has remarkable effects on the physical properties of organic compounds such as solubility and melting point. In general, higher melting temperatures and lower solubilities, are the key properties of crystalline symmetrical molecules [170]. However, we did not have any information about the ΔE_d (and even ΔE_v) value of the MM3411 anion, but it was assumed that an asymmetric anion might have higher aqueous solubility due to disruption in crystal packing [171]. Hence, aliphatic anion “4-(dimethyl(3-sulfonatopropyl)ammonio)butane-1-sulfonate” MM3411 and its corresponding lithium and sodium salts were prepared (**paper II & III**), via a three-step procedure (figure 13).

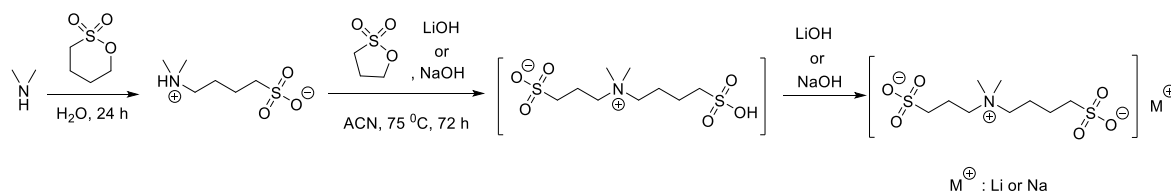


Figure 13. Synthesis route of LiMM3411 and NaMM3411 (Reproduced from (**paper II**) published by Chemical Communication (ChemComm) © Royal Society of Chemistry.

In the first step, dimethyl ammonio-butanedisulfonate (ZDMBS) as the intermediate, was obtained by nucleophilic substitution reaction between 1,4-butanedisulfone and a cold aqueous solution of di-methylamine over 24 hours. In the second step, a binuclear nucleophilic substitution reaction between stoichiometric amounts of ZDMBS and 1,3-propanedisulfone in the presence of LiOH or NaOH in anhydrous acetonitrile, resulted in, 3-(dimethyl(4-sulfobutyl)ammonio)propane-1-sulfonic acid HMM3411 in 96% yield after recrystallization in methanol. At the final step by treating the HMM3411 with LiOH or NaOH solution, LiMM3411 and NaMM3411 were achieved in 99% and 98% yield respectively.

HMM3411: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 3.31 (t, 2H, NCH_2); 3.22 (t, 2H, NCH_2); 2.96 (s, 6H, $2\times\text{CH}_3$); 2.82 (t, 4H, SCH_2); 2.06 (m, 2H, $-\text{CH}_2-$); 1.75 (m, 2H, $-\text{CH}_2-$); 1.65 (m, 2H, $-\text{CH}_2-$) ppm.
 $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 63.54 (NCH_2); 62.25 (NCH_2); 50.4 (SCH_2); 49.91 (SCH_2); 47.17 ($2\times\text{CH}_3$); 20.99 (CH_2); 20.77 (CH_2); 18.04 (CH_2) ppm.

LiMM3411: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 3.33 (t, 2H, NCH_2); 3.24 (t, 2H, NCH_2); 2.96 (s, 6H, $2\times\text{CH}_3$); 2.84 (t, 4H, SCH_2); 2.08 (m, 2H, $-\text{CH}_2-$); 1.80 (m, 2H, $-\text{CH}_2-$); 1.67 (m, 2H, $-\text{CH}_2-$) ppm.
 $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 63.55 (NCH_2); 62.27 (NCH_2); 50.35 (SCH_2); 49.89 (SCH_2); 47.15

(2xCH₃); 20.97 (CH₂); 20.75 (CH₂); 18.03 (CH₂) ppm. Elem. Anal. Calc.: (LiC₉H₂₀NO₆S₂·0.5H₂O): C, 33.96; H, 6.75; N, 4.4; S, 20.15; Li, 2.18. Found: C, 33.98; H, 6.95; N, 4.00; S, 19.6; Li: 1.90.

NaMM3411: ¹H-NMR (400 MHz, D₂O) δ = 3.33 (t, 2H, NCH₂); 3.24 (t, 2H, NCH₂); 2.96 (s, 6H, 2xCH₃); 2.84 (t, 4H, SCH₂); 2.08 (m, 2H, -CH₂-); 1.80 (m, 2H, -CH₂-); 1.67 (m, 2H, -CH₂-) ppm. ¹³C-NMR (100 MHz, D₂O) δ: 63.55 (NCH₂); 62.24 (NCH₂); 50.39 (SCH₂) 49.89 (SCH₂); 47.15 (2xCH₃); 20.96 (CH₂); 20.75 (CH₂); 18.03 (CH₂) ppm. Elem. Anal. Calc.: (NaC₉H₂₀NO₆S₂·0.5 H₂O): C, 32.33; H, 6.33; N, 4.19; S, 19.18. Found: C, 32.7; H, 6.61; N, 4.36; S, 18.75.

4.2. Pyridinium based anions

Among the proposed pseudo-delocalized pyridinium based anions, the anions containing sulfonate groups showed (table 3.) higher anion oxidation potential compared to anion with carboxylate group, although the dissociation potential were quite similar (with one exception due to the presence of one carbon spacer between sulfonate group and pyridinium ring). But when these anions considered for chemical synthesis, some issues such as very costly and even availability of starting materials emerged. Therefore, here the anion with carboxylate groups and another anion which was hybrid (containing both carboxylate and sulfonate groups) were synthesized.

The abbreviation of heterocyclic anions was chosen by a mix of digits and letters. For example, the anion 1-methylpyridinium-3,5-disulfonate (figure 14a), has been named as MM35py. MM stands for “Mickey Mouse”, the digits show the atom numbers in the ring that connected to the negative groups and the last two letters show the brief name of the ring.

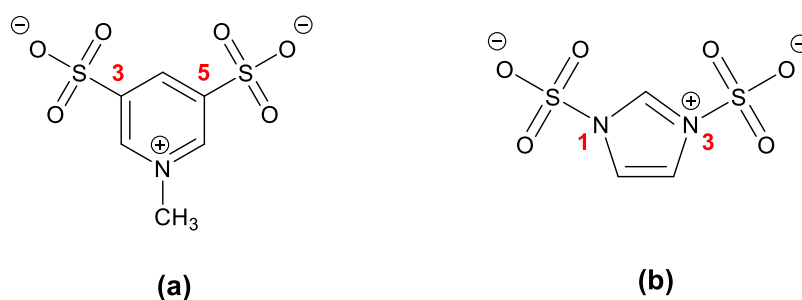
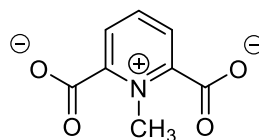


Figure 14. Schematic of **a)** 1-methylpyridinium-3,5-disulfonate (MM35py) and **b)** Imidazolium-1,3-disulfonate (MM13Im).

4.2.1. Synthesis of MM26py



The synthesis of 1-methylpyridinium-2,6-dicarboxylate (MM26py) and the corresponding lithium and sodium salts were conducted via a two-step synthesis procedure (figure 15).

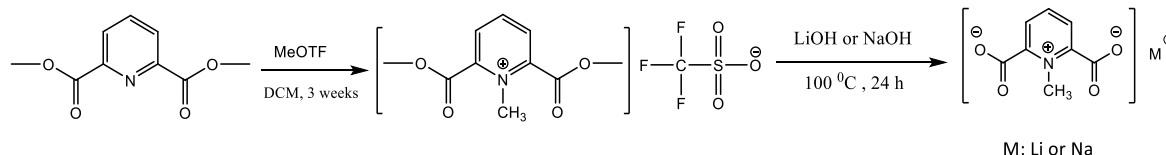


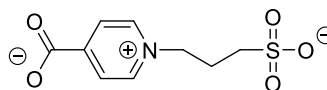
Figure 15. Synthesis route of LiMM26py and NaMM26py (Reproduced from (**paper IV**) published by Physical Chemistry Chemical Physics (PCCP) © Royal Society of Chemistry).

The first step of synthesis was inspired by previously reported work [172, 173]. Treatment of dimethyl 2,6-pyridinedicarboxylate was performed with a strong alkylating agent such as methyl trifluoromethanesulfonate (MeOTf) in anhydrous dichloromethane (DCM) under reflux at 40 °C over 3 weeks. The reaction mixture was cooled to room temperature and diluted with diethyl ether. Then the crude needle-like product was left to precipitate during a 24 h period in the fridge (~5 °C). Recrystallization of intermediate from ethyl acetate, gave 2,6-dimethoxycarbonyl-1-methylpyridinium trifluoromethanesulfonate in 96% yield. The second step proceeded with hydrolysis of intermediate in basic condition with the respective bases LiOH or NaOH over 24 h, followed by recrystallization of crude product from methanol, yielding LiMM26py (86%) and NaMM26py (83%).

LiMM26py: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 4.14 (s, 3H, NCH_3); 7.77 (d, 2H, 2xCH); 8.37 (t, 1H, CH) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 43.3 (NCH_3); 124.3 (2xCH); 146.8 (CH); 152.3 (2xCC); 165.9 (CO_2) ppm. Elem. Anal.: Calc. ($\text{LiC}_8\text{H}_6\text{NO}_4 \cdot 0.6 \text{H}_2\text{O}$): C, 48.56; H, 3.67; N, 7.08; Li, 3.51. Found: C, 48.44; H, 3.99; N, 7.18; Li: 3.53. LC-MS: $m/z=182$ ($\text{M}^-_{\text{anions}+2}$), 180 ($\text{M}^-_{\text{anions}}$).

NaMM26py: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 4.14 (s, 3H, NCH_3); 7.77 (d, 2H, 2xCH); 8.37 (t, 1H, CH) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 43.3 (NCH_3); 124.3 (2xCH); 146.8 (CH); 152.3 (2xCC); 165.9 (CO_2) ppm. Elem. Anal.: Calc. ($\text{NaC}_8\text{H}_6\text{NO}_4 \cdot 0.45 \text{H}_2\text{O}$): C, 45.49; H, 3.29; N, 6.63; Na, 10.88. Found: C, 45.55; H, 3.55; N, 6.97; Na: 10.87. LC-MS: $m/z=182$ ($\text{M}^-_{\text{anions}+2}$), 180 ($\text{M}^-_{\text{anions}}$).

4.2.2. Synthesis of MM14py



The synthesis of hybrid pseudo-delocalized anion, based on two different negatively charged groups, were tried because of two main purposes. Firstly, investigating the influence of hybrid anions on salts properties (solubility and thermal stability compare to proposed pyridinium based pseudo-delocalized anions) and secondly trying to make ionic liquid (IL) with the use of this anion. Since, the synthesis of lithium and sodium salts based on MM14py anion has been reported in this thesis for the first time, therefore full details of synthesis method and characterization of both lithium and sodium salts are also provided here.

The synthesis of 1-(3-sulfonatopropyl)pyridinium-4-carboxylate (MM14py) was performed in two successive steps (figure 16). However, the first step of synthesis procedure, previously had been reported [174], but here we performed it through a different synthesis route (as below), which resulted an increase in the reaction yield from 62% [174] to 77%.

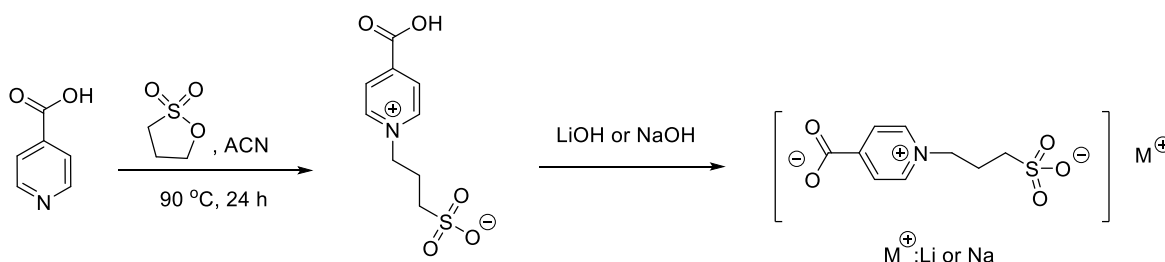


Figure 16. Synthesis route of LiMM14py and NaMM14py (unpublished).

In the first step, 3-(4-carboxypyridinium)propane-1-sulfonic acid (HMM14py) was synthesized as a slurry containing commercially available starting materials isonicotinic acid (1.36 g, 11.04 mmol) and 1,3 propane sultone (2 mL, 22.08 mmol) in 50 mL anhydrous acetonitrile at 90 °C for 24 hours. When reaction completion was verified by NMR, the crude product was filtered off and dissolved in 10 mL water. Before removing water *in vacuo*, by filtration unsolvable white supernatant was isolated. The desired product was further purified by recrystallization from ethanol and drying in vacuum oven at 70 °C for 24 hours, afforded the target compound as colorless crystals (2.1 g, 8.6 mmol), corresponding to 77% yield. By neutralization of HMM14py (1 g, 4.1 mmol) with LiOH or NaOH solution followed by water removal *in vacuo* and drying in vacuum oven at 70 °C for 72 hours,

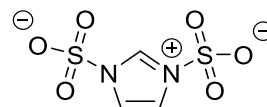
corresponding lithium or sodium salts LiMM14py (1.0 g, 3.98 mmol, 97%) and NaMM14py (1.03 g, 3.74 mmol, 94%), were collected.

LiMM14py: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 2.34 (m, 2H, $-\text{CH}_2-$); 2.85 (t, 2H, $\text{CH}_2\text{-S}$); 4.69 (t, $\text{CH}_2\text{-N}$) 8.32 (d, 2H, CH); 8.90 (d, 2H, CH) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 20.67; 46.69; 60.10; 127.7; 145.5; 148.9; 165.4 ppm. Elem. Anal.: Calc. ($\text{LiC}_9\text{H}_{10}\text{NO}_5\text{S} \cdot 0.15 \text{H}_2\text{O}$): C, 42.58; H, 4.09; N, 5.52; S, 12.63; Li, 2.73. Found: C, 42.63; H, 4.11; N, 5.62; S, 12.74; Li: 2.71. LC-MS: $m/z=246.3$ ($\text{M}^-_{\text{anions}+2}$), 244.3 ($\text{M}^-_{\text{anions}}$).

NaMM14py: $^1\text{H-NMR}$ (400 MHz, D_2O) δ = 2.34 (m, 2H, $-\text{CH}_2-$); 2.85 (t, 2H, $\text{CH}_2\text{-S}$); 4.69 (t, $\text{CH}_2\text{-N}$) 8.32 (d, 2H, CH); 8.90 (d, 2H, CH) ppm. $^{13}\text{C-NMR}$ (100 MHz, D_2O) δ : 20.67; 46.69; 60.10; 127.7; 145.5; 148.9; 165.4 ppm. Elem. Anal.: Calc. ($\text{NaC}_9\text{H}_{10}\text{NO}_5\text{S} \cdot 0.4 \text{H}_2\text{O}$): C, 39.39; H, 3.97; N, 5.10; S, 11.68; Na, 8.38. Found: C, 39.32; H, 3.70; N, 4.99; S, 11.56; Na: 8.63. LC-MS: $m/z=246.3$ ($\text{M}^-_{\text{anions}+2}$), 244.3 ($\text{M}^-_{\text{anions}}$).

4.3. Synthesis towards other pseudo-delocalized anions

Besides those of pseudo-delocalized anions, that were synthesized, examined and published as battery electrolyte salts, we also tried hard to synthesize other anions as well but unfortunately for different reasons, we were not successful in isolating the desired salts. Therefore, in this section, the applied synthetic methods for some of these anions were presented with the emphasis on why we could not manage to synthesize them.



4.3.1. Toward synthesis of MM13Im

Synthesis of pseudo-delocalized salt based on imidazolium-1,3-disulfonate (MM13Im) anion was of interest to us, due to having the highest anion oxidation potential among the heterocyclic and aliphatic based anions, lower dissociation energy compares to LiPF₆ and availability of starting materials with reasonable price. However, several attempts were performed to synthesize this anion, but unfortunately, the desired salt was unattainable. Attempted synthesis procedure to reach the salt can be found in figure 17.

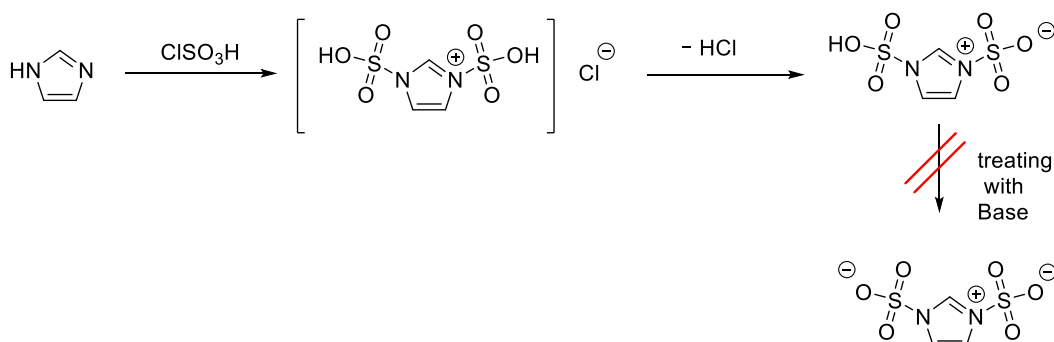


Figure 17. Attempted synthesis route of salt based on MM13Im anion.

As it has been shown, firstly imidazole must be treated with chlorosulfonic acid in dry dichloromethane to yield 1,3-disulfonic acid imidazolium chloride (DSImCl), according to the previously reported work [175]. This product is a protonated ionic liquid (IL) that has been utilized as a catalyst in organic synthesis. While, the synthesis of DSImCl was quite straight forward, but in the beginning, it was so challenging for us. However, after many efforts, we succeeded to synthesize it without any difficulties on multi grams scale.

Removing hydrochloric acid in the second step was tried through different methods, in the following, some of them are presented.

4.3.1.1. Treatment of DSImCl by silver oxide

The first try for making zwitterion from corresponding IL (DSImCl), was conducted by mixing DSImCl with silver oxide(I) in water presence at room temperature (figure 18). Indeed, we expected that the reaction proceeds as figure 18 and by the elimination of hydrochloric acid, zwitterion obtains.

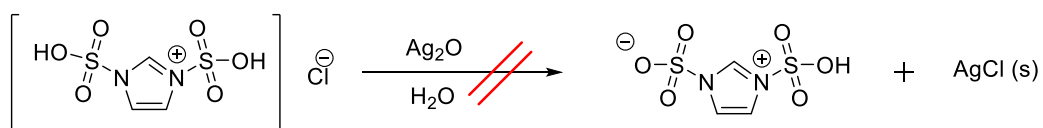


Figure 18. Attempted method to remove HCl by silver oxide.

This strategy was selected due to the insolubility of silver halide and in contrast solubility of zwitterion in water. Indeed, we expected that the reaction proceeds as figure 18 and by the elimination of hydrochloric acid, zwitterion obtains. However, instead of obtaining zwitterion as the intermediate, two silver salts based on chloride and 1,3-disulfonate imidazolium were collected which were insoluble in water (figure 19).

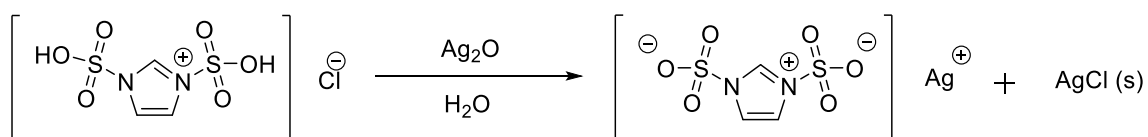
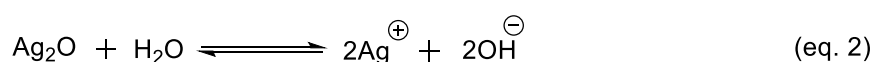


Figure 19. Treatment of DSImCl by silver oxide.

This result could be due to its intrinsic tendency of silver oxide to react with water in acidic or neutral solution [176], which represents by (eq. 2):



Indeed, the hydroxide anion can easily react with the protons in DSImCl and then silver cation can compensate the required charge to make silver 1,3-disulfonate imidazolium.

4.3.1.2. Expelling of hydrochloric acid by heat

Another approach for expelling of HCl, was performed at elevated temperature. By running thermogravimetric analysis (TGA) coupled to infrared spectroscopy (TGA-IR) on DSImCl, it was observed that HCl can be released between *ca.* 130-140 °C. Therefore, HCl removal experiment for 10 mg of DSImCl under nitrogen flow and using oil bath at elevated temperature was accomplished in 24 hours (figure 20). During this period the experiment was monitored by pH paper to verify the pH of released gas (HCl). Therefore, after 24 hours, when no changing in pH paper color was observed, the experiment was proceeded for 1 more hour, to ascertain the removal of all HCl.

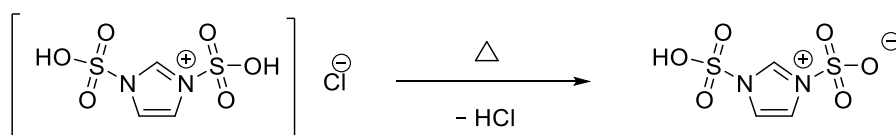


Figure 20. Removing of hydrochloric acid at elevated temperature.

The dark brownish product was analyzed with elemental analysis (table 4). While the result showed that there is not any chlorine in the product, but an extra amount of hydrogen indicated that it might be very hygroscopic. Nevertheless, we tried to perform the experiment on a larger scale (1 g), but we never managed to get the desired intermediate again.

Table 4. Elemental analysis designation after expelling hydrochloric acid from DSImCl.

Sample designation	% C	% H	% N	% S	% Cl
HMM13Im- found	15,98	3,81	11,60	21,41	0,00
HMM13Im- theoretical	15,79	1,77	12,28	28,10	-

4.3.1.3. Hydrochloric acid trapping by pyridine

Another alternative to trap HCl was examined by pyridine as a hydrochloric acid scavenger [177]. The lone pair on nitrogen in pyridine ring form bond with hydrogen and create a positive charge that can be compensated with the negative charge on chlorine (figure 21).

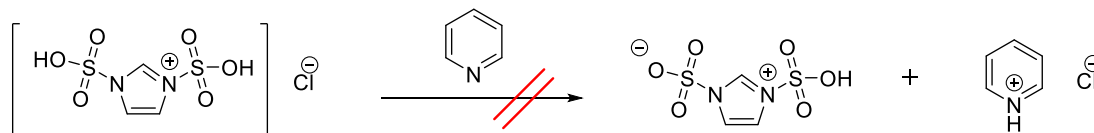


Figure 21. Hydrochloric acid removal by pyridine.

The experiment was exerted with the immiscible mixture containing DSImCl (0.5 g) in 30 mL pyridine for 5 days at room temperature. However, since no change in the chlorine amount was observed according to elemental analysis, the experiment was repeated with the same amount of starting materials at higher temperature (70 °C). As no remarkable evidence to show if chlorine amount has been reduced, therefore the experiment was stopped without any significant result. It is speculated that the insolubility of IL in pyridine has led to the failure of this method.

Various approaches to removing hydrogen chloride (HCl) from DSImCl and creating protonated zwitterion, were examined but almost all of them were failed except in one case (section 4.3.1.2.), where the small scale of DSImCl was handled. However, the elemental analysis result was acceptable (no trace of chlorine), but it also revealed the hygroscopic character of protonated zwitterion which can create other problems toward the isolating of favored salt. As we could not obtain a large scale of protonated zwitterion, therefore we examined another alternative in the following section.

4.3.2. Toward MM13Im synthesis by inorganic salt

Treating of 1,3-disulfonicacid-imidazolium chloride with inorganic salts in acetonitrile was another strategy, that tried several times. But here only lithium phosphate (Li_3PO_4) is presented (figure 22).

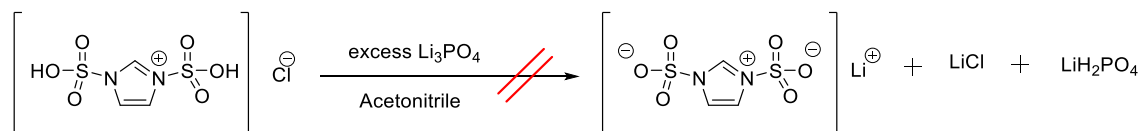


Figure 22. Neutralizing of IL by lithium phosphate.

The reaction was made as a slurry over a few days. Acetonitrile was selected as the solvent because in general, all the phosphate species are insoluble in solvents such as acetonitrile (or any other solvents rather than water) and also the lithium chloride solubility is quite low in this solvent. Hence, with the hope that LiMM13Im is soluble in acetonitrile and can be easily obtained by evaporation, the experiment was run for seven days.

By filtering the white precipitate, the solid and liquid phases were collected separately. However, upon removal of the solvent in rotavapor, nothing remained in the container. Therefore, apparently the desired salt together with starting materials and other by-products were all insoluble in acetonitrile.

The NMR result on solid part, could not be useful in this case, because there was not any major difference between the H-NMR spectrum of DSImCl and the corresponding lithium salt (LiMM13Im), except the acidic protons that could not be even detected by NMR when D_2O was used (the only NMR solvent, that dissolved solid part entirely). Meanwhile, LC-MS was an inefficient analytical technique as well, because the presence of pseudo-delocalized anions could be determined only by selecting positive mode on the mass spectrometer. By this technique, both of the negatively charged groups are protonated and the mass of anions detected as $(M^+ + 2)$ which is similar to the precursor.

Nevertheless, both NMR and LC-MS analysis on white solid was performed and in both analytical techniques trace of imidazole was observed. We speculate that phosphate anion can act as a base and cause detaching of sulfonate groups, similar to previously reported work, in which aqueous sodium hydroxide caused expelling of sulfonate group from imidazole ring [175]. Several purification methods such as recrystallization and Soxhlet extraction were exerted, but we could not isolate the pure salt.

4.3.3. Microwave assisted synthesis

Microwave (MW) based synthesis is considered as an efficient technique in the chemical synthesis field due to reduced reaction time, reduced energy consumption and in some cases higher purity or yield. Despite the usefulness of this technique for organic synthesis, still, there is a lack of knowledge about the effective interaction between electromagnetic radiation and matter [178]. Nevertheless, MW plays an important role in organic synthesis, because often, it can reduce the reaction time from days to hours or even minutes.

Here, in parallel to the synthesis of pseudo-delocalized anions belong to the initial proposal [25], the possibility of design and preparing other anions (figure 23), based on this concept by the aid of MW synthesis were also examined. Although in nearly all cases, the synthesis was abandoned because of sterically hindered of intermediate. As an example, the synthesis of MM2233 (figure 23) was presented in this section.¹

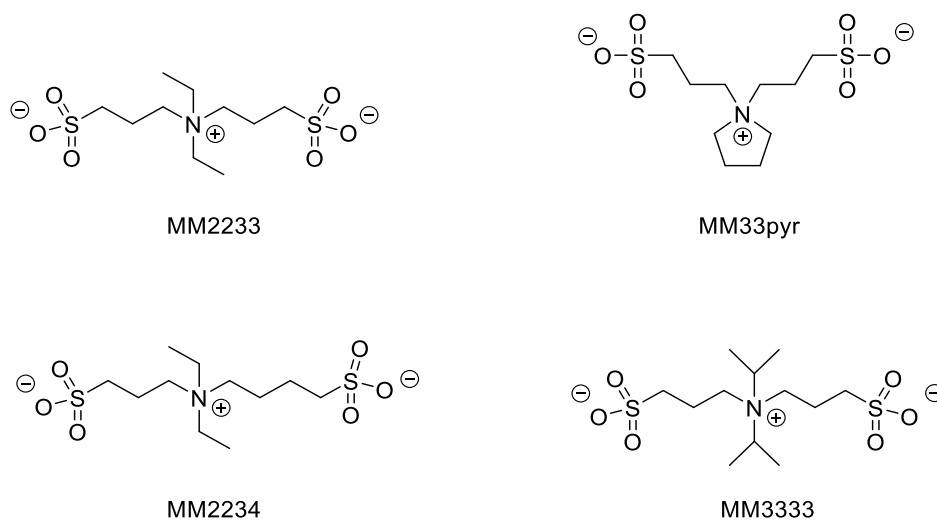


Figure 23. Chemical structures of other pseudo-delocalized anions.

¹ This experiment was performed partially by “Raphaëlle Houdeville” from the “Higher school of organic and mineral chemistry (ESCOM), Compiègne, Hauts de France” as an internship master student at Chalmers university of technology.

4.3.3.1. Toward synthesis of MM2233

The synthesis of protonated 3,3'-(diethylammonio)bis(propane-1-sulfonic acid) (HMM2233) from commercially available starting materials such as diethylamine and 1,3-propane sultone and lithium hydroxide was conducted in two consecutive steps (figure 24).

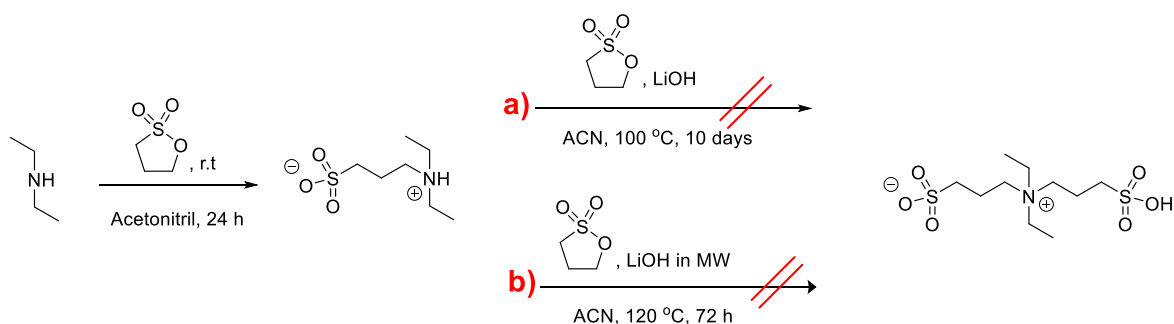


Figure 24. Synthesis route for MM2233.

In first step zwitterion 3-(diethylammonio)propane-1-sulfonate (Z223) was obtained by using 1,3-propane sultone and three times excess of diethylamine in 50 mL of acetonitrile over 24 hours. Once the reaction completion was verified by NMR, crude white intermediate Z223 was collected and recrystallized from ethanol and dried in the oven. The second step was carried out by mixing Z223, lithium hydroxide and 1,3-propane sultone in 50 mL of acetonitrile over 10 days at 100 °C (figure 24a). But due to low reaction yield (>10%), we preferred to perform the experiment in the MW reactor (figure 24b) to save time and perhaps increase the reaction yield. However, after running the experiment for 72 hours at 120 °C in MW, we did not observe any remarkable differences in reaction yield ($\approx 12\%$). Indeed, steric hindrance was the big barrier for S_N2 reaction in the second step that was created by two ethyl groups together with propane sulfonate on nitrogen in Z223, which caused low reaction yield.

Other anions in figure 23 also suffered from this restriction. However, the steric hindrance effect on MM2234 was quite similar to MM2233, but it even became worse in the case of MM33pyr and MM3333. While in former pyrrolidine ring and propane sulfonate, made a big obstacle for S_N2 reaction, in the latter, it caused by two isopropyl groups and propane sulfonate. Surrounding nitrogen by alkyl groups in pyrrolidine ring and amine, not only led to prolong reaction time at first step to 6 days and 3 weeks respectively, but it also caused that the second step of reaction does not proceed at all, therefore no favored product could be collected.

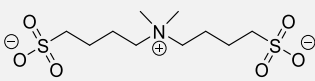
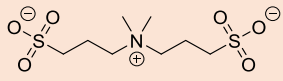
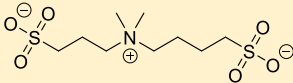
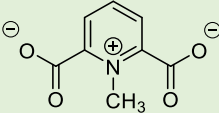
Chapter 5

This chapter provides a brief summary of the results contained in the appended papers at the end of this thesis.

Results and Observations

In this section, it has been attempted to present observations and findings through summarizing some of the key properties of synthesized salt (table 5). The aim is to help the readers understand the results in greater detail.

Table 5. Some properties of synthesized salts based on pseudo-delocalized anion concept.

Anion structures	Salts	T _d (°C)	Solubility in water (m)	Tested electrolyte
	LiMM4411	325	< 6	low voltage aqueous electrolyte
	NaMM4411	315	< 6	
	LiMM3311	265	< 6	solid state electrolyte
	NaMM3311	275	< 6	
	LiMM3411	285	< 8	solid state and WiBs electrolyte
	NaMM3411	275	-	solid state electrolyte
	LiMM26py	150	< 9	medium voltage IL-based electrolyte
	NaMM26py	200	< 8.2	

5.1. MM4411 (paper I)

In **paper I**, the first fluorine-free salts based on pseudo-delocalized concept were presented. From the synthesis aspect, both salts were synthesized from inexpensive and readily available materials and collected as the salts in excellent yield. The synthesis procedures were conducted entirely in water as the solvent. The commercially available dimethylamine aqueous solution and 1,4-butane sultone were used initially as starting material which afforded zwitterion (ZDMBS) in high yield (96%). Synthesizing desired salts were conducted via bimolecular nucleophilic substitution (S_N2) reaction between ZDMBS and 1,4-butane sultone in the presence of the corresponding base (LiOH or NaOH). However, the second step was temperature dependence as it was monitored by NMR. Indeed, increasing the temperature leading to faster completion but by the expenditure of reaction yield (table 6), because at elevated temperature 1,4-butane sultone will react with water, resulted in lower reaction yield. Therefore, to obtain the product in higher yield and purity, 35 °C was selected as the reaction temperature. By this optimized synthetic route, the analytically pure target salts were collected in excellent yield (LiMM4411: 92% and NaMM4411: 90%) on a multigram scale. From the chemistry point of view, the synthesis of both non-fluorinated salts was done entirely in water as the solvent, without consuming any organic solvent (however, favored salts were washed with chloroform and recrystallized from methanol) and purification was done without the use of any column chromatography. From the physical properties aspect, both of the salts were thermally stable (over 300 °C) and fluorine-free compared to popular fluorine contains salts. However, their poor solubility in organic solvents which was confirmed by x-ray crystallography and quite good solubility in aqueous solvent, pave the way for their application in low voltage aqueous battery.

Table 6. Optimization of reaction conditions.

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. MM3311 (paper II)

In **paper II**, another analog of fluorine-free aliphatic salts based on the pseudo-delocalized concept with three carbon spacers were examined. Since previously synthesized salts in **paper I** showed insolubility in conventional electrolyte solvents, hence to improve solubility, synthesis of aliphatic salts contains shorter alkyl chain was of interest. Both LiMM3311 and NaMM3311 salts were synthesized in three consecutive steps. Firstly, monomeric zwitterion Z311 was obtained in high purity and yield (96%) by using the commercially available dimethylamine and 1,3-propane sultone as the starting material in aqueous media at 0 °C in 30 minutes. Followed by stirring a slurry of stoichiometric amounts of Z311, LiOH or NaOH and 1,3-propane sultone in anhydrous acetonitrile at 70 °C. Albeit, using anhydrous acetonitrile in second step was essential, due to the high reactivity of 1,3-propane sultone in water, which can be compared with the reaction of 1,4-butane sultone in **paper (I)**. Solvent modification led to some remarkable changes in the synthesis process. Initially, the reaction temperature was raised to 70 °C compared to 35 °C in water, because in lower temperature the completion of reaction would take longer (10 to 14 days). On the other hand, as was mentioned before (**paper I**) the desired salts were obtained in two steps, but here instead, protonated form of favored anions, HMM3311 in high yield (94%) was achieved. In addition, a colorless byproduct was also isolated by filtration after dissolving the mixture in water. We speculated that reaction between 1,3-propane sultone and acetonitrile in presence of base at elevated temperature cause production of this supernatant byproduct, however, its chemical composition never uncovered due to its insolubility in most of the conventional organic solvents. In the final step, the neutralization of HMM3311 by an aqueous solution of lithium hydroxide or sodium hydroxide resulted in LiMM3311 (83%) and NaMM3311 (82%) in high purity. The salts' solubility test revealed that organic electrolyte solvents are not good candidates to dissolve them, because of the strong interaction between the metal ion and the anion. Therefore, in **paper (II)** by mixing these salts with standard battery salt LiTFSI (making eutectic mixtures), novel solvent-free liquid electrolytes were prepared. The thermal stability of these novel solid electrolytes contains pseudo-delocalized anion salt together with organic solvent elimination, resulted a super-cooled electrolyte for LIB and SIB future applications.

5.3. MM3411 (paper II & III)

Asymmetric salts based on MM3411 pseudo-delocalized anion were other alternatives to overcome the low solubility of aliphatic salts. The salts synthesis was conducted through a three-step synthesis route similar to synthesis procedures that were exerted for the salts based on MM3311 anion. First, the addition of 1,4-butane sultone to the aqueous solution of di-methyl amine during 24 hours at low temperature resulted intermediate ZDMBS. In the second step, HMM3411 and a colorless supernatant were collected as the products of the reaction between ZDMBS, 1,3-propane and corresponding base in anhydrous acetonitrile at 70 °C for 72 h. However, before the treatment of HMM3411 with LiOH or NaOH solution, the supernatant byproduct was isolated from the desired product by dissolving in water. In the third step, LiMM3411 (99%) and NaMM3411 (98%) were obtained as pure colorless salts.

Unorganized packing structure due to anion asymmetry and high thermal stability (*ca.* 280 °C) created specific properties for these salts. As it has presented in **paper (II)**, the solvent-free liquid electrolyte can be obtained in the presence of 20-30 mole% of LiMM3411. In fact, preventing recrystallization of LiTFSI when combined with LiMM3411 was very handy and useful, because this ability helped to prepare a water-in-bisalt electrolyte (**paper III**) with a record salt concentration (31.4 m LiTFSI + 7.9 m LiMM3411) that allows stable SEI formation on the anode surface.

5.4. Biological activity of aliphatic anions

Heterocyclic sulfonic esters or sultones are a group of alkylating agents that provide sulfoalkyl chain in organic and medicinal synthesis. Sultones based on 4 to 6-membered ring are the most known ones, although 7-membered or even higher have been synthesized as well [179]. Despite wide applications of these alkylating agents in the chemical industry, there are still some debates about the carcinogenic activity of these substances. As an example, 1,3-propane sultone (figure 25a) is one of the carcinogenic and genotoxic compounds [180] that has been also in used by us as starting material for the synthesis of various aliphatic pseudo-delocalized anions. However, to use 1,3-propane sultone even at small scale, we needed special permission from the “Swedish work environmental authority” or “Arbetsmiljöverket”, which was granted to us after inspecting our working environment by this authority. Although we have used 1,4-butane sultone (figure 25b) which is carcinogenic as well [181], but because of its less reactivity, no special permission was required.

Regard to the chemical characterization of aliphatic salts, there were not any sultones trace in the desired salts. Nevertheless, we were also eager to test these salts from the biological activity aspect. Therefore, NaMM3311 and NaMM4411 were sent to Copenhagen university, department of veterinary and animal sciences for further evaluations.

According to the report by our colleagues, both salts were dissolved in MiliQ water at the concentration of 250 $\mu\text{g} / \text{ml}$, to examine their capability of inhibiting the growth of the bacteria (*Staphylococcus aureus*). However, in such a high concentration no biological effects were detected. Indeed, the biological experiment results verified that these salts are safe to handle and use as electrolyte salts.

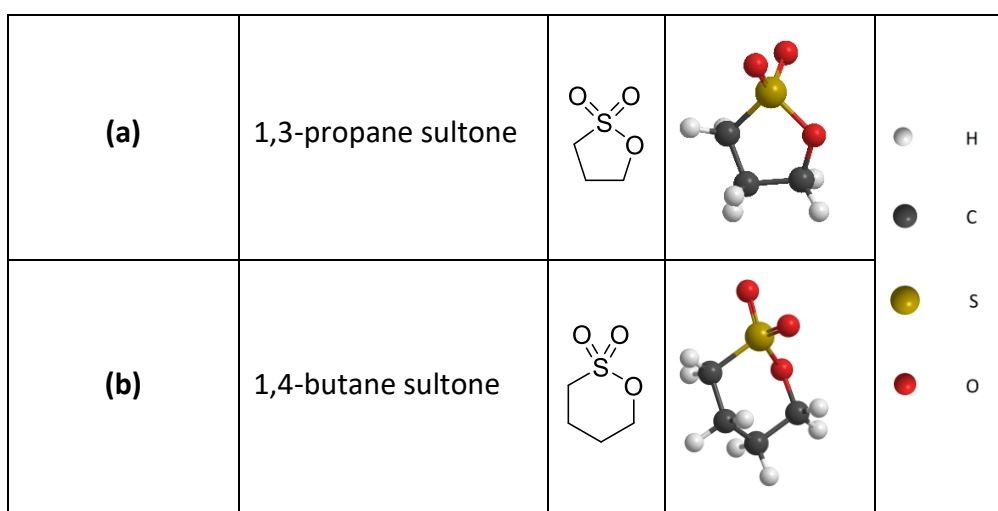


Figure 25. Chemical structures of **a)** 1,3 propane sultone and **b)** 1,4-butane sultone.

5.5. MM26py (paper IV)

The synthesis of LiMM26py and NaMM26py was performed through a two-step synthetic procedure. Firstly pyridine-2,6-dicarboxylatedimethylester was alkylated by strong alkylating agent as methyl trifluoromethanesulfonate (MeOTf). But, because of steric and electronic effects, the reactivity of the pyridine was slightly low. During the alkylating process, we noticed that time is a more efficient factor to increase the reaction yield rather than using the excess of alkylating agent. By increasing reaction time from two weeks [173] to three weeks (**paper IV**), improving reaction yield as 53% [173] to 96% (**paper IV**) was observed, even by reducing the amount of MeOTf from 3 to 1.3 molar equivalent. In the second step, hydrolysis of the ester (figure 26) was carried out in basic solution, not only due to the need of metal cation (Li, Na) as a counter-ion but also because of the irreversibility of the ester hydrolysis reaction under basic conditions.

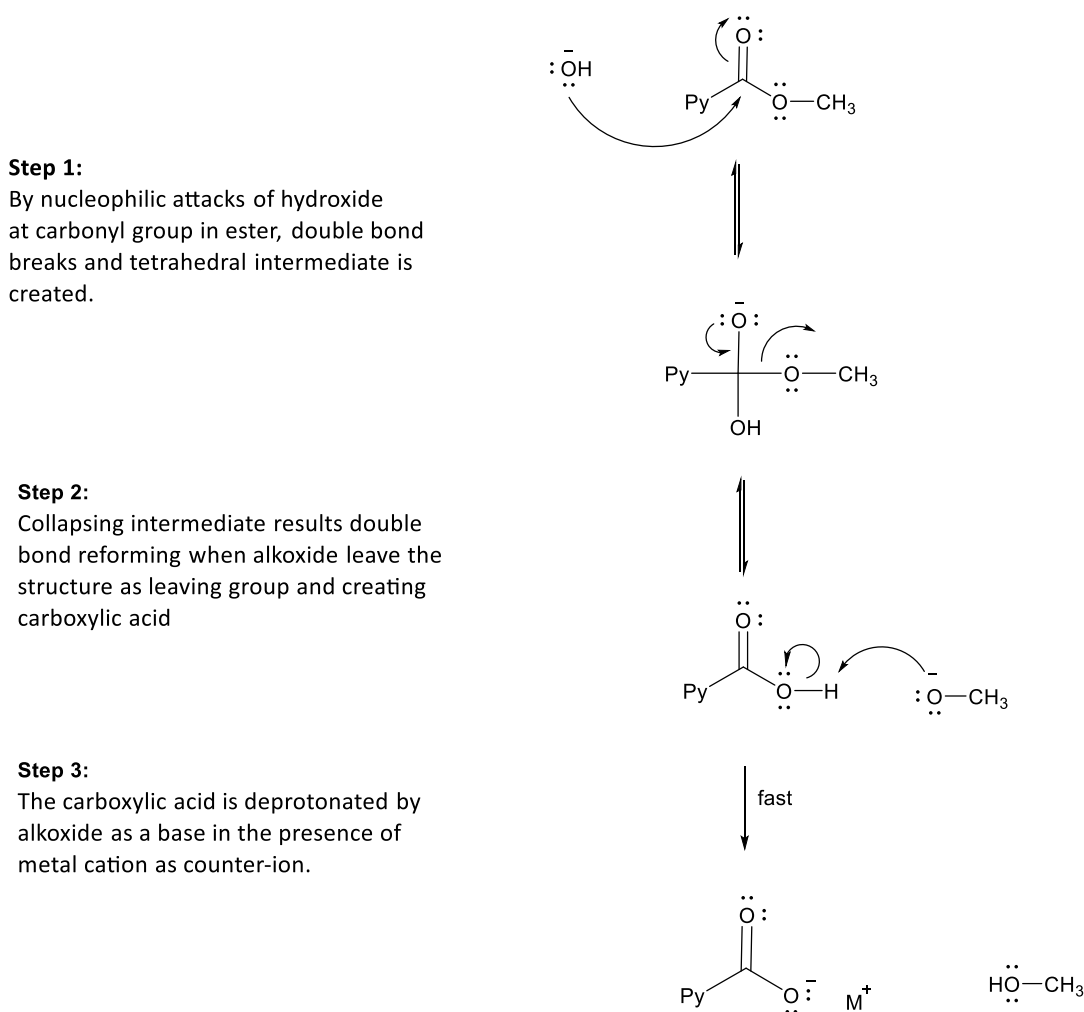


Figure 26: Ester hydrolysis mechanism in basic condition.

Furthermore, the ester hydrolysis under basic conditions resulted in much higher yields (LiMM26py: 86% and NaMM26py: 83%) as compared to under acidic conditions (12% yield) [173] Combined these optimized synthesis procedures furnish the target salts in excellent yield with high analytical purity. By dissolving the synthesized pyridinium salts in an ionic liquid matrix (Pyr14TFSI), ionic liquid (IL) based electrolytes were prepared. The obtained electrolytes showed good thermal stability up to 200 °C and the electrochemical stability windows between 2.3 and 2.5 V, which confirm the applications of these electrolytes in medium-voltage LIBs and SIBs.

Chapter 6

Conclusion Remarks and Outlook

The electrolyte is one of the main components of the electrochemical cell which plays an important role in battery's safety. Depends on the used salt(s) and solvent(s), each electrolyte has its pros and cons. Although organic liquid electrolyte based on fluorinated salts, possess larger output voltage than aqueous based electrolytes, but suffer severely from safety issues. The first action toward creating safer LIB (SIB) electrolyte has covered in this thesis by synthesizing the first generation of non-fluorinated Mickey Mouse™ anions based on the pseudo-delocalized concept. Combining the theoretical calculations and experimental results, confirmed the low solubility of these salts in conventional organic solvents. However, this limitation directed the project toward exploring electrolytes with safer solvents (water and IL) or even solvent-free. Alongside good futures of these fluorine-free salts, some drawbacks also accompany them. In order to further improve the salt performances as LIB and SIB electrolytes, the following suggestions are presented;

- ❖ Synthesis of the second generation of fluorine-free aliphatic anions that benefited from shorter alkyl chains and also asymmetry perhaps can improve the solubility challenges. Because shorter alkyl chain could avoid trapping of the metal cation and in parallel asymmetry can increase salts solubility which already has been observed in MM3411 anion.
- ❖ One possible strategy to modify salts' solubility and ion conductivity can be achieved further by softening the $-\text{SO}_3^-$ moieties. Replacing one of the oxygen atoms with more weakly coordinating unite *e.g.* (-NCN- or -N(SO₂CF₃)-), can "soften" the sulfonate group and results in higher solubility.

- ❖ Synthesizing of salts based on hybrid pseudo-delocalized anions is another feasible approach to overcome solubility and thermal stability restrictions. In this case, the anion has two different withdrawing groups. one example of hybrid anions has been presented in section (4.2.2).
- ❖ Another Alternative might be trying to synthesis some other salts based on the pseudo-delocalized concept, which showed more promising properties similar to common fluorinated salt, but more challenging from the synthesis aspect. They can be from any other subsets of MM anions like pyridine-, imidazole- or even spiro-based.

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