



Optimization of porous polymer electrolyte for quasi-solid-state electrical double layer supercapacitor



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ABSTRACT

We report the poly(vinylidene fluoride-co-hexfluoropropylene) (PVdF-HFP) based porous polymer electrolyte membranes, prepared via phase-inversion/solvent-nonsolvent methods, activated with an organic liquid electrolyte ethylene carbonate (EC):propylene carbonate (PC)-NaClO₄ for the application in electric double layer capacitor (EDLC). The simple, quick and environment-friendly phase-inversion method, involving condensing steam as non-solvent, has been taken as the optimized process to obtain the porous PVdF-HFP film. The films of porous PVdF-HFP and the electrolyte (after soaking with liquid electrolyte) have been characterized for their morphological/structural aspects, porosity, liquid electrolyte retention, interaction with electrolyte, thermal properties, electrochemical stability and ionic conductivity. A pore-formation mechanism during phase-inversion at 100 °C has been proposed on the basis of thermal studies. The electrolyte film has been found to have excellent mechanical flexibility, porosity (~80%), electrolyte retention (~400%), ionic conductivity (~2 mS cm⁻¹ at room temperature), and electrochemical stability window (ESW) of ~4.35 V. The EDLC, fabricated with activated carbon electrodes and porous polymer electrolyte, exhibits excellent performance characteristics in terms of the specific capacitance (~150 F g⁻¹, evaluated from EIS), specific energy (~17.7 Wh kg⁻¹) and specific power (14.3 kW kg⁻¹). The device shows stable specific capacitance (after ~17% initial fading) and high Coulombic efficiency (over 99%) for ~10,000 charge-discharge cycles.

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1. Introduction

Polymer-based electrolytes are widely used in energy storage devices like ion-batteries and supercapacitors due to their various advantageous properties including leakage prevention, flexibility, mechanical/dimensional stability, low dendrite formation tendency, etc. [1–4]. They are generally categorized in two broad classes namely: (i) solvent-free solid polymer electrolytes (SPEs), and (ii) gel polymer electrolytes (GPEs) [1–4]. While SPEs increase device safety by preventing direct contact between the electrodes, they have lower ionic conductivity than the bulk liquid electrolytes and also suffer from problems like poor interfacial contacts at electrolyte-electrode interfaces [3–6]. On the other hand, GPEs are a class of polymer electrolytes comprising aqueous, organic or ionic liquid based liquid electrolytes immobilized in host polymers e.g. poly vinylidene fluoride (PVdF), poly vinylidene fluoride-co-

hexafluoropropylene (PVdF-HFP), poly methyl methacrylate (PMMA), poly ethylene oxide (PEO), etc. [7–16]. Such electrolytes are of quasi-solid state nature offering liquid-like ionic conductivity of the order of 10⁻⁴–10⁻² S cm⁻¹ at room or ambient temperatures. Although these electrolytes are widely used these days in various energy storage applications e.g. Li/Na-ion batteries, supercapacitors etc. [7,13–20], they suffer from few drawbacks including poor mechanical and thermal stabilities.

Another important class of polymer-based electrolytes, referred as porous polymer electrolytes (PPEs) or microporous gel polymer electrolytes (MPEs), was introduced by Tarascon and coworkers [21]. The first PPE was prepared by the extraction/activation process in which di-butyl phthalate (DBP) was extracted from the solvent-cast film of PVdF-HFP and DBP mixture by solvent-extraction process [21]. This process was followed by soaking of liquid electrolyte (ethylene carbonate (EC)-dimethyl carbonate (DMC)-LiPF₆), referred as activation process. However, the extraction method to prepare porous membranes has been found to be tedious and expensive due to the large consumption of organic solvents to extract DBP like components [22,23]. Thereafter, the phase-inversion technique has become a popular method to

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prepare porous films of polymers, introduced by Du Pasquier et al. [24]. In this method, the solvent/non-solvent mixture is allowed to evaporate simultaneously from the polymer solution, which is cast to prepare the film. Thereafter, various PPEs have been reported based on porous polymer membranes prepared from different host polymers e.g. PVdF, PVdF-HFP, PEO, PMMA, polyacrylonitrile (PAN), polyvinyl carbonate (PVC), etc. [25–38]. The porous membranes have been activated by different organic liquid electrolytes viz: $\text{LiPF}_6/\text{EC-PC}$ [21], $\text{LiPF}_6/\text{EC-DMC}$ [25,31,38], $\text{LiClO}_4/\text{EC-PC}$ [26,28,34], $\text{LiClO}_4/\text{EC-DMC}$ [27], $\text{LiBF}_4/\text{EC-DMC}$ [27], $\text{LiPF}_6/\text{EC-DEC}$ [29,36], $\text{LiClO}_4/\text{EC-DEC}$ [30], $\text{LiPF}_6/\text{EC-DMC-EMC}$ [32,33,37], $\text{LiTFSI}/\text{EC-DMC}$ [37], $\text{LiBOB}/\text{EC-DMC}$ [37], $\text{LiClO}_4\text{-BMIMBF}_4$ [36], etc., to develop potential PPEs. The room temperature ionic conductivity values reported for such porous electrolytes are of the order of 10^{-3} – $10^{-2} \text{ S cm}^{-1}$. Such electrolytes have been reported for use as promising separators/electrolytes in lithium-ion systems. Few porous systems have been reported for sodium ion batteries also e.g. a porous PVdF-HFP film has been reported offering ionic conductivity of $0.60 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature after activation with 1 M NaClO_4 in EC:DC:DEC and shows better electrochemical performance compared to commercial (Celgard 2730) membrane [23].

Electrical double layer capacitors (EDLCs), also referred as supercapacitors, are a class of energy storage devices, in which high surface area porous carbon electrodes are employed to form electrochemical cells, separated by liquid or polymer-based electrolytes [39–43]. Various forms of carbon are used in EDLC electrodes including, primarily, activated carbon (AC; powder, fibre or fabric) [39–45], carbon nanotubes (CNTs) [16,41,42,46,47], carbon nanofibres (CNFs) [48–50], carbon aerogels [51] and graphene [17,40,52,53,56]. Most of the reported EDLCs are based on liquid electrolytes, which are soaked with different types of commercially available separators [41,42,51–55]. In recent years, the gel polymer electrolytes have been widely reported as separators/electrolytes in EDLCs due to their advantageous properties including their high ionic conductivity and flexible nature [16,17,45–47,49]. Except a few studies [57–59], the PPEs have been hardly used as electrolytes in EDLCs/supercapacitors, despite their excellent electrochemical and mechanical properties. In the present study, we report the porous polymer electrolytes based on PVdF-HFP porous films, prepared by phase-inversion technique using two different combinations of solvents and non-solvents namely DMF/glycerol and DMF/water (steam), activated by the liquid electrolyte EC-PC- NaClO_4 . Morphological, structural, porosity and electrochemical studies have been performed to test the suitability of PPEs as EDLC-electrolyte. The optimized PPE film has been employed to fabricate EDLCs using commercial activated carbon electrodes. The performance of the EDLC cells has been evaluated by a.c. impedance spectroscopy, cyclic voltammetry and galvanostatic charge–discharge tests.

2. Experimental

2.1. Preparation of porous films

PVdF-HFP (average molecular weight $\sim 400,000$) was procured from Sigma-Aldrich and used as received. DMF (AR grade) and

glycerol (GR grade) were obtained from Spectrochem (India) and Merck, respectively. Porous PVdF-HFP films were prepared by phase-inversion (PI) and solvent-nonsolvent (SNS) methods. In the phase-inversion process, steam at the atmospheric pressure was used as the non-solvent, and DMF was employed as the solvent. 1 g of P(VdF-HFP) was dissolved in 20 ml of DMF by continuous stirring for 12 hours at $\sim 80^\circ\text{C}$ using a magnetic stirrer. After full dissolution, the solution was poured in a glass petridish. The solution in the petridish was then kept in the steam atmosphere at 100°C at normal pressure ($\sim 1 \text{ atm}$). The humid atmosphere initiates a diffusive injection of water (non-solvent) in the solution [60], whereas the heat from the injected water helps in the evaporation of DMF. After the slow cooling, the phase separation started quickly and film like texture was obtained within the first 15 minutes. The complete removal of DMF happened in about 1 hour after which the light-brownish and smooth porous film was peeled-off from the dish. The film was washed with double distilled water once or twice and kept to dry in a vacuum oven at $\sim 60^\circ\text{C}$ overnight.

In the solvent-nonsolvent process, the glycerol was used as the non-solvent and pore inducer, and DMF as the solvent. The PVdF-HFP solution was stirred thoroughly for 12 hours at $\sim 80^\circ\text{C}$ and then kept for vacuum drying in a glass petri-dish at $\sim 80^\circ\text{C}$ until the complete evaporation of DMF. The glycerol was then washed away with double-distilled water. A porous and smooth film was obtained which was further dried at 60°C to remove the traces of water. Five porous films were prepared using the solvent/non-solvent method by varying the amount of glycerol (non-solvent), i.e. 1, 2, 3, 4 and 5 ml of glycerol in 20 ml DMF. The film made by phase-inversion process is coded as PI-film while the films made by solvent/non-solvent process are given the code SNS- x ($x = 1, 2, 3, 4, 5 \text{ ml of glycerol}$). Table 1 summarizes the method of preparation, codes, etc.

2.2. Physical characterization of porous polymer electrolytes

The morphology and structure of the porous films was characterized using field-emission scanning electron microscopy (FESEM) and high resolution X-ray diffraction (HR-XRD). Fourier-transform infrared (FTIR) spectroscopy was also used to identify different possible interactions of the salt-solvent-polymer. FESEM was performed using a TESCAN MIRA3 LMH (Czechoslovakia) instrument, set at a potential difference of 20 kV. Samples for FESEM were sputtered with gold to prepare conductive surfaces. The HR-XRD was performed on an X-ray diffractometer (D8 Discover, Bruker AXS Analytical Instruments, Germany) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) with 2θ varying from 5 to 60° at a scan rate of 2° min^{-1} . FTIR measurements were performed on a Spectrum RX I FT-IR Spectrophotometer (Perkin-Elmer, USA) in the wave number range from 400 to 4000 cm^{-1} . The spectra were recorded by averaging 32 scans per sample with an optical resolution of 4 cm^{-1} . Thermo-gravimetric analysis (TGA) was done on a Perkin Elmer TGA7 system from room temperature to 600°C at a heating rate of $10^\circ\text{C min}^{-1}$ in dry N_2 atmosphere. The modulated differential scanning calorimetry (mDSC) was performed using Differential Scanning Calorimeter (model Q100, TA Instruments) for the temperature range from -80°C to 180°C at a heating rate of 3°C min^{-1} in static N_2 atmosphere. The samples were kept in sealed aluminum pans for the DSC analysis.

Table 1

Name and codes of films prepared by various methods .

Method of preparation	Solvent	Non-solvent	Codes
Solvent-cast	Acetone	–	–
Phase Inversion	DMF (20 ml)	Steam/Water	PI
Solvent Non-solvent	DMF (20 ml)	Glycerol (x ml), 'x' = 1, 2, 3, 4, 5	SNS-'x'

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