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Electroactive poly(vinylidene fluoride) fluoride separator for sodium ion battery with high coulombic efficiency

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ABSTRACT

Electroactive separators are recent interest in self-charging rechargeable batteries. In this study, electrospun polyvinylidene fluoride (PVDF) is characterized as an electroactive separator for Na-ion batteries. The intrinsic β-phase with high porosity of the separator is confirmed from X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Field emission scanning electron microscopy (FESEM) and Atomic Force Microscopy (AFM) studies. The electroactive separator is immersed in 1M $NaClO_4$-ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by weight) solution. The physicochemical characteristics of electroactive separator electrolyte (EaSE) were investigated using sodium ion conductivity, ion transference number and contact angle measurements. Linear and cyclic voltammetry studies were also carried out for the electrolyte system to evaluate oxidation stability window. The inherent β-phases of the separator as obtained by electrospinning has an ionic conductivity of ~7.38×10^{-4} S cm^{-1} under ambient condition. Sodium ion cell made from EaSE with $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ as cathode and Na metal as anode has displayed a stable cycle performance with a coulombic efficiency of 92% after 90 cycles.

1. Introduction

Sodium ion batteries (SIB) are among the emerging rechargeable batteries for portable electronics in recent years. Sodium (Na) based compounds have made a comeback due to increased cost of Li metal. Apart from the low cost, natural abundance of sodium and its satisfactory electrochemical potential (−2.7 V) on standard hydrogen electrode makes it attractive for the rechargeable batteries [1–3]. Some cathode and anode materials have been identified and tested for Na battery application [2,4]. The electrolyte separator system (ESS) is also one of the critical aspects of the galvanostatic charging-discharging processes [4]. The primary function of the ESS is to insulate the electrodes while maintaining the reservoir of electrolyte and control of Na ions transport. Though this area is not explored extensively for Na-ion batteries, separators like polypropylene, glass fiber [5] polyethylene oxide and polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) are being regularly used [6].

The electroactive polyvinylidene fluoride (PVDF) are piezoelectric in nature and have numerous applications in actuators, sensors and energy harvesters etc. Electroactive separator electrolyte (EaSE) based on PVDF have attracted considerable attention in Li-ion batteries for self-charging power cell that hybridizes the mechanical and chemical energy for self-charging of the battery [7–10]. The EaSE system consists of ionic salt as the electrolyte in the electroactive polymer matrix separator.

PVDF is a semi-crystalline polymer with a good affinity for polar organic electrolytes. It mainly exists in five different crystalline phases namely, α, β, and γ where β and γ are polar lattices. The β phase is the most electroactive one with a dipole moment of 8×10^{-30} cm electroactive in nature. The electroactive phases are inherent due to the spatial arrangement of electric dipoles contributed by the polar C–F bonds in the polymer chain. In recent years, ionic conductivity and oxidation stability of polyvinylidene fluoride and its copolymers poly(vinylidene fluoride-co-tri-fluoroethylene), PVDF-TrFE, polyvinylidene fluoride-co-hexa-fluoroporpylene, PVDF-HFP [9–12] have been improved in the organic solvent electrolyte. These are widely used as polymer separator for lithium ion battery due to their high dielectric constant and strong electron withdrawing functional groups, which can also be advantageous to the dissociation of sodium salts; however only a few reports are available based on the study of ionic conductivity of Na with the PVDF ESS [6,13]. The safety of the ESS can also been improved using PVdF-glass fiber mats composite [14].

Though the β phase is electroactive, it is relatively more crystalline and hence it is believed that the high crystallinity could cause low ionic conductivity and low stability due to the reduced migration rate

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of lithium ions in the crystalline phase. Efforts were directed towards lowering the crystallinity of non-woven mats by suitable PVDF copolymers or modified PVDF [10]. Alternatively one can improve the porosity and the wettability of the separator to increase the ionic conductivity and to reduce the cell resistance [15]. The electroactive phases of PVDF are obtained by several techniques such as solution casting, spin coating and Langmuir–Blodgett deposition. But these microporous membranes are handicapped by low porosity and poor wettability [10, 16–18]. Electrospinning is another useful technique to obtain non-woven mats with fiber diameters ranging from micrometers to a few nanometers. In electrospinning, the β phase is formed through in-situ poling and stretching of the polymer solution [19]. Electrospun fibrous membranes have advantages of high porosity, interconnected open pore web network structure, large surface area, which are essential for proper electrolyte uptake and ionic conductivity [9]. The crystalline electroactive and highly porous PVDF membrane produced by electrospinning are reported in the current work. Above 90 cycles are observed retaining coulombic efficiency of more than 90% of the sodium cells composed of $Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ cathode and Na metal anode.

2. Experimental

2.1. Optimization of the electrospinning process

Several experiments are performed by optimizing the process parameters to get bead free and uniform, but smaller average fiber diameter with electroactive phase. Various parameters like polymer concentration, voltage, flow rate, needle to collector distance, temperature etc. influence the physical features of the polymer membrane [20–22]. Dimethyl sulfoxide (DMSO) is used as the major solvent in our experiment. Guo et al. [23] reported that DMSO can cause instability as its high dielectric constant leads to misalignment of fibers. But the solvents with lower dielectric constants contain less free charge available at the surface and hence, diminishes the electrostatic repulsion. The addition of acetone, which has a dielectric constant of 21, decreased the instability and helped in the formation of aligned fibers. Acetone can also make the solvent more volatile that can stabilize the jet for longer distances from the spinneret to the drum collector fixed at 1200 rpm and thereby can improve the fiber alignment. PVDF is dissolved in DMSO/acetone mixtures optimized to 8:2 by weight ratio. In this study, we varied polymer concentration and voltage for the optimization are varied while keeping flow rate, needle to collector distance, temperature and humidity at a fixed value. The critical parameter to get a bead free structure with electroactive phase is the voltage, and it was varied from 10 kV, 15 kV, 20 kV and 25 kV respectively. The increase in solution concentration further improves the viscosity of the solution. Higher viscosity aids in the formation of smooth and uniform fibers as it attains enough entanglement concentration [21]. Thus, it also helps in reducing the formation of beads. The fiber diameter is decreased with an increase in voltage at all the concentration levels and, bead formation is also suppressed with the applied voltage. With increase in net charge built up on the surface, the electrostatic repulsion is increased. Considering the high electrostatic field and PVDF concentration of the electrospinning process, the electroactive phase is formed through in-situ poling and mechanical stretching of the polymer solution.

2.2. Preparation of EaSE and cathode

The PVDF powder (average M_w ~ 534,000), DMSO and Sodium perchlorate ($NaClO_4$) are purchased from Alfa Aesar; EC and DEC purchased from Sigma-Aldrich was used without further purification. The polymer solution for electrospinning is prepared by adding 19% by weight of PVDF to 10 mL of DMSO. Considering the high boiling point of DMSO, the temperature during electrospinning is increased to a higher 44 ± 1 °C using an IR light source and the temperature continuously monitored using a thermometer placed inside the electrospinning chamber. The humidity, needle to collector (drum collector) distance, applied voltage, spinning time and the flow rate were 30 ± 2%, 10 cm, 25 kV, 6 h and 0.5 mlph respectively. The microporous membranes obtained after electrospinning are swollen by immersing in 1M $NaClO_4$-EC: DEC (1:1 by weight) solution to form EaSE. The immersion is carried out inside an argon filled glovebox.

$Na_{0.66}Fe_{0.5}Mn_{0.5}O_2$ is prepared by a solid-state reaction using high purity starting precursors of Na_2CO_3, Fe_2O_3, and Mn_2O_3.·The appropriate stoichiometric amounts of these starting materials were ground using a mortar and pestle and pressed into pellets. These pellets are heat-treated at 900 °C for 12 h in air. The pellets are quenched to room temperature by using a copper plate and stored in the glovebox. The cathode electrode is prepared by mixing active material, acetylene black and PVDF binder (8:1:1) in the weight ratio and pasted onto the aluminium current collector [24].

2.3. Physico-chemical characterization of EaSE

X-ray diffraction (XRD) pattern of the PVDF membrane is recorded using a Bruker diffractometer with Cu Kα radiation (λ = 1.54 A).The crystallinity of the membrane is found by peak deconvolution method. The percentage of β crystallinity of membrane is calculated using Eq. (1) [25].

$$\text{Crystallinity of } \beta\ (\%) = \left(A_\beta/(A_\alpha + A_\beta)\right) \times 100\% \tag{1}$$

where A_β, A_α are respectively the area of the β-phase and α-phases.

FTIR spectra (Nexus-870) in ATR mode in the region of 4000–600 cm^{-1} and 32 scans are collected with a spectral resolution of 0.5 cm^{-1}. An average of three scans for each sample is taken for the measurement. Morphology of the polymer membrane is then observed using Field emission scanning electron microscope (Merlin, Germany). Atomic Force Microscope (Agilent 5500) in tapping mode is used to obtain the 3-dimensional topography image of the sample. The porosity is estimated from Eq. (2) [9].

$$\text{Porosity } (\%) = ((Mw - Md)/(\rho_b \times V_m)) \times 100\% \tag{2}$$

where M_w and M_d, ρ_b and are V_m masses of the wet and dry membrane, the density of butanol and the geometric volume of the membrane, respectively.

The static contact angle of 5 μL electrolyte droplet is measured using Contact Angle Goniometer (Rame-Hart instrument & Co. Model no-90F2). It is measured between the electrolyte and the separator to describe the features of electrolyte wettability. Electrolyte uptake by the membrane is assessed by soaking the membrane (1.4 × 1.4 cm^2) in the liquid electrolyte, 1 M $NaClO_4$ in EC/DEC solution. The weight of the wet membrane is measured after removing the excess electrolyte on the surface by using a tissue paper. Electrolyte uptake is calculated using the Eq. (3).

$$\text{Electrolyte uptake}, S_W(\%) = \left((M_{wet} - M_{dry})/M_{dry}\right) \times 100\% \tag{3}$$

where M_{wet} and M_{dry} are the masses of liquid electrolyte soaked and dry membrane respectively.

The ionic conductivity of EaSE is measured by AC impedance spectroscopy using electrochemical workstation (Hioki 3532–50 LCR tester) with in a frequency range of 50 Hz to 1 MHz with 10 mV of AC amplitude at various temperatures. The soaked separator is sandwiched between two stainless steel (SS/EaSE/SS system) and sealed in CR2032 coin cell shells. The ionic conductivity of the separator (σ) is calculated using the equation:

$$\sigma = t/(R_{EaSE} \times A) \tag{4}$$

where R_{EaSE} is the resistance obtained from the intercept of the Nyquist plot with the real axis, the membrane thickness (t), and the electrode