



Theoretical and practical energy limitations of organic and ionic liquid-based electrolytes for high voltage electrochemical double layer capacitors



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HIGHLIGHTS

- Importance of salt concentration for the development of high energy supercapacitors.
- High voltage PC-based electrolytes feature promising properties.
- Ionic liquids-based EDLCs display limited power at room temperature.

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ABSTRACT

In EDLCs the energy is stored in the double layer formed by the ions of the electrolyte. Hence, during charge–discharge the ion concentration changes and therefore also the electrolyte should be considered as active material. In the past it has been shown that the performance of EDLCs based on non-aqueous electrolytes is mainly limited by ion concentration of the electrolytes. Taking this point into account, we considered the influence of the salt concentration on the theoretical and practical energy of high voltage EDLCs containing innovative electrolytes with the aim to understand the advantages and the limits related to their use.

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1. Introduction

Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, are today advancing as one of the most promising energy storage technology [1,2]. In EDLCs the charge is electrostatically stored at the electrode–electrolyte interface and because of this storage mechanism these devices can be charged and discharged within seconds, they feature high power (up to 10 kW kg⁻¹) and an extremely high cycle life (>500,000) [3]. Currently, the commercial available EDLCs contain activated carbon as active material and electrolytes based on quaternary ammonium salt dissolved in organic solvents (acetonitrile (ACN) or propylene carbonate (PC)). The operative voltage of these EDLCs is in the range of 2.3–2.7 V [4]. EDLCs are nowadays conveniently used in a large number of applications where rapid charge–discharge capability

and reliability are required [5]. In the last years, they have also been proposed for high power/energy applications such as hybrid and electric vehicles, power quality systems and smart grids [5]. However, in order to be effectively introduced into these new applications, the performance of EDLCs needs to be improved, particularly in terms of specific energy.

The specific energy of EDLCs is defined by the equation $E = 1/2CU^2$, where C and U are the capacitance and operative voltage of the EDLC, respectively. Hence, the energy density of EDLCs can be improved by increasing the specific capacitance of the electrode material and/or the operative cell voltage. Regarding electrode materials, several carbonaceous materials such as carbon blacks, carbon aerogels or carbon nanotubes have been proposed as alternatives for activated carbons [1,6–9]. All proposed materials feature interesting properties. Nevertheless, when used in composite electrodes (with mass loading higher than 2 mg cm⁻²), the specific capacitance reported for these alternative materials is in the order of 100–150 F g⁻¹. Hence, such alternative materials do not outperform significantly activated carbon-based electrodes. Taking

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this point into account, the greatest progress for carbon-based EDLCs can be presently expected from an increase of the operative voltage.

In the last years, many groups worked on the development of alternative electrolytes for high voltage (>3 V) EDLCs. Among the alternative electrolytes proposed so far, ionic liquids (ILs) are currently considered as one of the most promising. Several groups suggested the use of ILs as electrolytes for supercapacitors. These studies showed that IL-based EDLCs with operative voltages of 3.5 V (or even higher) can be realized [10–13]. This high cell voltage leads to a considerable increment of the energy of these devices. However, due to higher viscosities and lower conductivities of the ILs compared to that of ACN and PC-based systems, the power of IL-based EDLCs appears limited, especially at room temperature. In order to improve the power of high voltage EDLCs, the use of electrolytes containing mixtures of organic solvents (PC or ACN) and ILs has also been proposed [14–16]. Depending on the IL/organic solvent ratio, such mixtures can feature high conductivity, low viscosity and wide ESW. Hence, these characteristics enable the development of high performance devices [15,17,18]. In these electrolytes, the ILs simply act as a conducting salt, and it is important to notice that these mixtures can feature much higher salt concentration compared to conventional electrolytes.

Zhang et al. showed that the performance of EDLCs based on non-aqueous electrolytes is mainly limited by ion concentration of the electrolyte [19,20]. For this reason, the use of highly concentrated electrolytes, e.g. mixtures of ILs and organic solvents, appears promising. But even more, the utilization of solvent-free electrolytes, e.g. pure ILs, is desirable for the increment of the energy density of EDLCs. Although the salt concentration appears an aspect of great importance in view of the development of innovative electrolytes, it is interesting to note that a detailed investigation about the influence of this parameter on the energy of EDLCs containing the above mentioned alternative electrolytes has not been carried out, so far.

In this manuscript, we considered the influence of the salt concentration on the theoretical and practical energy of high voltage EDLCs containing pure IL and PC-based electrolytes. Initially, following the approach proposed by Zhang et al., the theoretical influence of the electrolyte on the energy density of EDLCs is considered. Afterwards, the physicochemical characteristics, such as conductivity, viscosity, etc., of 5 non-conventional electrolytes for high voltage EDLCs are compared with those of conventional electrolytes. Finally, the impact of different electrolytes on the theoretical and practical energy limitations of EDLCs is critically discussed.

2. Experimental

The organic solvents ACN (Sigma–Aldrich, Germany) and PC (UBE, Japan), the conducting salts tetraethylammonium tetrafluoroborate (Et_4NBF_4 , Sigma–Aldrich, Germany), and N-methyl-N-butyl pyrrolidinium tetrafluoroborate ($\text{PYR}_{14}\text{BF}_4$, Iolitec, Germany) are commercially available and were used as received without any further purification.

The ionic liquids tetraethylammonium bis-[(trifluoromethyl)sulfonyl]imide (Et_3NHTFSI), trimethylsulfonium bis-[(trifluoromethyl)sulfonyl]imide (Me_3STFSI) and N-methyl-N-butyl pyrrolidinium bis-[(trifluoromethyl)sulfonyl]imide ($\text{PYR}_{14}\text{TFSI}$) were synthesized according to procedures described in references [21–24].

All electrolytes (except the solvent-free) were prepared in an argon filled glove box and the concentration of all of them can be found in Table 1. Their water contents were evaluated using an automated Karl-Fischer titrator. As reported in Table 1, all investigated electrolytes contained less than 25 ppm of water.

Composite electrodes containing activated carbon (DLC Super 30, Norit) as the active material were coated on Al foil following the procedure reported in Ref. [9]. The activated carbon is mainly microporous (92% of micropore volume, $0.78 \text{ cm}^3 \text{ g}^{-1}$), has a specific surface area (BET) about $1410 \text{ m}^2 \text{ g}^{-1}$ and the oxygen surface functionality is about 4–5% (95% carbon) [25]. The composition of the dry electrodes was 90% of AC, 5% conducting agent (C65, TIMCAL) and 5% sodium carboxymethyl-cellulose binder (CMC, Walocel CRT 2000 PPA 12 from Dow Wolff Cellulosics). The activated carbon loading on the electrodes was in the range of 6 mg per cell, and the electrode area was 1.13 cm^2 . The electrode coating density (referred to the whole electrode mass loading and dry coating thickness) was about 0.5 g cm^{-3} for all electrodes.

Electrochemical investigations were carried out with Swagelok®-type cells. The cells were assembled in an Argon-filled glove box with oxygen and water contents lower than 1 ppm. Experiments were carried out using 2-electrode configuration. Whatman GF/D glass microfiber filter of $675 \mu\text{m}$ in thickness and 12 mm in diameter served as a separator in all experiments. It was drenched with 120 μL of electrolyte solution.

The electrochemical cycling tests were performed at $20 \text{ }^\circ\text{C}$ (controlled temperature) using a VMP multichannel potentiostatic–galvanostatic system (Biologic Science Instrument, France). Galvanostatic charge–discharge cycling was carried out using current densities ranging from 0.1 to 10 A g^{-1} .

Table 1
Comparison of the water content, ionic conductivity (at $20 \text{ }^\circ\text{C}$), viscosity ($25 \text{ }^\circ\text{C}$) and ESW (at $20 \text{ }^\circ\text{C}$, on platinum working electrode, 1 mV s^{-1} scan rate, 0.1 mA cm^{-2} threshold value) of the considered electrolytes. In the table also the maximum operative voltage and suitable ratio between positive and negative AC electrode for such voltage are also indicated.

Electrolyte	Water content (ppm)	Conductivity ($20 \text{ }^\circ\text{C}$) / mS cm^{-1}	Viscosity ($25 \text{ }^\circ\text{C}$) / mPa s	ESW ($20 \text{ }^\circ\text{C}$) / V	Maximum operative voltage in EDLCs / V	Ratio of activated carbon loading on electrodes in EDLCs / m^2/m^3
$\text{PYR}_{14}\text{TFSI}$	<9	2.2	77.1	5.6	3.7	1.30
Et_3NHTFSI	<10	4	39	3.8	2.4	0.5
3.8 M Me_3STFSI in PC	<5	5.4	31	4.8	2.9	1.2
1.5 M $\text{PYR}_{14}\text{TFSI}$ in PC	<10	10.4	5.6	5.4	3.5	1.3
1.9 M $\text{PYR}_{14}\text{BF}_4$ in PC	<24	10.2	6.3	5.5	3.2	1.6
1.0 M Et_4NBF_4 in PC	<11	14.5	2.5	4.9	2.7	1.0
1.0 M Et_4NBF_4 in ACN	<7	56.1	0.6	4.0	2.7	1.0

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