

# OVERVIEW OF NON-AQUEOUS ELECTROLYTES FOR SUPERCAPACITORS

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## ABSTRACT

This paper relates to energy storage devices such as supercapacitors and non-aqueous electrolytes suitable for use in these systems. The electrochemical and physical properties of the electrolytes are the key factors in determining the internal resistance (esr) and the power output capability of the supercapacitors. Discussed electrolyte systems are: blended electrolytes, gel polymer electrolytes and ionic liquid

## 1. INTRODUCTION

Supercapacitors, also known as ultracapacitors, electric double layer capacitors (EDLCs) or electrochemical supercapacitors are the electrochemical energy storage devices in which the electric charge is stored in the electrical double layer formed at the interface between electrode and an electrolyte solution. These devices can provide high power capability, excellent reversibility and long cycle life. Typically they exhibit 20-200 times larger capacitance per unit volume or mass than conventional capacitors. [1,2,3]

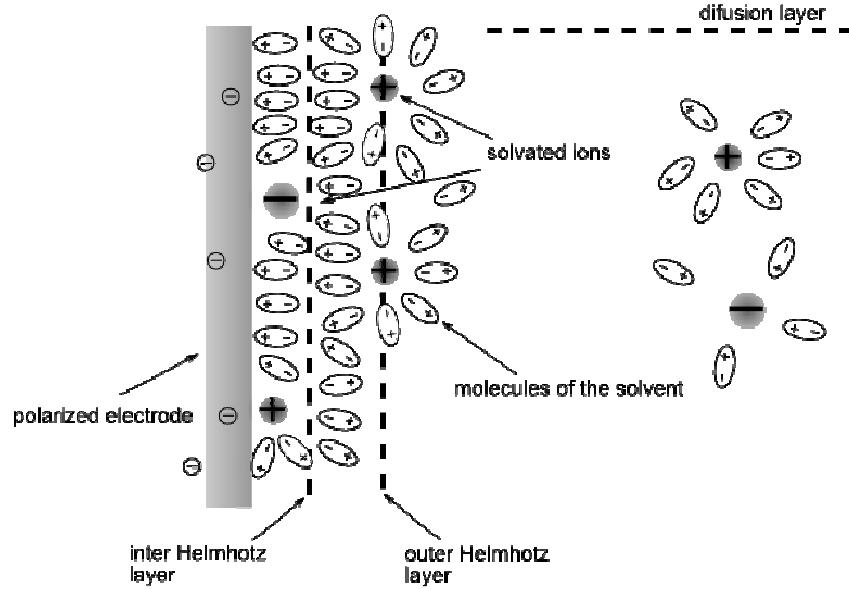
Supercapacitors can be used in hundreds of applications. Their relatively high power density makes them ideal for parallel combination with batteries that have high energy density to ram the hybrid energy storage systems. When a load requires not constant energy, the battery system supplemented by supercapacitor allows delivering the high amount of energy in the short time period from the charged supercapacitor. This reduces a load on the battery and in many cases extends the lifetime of rechargeable batteries. [1, 2, 3]

## 2. PRICIPLES AND ENERGY STORAGE MECHANISM OF THE SUPERCAPACITORS

EDLCs store the electric charge directly across the interface, this is a true capacitance effect (fig. 1). The mechanism of surface charge generation can be enumerated as: surface dissociation and ion adsorption from solution. The capacitance arises from an electrochemical double layer (DL) directly analogous to a parallel plate capacitor. The thickness of the DL is in the order of  $5 - 10 \cdot 10^{-10}$  m depends on the concentration of the electrolyte and size of ions. The double layer capacity is about  $10 - 20 \mu\text{m}^2$  for a smooth electrode in concentrated electrolyte solution. As an electrode material are used highly porous carbon par-

ticles with a very high surface area. This area is in the range from 100 m<sup>2</sup> to 2500 m<sup>2</sup> per gram. The current collector is generally a metal foil.

The porous separator, filled by electrolyte, is employed to physically isolate the carbon electrodes and prevent electrical shorting of the electrodes.



**Figure 1:** Bockris Devanathan Müller double layer model

The capacity [F] can be estimated according to equation:

$$C = \epsilon_0 \epsilon_r \frac{S}{l} \quad (1)$$

where  $\epsilon_r$  is the double layer dielectric constant, the  $l$  [m] is the thickness of the DL and  $S$  [m<sup>2</sup>] is the electrode surface area. [1, 2, 3, 4]

## 2.1. ELECTROLYTE FACTOR IN THE SUPERCAPACITORS

The electrolyte is typically one or more solvents containing one or more dissolved ionic species. In many cases, the physical and electrochemical properties of the electrolyte are a key factor in determining in the internal resistance (esr) of the supercapacitor and the power properties.

The energy [J] storage in the supercapacitor can be described by the equation

$$E = \frac{1}{2} C U^2 \quad (2)$$

where  $U$  [V] is the operating voltage.

The another measure of supercapacitor performance is the ability to store and release the energy rapidly, it is the power  $P$  [W] of supercapacitor and is given by

$$P = \frac{U^2}{4R} \quad (3)$$

where  $R$  [ $\Omega$ ] is the internal resistance.

As can be deduced from equations 1 and 2, the energy and power performance are highly dependent at the operating voltage and internal resistance. These two factors are mainly given by the conductivity and voltage range of the electrolyte.

The two principal factors involved in conductance are:

- a) concentration of free charge carries (cations and anions)
- b) ionic mobility or conductance contribution per dissociated ion in the electrolyte

There are also a number of sub-factors which influence these two general factors:

- a) solubility of the selected salt
- b) degree of dissociation into free ions and factors such as extent of cation-anion association or pairing of ions of the dissolved salt. This in turn is influenced by the salt concentration, temperature and the dielectric constant of the solvent
- c) viscosity of the solvent, which is a temperature dependent property. As temperature increases, there is a corresponding decrease in viscosity

There is also the necessity for the solvent to be chemically stable. Stability is important when one considers that supercapacitor must charge and discharge many hundreds or thousands of times during the operational lifetime of the supercapacitor. [1, 4]

### 3. NON-AQUEOUS ELECTROLYTE SYSTEMS

The use of non-aqueous electrolytes for electrochemical capacitors is, in principle, preferred since higher operating voltages  $U$  can be utilized due to the larger decomposition limits of such electrolyte solutions. Since the stored energy increases as  $U^2$  (equation 2), this is an obvious advantage over aqueous systems.

#### 3.1. BLENDED ELECTROLYTES

The non-aqueous electrolyte of the supercapacitor contains a solution of a conductive salt dissolved in a solvent. The most common solvents are in the table 1.

Solvent	Bp.	Mp.	Permittivity	Viscosity (25 °C)
Propylene carbonate	241°C	-55°C	65	2.8 mPa·s
Dimethylsulfoxide	189°C	18.5°C	29.8	1.996 mPa·s
N, N dimethylformamide	153°C	-61°C	30.9	0.92 mPa·s
Ethylene carbonate	260°C	37°C	95	1.92 mPa·s (40)
Diethyl carbonate	128°C	-48°C	-	0.795 mPa·s
Acetonitrile	82°C	-45°C	38	0.369 mPa·s
Sulfolane	285	26	14.8	10 mPa·s
$\gamma$ -butyrolactone	204	-44	42	1.7 mPa·s

**Table 1:** Properties of some non-aqueous solvents

The major factor for choosing a suitable salt are important discharging and decomposing potentials of the solute ionic species. The preferred solutes are tetraalkylammonium salts of anions that are difficult to discharge, such as  $(PF_6)^-$ ,  $(BF_4)^-$  and  $(AsF_6)^-$ .  $Li^+$  salts could

be also used provided the cathodic limit for Li metal deposition is not reached on charging of the capacitor.

The choice of solvents usually follows the same principles as for Li battery systems, although stability to reaction with Li is no longer critical factor. [1, 4, 7]

### 3.2. GEL POLYMER ELECTROLYTES

The gel polymer electrolytes continue to attract attention since their introduction by M. Armand. So far various systems have been extensively investigated in high-energy lithium-ion batteries, electric double-layer supercapacitors, fuel cells, and chemical sensors. The operating voltage is about 4 V and conductivity up to 10 mS/cm.

In principle the gel polymer electrolyte can be classified as the two-phase system composed of ionically conducting medium entrapped in host polymer matrix. The most important ionic conductors are proton ( $H^+$ ) and lithium ( $Li^+$ ) based electrolytes. The first one are known for their high conductivity with the  $H^+$  donors originating from e.g. sulphuric ( $H_2SO_4$ ) or phosphoric ( $H_3PO_4$ ) acid. In the second group mobile  $Li^+$  species are provided by dissolution of lithium perchlorates ( $LiClO_4$ ), fluorophosphates ( $LiPF_6$ ) or fluoroborates ( $LiBF_4$ ) in aprotic solvents. Furthermore the sodium, potassium or ammonium based electrolytes are known. Among others acetonitrile, propylene and ethylene carbonates are the most common choices of aprotic solvents.

The polymer matrix, based on poly(propylene), poly(vinylidene difluoride), poly(tetrafluoroethylene), poly(ethylene oxide) (PEO), polyaniline (PANI), poly(methyl methacrylate) (PMMA), ensures desired mechanical properties resulting in self-standing gel polymer electrolyte. [5, 6]

Gel polymer electrolytes have several advantages:

- volatile organic solvent is not incorporated
- supercapacitors can be made of any size and shape and
- light weight and high energy density battery can be made.

### 3.3. IONIC LIQUID ELECTROLYTES

Covalent supercapacitor electrolyte technology is based on a family of salts known as hydrophobic ionic liquids (IL). These materials possess a unique set of physical, chemical and electrochemical properties that strongly favor their use as electrolytes in supercapacitors. IL technology is based on the judicious pairing of delocalized heterocyclic organic cations and charge stabilized organic and inorganic anions.

Properties of the ionic liquid:

- ion concentration from 4 M to 6 M
- wide working temperature, from  $-90\text{ }^\circ\text{C}$  to  $400\text{ }^\circ\text{C}$
- non-flammable with low toxicity
- non-corrosive to electrode and packing components at elevated temperatures
- isothermal stabilities approaching  $300\text{ }^\circ\text{C}$  with no measurable vapor pressure

The viscosities of IL are minimally two orders of magnitude greater than those of most common molecular solvents. Thus the typically ionic conductivity is in the range from 4 to

14 mS/cm at 22 °C. This conductivity is insufficient for supercapacitors at room temperature and below, but are suitable for high temperature applications. [5, 7]

#### **4. CONCLUSION**

In this paper were briefly summarized properties of the 3 general non-aqueous electrolytes. The electrochemical and physical properties of the electrolytes are the important factors influencing parameters of the supercapacitors such as internal resistance, working potential and currents.

#### **ACKNOWLEDGEMENTS**

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#### **REFERENCES**

- [1] CONWAY B.E., Elektrochemical Supercapacitors: Scientific Fundament and Technological Application, Kluwer Academic, New York, 1999, 698 s, ISBN 0-306-45736-9
- [2] U.S. Department of Energy, Basic Research Needs for Electrical Energy Storage, Report of the Basic Energy Science Workshop on Electrical Energy Storage, April 2-4 2007, [cit.1.4.2009]. Available from [www: http://www.er.doe.gov/bes/reports/files/EES\\_rpt.pdf](http://www.er.doe.gov/bes/reports/files/EES_rpt.pdf)
- [3] CAP-XX LTD. Electrolyte for an energy storage devices. USA Patent, US 7,341,514 B2. 208-01-01.
- [4] Makoto Ue, Kazuhiko Ida, Shoichiro Mori, J. Electrochem.Soc., 141, 11, (1994)
- [5] KREJZA, O. Gel polymer electrolytes for electrochromic devices. Brno: Brno University of Technology, Faculty of Electrical Engineering and Communications, 2009. 117 s. Tutor Prof. Ing. Jiří Vondrák, DrSc.
- [6] SEKHON, S. S., Bull. Mater. Sci., 26, 3,(2003)