

Solid-state electric double layer capacitors fabricated with plastic crystal based flexible gel polymer electrolytes: Effective role of electrolyte anions



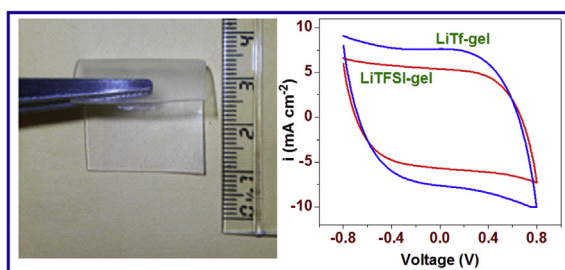
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HIGHLIGHTS

- Flexible EDLCs with succinonitrile based gel electrolyte membranes are reported.
- Anionic size of salts in gel electrolytes plays important role on capacitive performance.
- Li-triflate incorporated gel electrolyte shows better performance over LiTFSI-based gel.
- Highest specific capacitance, energy and power are 240 F g^{-1} , 39 Wh kg^{-1} and 19 kW kg^{-1} , respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

Flexible gel polymer electrolyte (GPE) thick films incorporated with solutions of lithium trifluoromethanesulfonate (Li-triflate or LiTf) and lithium bis trifluoromethane-sulfonimide (LiTFSI) in a plastic crystal succinonitrile (SN), entrapped in poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) have been prepared and characterized. The films have been used as electrolytes in the electrical double layer capacitors (EDLCs). Coconut-shell derived activated carbon with high specific surface area ($\sim 2100 \text{ m}^2 \text{ g}^{-1}$) and mixed (micro- and meso-) porosity has been used as EDLC electrodes. The structural, thermal, and electrochemical characterization of the GPEs have been performed using scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), impedance measurements and cyclic voltammetry. The high ionic conductivity ($\sim 10^{-3} \text{ S cm}^{-1}$ at 25°C), good electrochemical stability window ($>4.0 \text{ V}$) and flexible nature of the free-standing films of GPEs show their competence in the fabrication of EDLCs. The EDLCs have been tested using electrochemical impedance spectroscopy, cyclic voltammetry, and charge–discharge studies. The EDLCs using LiTf based electrolyte have been found to give higher values of specific capacitance, specific energy, power density (240 – 280 F g^{-1} , $\sim 39 \text{ Wh kg}^{-1}$ and $\sim 19 \text{ kW kg}^{-1}$, respectively) than the EDLC cell with LiTFSI based gel electrolyte. EDLCs have been found to show stable performance for $\sim 10^4$ charge–discharge cycles. The comparative studies indicate the effective role of electrolyte anions on the capacitive performance of the solid-state EDLCs.

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1. Introduction

Electrochemical supercapacitors are energy storage devices,

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which are known for their high specific capacitance, high specific power, moderate specific energy, long cycle life and operational safety [1–6]. Electrical double layer capacitors (EDLCs) and redox supercapacitors (or pseudocapacitors) are two important classes of supercapacitors with symmetrical electrodes, classified on the basis of the types of electrode materials employed and charge-storage mechanisms [1,5,6]. In pseudocapacitors, fast redox reactions in electrode materials (transition metal oxides or conducting polymers), interfaced with electrolyte are responsible for high capacitance, whereas the charge storage at the interface between a polarizable electrode (e.g. different forms of carbon) and an electrolyte is accountable for the high capacitance in EDLCs [1–6]. Amongst various forms of carbon, activated carbons extracted from various sources e.g. poly acrylonitrile (PAN) [7], coal-tar pitch [8], carbides [9], including biomaterials namely; coconut shell [10], coffee shell [11], tea-leaves [12], poplar wood [13], etc. are the potential materials to be used as capacitor electrodes to develop cost-effective EDLCs with high specific capacitance.

Liquid electrolytes, in aqueous or organic media, are generally employed as separators in most of the reported EDLCs/supercapacitors [1,6,14,15], which suffer from various limitations/drawbacks including bulky size, corrosion with electrodes and/or current collectors, self-discharge, electrolyte leakage, etc. The gel polymer electrolytes (GPEs), in the form of free standing thick films, have recently been proven to be the prospective substitutes of liquid electrolytes for their applications in electrochemical devices [6,16–18]. GPEs, comprising liquid electrolytes (e.g. salt solutions in polar organic solvents) immobilized in host polymers like poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP), poly(methyl methacrylate) (PMMA), PAN, etc. [15–19], possess liquid-like ionic conductivity with uniform electrolyte distribution and solid-like mechanical integrity [6,15–24]. GPEs have been modified in various ways to improve their mechanical, thermal and electrochemical properties, which include the addition of active or passive ceramic fillers to form their composites [25–27] and the use of ionic liquids (ILs) as solvents/plasticizers to replace organic solvents like propylene carbonate (PC), ethylene carbonate (EC), etc. [25–30]. The replacement of volatile and flammable organic solvents by non-volatile, non-flammable and high ion conducting ILs is an approach to obtain GPEs with excellent thermal and electrochemical stabilities. However, such GPEs possess cumbersome ionic conduction process due to the mobility of component ions of ILs along with the conduction of Li^+ like target ions from the salts [31].

Recently, few polymer-based electrolytes are reported employing a non-ionic plastic crystalline material succinonitrile (SN) as solid solvent/plasticizer to replace organic solvents or ILs [32–38]. Such emerging electrolytes are the materials of technological interest due to their non-volatile and less flammable character as compared to liquid organic solvents like acetonitrile, PC, etc., ability of proper electrode-electrolyte contacts in devices and safely concern. Plastic crystals are basically the compounds formed by disk like molecules having short range rotational disorder but retaining long range translational order [39,40]. SN has been mostly used to form polymer electrolytes/GPEs as it possesses high dielectric constant (~55 at room temperature) due to its polar character and hence it shows the ability to dissociate the salts for high ionic conductivity [32–36]. Further, in its trans-gauche isomer form, which involves rotation of molecules about the central C–C bond, the SN molecules help to increase the mobility of ions in the electrolytes via paddle-wheel mechanism [36,39,41]. However, the binary SN/salt electrolyte systems [39] lack the mechanical integrity. So, the formation of GPEs by immobilizing these binary systems in host polymers like PVdF-HFP, PMMA, PAN, PEO, etc. is a useful approach to obtain free-standing and flexible films with

excellent electrochemical properties including high ionic conductivity [32–38].

Lithium ion conducting GPEs are well studied systems containing a variety of Li-salts with different bulky anions e.g. ClO_4^- , BF_4^- , PF_6^- , AsF_6^- , CF_3SO_3^- (triflate), $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ (TFSI), etc. [16,17]. Each anion has some merits and demerits from the application point of view, particularly, in batteries and supercapacitors. We have prepared two SN-based GPE films in the present work using two Li-salts namely; lithium trifluoromethanesulfonate (Li-triflate or LiTf) and lithium bis(trifluoromethane sulfonyl)imide (LiTFSI), and compared their performance in EDLCs. These LiTf and LiTFSI salts have enough capability to replace hazardous LiClO_4 , the thermally unstable LiPF_6 and LiBF_4 , the toxic LiAsF_6 in electrochemical applications, particularly in Li-batteries [42]. These sulfonate ($-\text{SO}_3^-$) containing species become the anions of choice because they are highly resistant to oxidation, thermally stable, nontoxic, and insensitive to ambient moisture as compared to many Li-salts [42]. The imide (TFSI) anion, which is stabilized with two triflic groups, has proven to offer excellent electrochemical properties. Because of the high dissociation constant, the lithium salt LiTFSI shows the highest ionic conductivity in organic media, higher than LiTf, although the average ionic mobility of LiTf is higher than that of LiTFSI [42].

In this paper, we report the studies on GPEs comprising the solution of LiTf or LiTFSI in a plastic crystalline material SN, immobilized in a host polymer PVdF-HFP for their application as electrolytes to fabricate EDLCs. Structural/morphological, thermal and electrochemical properties of the GPEs have been characterized using various physical techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), thermo-gravimetric analysis (TGA), impedance/electrical conductivity measurements and linear sweep voltammetry. The symmetrical EDLCs have been fabricated with activated carbon electrodes (containing mixed micro- and mesoporosity, derived from coconut shell) and their performance has been tested using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV), galvanostatic charge–discharge and prolonged cyclic test. Studies indicate that the nature of Li-salts in GPEs, particularly the ionic dissociation of salts in a common dielectric medium and the anionic sizes, play the important role on the capacitive performance of EDLCs.

2. Experimental

2.1. Preparation of SN-based gel polymer electrolytes

The co-polymer, PVdF-HFP (average MW ~400 000), succinonitrile (SN), lithium salts namely: lithium trifluoromethanesulfonate (Li-triflate or LiTf) and lithium bis(trifluoromethane-sulfonyl)imide (LiTFSI) were procured from Sigma–Aldrich and used without further purification. The lithium salts were vacuum dried at $\sim 80^\circ\text{C}$ for ~ 12 h prior to use. The PVdF-HFP and SN were vacuum dried at room temperature. The GPE films were prepared by “solution-cast” technique. Following this technique, 5 mol% solution of LiTf or LiTFSI in SN was prepared separately in a common solvent acetone. These solutions were added to the host polymer PVdF-HFP (separately dissolved in acetone) in 80:20 (w/w) ratio and stirred thoroughly using magnetic stirrer at room temperature for ~ 24 h until the mixture appeared to be homogeneous. The mixtures were cast over glass petridishes and allowed to evaporate the common solvent acetone slowly. Finally, free-standing GPE films of thickness ~ 350 – 400 μm were obtained. All the GPE films were stored in dry atmosphere to avoid moisture adsorption. The compositions of GPEs are expressed as follows:

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