

The influence of electrochemical stability and solubility of conductive salts on the behavior of high voltage electrochemical double layer capacitors

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Electrochemical double layer capacitors (EDLCs), also known as supercapacitors, display high power ($10 \text{ kW}\cdot\text{kg}^{-1}$) and extremely high cycle life (up to millions of cycles) [1]. Because of these characteristics EDLCs are currently considered as one of the most important electrochemical storage devices, and they are used in an increasing number of applications [1]. Commercially available EDLCs contain activated carbon (AC) as active material and quaternary ammonium salts (typically tetraethylammonium tetrafluoroborate, Et_4NBF_4) in propylene carbonate (PC) or acetonitrile (ACN) as electrolyte. These EDLCs have operative voltages in the order of 2.7 – 2.8 V and their energy is in the order of 5 Wh kg^{-1} . This specific energy is enough to fulfill the need of present applications. However, in order to enlarge the number of applications (and consequently the market) of EDLCs, higher energy is needed. For this reason, tremendous efforts have been conducted in the last years in order to increase the energy of these devices [2].

The energy (E) of EDLCs is described by the equation $E=1/2CV^2$, where C and V are the capacitance and operative voltage of the EDLCs, respectively. Considering this expression, it appears evident that the most convenient way to increase the energy of EDLCs is to increase the operative voltage of these devices. Several studies showed that it is not possible to realize EDLCs with operative voltage higher than 3V and stable performance when activated carbons are used in combination with the state-of-the-art electrolytes [3]. Therefore, in order to overcome this limitation, in the last years new types of electrolytes have been proposed and used for the realization of high voltage EDLCs [4].

It is well known that the properties of the conducting salts, particularly its electrochemical stability and its solubility in the solvent, might play a crucial role for the development of high performance (and high voltage) EDLC since they affect the physical-chemical properties of the electrolytes as well as the double layer formation [1]. Even so, to the best of our knowledge, only a limited number of works focused on the investigation of conducting salts for EDLCs. Ue et al. considered the influence of several quaternary ammonium salts on the conductivity and electrochemical stability window (EWS) in PC-based electrolyte [5]. Zheng et al. considered the influence of the Et_4NBF_4 concentration in PC-based electrolytes on the energy of EDLCs [6]. Only recently a new conducting salt, spiro-(1,1*)-bipyrrrolidinium tetrafluoroborate, has been proposed as alternative to Et_4NBF_4 [7].

In this paper we report about the use of different conductive salts for the realization of advanced EDLCs. The influence of the electrochemical stability of the conducting salts on the operative voltage of EDLCs

has been investigated. Moreover, also the influence of the solubility of these salts in PC on the performance of high voltage EDLCs has been taken into account. The results of this investigation show that a proper selection of ions might allow the design of conductive salt able to improve the performance of PC-based EDLCs. As example, using the conducting salt *N*-butyl-*N*-methylpyrrolidinium tetrafluoroborate ($\text{PYR}_{14}\text{BF}_4$) it is possible to realize EDLCs with an operative voltage of 3.2V. These high voltage EDLCs display higher energy and power compared to conventional PC-based EDLCs. Moreover, thanks to the stability of this electrolyte, these EDLCs display good performance during charge-discharge tests as well as float tests carried out using an operative voltage of 3.2V [8].

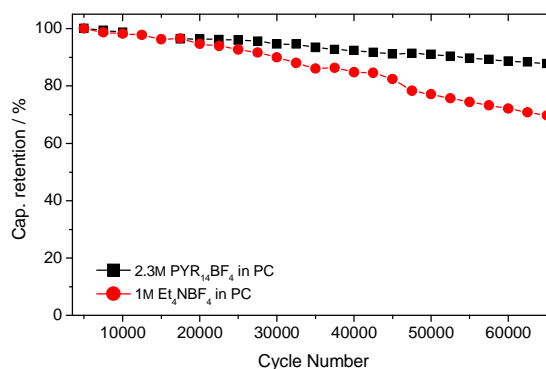


Fig. 1 Capacitance retention vs. cycle number of EDLCs containing 2.3M $\text{PYR}_{14}\text{BF}_4$ in PC and 1M Et_4NBF_4 in PC as electrolytes obtained from galvanostatic charge-discharge tests carried out using a cell voltage of 3.2 V and current of 10 mA cm^{-2} .

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