

Novel Electrolytes for Supercapacitors

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ABSTRACT

Nowadays supercapacitors (also called electric double-layer capacitors or ultracapacitors) rank together with batteries among the most important devices to store energy. Although both technologies are closely related to each other, there are big differences regarding energy and power density: While supercapacitors have a lower energy density compared to batteries, they have a much higher power density than batteries. Thus it is possible to charge and recharge supercapacitors within only a few seconds. Beyond this they can provide electrical power extremely fast and have a long cycle life (> 500 000 cycles) [1].

In this context, supercapacitors using ionic liquids (ILs) as novel electrolytes have gained much attention because of their interesting profiles of physical and chemical properties [2], such as tunable viscosities and conductivities, chemical and thermal stability as well as large electrochemical windows, and incombustibility at temperatures below their decomposition point [3].

Keywords: ionic liquids, supercapacitors, electrolytes, conductivity, viscosity

1 INTRODUCTION

Electric double-layer capacitors (EDLCs) have gained much attention through the last years due to the increasing demand for power electronics for back-up memories and peak power saving [4]. Especially the field of automotive benefits from a very fast reacting kinetic energy recovery system. This system is capable to recover very short and high currents that occur under braking [5]. The recovered energy is stored in the before mentioned supercapacitors for later use under acceleration. This reversible mechanism is based on ion adsorption onto active materials that have a high specific surface area. This so called electric double layer is formed at the interface between electrodes and electrolyte (Figure 1) [6]. The energy stored in a capacitor is dependent on the applied voltage between electrodes. The limitation is the electrochemical stability of the electrolyte so called “electrochemical window”. Ionic Liquids have wide range of electrochemical stability up to 5V and they have been already tested in double-layer capacitors showing an excellent performance. The advantageous properties like high power density, high capacitance and a long cycle life make supercapacitors suitable for electrical energy storage [7].

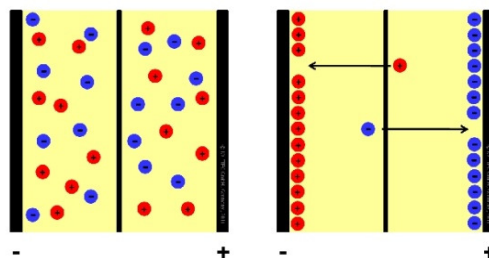


Figure 1: Composition and operating mode of a supercap

In commercially available supercapacitors aqueous solutions such as sulfuric acid, potassium hydroxide or quaternary ammonium salts and organic electrolytes based on acetonitrile, polypropylene or other organic solvents are commonly used. Main disadvantages of these electrolytes are low decomposition voltage and low ion conductivity. To overcome these problems much effort has been made in finding alternatives to these conventional electrolytes [8]. Very promising candidates are ionic liquids. These new class of electrolytes consists entirely of ions and is liquid below 100°C. Their impressive properties like large electrochemical stability, wide liquid range, high thermal and chemical stability, negligible vapor pressure, incombustibility and relatively high ionic conductivity match perfectly with the requirements of electrolytes for supercapacitors. Therefore ionic liquids have been used in different applications in the field of electrochemistry as in lithium batteries, fuel cells, bio-batteries and also in supercapacitors [9].

2 IONIC LIQUIDS

As mentioned above tetra alkyl ammonium salts in acetonitrile, which show an acceptable combination of good conductivity and a broad electrochemical window, are commonly used in electric double layer capacitors. Unfortunately this kind of electrolytes owns due to organic solvents' vapor pressure a big drawback at high temperatures and voltages: solvent's high risk of inflammability. This is where ionic liquids come in. Structurally and chemically similar to these tetra alkyl ammonium salts but having much lower melting points ionic liquids are particularly suitable for applications in supercapacitors. Without an additional organic solvent e.g. acetonitrile or ethylene or propylene carbonate they stay liquid over a wide temperature range (-35°C to 250°C). Adequate ionic liquids do not have any propensity for vaporization [10].

In the last years many ionic liquids containing aromatic and aliphatic cations such as imidazolium, pyridinium, pyrrolidinium, tetraalkyl ammonium, sulfonium have been subject to investigation for EDLC applications [11].

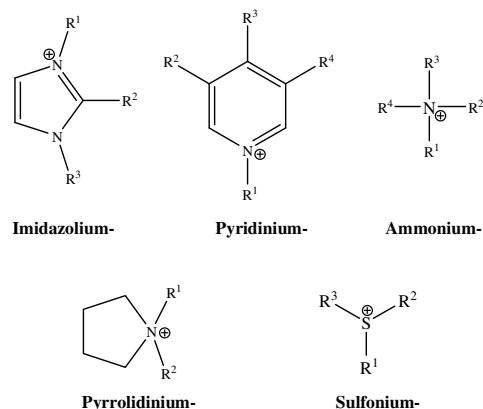


Figure 2: Cations investigated for supercap applications

Major advances in research and development of ionic liquids electrolytes have concerned quaternary ammonium-based ionic liquids because of their higher cathodic stability compared to their aromatic counterparts. Unfortunately very few aliphatic quaternary ammonium salts e.g. such as N, N-diethyl- N-(2-methoxyethyl)-N-methylammonium tetrafluoroborate (DEME BF₄) have been commercialized despite their higher conductivity and wider decomposition potential as compared to aromatic IL such as 1-ethyl-3-methylimidazolium (EMIM BF₄). Nisshinbo Industries Inc. in Japan has developed large size EDCLs applying DEME BF₄ diluted with PC as electrolyte. These EDLCs have an extremely high charge and discharge performance even at temperatures below -40°C [6, 12].

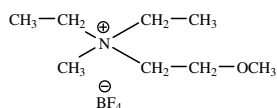


Figure 2: Schematic illustration of the molecular structure of DEME BF₄ [6]

The outstanding performance is closely connected to the higher solubility of quaternary ammonium type ionic liquids in the carbonate solvent compared to the solubility of solid quaternary ammonium salts. With this ionic liquid it is possible to achieve higher ion concentration resulting in a higher capacitance of the EDLC. In contrary, some solid ammonium salts tend to precipitate at low temperatures because of their low solubility. This results in a significant drop in capacitance at low temperatures. Whereas DEME BF₄ gives in combination with PC a homogenously mixed uniform electrolyte which shows no precipitation of the salt at decreased temperatures [6, 13].

Also various other ionic liquids have been investigated through the last years. Different cations and anions were combined to achieve the best properties for electrochemical applications. A major limitation of ionic liquids is despite that they are liquid over a broad temperature range their relatively high viscosity at low temperatures. This property has a major impact on ion mass transport which is necessary for forming the electric double layer. Many ionic liquids show a very good performance above ambient temperature but increased viscosity at sub-ambient temperatures what effects increasing internal resistance and corresponding decrease in power output. To cope with this task much effort has been done to decrease the viscosity and to improve the conductivity of ionic liquids [14]. One approach is to blend ionic liquids with different organic solvents. For example McEwen et al. [15] had successfully increased the conductivity of 1-Ethyl-3-methylimidazolium hexafluorophosphate (EMIM PF₆), which is solid at room temperature, by mixing with several carbonate solvents such as propylene carbonate (PC), ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) or ethyl methyl carbonate (EMC). The highest conductivity (26 mS/cm at 25°C) was obtained for a mixture of EMIM PF₆ in EC-DMC (1:1 v/v) [14].

A second approach to influence the conductivity positively is preparing binary ionic liquid mixtures. By influencing the viscosity it is possible to have an impact on the conductivity. In our laboratories we could show that the viscosity of ionic liquids can be significantly reduced by using eutectic mixtures [16].

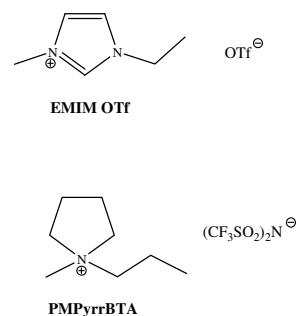


Figure 3: Chemical structure of the investigated ionic liquids

Because of the high electrochemical stability of the anions we chose ionic liquids based on bis(trifluoromethylsulfonyl)amide or trifluoromethyl sulfonate namely 1-ethyl-3-methyl imidazolium trifluoromethylsulfonate (EMIM OTf) and 1-Methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)amide (PMPyrr BTA) (Figure 3). We tested some mixtures in different ratios.

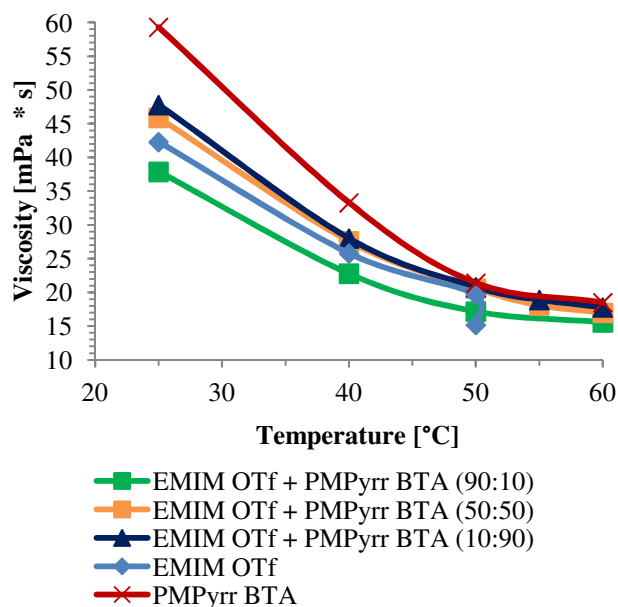


Figure 4: Temperature-dependent viscosity of selected ionic liquids' mixtures

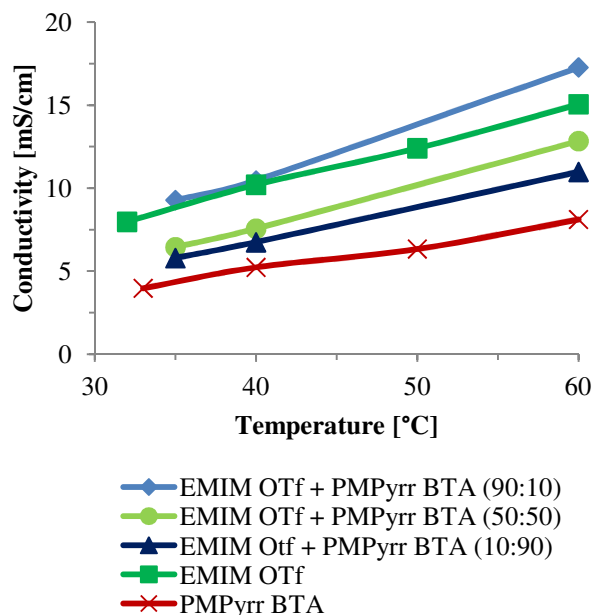


Figure 5: Temperature-dependent conductivity of selected ionic liquids' mixtures

Our results showed that the ratio of 90:10 mol % of EMIM OTf/PMPyrr BTA had in comparison to the neat ionic liquids a significantly lower viscosity (Figure 4). The measurements of the conductivity displayed with decreasing viscosity an increase in conductivity. As expected the 90 : 10 mol % mixture of EMIM OTf/PMPyrr BTA showed the highest values of

conductivity (Figure 5). So, using binary mixtures of ionic liquids has a great potential for electrochemical applications [16].

3 CONCLUSIONS

These results show that ionic liquids mixed either with organic solvents or with another ionic liquid are a promising alternative to conventional electrolytes. The electrochemical and physical properties of ionic liquids meet many requirements of electrolytes for electrochemical applications.

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