

THESIS FOR THE DEGREE OF LICENTIATE OF ENGINEERING

Novel electrolytes for next-generation hybrid supercapacitors

Investigating the interaction between electrolyte and electrode

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ABSTRACT

The storage of electrical energy is of utmost importance in today's society, ranging from cell phones to large scale energy storage of intermittent electricity sources. Batteries, that are most commonly used, struggle with low power density and limited cycle lifetime. Supercapacitors are seen as an alternative to batteries with their high-power density and almost unlimited cycle lifetime. However, supercapacitors only use the surface of the electrode which reduces the energy content compared to batteries. The low energy density limits their use in different applications where they otherwise would have been suitable. To increase the energy density metal oxides, such as MnO_2 , RuO or VO_2 , with higher energy content than carbon are often added to the electrodes. The total energy is also proportional to the voltage window, squared, in which the device operates. The normal limiting factor of the voltage window is the electrolyte, all electrolytes breaks down if polarized to sufficiently high or low potentials. Choosing an electrolyte with a large voltage window will also increase the energy content of the cell.

This thesis focuses on combining these two approaches to increase the energy density even further by investigating novel, high-energy, electrolytes and their interactions with MnO_2 and VO_2 based electrodes. Electrochemical measurements and physical characterization of the electrolytes are used to determine important parameters for optimal performance of the electrodes. The results show that by using protic ionic liquids the contribution of MnO_2 -electrodes to the total energy content can be increased while the potential window is widened. Highly-concentrated aqueous NaTFSI electrolytes present a promising, cheap, alternative with a larger potential window compared to standard aqueous electrolytes. VO_2 -electrodes performs well but with a limited cycle lifetime in the NaTFSI electrolyte and have higher energy density combined with retained power density.

Keywords: Hybrid supercapacitors, ionic liquids, MnO_2 , VO_2 , non-aqueous, superconcentrated, NaTFSI, pseudocapacitance

List of publications

This thesis is based on the work containing the following papers:

1. High energy-density hybrid supercapacitors: Combining high-voltage window ionic liquids with MnO₂-nanomaterials

Simon Lindberg, Steffen Jeschke, Matthew Sadd, Muhammad Abdelhamid, Thierry Brousse, Jean Le Bideau, Patrik Johansson, Aleksandar Matic

2. Application of a highly-concentrated aqueous NaTFSI electrolyte to a VO₂/Carbon hybrid supercapacitor

Simon Lindberg, Ndeye Maty Ndiaye Fall, Ncholu Manyala, Patrik Johansson, Aleksandar Matic

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List of acronyms

| | |
|---|------------------------------------|
| HSC | Hybrid supercapacitor |
| LIC | Lithium ion capacitor |
| SIC | Sodium ion capacitor |
| CV | Cyclic voltammetry |
| MnO ₂ | Manganese oxide |
| RuO | Ruthenium oxide |
| VO ₂ | Vanadium oxide |
| IL | Ionic liquid |
| BMIM | 1-Butyl-3-Methylimidazolium |
| EMIM | 1-Ethyl-3-Methylimidazolium |
| TFSI | bis(trifluoromethanesulfonyl)imide |
| Cl | Chloride |
| KOH | Potassium hydroxide |
| H ₂ SO ₄ | Sulfuric acid |
| HCl | Hydrochloric acid |
| Li ₂ SO ₄ | Lithium sulfate |
| AC | Activated carbon |
| PbO ₂ | Lead oxide |
| Ni ₂ (OH) | Nickel hydroxide |
| Li ₄ Ti ₅ O ₁₂ | Lithium titanate |
| SiC | Silicon carbide |
| MWCNT | Multi-walled carbon nanotubes |
| MoO ₂ | Molybdenum oxide |
| TiO ₂ | Titanium dioxide |
| rGO | Reduced graphene oxide |
| SnO ₂ | Tin oxide |
| AgCl | Silver chloride |
| SHE | Standard hydrogen electrode |

1 Introduction

Today's society requires more electrical energy storage than ever before [1-2], ranging from powering your smart-watch on your wrist to electric cars and storing energy in solar and wind power dominant energy systems. The wide range of applications requires energy storage systems with different properties regarding energy and power density, cyclability and other characteristics. Traditionally batteries of different types have dominated the market of electrical energy storage [1], however, several applications would benefit from energy storage with different properties. Some important drawbacks of batteries are the low power density, slow charging times and limited cycle lifetime.

An alternative technology to batteries, when the drawbacks are too important to neglect, are so called supercapacitors. Supercapacitors have been around since the seventies and is a development of traditional capacitors used as components in electronics. They have extremely high-power density, long cycle lifetime and low material cost compared to batteries. These benefits have opened up to some different applications, but they are limited to applications where energy density is not essential or there is no limit in space available, such as industrial back-up power and brake energy regeneration [3]. But the ongoing research is improving the energy density and there is, for example, an electrical bus system in Singapore relying solely on supercapacitors for energy storage [4]. However, in other applications, such as the automotive industry, the energy density is in most cases too low to consider supercapacitors as an option.

The main technological differences between supercapacitors and batteries lie in the mechanism for storing energy. Batteries rely on chemical reactions taking place inside the bulk of the electrodes. This leads to high energy content but reduces the power since the transport of ions in and out of the electrode is quite slow. Supercapacitors on the other hand store energy at the electrolyte – electrode interface as double layers, this increases the power density. However, not using the bulk of the electrode decreases the energy density compared to batteries.

The energy that can be stored in a supercapacitor is proportional to the width of the voltage window squared and the area and thickness of the double-layer of ions at the surface. However, the surface area cannot be infinitely large and increasing the area of the electrodes also comes with the cost of reduced density leading to reduced volumetric capacitance. The development to increase the energy density has mainly followed two different routes [5]. The first route is using non-aqueous electrolytes in symmetric carbon/carbon cells to increase the voltage window of the device. The non-aqueous electrolytes have mainly been organic solvents together with a salt. These electrolytes are flammable and have high vapor pressures, leading to possible safety concerns. The latest approach in electrolyte research focuses instead on a special type of solvents called ionic liquids, which are non-flammable, have a low vapor pressure and possess even larger voltage windows than most organic solvents. They are also easy to tailor and can be made to possess various other different properties.

The second route have been to add battery type materials that have larger energy content than carbon, i.e. electrochemically active materials, to the electrode [6, 7]. Common materials are RuO_2 , MnO_2 and different conducting polymers. These electrodes, however, are mostly used in combination with aqueous electrolytes. Combining non-aqueous electrolytes with electrochemically active electrodes is not done frequently but the possible gain in energy content is promising [6].

This work focuses on developing an understanding of the properties required of novel electrolytes to be able to interact with electrochemically active electrodes. The electrolytes investigated are ionic liquid-based electrolytes and a highly-concentrated aqueous electrolyte that both potentially could be safe and cheap options with large voltage windows coupled with optimized interactions with the metal oxides added to the electrodes.

The hypothesis of the first paper was that the interaction between MnO_2 -electrode material and ionic liquids can be tuned by adding functional groups to the cation with different abilities to form hydrogen bonds and the research questions were exactly how this electrolyte/electrode interactions behave electrochemically and how the addition of a Li-salt affects the interaction. Normally in aqueous electrolyte the salt is essential but how does it work with the IL-electrolytes?

For the second paper the hypothesis was that we can make a hybrid device that uses a super concentrated electrolyte that expands the voltage window and improves performance. To investigate this VO_2 was chosen as electrode material, since not much previous research has been done on exotic electrolytes with this system. The research question was how to prepare the electrode material for optimal performance and how the interaction between the electrolyte and electrode material work.

2 Hybrid & asymmetric supercapacitors

Capacitors have been around for a very long time and can be seen as the simplest form of energy storage where the charge is stored as double layers at adjacent conducting metal plates. The term ‘supercapacitor’ was coined in 1971 by NEC after patents and research by General Electric in the 1950-60’s, when experimenting on using activated carbon on aluminum foil electrodes in capacitors. Howard Becker was the first to note the exceptional capacity acquired by these aluminum/activated carbon electrodes described in his patent from 1957 [8]. He assigned the extra capacitance to charge stored in the activated carbon itself, however, the origin is actually only surface charge and the high specific surface area of the carbon, reaching more than 3000 m²/g [9]. The capacitance of these early supercapacitors was 10 to 100 times higher than traditional capacitors.

In supercapacitors the charge is stored as Helmholtz double-layers consisting of the ionic species present in the electrolyte. Since the charge is stored in the actual electrolyte the formation and dissolution of these layers are very fast, leading to high power densities and long cycle lifetime. However, the energy content was low so the applications were limited to back-up power for the memories of early computers. Although the performance of supercapacitors has been improved since then by better activated carbons and novel organic electrolytes enabling higher voltage and higher energy density, the applications of supercapacitors are still mostly limited to different forms of industrial back-up power.

In the following decades, fundamental research was performed by Brian Evans Conway, beginning in the mid 70’s to the 1990’s, investigating and characterizing different materials, coining terms such as pseudocapacitance and faradaic materials. He specified the difference between batteries and supercapacitors and laid the ground for hybrid devices, combining both battery and supercapacitor materials for improved energy density [10].

Based on the work of Conway, next generation supercapacitors can, generally, be divided into two categories: Hybrid and asymmetric supercapacitors. A hybrid supercapacitor (HSC) is a device that combines the high energy content of a battery material with the speed and power of a supercapacitor material [11]. This combination is materialized by the use of a battery type insertion/desertion electrode combined with a capacitive electrode, such as activated carbon. A certain sub-type of HSCs are metal-ion capacitors, where the anode is an electrode with pre-inserted metal-ions to change the potential of the electrode, potentially enabling a larger voltage window of the cell. The most common types are Li-ion capacitors (LIC) and Na-ion capacitors (SIC) but also Al-ion capacitors have been successfully realized [12]. The research in this area follows the research in the battery field very closely and often builds on to progress made there concerning new materials.

Another special class of HSCs worth mention have transferred the electrochemically active material from the electrode to the electrolyte. This approach enables, generally very high-power densities since the conductivity of the electrolyte is larger than that of solid materials. However, to enable a high energy density the solubility of the active material in the electrolyte should be high to reduce the amount of electrolyte needed to increase the specific energy density.

Asymmetric supercapacitors on the other hand do not have a real intercalation type electrode but rely on reactions between the ions in the electrolyte and the electrode surface, although there can be some intercalation during charge and discharge, depending on the morphology of the material [13]. The electrochemical behavior of the asymmetric cell is very similar to traditional supercapacitors while HSCs often behave completely different. The cell-design of

HSCs and LICs/SICs are in principle the same. A typical coin cell can be seen in Figure 1 of either HSC or an asymmetric supercapacitor.

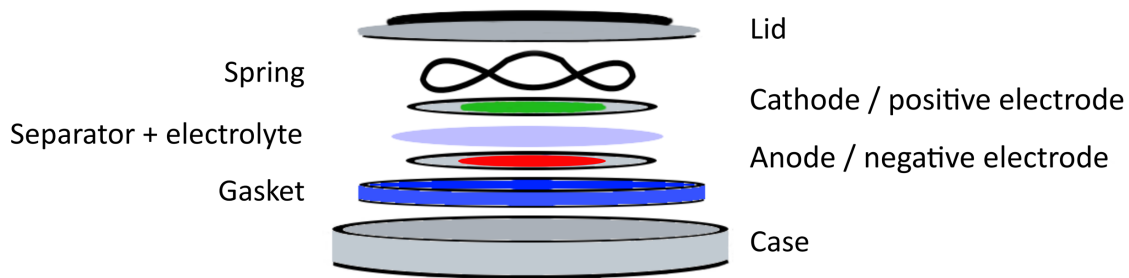


Figure 1. Schematic of a full cell in a coin cell casing.

2.1 Operation and functionality

The characteristics of these next generation supercapacitors differ from traditional supercapacitors due to the deliberate addition of materials contributing to the capacitance through electrochemical reactions. This can be seen in the difference of the electrochemical response between traditional supercapacitors and hybrid supercapacitors. A traditional supercapacitor has a strictly linear voltage profile during constant current charge/discharge and a rectangular cyclic voltammogram [14, 7]. Hybrid and asymmetric supercapacitors rely on electrochemical reactions, where the CVs of a hybrid show one or several peaks and in an asymmetric supercapacitor the peaks are only visible at slower scan speeds [7]. A Schematic figure, comparing traditional supercapacitor material and hybrid supercapacitor material, can be seen in Figure 2.

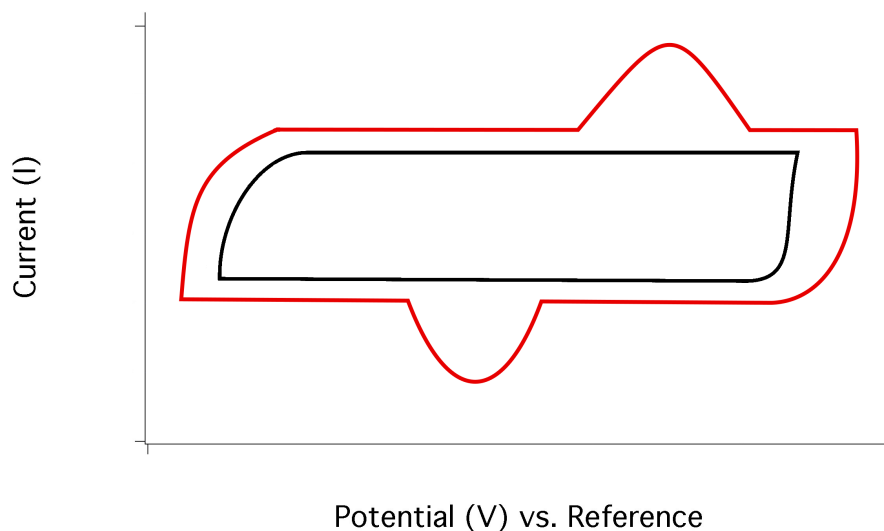


Figure 2. Schematic cyclic voltammograms of a traditional supercapacitor material (black) and a next-generation or faradaic supercapacitor material (red).

The peaks in the CV indicate at which potential the electrochemical reactions take place and the peak position and shape vary depending on the electrochemically active species in the electrode and type of electrolyte. Since the electrochemical reactions depend on the electrolyte, the choice of electrolyte needs to be taken into consideration for optimal performance in greater extent than for traditional supercapacitors.

When comparing HSCs and asymmetric supercapacitors with traditional supercapacitors one has to take the expected lifetime into consideration. Traditional supercapacitors have the advantage that they can have a cycle lifetime stretching over several million cycles [14]. This is due to the fact that no chemical reactions take place in the cell and the lifetime is instead limited by evaporation of the electrolyte rather than actual degradation of the electrodes or electrolyte. When using a lithium insertion electrode in a LIC, the cycle life time is often decreased due to the strain that the Li-insertion/extraction mechanism puts on the electrode. However, they can still have substantially longer cycle lifetime than batteries (>10000 cycles) [15, 16].

The lifetime of asymmetric capacitors and HSCs varies considerably depending on which materials are used in the electrode or electrolyte. A common problem when using metal oxides, sulfides or other compounds in the electrodes is the dissolution of metal complexes into the electrolyte during cycling [5]. This is of course detrimental to the performance, but the effect depends on the electrolyte, and by choosing a suitable electrolyte this side-effect can be limited. There are studies that show exceptional cycle lifetime, up to 100000 cycles, of asymmetric supercapacitors using a pseudo-capacitive MnO₂ electrode [17]. If the active material instead is in the electrolyte the lifetime can also be limited due to side-reactions between the solvent and the additive or deposition of insoluble side-products on the electrode.

Another parameter of importance is the self-discharge, which means that the potential of a charged cell will decrease over time without drawing any current. In traditional supercapacitors this is due to that the ions in the double-layers, which are formed in the electrolyte, will dissipate over time and when the double-layers dissipate the potential will decrease at the same rate. The issue is similar in HSCs, since the redox reactions mostly take place at the surface, the ions can still diffuse into the bulk of the electrolyte without extracting a current. In LICs this is less of a problem since the removal of intercalated Li-ions is a slower process [18].

Traditionally when evaluating capacitors and supercapacitors, the capacitance has been used as a measure of the performance. Capacitance has the unit Farad (F) were 1 Farad is defined as the charge between two surfaces, when charged with one Coulomb creates a potential difference of 1V. This unit works well for electrodes were the current is constant over the voltage interval which is the case for traditional capacitors and supercapacitors. For HSCs, LICs and asymmetric supercapacitors, the voltage profiles during charge/discharge are no longer constant, with a few exceptions: The most notable ones being MnO₂ and RuO₂. This means that capacitance is no longer a good way to determine the performance [19]. To evaluate and compare the performance of electrodes, or electrochemically active electrolytes, where the current is not constant the specific capacity (mAh/g) is a more suitable quantity. The specific capacity can be calculated from constant current cycling according to Eq. 1:

$$\text{Specific capacity } \left(\frac{\text{mAh}}{\text{g}}\right) = \frac{I \cdot t}{m} \quad (1)$$

where I is the constant current, t is the duration of the charge/discharge in hours and m is the mass of the electrode.

To evaluate and assess full cells, power density (W/g) and energy density (Wh/g) are more interesting figures of merit. For supercapacitors, HSCs and LICs it is important to measure the energy content at relevant time scales. Since all of these devices are supposed to operate at a high power, charge/discharge times should not exceed 60s in total for the device to be a complement to batteries [20]. The specific energy can be calculated according to Eq. 2, where

I is the current in A, t is the time in hours to charge or discharge, m is the mass in gram and ΔV is the voltage window.

$$\text{Specific Energy } \left(\frac{Wh}{g}\right) = \frac{I \cdot t \cdot \Delta V}{m} \quad (2)$$

From the equation it is possible to discern that the energy density is strongly depending on the voltage window. If we double the voltage window, while maintaining the constant current, the time and ΔV will both be twice as large, leading to 4 times higher energy density. To calculate the average power density the total energy density is divided by the discharge/charge time in hours.

Since the energy storage mechanism is different in traditional, asymmetric supercapacitors and HSCs, the factors of importance for the energy content are also different. In traditional supercapacitors the energy content is determined by the thickness and surface area of the double-layer at the electrode surfaces. In HSCs and asymmetric supercapacitors, the energy content is determined by the characteristics of the electrochemically active material in the cell. For solid materials in the electrodes the surface area, the number of oxidation states that are accessible in the specific system and the conductivity of the material are all important properties [14]. For electrochemically active electrolytes the number of oxidation states available in the compound and the amount of active species in the electrolyte determines the contribution to the total energy content. All of these factors combined with the area and thickness of double layer makes out the total energy content. In LICs the potential of the anode is much lower compared to the cathode and that enables a wider electrochemical window to be used, and the energy content is determined by how many ions that can be extracted from the anode [11].

For supercapacitor applications, power is a very important factor. To investigate the high-power properties the scan speed needs to be high. When changing the relative scan speed the contributions from the different mechanisms mentioned above also change. At very high scan speeds, the contribution from the electrochemical reactions in the active materials are reduced and a larger contribution to the total energy stored comes instead from double layers at the surface of the electrodes [21]. The distribution between double layer and faradaic contributions to the energy stored depends on the electrochemical properties of the material, but in general a high surface area and a high conductivity of the electrochemically active material improves energy storage at high power. However, if the electrolyte itself contains the electrochemically active material, and if the reactions are fast, the contribution from the redox-reactions can be very high resulting in high energy content even at high-power rates.

To increase the energy content in supercapacitors, using electrolytes with large voltage windows is a good strategy. However, for electrochemically active materials in general the research in this area is very limited due to the simplicity and high conductivity of aqueous electrolytes. According to Zhong et al around 80% of all articles published on HSCs and asymmetric supercapacitors with electrochemically active materials added to the electrode use aqueous electrolytes [5], which limits the energy content due to the narrow voltage window of water. The few articles that have been published on both non-aqueous electrolytes and hybrid supercapacitors have been limited to special systems, often lacking a wider scope to define what makes a good electrolyte for different electrode materials. In the work presented in this thesis the aim is to do a more systematic study of the interaction between a certain class of solvents, i.e. ionic liquids, and electrodes with MnO_2 as the electrochemically active material. This would

allow both a wide voltage window and an increased gravimetric capacity due to the contributions from the MnO₂ material.

However, a way to increase the voltage window while retaining the relative low cost of aqueous electrolytes has been proposed by increasing the salt concentration. Recent studies [22]–[24] have shown that by using aqueous electrolytes with up to 21m LiTFSI increases the voltage window to 2.4V. The increased potential window is explained by the formation of an SEI layer that reduces the reactivity of water and that the water molecules are tightly bounded to the cations. The first studies focused on traditional lithium ion batteries, however, there are some studies [25,26] using the same strategy on both supercapacitors and HSC. However, the study on HSC used a relatively low concentration of 5m LiTFSI which does not really qualify for a ‘water-in-salt’ electrolyte. In Paper 2 we have used an 8m NaTFSI which is on the border to the region where all H₂O molecules are coordinated to cations, to maximize the conductivity of the electrolyte. This approach could lead to an increased voltage window compared with traditional aqueous electrolytes combined with high capacity inorganic electrode materials.

2.2 Electrolytes

The electrolyte is a very important component of a supercapacitor. It carries charges between the electrodes in the cell and interacts with the electrodes enabling the different electrochemical reactions to take place. Electrolytes can either be gels [27] or liquids [28]–[30]. In this work we have focused on liquid electrolytes which are most suitable for supercapacitor applications. A liquid electrolyte consists of one or more solvents and one or more salts, depending on the specific device [5]. For traditional supercapacitors the solvent is usually an organic solvent [5] with low viscosity and a large voltage window, combined with a salt that forms the double layers. The low viscosity is important to ensure a high conductivity which allows for high power content of the device. The large voltage window is important for the energy content according to Equation 3 below where E is the energy content, C is the capacitance and V is the width of the voltage window.

$$E = \frac{1}{2} CV^2 \quad (3)$$

Even though a wide electrochemical window is important for the energy content, a majority of the research performed is using aqueous electrolytes for cells with electrochemically active materials. When using water as the solvent your voltage window is normally limited to 1.23V vs. SHE due to water splitting [5], which can be compared to around 3V for many organic solvents. The reason why water is the most commonly used solvent is because of the extremely high conductivity that can be achieved, it is an easy solvent to work with and very safe.

In the case of MnO₂-electrodes previous research has proposed that the contribution from the MnO₂ can not only be attributed to the interaction with the ions from the added salt. Brousse et al have attributed the increased performance to the insertion of protons into the surface of the MnO₂ material, even though the electrolyte itself does not contain any acids [31]. This could explain why MnO₂ electrodes generally have a lower capacitance in aprotic organic electrolytes. But the energy density would nonetheless benefit from using electrolytes with a wider electrochemical stability window, combined with an electrochemically active electrode material contributing with a higher capacitance compared to carbon.

2.2.1 Ionic liquid electrolytes

A new type of solvents that have recently attracted a lot of attention are so called ionic liquids, or ILs. An example of a common IL can be seen in Figure 3.

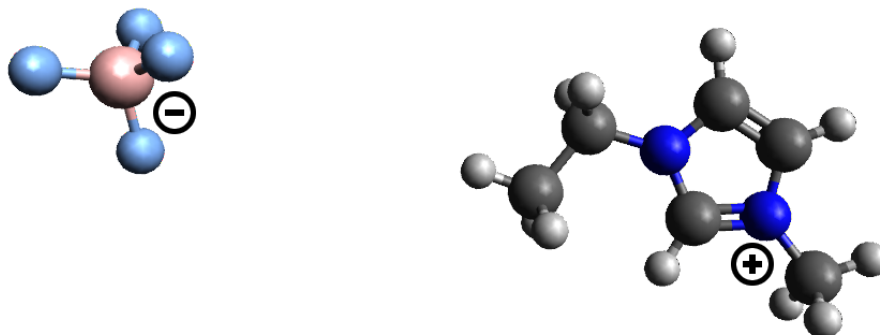


Figure 3. Schematic figure of an ionic liquid consisting of the 1-ethyl-3-methylimidazolium cation (right) and the tetrafluoroborate anion (left) making up the IL EMIM BF₄.

ILs consists only of ions [5], like a salt, but different from traditional salts they have a melting point below room temperature. ILs are of interest as electrolytes because they can have a very wide voltage window (>4.5V) [28], they are non-flammable, relatively non-toxic and have a very low vapor pressure compared to other solvents commonly used in electrolytes. They are also easy to modify for different needs by combining anions and cations, or by adding different functional groups to obtain certain properties. By using ILs we hope that we can tailor the ions to optimize the performance when used together with different electrochemically active electrode materials. An example of such tailoring that can be beneficial for supercapacitors in general can be seen in Figure 4, where one ion is replaced in each step resulting in different properties of the new ILs.

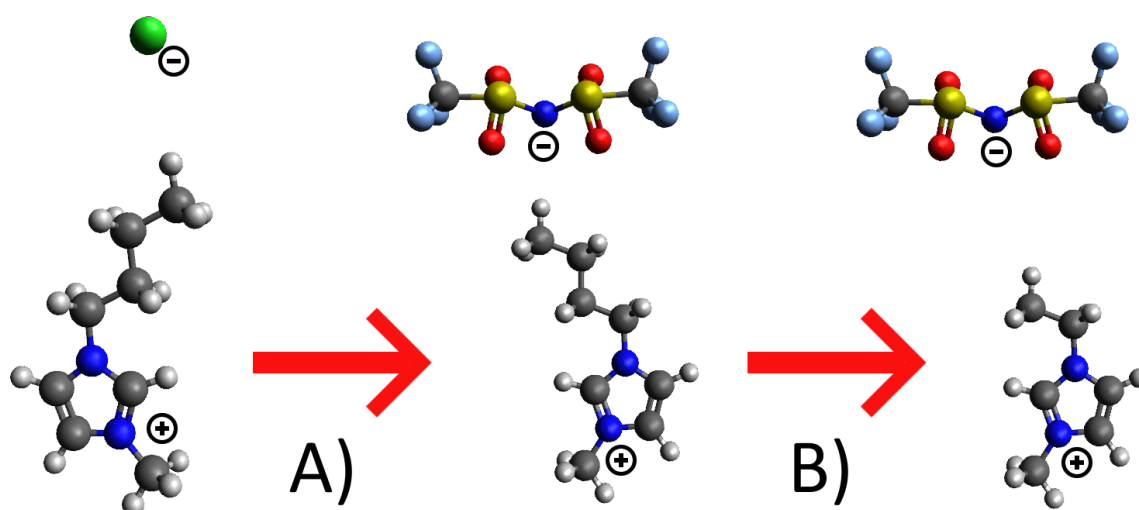


Figure 4. Three different ILs: BMIM-Cl (left), BMIM-TFSI (middle) and EMIM-TFSI (right) where one ion is replaced in each step.

Replacing the small chloride-anion with the larger bis(trifluoromethylsulfonyl)imide-anion in step A will drastically reduce the melting point, from 338K of BMIM-Cl [32] to 267K of

BMIM-TFSI [33]. Removing the long side chain in step B reduces viscosity at room temperature from 0.052 Pas of BMIM-TFSI [34] to 0.034 Pas of EMIM-TFSI [34] with only lowering the melting point with about 4K to 263K for EMIM-TFSI [35]. However, when trying to optimize one property it is important to consider the effect the new ions will have on other important properties such as electrochemical stability.

As mentioned before, a high conductivity of the electrolyte is important for high power applications such as supercapacitors. Aqueous electrolytes with KOH or H₂SO₄ added can have conductivities up to 800 mS/cm. Organic electrolytes often have an order of magnitude lower while ILs can have even lower conductivities [5], which we showed in Paper I of this thesis. A lower conductivity will result in higher resistance of the cell and a lower energy density at high power rates. An example that emphasizes these requirements was made by Reber et al, by comparing two similar aqueous electrolytes but with different conductivities, 5 and 50 mS/cm, respectively showing that using the electrolyte with higher conductivity will result in superior energy and power content [25].

ILs often struggle with a too low conductivity at room temperature for supercapacitor applications. However, by increasing the temperature the conductivity can be improved [36]. Even though the high-power performance is limited in ILs by the low conductivity at room temperature it is still possible to investigate the interaction between the IL and the material by measuring and comparing the CV at slower scan speeds using different ionic liquids.

However, the conductivities of aqueous electrolytes can be difficult to compare with the ones of pure ILs, since there are only ions present in the latter. Another important factor regarding the conductivity to take into account is what is actually being conducted. This is not answered by a simple conductivity measurement but requires more complicated methods to track different ionic species.

A physical property that is linked to conductivity is the viscosity of the electrolyte and ILs also often have high viscosities at room temperature. If an electrolyte is too viscous it might not wet the surface of the electrode and since a high active surface area is paramount for supercapacitor performance a high viscosity can be detrimental. The strategies to improve the conductivity can also be used to decrease the viscosity: Increasing the temperature and adding organic solvents.

Traditional electrolytes consist of a solvent and a salt is added to interact with the form the double layers at the electrode surfaces. In aqueous electrolytes neutral alkali-metal based salts are most often added, either neutral such as Li₂SO₄, acidic such as HCl or alkaline KOH. When using an IL, there are several charged species contributing to the conductivity, so a question raised in the first paper is what the effect on the MnO₂ interaction the addition of LiTFSI has when used in IL as electrolytes?

In the first paper we have focused on investigating what makes an ion in an ionic liquid interact with MnO₂ electrode materials. MnO₂ is mainly used as a positive electrode so focus has been on the cation. An interesting property that is not related to the physical property of the IL itself is the ability to donate protons. There are some previous results that indicate an increased capacitance when adding more acid to the IL [37]. However, no systematic study has been performed on neat ILs or investigating the interaction using cations with different ability to donate protons. The ability of a molecule to donate protons is determined by the local structure and which atomic species the protons are bound to. Generally, elements that are strongly electronegative, such as sulfur, nitrogen and oxygen, bond less strongly to protons. By attaching

different chemical groups to the cation this ability can be modified. As an example, two imidazolium-based cations with very different ability to donate protons can be seen in Figure 5. The functional groups have different proton donating abilities: The proton attached to the sulfur in A) is more easily donated while in B) all protons are bonded to carbon which make them unlikely to be donated. By keeping the anion and the backbone of the cation constant it is possible to vary the functional group attached to the cation thus varying the properties. Potential faradaic contribution of the MnO_2 material when using different cations can then be investigated while keeping the anion constant. Thus, keeping the ionic liquids similar, but with very different proton donating properties, it is possible to rule out other effects such as viscosity and conductivity on the interaction with the MnO_2 .

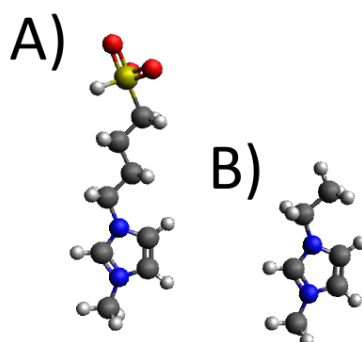


Figure 5. Comparison of two imidazolium-based ions with functional groups having different proton properties: A) protic, B) aprotic.

2.3 Electrode materials

For electrodes where the charge is stored as double layers the electrode should be inert to any chemical reaction, have a high surface area and good conductivity. The most common electrode material for these kinds of electrodes is activated carbon (AC). AC can have extremely high specific surface area, relatively high conductivity and is inert in most electrolytes. It is also rather cheap which makes it the most used material in supercapacitors today. The high surface area is linked to a large porosity, which leads to a quite low gravimetric density. The lower density of AC on the other hand reduces the volumetric capacitance which leads to light but bulky devices. For some applications this is not a problem, but for more demanding uses, such as in electrical cars, the devices need to be as compact as possible. The low volumetric capacitance of carbon and the difficulty to further increase the gravimetric capacitance are the main reasons research is being aimed at electrode materials with electrochemical reactions that increases the volumetric energy content.

In general, electrochemically active materials used in supercapacitor electrodes can be divided in to two categories: redox-reaction or insertion/desertion types. A schematic comparison between these two types and activated carbon can be seen in Figure 6. The redox-reaction type materials rely mostly on surface reactions although some insertion and desertion of different ions can occur as well.

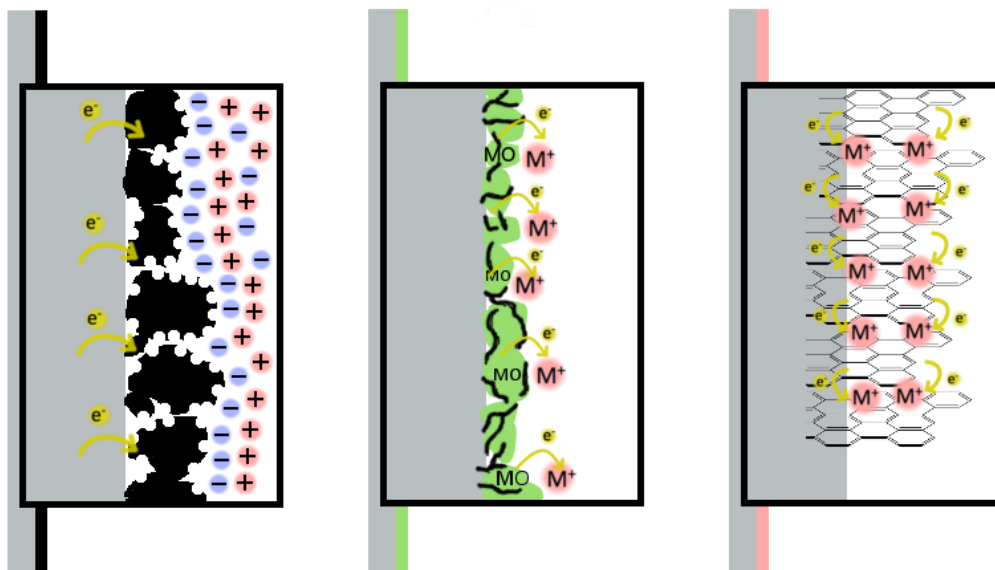


Figure 6. Schematics of the three different types of supercapacitor materials and the electron transport during charging: Left) Activated carbon, Middle) Surface redox-reaction of metal oxide and Right) Insertion/desertion type electrode.

2.3.1 Redox-active electrode materials

Redox active materials can be defined as materials having the ability to reversibly switch between different oxidation states. These types of materials can then be divided into two categories: pseudo-capacitive and faradaic. The difference between these two lies in the electrochemical response during charge/discharge. For a material to be pseudo-capacitive it needs to have a linear response in the potential when a current is applied, or a rectangular CV resembling the shape of the curve of pure double-layer charge storage. If a material is faradaic it often has a non-linear CV showing one or more peaks. Examples of faradaic materials used in supercapacitor applications are PbO_2 , $\text{Ni}_2(\text{OH})$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. However, not only metal oxides are of interest, perhaps the cheapest way to add faradaic properties to carbon materials is by adding hetero-atoms or different surface groups. These types of carbons have very high specific capacitance but they tend to struggle with stability and the need of acid electrolytes makes them more difficult to commercialize.

Another group of non-metallic redox-active materials often used as electrodes in supercapacitors are conducting polymers. Conducting polymers conduct electricity through conjugated monomers formed by chemical oxidation or electrochemical oxidation. The charge storage in the polymer is also connected to the doping, depending on the polymer and the polarity the charge can be stored as either n- or p-type charge carriers [38]. The biggest benefit of using conducting polymers is that the bulk of the material also can be used, compared to AC where only the surface is used. This increases the energy content compared to AC, however to access the bulk the ions need to diffuse into the polymer. The insertion of ions is slower in the polymer so the power density is reduced [39].

The first pseudo-capacitive material investigated for supercapacitor applications was RuO_2 . It was found that the material had many beneficial properties such as low resistivity, high density

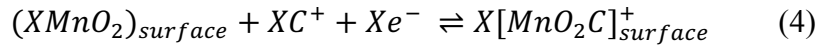
and high capacitance [40]. Another widely investigated material is MnO₂. A comparison of the performance of RuO₂, MnO₂ and AC electrodes can be seen in Table 1.

Table 1. Summary of capacitance measured in different electrode materials.

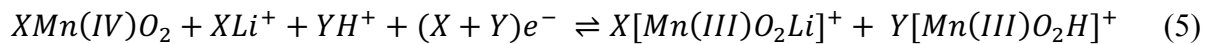
| Electrode Materials | Gravimetric capacitance (F/g) | Volumetric capacitance (F/cm ³) |
|-----------------------------------|-------------------------------|---|
| AC derived from SiC [41] | 175 | 122 |
| Hydrous RuO ₂ [41] | 650 | 1300 |
| MnO ₂ , thin film [42] | 1145 | 1100 |
| MnO ₂ /MWCNT [43] | 290 | 200 |

As we can see RuO₂ has the best volumetric performance. However, RuO₂ is expensive, shows some toxicity in the environment and it requires acidic electrolytes for optimal performance. Our work has instead focused on MnO₂ as a cheap and safe alternative to improve the capacitance. MnO₂ has a large theoretical capacitance, 1380 F/g, but due to a large electrical resistivity the practical capacitance is much lower. However, as we can see in Table 1, when using MnO₂-thin films values very close to the theoretical limit can be obtained. However, for more practical electrodes, such as a MnO₂/MWCNT composite, the capacitance becomes much lower, but it is still possible to achieve higher capacitance than with activated carbon.

The charge storage mechanism in MnO₂ involves changing the oxidation number of the manganese atom from +4 to +3 in the presence of a suitable cation, C⁺. A general mechanism could be described through Equation 4, regardless of which solvent used and with a salt consisting of a generic cation C⁺ present in the electrolyte.



Research has shown that the alkali-metal cations cannot alone explain the capacitance of MnO₂ materials, which shows higher capacitance when cycled in aqueous electrolytes. Brousse et al showed that in aqueous electrolytes protons also play a part in the charge storage, even if the electrolyte is at nearly neutral conditions [44]. The suggested mechanism in aqueous solution can be found in Equation 5, where we see how the protons take on a role very similar to the added cations. However, the protons are more likely to be inserted into the outer layers of the MnO₂ material and not only act on the surface. This might not be so surprising, protons are also important for the capacitance of other materials like PbO₂, RuO₂ and MoO₂. However, whereas other electrode materials are stable in acidic electrolytes, this is not the case for MnO₂[45].



Moving on from the mechanisms in aqueous electrolytes, there has been some research on pseudo-capacitive materials in non-aqueous electrolytes. Rochefort et al investigated how protic ILs interact with RuO₂ electrodes [46] and Ruiz et al proved that MnO₂-electrodes perform better in protic ionic liquids with an excess of acid than at acid-base equilibrium [37]. However, no systematic study has been done on the topic on how the ionic species in the ionic liquid affects the performance of electrochemically active supercapacitor materials in general or MnO₂ in particular. By using a systematic approach, we can identify how the proton availability of a cation in an ionic liquid affects the performance of the MnO₂ material and suggest the interaction mechanism, see Paper I.

2.3.2 Insertion/desertion type electrodes

These types of electrodes, use the bulk of the material to store charge in contrast to the pseudo-capacitive and faradaic materials that mostly utilize the surface or the outer layers of the material. The most common technique is to pre-insert Li^+ or Na^+ in a suitable material such as graphite/graphene [47], silicon [48] or TiO_2 [49] and use the electrode on the negative side in the cell. These types of supercapacitors can have very high energy densities, examples can be found in Table 2. However, there are drawbacks. Pre-lithiation is the most common way to ‘fill up’ the material with Li-ion. This means that the electrode must first be assembled in a separate cell where the potential is slowly lowered towards 0V vs. Li/Li^+ , and then transferred to the full cell, which limits commercial use. However, there are examples of electrodes where the Li-ions are added either in the synthesis step [50] or in the cell so the Li-insertion become a part of the first cycle [51].

Generally, the desertion/insertion mechanism of Li-ions in solid materials is much slower than the double-layer formation or surface based redox reactions, which would lead to lower power-density, similar to that of traditional Li-ion batteries. To improve the power density, the active material is reduced in size to nanometer sized particles. This reduces the mass loading and energy content compared to batteries, but the smaller size increases the power density, moving the electrode towards supercapacitor power performance. An example of this can be found in the paper by Sun et al where they demonstrate the excellent performance of nanosized Sn-particles in a carbon matrix [52].

Table 2. Energy and power density of LICs: Lithium titanate/AC and tin oxide/reduced graphene oxide cells and the NIC nitrogen-doped hollow carbon nanowires/AC

| Electrode Materials | Energy Density (Wh/kg) | Power Density (W/kg) |
|--|-------------------------------|-----------------------------|
| $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{AC}$ [50] | 32.32 | 2466 |
| $\text{rGO}+\text{SnO}_2/\text{rGO}$ [53] | 12 | 10000 |
| N-HCNW/AC [54] | 37.5 | 9000 |

3 Experimental

The experimental techniques used in this work focus on the properties and behaviour of the electrolytes and electrolyte/electrode interaction. The conductivity was determined by electrical impedance spectroscopy, which is an easy technique to determine the average conductivity of ionic species in the electrolyte. It has some drawbacks since it is not possible to determine the conductivity of a particular ionic specie but for our experiments this is enough.

The electrochemical properties of the electrode/electrolyte interactions were investigated using cyclic voltammetry to compare and analyse the reactions taking place. Cyclic voltammetry is chosen since the scan properties can be kept constant for all samples. As an example: if a scan speed of 1 mV/s is chosen then different samples can all be compared at 1 mV/s, however if the current is scanned with 1 mA the voltage response will depend on the mass of the electrode and the capacity of your material so comparing and investigating electrochemical properties between different materials is much more difficult.

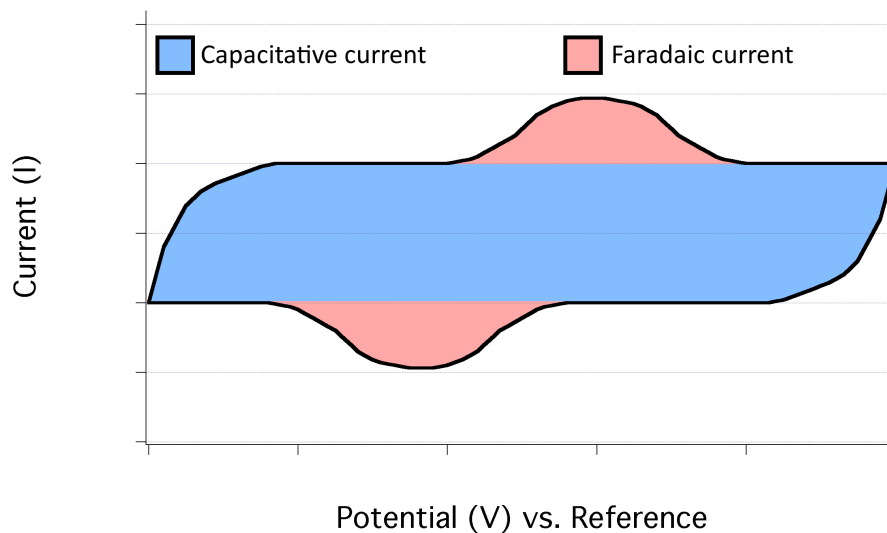


Figure 7. Typical CV of an electrode having both capacitive and faradaic contributions to the total current.

To properly evaluate an electrode using cyclic voltammetry, it is important to consider the scan speed and the potential window. At slower scan speed peaks from faradaic reactions are seen more clearly. However, the current will also be much lower so the noise will be more prominent. When cycling at higher scan speeds the peaks will be less pronounced, however it is still important to cycle the electrodes at higher scan speed to evaluate the electrochemical properties at scan speeds where the supercapacitor will operate.

In addition to investigating the electrochemical properties, the CV can also be used to calculate the charge stored in a certain material. By integrating the CV curve according to Eq. 6 the capacitance of the material is calculated.

$$\text{Specific capacitance} = \frac{1}{vW(\Delta V)} \int_{V_1}^{V_2} iVdV \quad (6)$$

In Eq. 6 W is the electrode mass (g), v is the scan speed (V/s), ΔV is the width of the voltage window and V_1 and V_2 are the integration limits. The different areas integrated to calculate charge/discharge performance for positive and negative electrodes are shown in Figure 8.

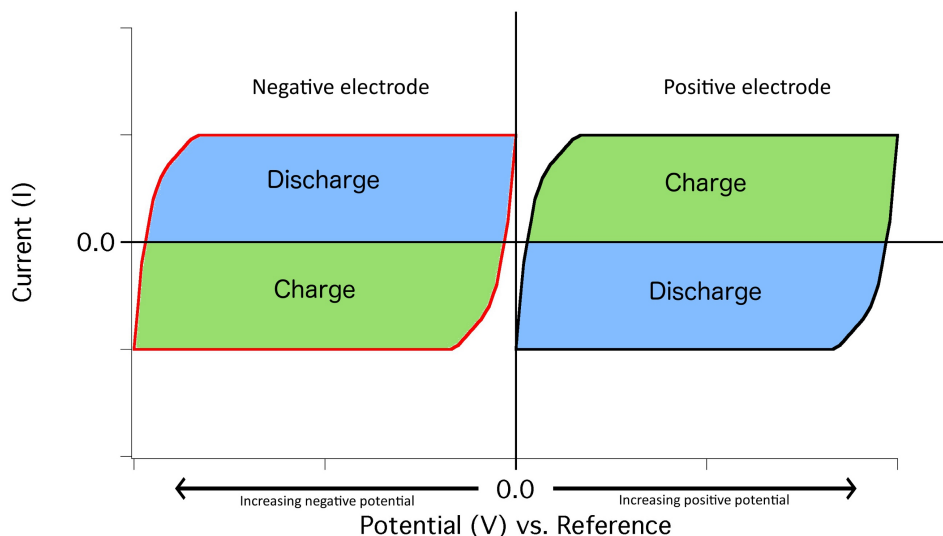


Figure 8. CVs of a negative and positive electrode highlighting areas of integration for charge and discharge calculations.

3.1 Electrochemical characterization

Supercapacitor materials are often divided into two categories: capacitive and faradaic depending on the charge storage mechanism involved. Capacitive processes are fast charge storage mechanisms and are characterized by a linear charge storage. The most common capacitive mechanism is from the formation of a so-called double layer at the surfaces of the electrodes. In the CV, seen in Figure 3, the capacitive part has a rectangular shape due to the speed and continuous change of the double layer. However, not only the formation of double layers results in rectangular contributions to the CV, fast red-ox reactions can yield the same shape. These reactions are often referred to as pseudo-capacitive and involve a transfer of an electron to, or from, the electrode together with a change in the oxidation number. Faradaic mechanisms also involve the transfer of electrons to/from the electrodes, however in this case the transfer is also coupled with a slower structural or chemical change in the electrode. These processes result in peaks in the CV. Pseudo-capacitive reactions are much faster than faradaic and will not result in any peaks in the CV at normal scan speeds where faradaic reactions will exhibit almost ‘battery-like’ CVs, seen in Figure 7.

To compare the performance, the current is kept constant while the cell charges and discharges, the method is called galvanostatic cycling or constant current cycling. This is to compare the performance using a method that is very similar to the charge/discharge it will experience in normal operation in applications.

3.1.1 Cyclic voltammetry

Cyclic voltammetry is an electrochemical characterization method in which a potential interval is scanned at a pre-set speed in V/s while the current is recorded [55]. The resulting plot (potential vs current) is referred to as a cyclic voltammogram (CV) and is vital for analysing and understanding the electrochemical processes occurring in the cell.

To analyse a certain material, some fundamental electrochemical principals need to be taken into consideration. To complete a circuit and to be able to charge/discharge a unit, only two connections are required. However, the potential of the working electrode or voltage of the cell will not be known or kept constant when the potential of the cell is changed. This makes analysis of the electrochemical properties difficult if not to say impossible. To define the potential at which you are cycling your electrode a reference is required. The reference should have a known and stable thermodynamic equilibrium. The reference is often designed so that a piece of metal is immersed into a solution containing the counter-ion in the redox couple. The solution is kept in a separate container, linked with the electrolyte through an ion conducting junction that will allow ions to pass from the electrolyte to the reference compartment. Common redox couples are Ag/AgCl, Hg/HgCl, Li/Li⁺ and Ag/Ag⁺.

In a non-aqueous electrolyte, and particularly if it is of limited supply, it might not be possible to use a traditional reference. An alternative to true references are so-called pseudo-references [56], examples of common pseudo-references are metal foils such as Ag, Pt, Pd or AgCl coated silver-foils. The pseudo-reference is immersed directly into the electrolyte. The main difference between a true and a pseudo-reference is that it lacks a thermodynamic equilibrium since there is no common anion present in the pseudo-reference system. As a consequence, the potential of the pseudo-reference is not known and will vary depending on electrolyte and temperature. To confirm the potential of the pseudo-reference, they are calibrated against a known potential of a redox couple such as ferrocene, in a particular system. Other issues that have to be taken into account are that the potential of the pseudo-reference changes over time and the pseudo-reference might only be stable in certain pH- or temperature-conditions. However, the benefits of using a pseudo-reference are many, such as low impedance due to the lack of an ion conducting junction, no contaminating ions and, above all they are sometimes the only option available to make 3-electrode measurements[56].

Besides the reference electrode, two more electrodes are required to complete the 3-electrode setup: A working electrode (WE) and a counter electrode (CE). The working electrode is the electrode of interest for the electrochemical measurements. It is the potential difference with this electrode that the reference measures and the current is recorded. The CE balances and accommodates for the electrochemical reactions taking place at the working electrode. For every electron transferred from or to the WE an electron needs to be transferred at the CE as well. The physical demands set on the CE is that it should have a larger specific surface area than the working electrode to ensure that electron transfers from fast reactions happening at the WE can be balanced by the formation of a double layer at the CE. It should also be inert to the specific electrolyte used. A typical setup used in the experiments in both papers can be seen in Figure 9, a setup that was chosen because it requires a small amount of electrolyte and can be properly sealed in a controlled environment.

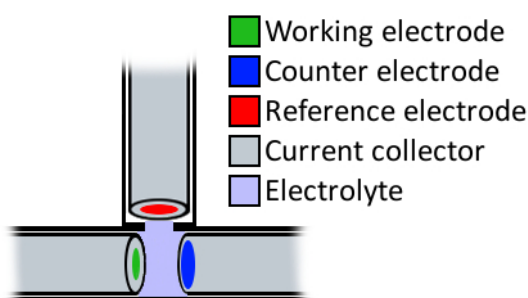


Figure 9. A typical 3-electrode setup used in this work minimizing electrolyte volume.

A cyclic voltammetry measurement is performed by cycling the WE between two potential limits at a certain scan speed. If the current is positive it means the working electrode is being oxidized and electrons will flow from the WE. If the current instead is negative the electrode is reduced and electrons will flow to the WE. A schematic of these processes can be seen in Figure 10 for both positive and negative electrode materials used in traditional supercapacitors.

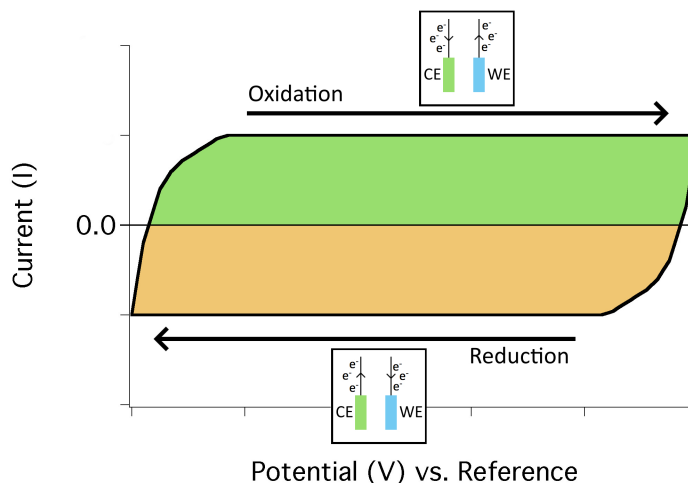


Figure 10. Illustrating the flow of electrons to and from the working electrode and counter electrode depending position in CV, including arrows indicating the scan direction.

3.1.2 Galvanostatic cycling

While cyclic voltammetry is used mainly for electrochemical measurements in supercapacitors, galvanostatic cycling, or constant current cycling, is used for performance measurements. Since this is a technique very similar to the normal operation of supercapacitors the values obtained show how well the cell performs in operation. The technique is based on keeping the current constant while the potential is increased or decreased depending on if the cell is charging or discharging. The experimental setup used in galvanostatic measurement can be the same 3-electrode cell shown in Figure 9, for performance evaluation of individual electrodes.

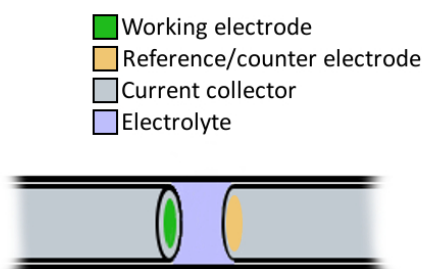


Figure 11. Schematic image of a full cell or 2-electrode setup, consisting of a positive electrode (left) and a negative (right).

To measure the performance of a real-world cell a slightly different cell design is used, called a 2-electrode cell or a full cell, which can be seen in Figure 11. The idea behind the setup is that the reference and the counter electrode have been merged into one, by convention this is the

negative electrode in a full cell. It also leads to that the potential of the reference is no longer constant and will be change as the cell is polarized. In the full cell we measure the combined response of both electrodes and how they perform together. In the 3-electrode setup it was important for the counter electrode to have a larger surface area than the working electrode. When using a full cell, the electrodes need to be balanced, for optimal performance. This means that the energy content of the electrodes should be the same. The fact that the reference is no longer constant and that the energy content of the electrode is balanced, makes it unsuitable to analyse the electrochemical reactions taking place.

The voltage profile in a galvanostatic experiment will depend on the properties of the electrodes, the electrolyte and the separator used in the cell. If only capacitive processes contribute to charge stored, the voltage profile will have the shape of a triangle. When faradaic reactions are contributing to the total charge stored, the shape of the curve will start to deviate from the triangular voltage profile. Depending on the actual electrochemical reactions taking place the profile will have different shapes. If the cell is cycled slowly and ions are inserted/extracted into/from the electrode, there will be plateaus in the profile. The same thing will happen, but to a lesser extent, for any faradaic reaction taking place at the electrode. At faster scan speeds or by using nano-sized particles of the active material, the profile will start to resemble a ‘shark-fin’ [57]. The reason in both cases are the surface reactions that will contribute to a larger extent to the total capacity [58]. An illustration of how the different contributions will affect the shape of the profile can be seen in Figure 12. From the potential response it is also possible to extract the IR-drop, simply by measuring the dV from the end of the charge to the beginning of the discharge.

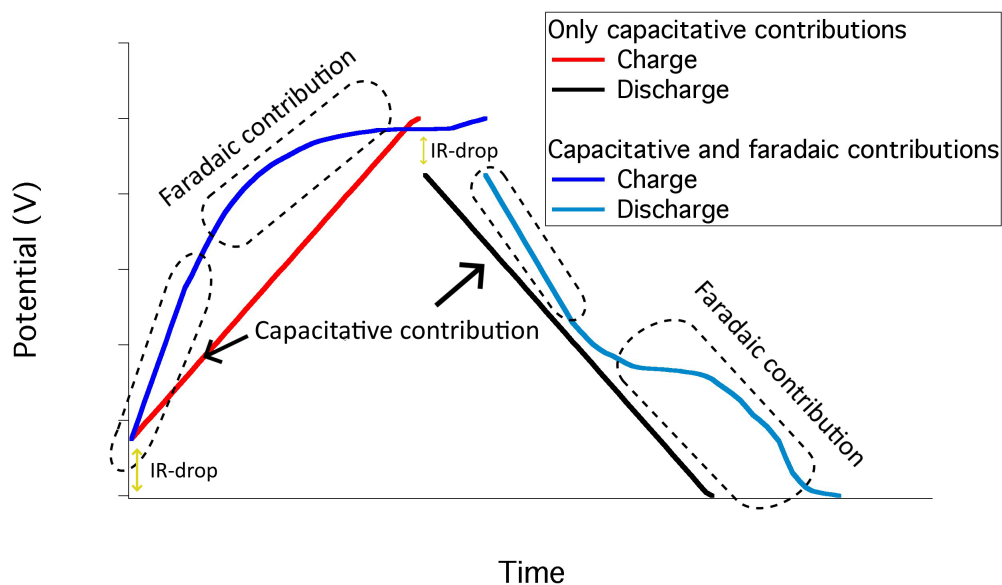


Figure 12. Two voltage profiles during charge/discharge at a constant current having a strictly capacitive behaviour and faradaic + capacitive behaviour, respectively.

To assess the performance of supercapacitors the measurement parameters need to be carefully chosen. Power is of great importance for supercapacitors, so the energy content should be calculated at a high-power density, to be a fair comparison. A rule of thumb is that the charge/discharge should take at the most 60s to assure a high-power content, but measurements at even faster scan speeds are of great importance [59]. To calculate how long time a charge discharge cycle at a specific current density takes, one should look at the current in the CVs at different scan speeds for an estimate. The resulting energy and power densities are often plotted

in a so called Ragone-plot where the energy- and power-density are plotted against each other to compare with previous results. A Ragone-plot with a typical supercapacitor performance curve is seen in Figure 13.

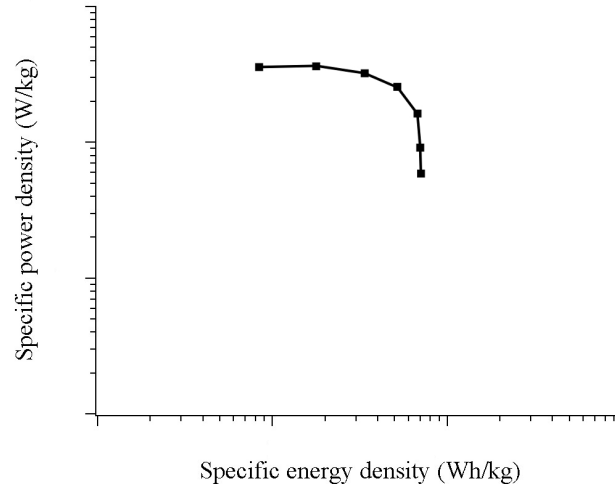


Figure 13. A typical Ragone-plot of a supercapacitor.

The full cell experiments are also used for cycle lifetime measurements where the cell is cycled for several thousand cycles to assess the lifetime.

3.2 Dielectric spectroscopy

Dielectric spectroscopy is a technique used to investigate the dynamics in different materials. The method is based on exposing materials to an alternating electric field at different frequencies. The response in term of impedance, current and phase angle is measured to analyse the different properties of the material. The frequency of the electrical field is chosen depending on which property of the material that is of interest.

For the measurements in this work the ionic conductivity has been the prime interest. Ionic conductivity is defined as the transport of ions, or rather ion-solvent clusters, through the bulk of the electrolyte. The ionic conductivity can be calculated, using the frequency, the dielectric constant and the imaginary part of the complex dielectric permittivity according to Eq. 7 [60].

$$\sigma = \omega \epsilon_0 \epsilon'' \quad (7)$$

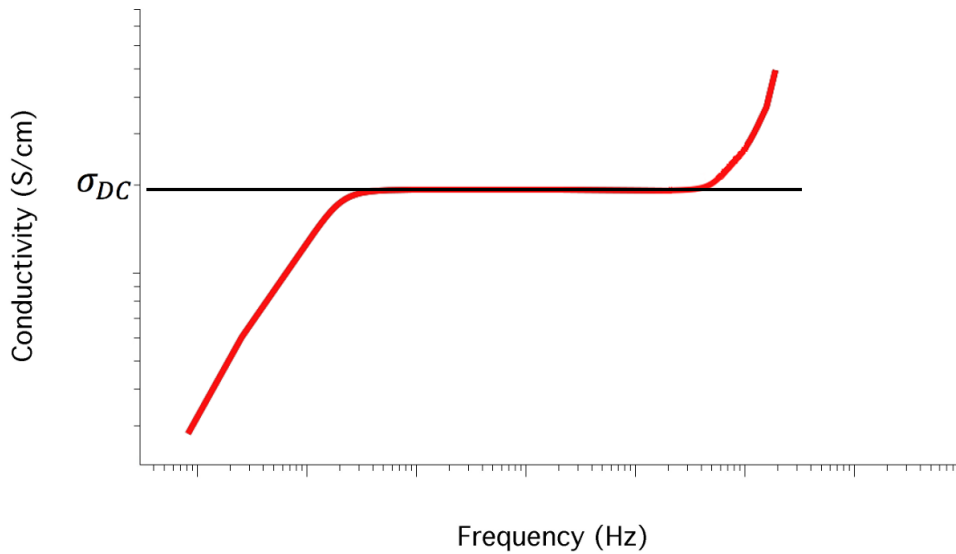


Figure 14. A typical curve plotting the logarithm of the frequency and conductivity of a liquid electrolyte.

When plotting the conductivity versus the frequency a plot similar to the one seen in Figure 14 is often obtained for liquid electrolytes. The different shapes of the plot in the different regions can be attributed to different mechanism in the electrolyte or electrolyte/current collector interface. The conductivity of a certain material is determined by analysing the frequency vs. conductivity plot seen in Figure 14 and identifying the frequency region where the conductivity is constant. In this interval the conductivity does not depend on the frequency and is often referred to as the DC conductivity and is identical to the ionic conductivity of the electrolyte [60]. However, it is important to understand that by simply doing a conductivity measurement one does not reveal the conductivity of the different ions present, but rather the average conductivity of the ions in the electrolyte. The resulting plot also tells us nothing about how the ions interact with the solvent and the configuration of the ion-solvent clusters that move through the electrolyte.

4 Results

The results from Paper I show that, by choosing ILs containing a cation with strong proton donating properties increases the capacity of a MnO_2 -cathode compared to similar cations with weaker or no proton donating properties. The proton donating properties of the cations were calculated in the form of pKa-values in different solvents. These are novel results that could enable tailoring IL electrolytes to optimize the MnO_2 contribution to the total capacity. Cycling the MnO_2 -electrode in a neat aprotic ionic liquid only shows a strictly rectangular CV with no faradaic contribution, while in the protic IL there are clear faradaic peaks present. Adding a salt to the aprotic IL invokes an electrochemical response from the MnO_2 , while in the protic IL the addition of the same salt suppresses the electrochemical reactions. This change in behavior is attributed to the interaction between the ions which might limit the cations from reaching the surface of the MnO_2 . However, the results also showed low capacities for the MnO_2 -electrodes in ILs at higher scan speeds. This limits the practical use and to improve this the addition of acetonitrile was investigated. The results showed some increase in capacity retention, but it still needs to be improved further for any practical applications of MnO_2 -IL based electrolytes.

The second paper used another oxide, VO_2 , which has not been so widely investigated as MnO_2 but previous work has shown good performance. Another approach on electrolyte design that has emerged lately is highly concentrated electrolyte. By increasing the salt concentration, the voltage window can be increased to up to 3V which is more than double of normal aqueous electrolytes, but conductivity is reduced with increased salt concentration. Two VO_2 -materials synthesized with the same method but with different nano-structures were investigated and the sample with the large surface area and more porous nanoparticles were shown to perform better in this particular electrolyte. The VO_2 was tested together with a highly concentrated 8m NaTFSI electrolyte to investigate if a high voltage, hybrid, supercapacitor could be realized. For this particular setup the voltage window was found to be 2.4V for the full cell and both the capacity and the voltage window in 8m NaTFSI exceeds that of 6M KOH. The conductivity of the electrolyte was large, enabling a high-power density. Cycle stability is not good enough but is better than some other previously presented results.

5 Conclusions and outlook

To conclude this work, I can say that by combining ILs and MnO₂-cathodes it is possible to expand the voltage window compared to aqueous electrolytes, the contribution of MnO₂-electrodes can be optimized by choosing the IL consisting of appropriate ions. In this case the cation should be able to donate protons easily to the MnO₂, while the anion should be electrochemically stable and enable a low viscosity of the electrolyte. However, the protic IL investigated in this work struggle with narrower potential windows compared to aprotic ILs. The high-power capabilities are also limited by the relatively low conductivity of the IL-based electrolyte. The addition of an alkali metal salt to this particular IL does not improve the capacity of the MnO₂-electrode, which can be related to the interaction between the different ionic species that might prevent the ions from interacting with the electrode.

Adding acetonitrile to the electrolyte improves the high-power performance slightly with increasing acetonitrile content. When LiTFSI is added the addition of acetonitrile is not recommended to this system since the capacity is reduced until reaching very high acetonitrile concentrations. Adding acetonitrile to an IL also increases the vapor pressure and induces a flammability so this might not be the best strategy to tackle the low performance. However, both the capacity and high-power density might be improved by increasing the operating temperature and since ILs have an exceptional high temperature stability this might a way forward.

For Paper II I can conclude that nanostructured VO₂ only performs well when the specific surface area is large enough to ensure a large exposure to the electrolyte. The surface area could possibly be increased even further by ball-milling the material.

By using a highly concentrated electrolyte the potential window is expanded compared both to normal, low concentration, neutral electrolytes and strongly alkaline electrolytes. However, in its neat state the cycle lifetime is limited probably due to dissolution of chemical complexes formed with the ions in the electrolyte. To improve this the effect of buffering, by adding NaOH, on the cycle lifetime and performance should be investigated. To gain a deeper understanding of this system, an in-depth analysis of the electrodes after cycling should be conducted by using XPS to analyze which oxidation states the Vanadium ion can access.

VO₂ electrodes should also be investigated using IL-based electrolytes to determine what properties of the ionic species are required. The combination IL+VO₂ is also interesting from possible synergies at higher temperatures: the conductivity of the IL will be increased and at the same time the VO₂-material has a semiconductor-metal transition at 80C, which would reduce resistivity in the electrode. To my knowledge no experiments have been done on such a system yet.

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