



Performance of solid state supercapacitors based on polymer electrolytes containing different ionic liquids



Girum Ayalneh Tiruye, David Muñoz-Torrero, Jesus Palma, Marc Anderson, Rebeca Marcilla*

Electrochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra 3, Parque Tecnológico de Móstoles, 28935, Móstoles, Spain

HIGHLIGHTS

- Different IL-b-PE are prepared by blending PILTFSI with 4 different ILs and used in SCs.
- Properties of IL-b-PE strongly depend on the nature of ILs & influences performance of SCs.
- σ of IL-b-PE with small anions (FSI and DCA) is higher than those with bigger anion (TFSI).
- SCs with IL-b-PE1 & 2 withstand 3.5 V while those with IL-b-PE3 & IL-b-PE4 is limited to 2.5 V.
- SC with IL-b-PE2 shows the best values of 150 F g^{-1} , 36 Wh kg^{-1} and 1170 W kg^{-1} at 3.5 V.

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ABSTRACT

Four Ionic Liquid based Polymer Electrolytes (IL-b-PE) were prepared by blending a Polymeric Ionic Liquid, Poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (PILTFSI), with four different ionic liquids: 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI) (IL-b-PE1), 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide (PYR₁₄FSI) (IL-b-PE2), 1-(2-hydroxy ethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HEMimTFSI) (IL-b-PE3), and 1-Butyl-1-methylpyrrolidinium dicyanamide, (PYR₁₄DCA) (IL-b-PE4). Physicochemical properties of IL-b-PE such as ionic conductivity, thermal and electrochemical stability were found to be dependent on the IL properties. For instance, ionic conductivity was significantly higher for IL-b-PE2 and IL-b-PE4 containing IL with small size anions (FSI and DCA) than IL-b-PE1 and IL-b-PE3 bearing IL with bigger anion (TFSI). On the other hand, wider electrochemical stability window (ESW) was found for IL-b-PE1 and IL-b-PE2 having ILs with electrochemically stable pyrrolidinium cation and FSI and TFSI anions. Solid state Supercapacitors (SCs) were assembled with activated carbon electrodes and their electrochemical performance was correlated with the polymer electrolyte properties. Best performance was obtained with SC having IL-b-PE2 that exhibited a good compromise between ionic conductivity and electrochemical window. Specific capacitance (C_{am}), real energy (E_{real}) & real power densities (P_{real}) as high as 150 F g^{-1} , 36 Wh kg^{-1} & 1170 W kg^{-1} were found at operating voltage of 3.5 V.

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1. Introduction

Supercapacitors (SCs), also named ultracapacitors or electric double layer capacitors (EDLCs), are electrochemical energy storage devices of preference when high power density and fast charge-discharge cycles are required. They store electrical energy by means of fast, reversible and simple formation of the double layer

in electrode/electrolyte interface [1–3]. Conventional SCs mostly utilize carbon electrodes with high specific surface area in combination with liquid electrolytes such as aqueous, organic, or more recently ionic liquids (ILs) [4,5]. Hence, the use of separators to avoid electric contacts between electrodes and heavy encapsulation materials to prevent liquid leakage is inevitable and make these SCs unsuitable to be integrated into textiles, microelectronics or lightweight energy storage systems [6].

One of the most promising strategies to design flexible and lightweight SCs is to replace liquid electrolytes by solid or quasi-solid polymer electrolytes thereby avoiding the strict sealing and

* Corresponding author.

E-mail address: rebeca.marcilla@imdea.org (R. Marcilla).

housing requirements [7]. So far, different families of polymer gel electrolytes have been investigated including aqueous and organic polymer gels, and more recently “iongels” which contain ionic liquids (ILs) [7–10]. In the case of aqueous polymer gel, hydrocarbon polymers such as polyvinyl alcohol (PVA) [11–13], poly(-methylmethacrylate) (PMMA) [14], perfluorosulfonic acid polymer (Nafion) [15–18] or sulfonated poly(ether ether ketone) (SPEEK) [19,20] were blended with acidic or basic aqueous electrolytes to obtain gel electrolytes with high ionic conductivity ranging from $2.5 \cdot 10^{-3}$ to $5 \cdot 10^{-2} \text{ Scm}^{-1}$ but with narrow electrochemical stability window (ESW) due to water electrolysis. Non-aqueous polymeric gels have also been examined as electrolytes of SCs. They consist of polar polymers matrixes such as polyethylene oxide (PEO) [21], poly(acrylonitrile) (PAN), polymethacrylate (PMA) [22] and copolymers of polyvinylidene difluoride (PVDF-HFP) swollen with organic electrolyte solution. However, the main disadvantage of both aqueous and non-aqueous polymer gel electrolytes in SCs is their low electrochemical stability window (ESW) which limits the device operating voltage up to 1 V for aqueous and 2.7 V for organic electrolytes and consequently restrains the energy and power densities of SCs. Moreover, the presence of volatile solvents in the device still makes it necessary to seal it to avoid possible evaporation.

In the last years, the development of iongels, which contain electrochemical stable and non-volatile ionic liquids in the polymer matrix, have attracted ever-increasing interest due to the unique characteristics of ILs. Several polymer matrices, including conventional PTFE [23], PVDF/-HFP [24–27], and polysaccharides [28,29] have been investigated in combination with ionic liquids to develop solid supercapacitors. Indeed, iongels present several advantages such as high thermal and electrochemical stability, high ionic conductivity, non-volatile and non-flammable components and appropriate mechanical properties that make them suitable for wide range of applications. Although ionic conductivity of those iongels (in the range of 10^{-4} – 10^{-2} Scm^{-1} at 25 °C) is generally lower than for hydrogels, they present some advantages such as higher electrochemical and thermal stability that make them promising candidates for high voltage electrochemical devices [30]. They can be prepared by simple blending of ILs with a polymer matrix [23,31,32] or by in-situ polymerization of a vinyl monomer in ILs [33]. As an example, PVDF-HFP was blended with 1-ethyl-3-methyl imidazolium tetrafluoroborate (EmimBF₄) and EmimTFSI and the resultant iongels were used in solid state SCs reaching specific energy value of 15 Wh kg^{-1} that was further improved up to 20 Wh kg^{-1} by adding a zeolite as conductivity enhancer. Other polymers such as PEO and PAN have been also jellified with ILs and used in solid SCs.

Polymeric ionic liquids (PILs) are a new class of functional polymers that combine the chemistry of ILs with the macromolecular architecture of polymers, providing the opportunity to create a new platform for the design of ionic liquid-based polymer electrolytes (IL-b-PE) with significantly improved properties [9]. The unique characteristic of PILs is that they have polymer-bearing ionic liquid features in their structures being more compatible with ILs to create more stable polymer electrolytes, hence better performance electrochemical devices [30,34]. Recently, we reported the use of a polymer electrolyte composed of Poly(-diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (PILTFSI) blended with 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI) in solid state SCs. Since both PIL and IL have the same anion (TFSI) and similar cation (pyrrolidinium) they present good compatibility, self-standing membrane even at high IL contents (up to 60% wt.), wide electrochemical stability window and high ionic conductivity. It was demonstrated that these solid state SCs could withstand high

voltages of 3.5 V resulting in real energy and real power densities as high as 32 Wh kg^{-1} and 800 W kg^{-1} respectively [35].

In this work we extend our research to different IL-b-PE to investigate the effect of the composition on the physicochemical properties of the polymer electrolytes. We report the synthesis of four different IL-b-PE having the same polymer matrix but different ILs and we analyze how the different properties of the ILs are translated to the polymer electrolytes and to the final performance of assembled solid state SCs.

2. Experimental

2.1. Materials

Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, $\geq 99\%$), 1-butyl-1-methylpyrrolidinium dicyanamide, (PYR₁₄DCA, $> 99.5\%$), 1-butyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide, (PYR₁₄FSI, $> 99.5\%$), 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide, (PYR₁₄TFSI, $\geq 99.5\%$) and 1-(2-hydroxy ethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HEMimTFSI, $\geq 99.5\%$) were purchased from Solvionic and stored inside the glove box. Poly(diallyldimethylammonium)chloride solution (pDADMAC) (average Mw 400,000 to 500,000, 20 wt % in H₂O) was obtained from Aldrich. Acetone (purity $\geq 99\%$) was used for the preparation of the electrolyte solution. NMP (N-methyl-2-pyrrolidone, analytical grade), polyvinylidene fluoride (PVDF, solution in water), carbon black (Alfa Aesar GmbH & Co KG, Germany) and activated carbon (Picatif BP 10, PICA) were used to prepare the carbon electrodes.

2.2. Preparation of ionic liquid based polymer electrolytes (IL-b-PE)

The polymeric ionic liquid, poly(diallyldimethylammonium) bis(trifluoromethanesulfonyl)imide (PILTFSI) was prepared by a simple ion exchange reaction from the commercially available poly(diallyldimethylammonium)chloride (pDADMAC) and Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) [34]. IL-b-PE solutions were prepared by dissolving 1.4 g of PILTFSI in 4 ml of acetone and adding the desired amount of ionic liquid; 2.1 g of PYR₁₄TFSI, PYR₁₄FSI, HEMimTFSI and 0.6 g of PYR₁₄DCA. Self-standing membranes were prepared by doctor blade technique using solvent casting method [35] and dried at 100 °C under vacuum overnight. The resulting polymer electrolytes were named IL-b-PE1, IL-b-PE2, IL-b-PE3 and IL-b-PE4, respectively. Scheme 1 also shows that IL-b-PE1, IL-b-PE2 and IL-b-PE3 membranes were colourless, transparent and flexible whereas IL-b-PE4 membrane was whitish and fragile.

2.3. Preparation of carbon electrodes and assembling of solid state supercapacitors

The method to prepare PICA carbon electrodes and the electrolyte impregnation process were explained in detail in our previous paper [35]. The composition of carbon electrodes was 80% of PICA activated carbon as active material (Picatif BP 10, $S_{\text{BET}} \sim 2000 \text{ m}^2 \text{ g}^{-1}$), 10% of carbon black as conductivity enhancer, and 10% of PVDF as polymeric binder. The electrode ink was prepared by mixing the three components in NMP using a ball-mill grinder. Doctor blade technique was used to spread the electrode ink onto aluminum current collector (25 μm thickness and 99% purity). After drying at 80 °C overnight, the carbon electrodes were cut into circular coin-shaped with 12 mm in diameter (geometrical area of 1.13 cm^2). The average thickness of carbon electrodes was about 100–160 μm corresponding to an average mass loading about 2–4 mgcm^{-2} .

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