Quasi-Solid State Polymer Electrolytes Based on PVdF-HFP Host Polymer for Sodium-Ion Secondary Batteries

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Abstract. Prices of lithium raw materials keep on increasing exponentially due to their heavy consumption for lithium batteries used in portable electronic devices as well as automobiles. Also, the global lithium deposits are very limited. Hence, sodium-ion batteries (SIBs) have been heavily investigated as cheaper alternatives to expensive lithium-ion batteries, mainly due to the abundance of sodium raw materials. However, one of the major bottlenecks faced by the material research community to commercialize SIBs is the poor ionic conductivity of sodium-ion conducting electrolytes at ambient temperature, especially in the solid-state. Very recently, quasi-solid state polymer electrolytes (QSSPEs) have been proposed to overcome this challenge. In this work, a set of OSSPEs have been synthesized by using poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) host polymer and NaBF4 ionic salt dissolved in EC/PC plasticizer/solvent mixture. The highest conducting composition; 6 PVdF-HFP: 14 NaBF4: 40 EC: 40 PC (wt.%); showed an ambient temperature ionic conductivity of 4.1×10^{-3} S cm⁻¹. The activation energy is almost same for all the sample compositions studied in this work suggesting that the activation process is mainly controlled by EC/PC. DC polarization test on highest conducting electrolyte composition with a configuration of SS/QSSPE/SS revealed that the electrolyte is predominantly ionic conductor with negligible electronic conductivity; a much desired property for a good electrolyte. Linear sweep voltammetric studies confirmed that the electrochemical stability window of the highest conducting electrolyte is about 3.6 V. This highest conducting electrolyte composition is found to be highly suitable for practical applications in sodium batteries.

Introduction

Due to ever increasing prices and limited global resources of lithium raw materials, search for alternative battery chemistries is becoming highly urgent. Sodium-ion batteries (SIBs) are the most promising alternative chemistries, because sodium is naturally abundant, low cost, low toxicity and has highly suitable redox potential; $E^{\circ}(Na/Na^{+}) = -2.71 \text{ V}$ [1-2]. However, one of the major bottlenecks for commercial production of SIBs is the poor ambient temperature ionic conductivities of sodium-ion conducting electrolytes, especially in the solid-state. Several liquid electrolytes such as organic liquids, aqueous liquids and ionic liquids have been investigated to overcome these challenges, but these liquid electrolytes pose leakage problems and safety issues; particularly there are potential fire hazards when aqueous electrolytes are used with sodium metal anodes [3]. Quasisolid state polymer electrolytes (QSSPEs) have been recently studied as electrolytes having intermediate properties between solids and liquids; which are simply formed with liquid electrolytes entrapped in some polymer matrices. They have high ambient temperature ionic conductivities with excellent dimensional and electrochemical properties. As far as sodium ion conducting QSSPEs are concerned, poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) is a most commonly used commercially available host polymer due to its good film-forming, high thermal and chemical stabilities. Electrochemical stability arises because of strong electron-withdrawing functional groups (-C-F-) [4]. Also, high dielectric constant ($\varepsilon_r = 8.4$) of PVdF-HFP helps to dissociate the ions well in the polymer medium. Further, the amorphous phase (HFP) present in the matrix helps to entrap large amount of liquid electrolyte and the crystalline phase (PVdF) provides mechanical support [4-5].

There are a few reports in the literature on PVdF-HFP based QSSPEs studied with sodium salts such as NaCF₃SO₃ and NaClO₄ [4-6]. To the best of our knowledge, there are no reports on sodium ion conducting QSSPEs synthesized with NaBF₄ ionic salt. In this work, several different compositions of PVdF-HFP: NaBF₄: EC: PC QSSPEs have been synthesized and characterized by electrochemical impedance spectroscopy (EIS), DC polarization and linear sweep voltammetry (LSV) techniques. The highest conducting composition; PVdF-HFP: NaBF₄: EC: PC (6: 14: 40: 40 wt.%); showed an ambient temperature ionic conductivity of 4.1×10^{-3} S cm⁻¹. In these electrolytes, NaBF₄ provides Na⁺ and BF₄⁻ ions necessary for ion conduction within the polymer matrix and the role of plasticizer/solvent (EC/PC) mixture is to decrease the glass transition temperature and soften the polymer host resulting higher segmental motion and hence increasing the ionic conductivity.

Materials and Methods

Five different compositions of PVdF-HFP: NaBF₄: EC: PC QSSPEs were synthesized as listed in Table 1. PVdF-HFP, NaBF₄, EC and PC, all purchased from Sigma-Aldrich, are the polymer host, ionic salt, plasticizer and the solvent, respectively. All the chemicals were used as received. For the synthesis of QSSPEs, required amount of NaBF₄, EC and PC were magnetically stirred at room temperature for 3 hours, then the required amount of PVdF-HFP was added and stirred again for 5 hours at 100 °C until homogenous slurry was obtained. The resulting slurry was kept overnight inside a desiccator to get the gel sample.

Metrohm Autolab (PGSTAT 128N) impedance analyzer in the frequency range from 1 Hz to 0.1 MHz was used for impedance measurements on disc shaped samples sandwiched between two spring-loaded stainless steel blocking electrodes (SS/QSSPE/SS) separated by an insulating spacer. The temperature of the samples was varied from 25 to 75 °C and the impedance data were recorded at 10 °C intervals on heating. The ionic conductivity of each sample was estimated by finding the bulk resistances in the respective Nyquist plots. DC polarization test was performed at room temperature on highest conducting sample under an applied voltage of 1V with a scan rate of 5 mV s⁻¹; stainless steel (SS) blocking electrodes were used to assemble the cell. The electrochemical window of the highest conducting sample was found from the linear sweep voltammetry (LSV) studies performed with a scan rate of 5 mV s⁻¹ for a cell configuration of SS/QSSPE/SS.

Sample	PVdF-HFP (wt.%)	NaBF4 (wt.%)	EC (wt.%)	PC (wt.%)
Α	14	06	40	40
В	12	08	40	40
С	10	10	40	40
D	08	12	40	40
E	06	14	40	40

Table 1: Sample compositions of five different PVdF-HFP-NaBF₄ based QSSPEs synthesized in this work

Results and Discussion

All five compositions (A, B, C, D and E) of QSSPEs were synthesized by systematically varying the EO/Na⁺ ratio and keeping both EC and PC fixed at 40 wt.%. EIS data were recorded by using Metrohm Autolab (PGSTAT 128N) impedance analyzer with an applied ac signal of 10 mV in the frequency range of 1 Hz to 0.1 MHz. Fig.1a shows the Nyquist plot representation of impedance data recorded at ambient temperature for all the compositions studied in this work.



Figure 1: (a) Nyquist plots at RT, and (b) σ vs 1/T plots for PVdF-HFP:NaBF4:EC:PC QSSPEs

The intercept of the Nyquist plots with the X-axis in Fig.1a gives rise to the bulk resistances (r_b) of the electrolytes. By using the bulk resistance values extracted from the respective Nyquist plots, the ionic conductivity values (σ) were calculated using equation (1).

$$\sigma = t/r_b A \tag{1}$$

where A is the cross-sectional area and t is the thickness of the electrolyte sample sandwiched between stainless steel blocking electrodes with the help of a non-conducting spacer.

The σ vs 1/T plots for all the compositions are shown in Fig.1b in the temperature range from 25 to 75 °C. As listed in Table 2, the highest ambient temperature ionic conductivity of 4.1×10^{-3} S cm⁻¹ was obtained for the sample E and all the other samples also showed ambient temperature ionic conductivities in the order of 10^{-3} S cm⁻¹, which is in agreement with a few other studies on PVdF-HFP based Na⁺ ion conducting QSSPEs synthesized with some other sodium salts [4-6]. The amorphous phase (HFP) present in the co-polymer matrix helps to entrap large amount of liquid electrolyte leading to high ambient temperature ionic conductivities. It was impossible to synthesize samples with weight percentage of PVdF-HFP polymer host below 6 % and above 14 % due to the difficulty in forming the gel. Further, as can be seen in Fig.1b, all the QSSPEs showed Arrhenius behavior of conductivity variation with inverse temperature satisfying the Arrhenius equation given in (2). Arrhenius behavior of conductivity variation was already reported for similar Na⁺ ion conducting QSSPE systems [4, 7-11].

$$\sigma(T) = \sigma_0 \, e^{-E_a/kT} \tag{2}$$

where σ_0 is the pre-exponential factor, E_a is the activation energy and k is the Boltzmann constant.

The activation energies (E_a) and pre-exponential factors (σ_0) for all the sample compositions were estimated from the slopes and intercepts respectively of the ln σ vs 1/T plots and are tabulated in Table 2 along with ambient temperature ionic conductivities. The activation energies almost remain constant within the range of 0.18 - 0.20 eV suggesting that the activation process is primarily dependent on the concentration of EC/PC rather than that of polymer host and NaBF₄ salt.

Fable 2: Conductivity at a	ambient temperature (σ_{RT})), pre-exponential fac	tor (σ_0) and the activation
ene	ergy (E_a) of PVdF-HFP: 1	NaBF4: EC: PC QSSI	PEs

Sample	σ _{RT} (S cm ⁻¹)	σ ₀ (S cm ⁻¹)	Ea (eV)
Α	3.0 x 10 ⁻³	6.0 x 10 ⁻³	0.19
В	2.8 x 10 ⁻³	6.7 x 10 ⁻³	0.20
С	3.2 x 10 ⁻³	4.5 x 10 ⁻³	0.19
D	3.4 x 10 ⁻³	5.1 x 10 ⁻³	0.19
Е	4.1 x 10 ⁻³	5.0 x 10 ⁻³	0.18

To study the ionic and electronic contributions to the conductivity, DC polarization test was performed on the highest conducting sample (sample E) by applying a 1V DC potential across the SS/QSSPE/SS cell. Fig.2a shows DC polarization current vs time plot recorded for 6 hours at a scan rate of 5 mV s⁻¹. As shown, current drops instantly to almost zero within a few minutes indicating that the electrolyte is a dominant ionic conductor. Mobility of ions is blocked within a few minutes due to the use of SS blocking electrodes. Obviously, the saturated current is arising due the motion of electrons. The ionic (t_i) and electronic (t_e) transference numbers were estimated from this DC polarization data and are found as 0.99 and 0.01 respectively for the highest conducting sample composition. The ionic transference number of almost close to unity is an essential property for an efficient electrolyte to avoid short-circuits within the cell [10]. LSV data was also recorded on sample E and is shown in Fig.2b. It is found from LSV that the electrochemical stability window (ESW) of the highest conducting composition is 3.6 V.



Figure 2: (a) DC polarization curve measured under an applied DC voltage of 1 V, and (b) LSV curve; both recorded with a scan rate of 5 mV s⁻¹ in the configuration SS/QSSPE/SS for the highest conducting composition, sample E

Conclusion

Among all the samples investigated in this work, the highest ambient temperature ionic conductivity of 4.1×10^{-3} S cm⁻¹ was observed for the composition PVdF-HFP: NaBF₄: EC: PC (6: 14: 40: 40 wt.%). The σ vs 1/T variation showed Arrhenius behavior for all the samples with almost same activation energies in the range 0.18 - 0.20 eV suggesting that the activation process is mainly controlled by the concentration of EC/PC. Highest conducting composition seems to be dominantly ionic conductor with an ionic transference number of 0.99 and negligible electronic transference number. From the LSV studies, electrochemical stability window of the highest conducting composition was found to be 3.6 V.

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