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An investigation about the cycling stability of supercapacitors containing protic ionic liquids as electrolyte components

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ABSTRACT

In the last years protic ionic liquids (PILs) have been proposed as novel electrolytes for supercapacitors. Nevertheless, so far the long term cycling stability of PIL-based supercapacitors has never been investigated in detail. Since high cycling stability is essential for such devices, a study about this aspect appears therefore of importance to understand the advantages and the limits of PIL-based systems. In this work we showed that using PILs as electrolytes it is possible to realize electrochemical double layer capacitors (EDLCs) with operative voltage as high as 2.4 V, able to feature good cycling stability in a broad range of temperature. Moreover, we also showed that the pseudo-capacitive behavior of activated carbon (ACs) in these electrolytes strongly depends on the water content and on the surface groups present on the ACs. When PILs with a lower content of water were used in combination with AC containing few surface groups, PIL-based supercapacitors exhibit specific capacitance comparable to classical organic electrolytes without any evident pseudo-capacitive contribution.

1. Introduction

Supercapacitors feature high power (up to 10 kW kg^{-1}) and extremely high cycle life (>500,000) and because of these characteristics they are currently considered as one of the most promising electrochemical storage devices [1,2]. The commercial available supercapacitors contain activated carbon as active material and either aqueous or organic solutions as electrolyte. In these devices, also called electrochemical double layer capacitors (EDLCs), the charge is stored at the interface between the electrode and the electrolyte [1]. Typically, EDLCs containing aqueous electrolyte have higher power than those containing organic electrolyte due to the higher conductivities and lower viscosities of aqueous electrolytes compared to the organic one. On the other hand, because of their higher operative voltage, the latter display higher energy compared to the former [1,2].

Ionic liquids (ILs) are molten salts with melting temperatures below 100 °C. ILs are non-flammable, they have negligible vapor pressure and they display high chemical and thermal stabilities [3]. Because of these characteristics they are considered as attracting electrolyte candidates for the realization of safe electrochemical devices. So far, most of the studies about the use of ILs in EDLCs have been carried out using aprotic ionic liquids (AILs). The results of these investigations indicated that the use of AIL-based electrolytes allows the realization of EDLCs with high energy and operative voltages significantly higher than 3 V [4,5]. A minor number of studies have been dedicated to the use of protic ionic liquids (PILs), which is another subset of ILs. PILs present all typical properties of ILs, but they have the advantage of being easier to synthesize and cheaper compared to aprotic ionic liquids [6–8]. Moreover, they are normally less viscous and they may have higher conductivities compared to AILs [9]. Taking into account these properties, also PILs could be interesting electrolyte candidates in electrochemical devices. In the past, the physicochemical properties of PIL-based electrolytes, meaning pure PILs as well as mixtures of PILs with organic solvents, have been investigated in view of their use as electrolytes for supercapacitors [9–13]. The results of this work showed that PIL-based electrolytes exhibit, like in the case of AILs, lower conductivity compared to conventional electrolyte (especially to ACN), but they might have interesting conductivity at low temperature [9–13]. Additionally, some works indicated that in PIL-based electrolytes ruthenium oxide [14,15] as well as activated carbon [12] might exhibit pseudo-capacitance due to the labile proton in PILs, which is participating on the fast redox reactions at the electrode/electrolyte interface. Nevertheless, to the best of our knowledge, the long term cycling stability of PIL-based supercapacitors has never been investigated in detail. Taking into account that high cycling stability is essential for supercapacitors, a study about this aspect appears of importance to understand the advantages and the limits of PIL-based supercapacitors.

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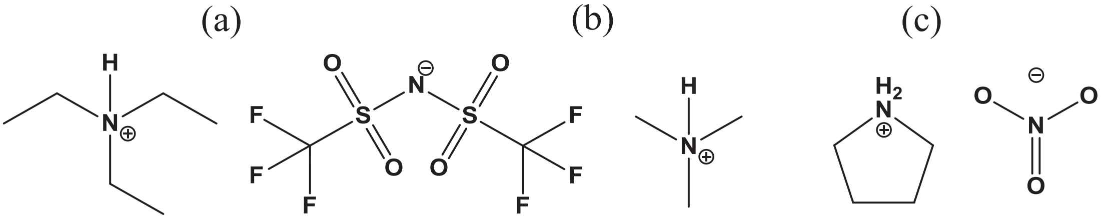

Fig. 1. Chemical structures of the protic ionic liquids (a) triethylammonium bis(tetrafluoromethylsulfonyl)imide ($Et_3NHTFSI$), (b) trimethylammonium bis(tetrafluoromethylsulfonyl)imide ($Me_3NHTFSI$) and (c) pyrrolidinium nitrate ($PYRNO_3$).

In this work we investigated the use of PIL-based electrolytes in EDLCs. Three different PILs have been selected for this study: triethylammonium bis(tetrafluoromethylsulfonyl)imide ($Et_3NHTFSI$), trimethylammonium bis(tetrafluoromethylsulfonyl)imide ($Me_3NHTFSI$) and pyrrolidinium nitrate ($PYRNO_3$). These PILs have been used either neat or in their mixtures with PC as electrolytes in carbon-based supercapacitors. Initially, the conductivity and the electrochemical stability windows of the considered PIL-based electrolytes were investigated and compared to that of conventional PC-based electrolyte. Afterwards, the cycling stability of PIL-based supercapacitors was evaluated at different temperatures, comprised between −20 and 60 °C. Finally, the energy and the power of the investigated devices was calculated and compared with those of the conventional PC-based EDLCs.

2. Experimental

The protic ionic liquids triethylammonium bis(tetrafluoromethylsulfonyl)imide ($Et_3NHTFSI$), trimethylammonium bis(tetrafluoromethylsulfonyl)imide ($Me_3NHTFSI$) and pyrrolidinium nitrate ($PYRNO_3$) were synthesized using procedures previously described in literature [13,16]. The chemical structures of the three PILs are reported in Fig. 1. The water content of $PYRNO_3$, $Me_3NHTFSI$ and $Et_3NHTFSI$ was lower than 80 ppm, 20 ppm and 10 ppm, respectively, as measured by automated Karl–Fischer titration. Propylene Carbonate (PC, battery grade UBE, Japan) was used as received. Three electrolytes were used for the electrochemical tests: neat $Et_3NHTFSI$ and the mixtures PC-$Me_3NHTFSI$ (1:1 wt.%) as well as PC-$PYRNO_3$ (1:1 wt.%). For convenience, in the following pages the mixtures PC-$Me_3NHTFSI$ (50 wt.%) and PC-$PYRNO_3$ (50 wt.%) will be indicated as PC-$Me_3NHTFSI$ and PC-$PYRNO_3$, respectively.

Conductivity measurements on the electrolytes were carried out by impedance spectroscopy, using a Solartron model 1260 impedance/gain-phase analyzer in a frequency region between 100 kHz and 100 Hz with an alternating voltage (AC) of 10 mV at OCV. The samples were placed in a sealed container equipped with platinum plated micro-electrode. The temperature was varied in the range from −40 °C to 60 °C and the sample was equilibrated at each temperature for 2 h prior to the measurement. The electrochemical stability windows (ESW) of the electrolytes were determined by linear sweet voltammetry (LSV) carried out using a scan rate of 1 mV s^{-1} in three-electrode cells with controlled temperature at 20 °C. The working electrode was a platinum micro-electrode (embedded in PEEK; active area = 0.79 mm^2) whereas the counter electrode consisted of an activated carbon electrode. As reference electrode a platinum wire was used. The cathodic and anodic stabilities of the electrolytes were determined by scanning the cell potential from the open circuit potential (OCP) to more negative (cathodic limit) or more positive (anodic limit) potentials. The oxidative and reductive potential limits were defined as the potentials where a current limit of 1 mA cm^{-2} was reached. For the measurement of each positive and negative limit fresh samples and cells were used.

The activated carbon (AC, DLC Super 30, BET specific surface area 1500 m^2 g^{-1}) was provided by Norit Activated Carbon. Sodium carboxymethylcellulose (CMC) was provided by Dow Wolff Cellulosics (Walocel CRT 200 PPA 12). As conducting agent, Super C65 (TIMCAL) was used. Carbon electrodes were prepared following a recipe similar to that indicated in reference [17]. The composition of the dry electrode was 90 wt.% AC, 5 wt.% Super C65 and 5 wt.% CMC. The average active material mass loading was comprised between 2 and 4 mg. The electrode area was 1.13 cm^2.

The electrochemical tests were carried out using Swagelok type cells, which were assembled in an argon-filled glove box with oxygen and water contents lower than 1 ppm. A Whatman GF/D glass microfiber filter (675 μm thickness and 13 mm diameter) was used as separator and drenched with 120 μL of electrolyte for all tests.

Cyclic voltammetry (CVs) and galvanostatic charge–discharge (GC) were carried out at controlled temperatures using a VMP multichannel potentiostatic–galvanostatic system (Biologic Science Instrument, France). In order to evaluate the maximum operative voltage of electrolytes CVs were carried out at 5 mV s^{-1} using a 3-electrode configuration. In these tests, the counter electrode was a carbon electrode (DLC Super 30, BET specific surface area 1500 m^2 g^{-1}) with a mass loading more than 10 times higher than that of the working carbon electrode and the separator was drenched with 150 μL of electrolyte. An Ag quasi-reference electrode was used as reference electrode. The supercapacitor performance was evaluated by galvanostatic charge–discharge tests carried out at temperatures ranging from −20 to 60 °C applying a current density of 10 mA cm^{-2}. The values of capacitance of active material (C_{am}), equivalent series resistance (ESR) and coulombic efficiency (η) have been calculated as indicated in reference [5]. The values of energy and power reported in Table 3 were calculated as indicated in references [5,16].

3. Results and Discussion

Table 1 compares the molecular weight, the water content and the aggregate state at room temperature (RT) of the PILs $Et_3NHTFSI$, $Me_3NHTFSI$ and $PYRNO_3$. As shown in the table, at RT $Me_3NHTFSI$ and $PYRNO_3$ are solid, and only $Et_3NHTFSI$ is liquid. It is very important to take into account that the physicochemical properties of PILs are strongly affected by the presence of impurities and, especially, by the amount of water present in the sample. Therefore the comparison of samples with marked difference in term of water content might be misleading, particularly when PILs (but more in

Table 1
Properties of someneatproticionicliquids, including molecular weight (MW), aggregate state at room temperature and water content.

Protic ionic liquid	MW (g mol^{-1})	Aggregate state at RT	Water content (ppm)
$Et_3NHTFSI$	382.4	Liquid	<10
$Me_3NHTFSI$	340.3	Solid	<20
$PYRNO_3$	142.1	Solid	<80