



# Investigation of methoxypropionitrile as co-solvent for ethylene carbonate based electrolyte in supercapacitors. A safe and wide temperature range electrolyte

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## ABSTRACT

The performances obtained with methoxypropionitrile/ethylene carbonate mixture based electrolytes were investigated in supercapacitor application. The incorporation of methoxypropionitrile allows a good compromise between electrochemical performances and safety issue to be exhibited in a wide temperature range. This improvement is associated with the decrease of electrolyte viscosity without compromising the salt solubility and dissociation. The highest conductivity values,  $20 \text{ mS cm}^{-1}$  at  $30^\circ\text{C}$  compared to  $14 \text{ mS cm}^{-1}$  in PC (propylene carbonate), were obtained with both 1 M tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) and spiro-(1,1')-bipyrrolidinium tetrafluoroborate (SBPBF<sub>4</sub>) salts. Bulk liquid state was conserved for these electrolytes in a wide temperature range. Then, interesting electrolyte conductivities were obtained at low temperature ( $5.2 \text{ mS cm}^{-1}$  at  $-25^\circ\text{C}$ ) which is twice that of PC + TEABF<sub>4</sub> 1 M electrolyte at the same conditions. Moreover, the capacitor performance of EC/MP based electrolyte is better than PC one at room temperature.

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## 1. Introduction

Electrical double layer capacitors (EDLCs) are promising charge-storage devices in which the charge storage ideally occurs entirely via electrostatic forces at the electrode/electrolyte interface [1,2]. Compared to redox processes commonly encountered in the bulk of battery electrodes, the electrical double-layer can be both charged and discharged efficiently at high rates and with high reversibility. As the energy density of EDLCs is proportional to the square of the cell voltage, the electrolyte electrochemical stability window is essential for EDLCs performances. Currently, the most commonly employed electrolytes for EDLCs consist of quaternary ammonium salts in either acetonitrile (ACN) or propylene carbonate (PC) as solvent [3]. Acetonitrile based electrolytes present high electrochemical stability and high conductivity even at low temperature (down to  $-40^\circ\text{C}$ ). However, it is flammable ( $F_p = 6^\circ\text{C}$ ) and harmful

liquid, thus supercapacitors based on acetonitrile electrolyte set some safety problems. With PC solvent, the safety is improved due to its high flash point ( $F_p = 135^\circ\text{C}$ ), but poor conductivity performances are obtained especially at low temperature. Other solvents, as  $\gamma$ -butyrolactone [4], dimethylketone [4], sulfolane [5], methoxyacetonitrile [6] and methoxypropionitrile [6] were investigated for EDLC. The conductivity values obtained with  $\gamma$ -butyrolactone and sulfolane solvents are low, due to their high viscosity; however a high electrochemical stability resulting in supercapacitors with high nominal voltage. Methoxyacetonitrile ( $\epsilon_r = 21$ ,  $\eta = 0.7 \text{ mPa s}$  at  $25^\circ\text{C}$ ) [6] and methoxypropionitrile (MP) ( $\epsilon_r = 36$ ,  $\eta = 1.1 \text{ mPa s}$  at  $25^\circ\text{C}$ ) [5] present adequate physico-chemical parameters which explain the high conductivity values [6]. These solvents present also a high electrochemical stability of  $5.7 \text{ V}$  [6] and a flash point higher than  $30^\circ\text{C}$ .

Many studies were performed on the optimization of the lithium-ion battery electrolyte, using solvent mixtures. In the case of supercapacitor electrolytes, only a few studies were done. Ding et al. [7] observed the increase of the electrolyte electrochemical stability and a decrease of the solidification temperature with the addition of  $\gamma$ -butyrolactone on ACN based electrolyte.

The salt used, which is often an ammonium salt, has also a major influence on the performances of the electrolyte (ionic conductivity, electrochemical stability). The most common salt is tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>); it has a low

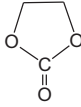
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**Table 1**  
Flash point, viscosity and dielectric constant of the solvents.

Solvent	Formula	FP (°C)	$\eta$ (mPa s) at 40 °C	$\epsilon_r$ at 25 °C
Ethylene carbonate (EC)		143	1.96	90
Methoxypropionitrile (MP)	CH <sub>3</sub> —O—CH <sub>2</sub> —CH <sub>2</sub> —CN	66	1.1	36

cost and presents a good electrochemical stability, but demonstrates a limited solubility in solvents of intermediate polarity. In order to improve the solubility and the low temperature performances, asymmetric ammonium cations were investigated. For example, triethylmethylammonium tetrafluoroborate allows the solubility limit to be enhanced without compromising the electrochemical stability and ionic conductivity [8]. The incorporation of an ether function in the ammonium cation [9,10] induces also an improvement of the salt solubility, but lower conductivities than TEABF<sub>4</sub> based electrolytes are demonstrated. The spiro-(1,1′)-bipyrrolidinium tetrafluoroborate (SBPBF<sub>4</sub>), a cyclic and symmetric salt, exhibits good performance as EDLC electrolyte [11]. A slight increase of conductivity is shown with SBPBF<sub>4</sub> in PC (0.65 M in PC; 10.9 mS cm<sup>-1</sup> at 25 °C) compared with TEABF<sub>4</sub> (0.65 M in PC; 10.6 mS cm<sup>-1</sup> at 25 °C) [6]. Furthermore SBPBF<sub>4</sub> is more soluble in a large variety of solvent mixtures [11].

The aim of this paper is to evaluate the properties of ethylene carbonate (EC)/MP mixtures as solvents for EDLC application, in view to improve the electrochemical performances, in a wide temperature range and without compromising the safety issues induced by EC. The EC is a polar solvent with a high viscosity, whereas methoxypropionitrile (MP) exhibits lower viscosity and an intermediate dielectric constant ( $\epsilon_r = 36$ ) (Table 1). The addition of MP in EC based electrolytes should improve the conductivity particularly at low temperature, due to the decrease of the electrolyte viscosity and mixing effect which reduces the electrolyte melting point without compromising the salt dissociation.

## 2. Experimental

### 2.1. Chemical products

EC and MP were purchased from Mitsubishi Chemical and ABCR respectively. They were purified by distillation, dried on 3 Å molecular sieves and stored in glove box (less than 3 ppm water). The purity of the solvents is higher than 99.9% (established by electrochemical investigation), whereas the amount of residual water is lower than 20 ppm (determined by Karl Fisher titration).

TEABF<sub>4</sub> was purchased from Fluka and SBPBF<sub>4</sub> was supplied by Batscap. The TEABF<sub>4</sub> salt was purified by recrystallization in 1,2-dichloroethane. The purified salt was dried by freeze drying and stored in a glove box. Electrolytes were prepared in glove box and exhibit water content below 20 ppm.

### 2.2. Measurements

#### 2.2.1. Thermal measurements

DSC tests were performed using a TA Instrument DSC 2920 CE. Samples of 3 mg were sealed in aluminum pans in glove box. Each sample was cooled from 40 °C to -100 °C and up to 40 °C at a rate of 5 K min<sup>-1</sup>. The melting and crystallization temperatures,  $T_m$  and  $T_c$  were determined at the top of melting and crystallization peaks respectively. For the boiling point determination, each sample was heated from room temperature up to 250 °C at a rate of 5° K min<sup>-1</sup>.

The electrolytes boiling point is taken at the beginning of the phenomenon.

#### 2.2.2. Viscosity measurement

The viscosity measurements were carried out on a TA Instrument AEG2 cone-plate rheometer using a stainless steel cone of 40 mm in diameter and angle  $\alpha$  of 2°. The device was protected from the surrounding atmosphere by a plastic glove box kept under nitrogen, to avoid water uptake during the measurement. The shear rate was fixed at 100 s<sup>-1</sup>, after ensuring the Newtonian behavior of each fluid studied. The measurements were carried out between 10 and 60 °C and repeated 3 times to ensure reproducibility; uncertainties of viscosity values are estimated to be  $\pm 0.06$  mPa s.

#### 2.2.3. Electrochemical measurements

Conductivity was measured using a Hewlett Packard 4192A impedancemeter controlled by software developed in the laboratory. The frequency range was 5 Hz–13 MHz and the amplitude of the sinusoidal signal was set at  $\pm 10$  mV. Measurements were performed at temperatures ranging from -30 to 60 °C in a thermostatic chamber (Vötsch models VTM 4004). The measurement is made after a temperature stabilization of 1.5 h. The conductivity, for the same electrolyte is determined twice in two different conductivity cells to check the reproducibility of measurements (conductivity accuracy values are estimated to be  $\pm 0.2$  mS cm<sup>-1</sup>). The cell constant was determined by using a 0.1 M KCl solution. The resistance of the cell in short-circuit and cables were subtracted to the overall measurement to obtain an accurate value of the electrolyte resistance. Cyclic voltammograms (CV) were recorded at 30 °C in a glove box. The counter electrode was a Pt wire, and the working electrode was Pt or a glassy carbon (diameter 3 mm). The scan rates used was 10 mV s<sup>-1</sup>. The reference electrode was an Ag wire in 10 mM AgNO<sub>3</sub> in acetonitrile +0.1 M tetrabutylammonium tetrafluoroborate. The measured potential can be converted to the NHE scale by adding 0.542 V [17]. The anodic and cathodic limits were defined as the potential at which the current density is equal to 0.3 mA cm<sup>-2</sup>.

For EDCL investigation, the electrode was supplied by Batscap. These electrodes contain 10% of PVDF and 10% of conductive additive; the carbon charge loading is equal to 2.94 mg cm<sup>-2</sup>. Previous experiments have demonstrated that these chemicals do not affect electrolyte stability (or have a minor effect). The electrodes were dried several days at 100 °C under vacuum and then stored in glove box. The electrochemical cell was assembled in a Swagelok type test cell using 1.13 cm<sup>2</sup> surface area electrodes. CV was performed in a two electrodes system (i.e. two identical carbon electrodes separated by a cellulose based separator (25  $\mu$ m, >70% of porosity)) at 100 mV s<sup>-1</sup> at 20 °C. Galvanostatic cycling was performed using a current density of  $\pm 9$  mA cm<sup>-2</sup>, with an operating voltage from 0V to 2.3V. The time constant of the system was determined using the "IR" drop at the initial portion of the discharge curve during the galvanostatic charge/discharge investigation.

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