



Eutectic mixture of Protic Ionic Liquids as an Electrolyte for Activated Carbon-Based Supercapacitors



L. Timperman*, A. Vigeant, M. Anouti

Université François Rabelais de Tours, Parc Grandmont, 37200 Tours, France

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ABSTRACT

One of the drawbacks of ionic liquids is that some of them are solid or very viscous at room temperature; this prevents their use as electrolytes in energy storage systems. One solution consists of a binary mixture of pure, solid salts with the formation of a eutectic, allowing it to be used at room temperature. This work describes, for the first time, the formulation and use of a binary mixture of protic ionic liquids (PILs) based on the same H-bond donor, pyrrolidinium cation, with nitrate ([Pyr][NO₃]) and bis(trifluoromethanesulfonyl) imide ([Pyr][TFSI]) anions as an electrolyte for carbon-based supercapacitors. The physico-chemical and thermal properties of mixtures as a function of composition and temperature were fully investigated and related to their electrochemical behavior as an electrolyte. The electrochemical characterization of some selected optimal compositions ($X_{[\text{Pyr}][\text{NO}_3]} = 0.64, 0.72, 0.80$) shows, at first, good capacitive behavior (up to 148 F g⁻¹) at a potential voltage of 2.0 V. Moreover, above 2.0 V, anion intercalation was observed, increasing the specific capacitance up to 209 F g⁻¹. At 2.5 V during cycling, the characteristic peak of anion intercalation/deintercalation decreases, caused by saturation of the positive electrode by anions. Finally, accelerated aging tests showed good capacity retention (> 80%) at 2.0 V during 110 hours for $X_{[\text{Pyr}][\text{NO}_3]} = 0.72$, at 25 °C. According to these results, the use of eutectic PIL binary mixtures is a promising way to design adapted electrolytes according to the material electrode for energy devices at room temperature.

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1. Introduction

Supercapacitors have been the subject of great interest because of their high-power storage capability, which is very desirable for applications in electric vehicles (EVs) and hybrid electric vehicles (HEVs) [1–3]. Carbon-based capacitors have attracted significant attention since these materials possess diversified morphologies with high stability and conductivity [4–9]. The electrical double-layer capacitors (EDLC), based on highly specific surface area carbon electrodes that operate by separation of charges at the electrode/electrolyte interface, are the most advanced and are already on the market [10]. Activated Carbons (ACs) are the most commonly used electrode materials for EDLC applications due to their relatively low cost and high surface area compared to other carbon materials. The attainable voltage of any supercapacitor device essentially depends on the electrolyte potential window, while the performance (power density and cyclability) depends both on the electrode nature and electrolyte properties, therefore,

the choice of the electrolyte is important. Although aqueous solutions are environment friendly and a low-cost solution, the low cell voltage attainable, and consequently low specific energy, is a disadvantage [11,12]. Organic electrolytes display a higher potential window, which is an advantage for high-energy applications; however, their main drawback is their volatility [13,14]. Owing to their unique properties of high chemical, thermal and electrochemical stability, good conductivity, low volatility, non-flammability and recyclability, ionic liquids (ILs) are considered as “key electrolytes” for the development of novel and safe electrochemical devices [15–19]. “Protic Ionic Liquids” (PILs) are referred to as a protic subgroup in the class of ambient temperature fluid systems, formed by the transfer of one proton between a Brønsted acid and a Brønsted base [20,21]. The labile proton creates donor and acceptor sites and can lead to the formation of hydrogen bonds [22]. These conducting electrolytes are starting to emerge as useful materials owing to their various potential applications, including electrolytes in batteries, fuel cells, double-layer capacitors and biosensors [23–33]. In the literature, some studies report the use of PILs [34–39], while there is a larger number of reports concerning aprotic ILs (AILs) [4,11,15–17,40–44] electrolyte formulations for supercapacitors. The main drawback of AILs is their transport

* Corresponding author. Tel.: +33 247366951; fax: +33 247367360.

E-mail address: laure.timperman@univ-tours.fr (L. Timperman).

properties (conductivity and viscosity) which are limiting for thermal condition of those electrochemical applications, i.e. room temperature.

Recently, AIL binary mixtures were reported as electrolytes for EDLC [45,46] and in mixtures with lithium salt for lithium ion battery systems [47,48]. For the latter, the results show a beneficial effect of the AIL mixture on electrochemical properties [47] and on the performance of the graphite electrode [48]. Moreover, EDLC can operate over a large temperature range, in a wide voltage window and at very high charge/discharge rates using a specific AIL binary mixture [45]. We have recently reported the use of PILs or AILs, pure or in mixtures with organic solvent (e.g. pyrrolidinium nitrate [49,50], triethylammonium bis(trifluoromethanesulfonyl) imide [34], or pyrrolidinium methane sulfonate in water [51], phosphonium tetrafluoroborate in acetonitrile [35], and sulfonium bis(trifluoromethane-sulfonyl) imide [52]). However, most of these ILs are solid or too viscous to be used in the pure form at room temperature, which is why they were mixed with a solvent or used at higher temperatures, such as 50 °C or 80 °C. The present work reports on the application at room temperature of PIL binary mixtures based on two PILs that are solid at this temperature: pyrrolidinium (HPyrr⁺) nitrate and pyrrolidinium (HPyrr⁺) bis(trifluoromethanesulfonyl) imide, which will be abbreviate, to simplify, as [Pyrr][NO₃] and [Pyrr][TFSI], respectively.

2. Experimental

2.1. Materials

Pyrrolidine (> 99%), hydrochloric acid (37%), nitric acid solution (68% in water) and 1,2-dichloroethane (DCE > 99%), commercially available from Sigma Aldrich, were used without further purification. Lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) ($\geq 99.0\%$) was obtained from Solvionic. Water was purified using a Mili-Q 18.3 M Ω system.

2.2. Preparation of PILs

Pyrrolidinium bis(trifluoromethanesulfonyl) imide ([Pyrr][TFSI]) PIL was synthesized by an equimolar metathesis method, as previously reported for triethylammonium bis(trifluoromethanesulfonyl) imide [34]. Pyrrolidinium nitrate [Pyrr][NO₃] was prepared according to the methodology previously described by our group [34,53].

In brief, for [Pyrr][NO₃] pyrrolidine (53.55 g) was firstly introduced into a three-necked round-bottom flask immersed in an ice bath and topped by a reflux condenser. A nitric acid solution (68.087 g) was added dropwise to the amine under vigorous stirring (30 min). As the acid-base reaction was slightly exothermic, an ice bath was used to maintain the temperature below 25 °C.

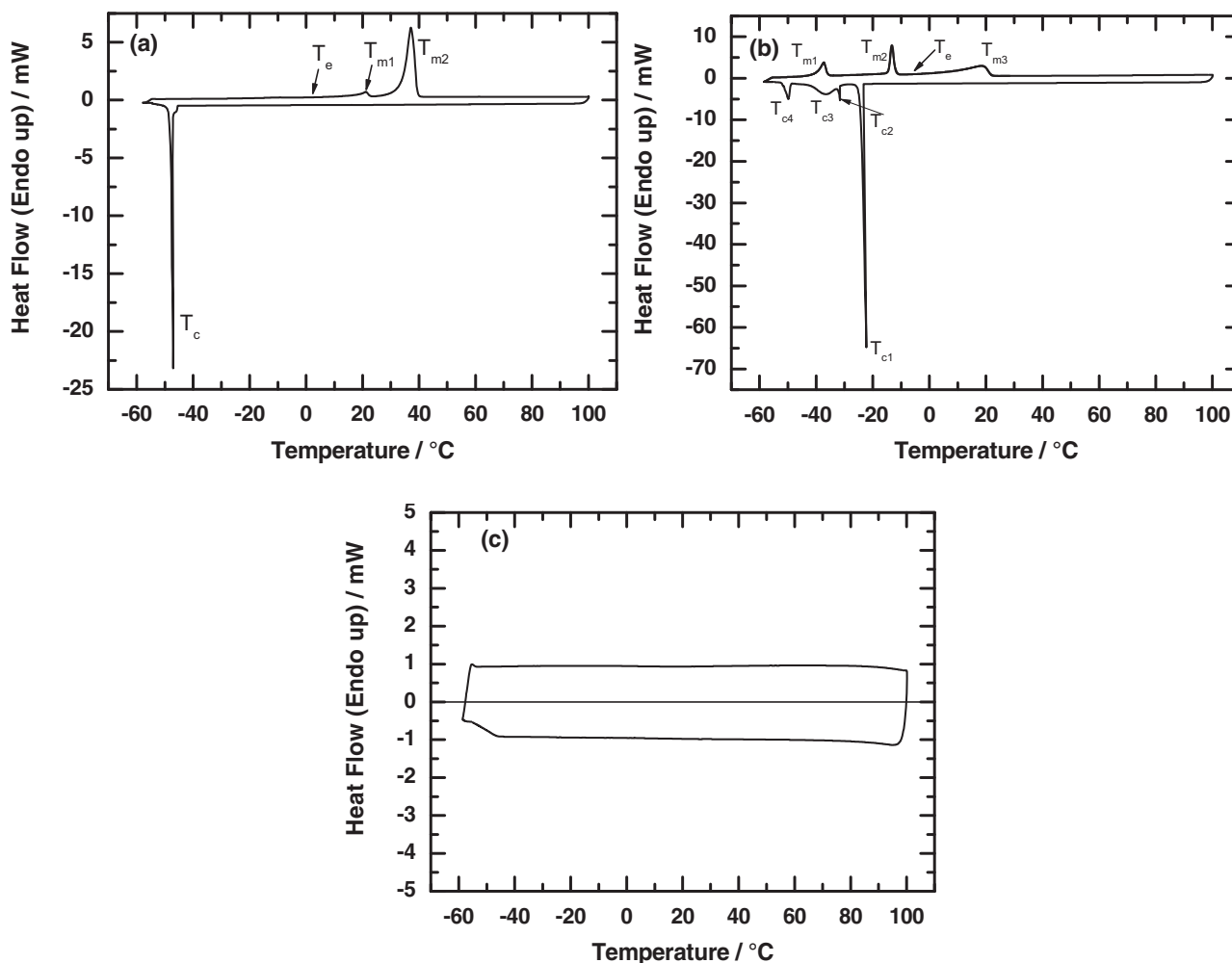


Fig. 1. DSC thermograms of pure [Pyrr][TFSI] (1000 ppm H₂O) (a), pure [Pyrr][NO₃] (1000 ppm H₂O) (b) and one binary mixture with $x[\text{Pyrr}][\text{NO}_3]=0.72$ (c), in the temperature range from -60 °C to 100 °C.

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