Conductivity Studies on Na⁺ -Ion Conducting 2-Phase Inorganic Composite Electrolyte and Composite Polymer Electrolyte

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Abstract— Investigations on ion transport property of Na⁺-ion conducting 2-phase composite solid electrolyte systems: [(1-x) NaCOOCH₃: x NaI] where x = 0, 3, 5, 7, 10, 15, 20, 25 wt.(%), have been reported. Sodium Acetate (NaA): NaCOOCH₃ acted as Iˢᵗ-phase host and active filler material NaI as IIⁿᵈ-phase dispersoid. Composition: [93NaA: 7NaI] exhibited highest room temperature conductivity with σ_{rt} ~1.38 x 10⁻⁶ S/cm which is approximately one orders of magnitude lager than that of pure host NaCOOCH₃ (σ_{rt} ~ 3.34 x 10⁻⁷ S/cm)[1]. In order to increase σ_{rt} further, prior to forming this CE, powder mixture of two constituent chemicals: NaA : NaI:: 93 :7 wt.(%), was subjected to high energy ball milling for different durations viz. 2,4,6,8,10,12,14,16 milling hrs. It was found that CE: [93NaA: 7NaI], prepared with 14-hour milled constituent chemicals, exhibited σ_{rt} ~ 5.21 x10⁻⁶ S/cm. This additional increase in σ_{rt} can be directly attributed to nano-ionic effect introduced at I & IIⁿᵈ –phase interface boundaries as a consequence of high energy ball milling. To synthesized CPEs 14 hour milled [93NaA:7NaI] were complexed in PEO, Composite Polymer electrolyte system [(1-x)PEO: x(93NaA:7NaI)] where x = 0, 3, 5, 7, 10, 12, 15, 20, 25 wt.(%), have been reported. SPE film [85PEO:15(93NaA:7NaI)] exhibiting optimum conducting composition with room temperature conductivity σ_{rt} ~ 3.32 x10⁻⁷ S/cm. The newly synthesized CE system and CPEs were then subjected to materials and ion transport property characterization studies, to evaluate its utilities in All-Solid-State battery applications.

1. INTRODUCTION

Two-phase inorganic composite solid electrolytes consist of a moderate ion conducting material which acts as Iˢᵗ-phase host and submicron (μm/nm) size particles of a chemically inert and electrically insulating ionic/non-ionic filler material as IIⁿᵈ-phase dispersoid. As a consequence of fractional dispersal of IIⁿᵈ-phase, σ_{rt} enhancement of 1-3 orders of magnitude could be achieved in Iˢᵗ-phase host material. Size of filler particles acts an important role in σ_{rt}- enhancement. Hence, smaller is the size, larger is the enhancement CEs exhibiting room temperature conductivity (σ_{rt}) ~ 10⁻¹ – 10⁻³ S/cm, are novel Solid State Ionic systems which can be potentially used for All-Solid-State battery applications. CEs attracted wide spread attention only after C.C. Liang reported for the first time ~ 50 times increase in Li⁺-ion conduction at room temperature simply by dispersing micron size particles of inert Al₂O₃ (IIⁿᵈ-phase) into LiI (Iˢᵗ-phase) [2]. Since then, variety of 2-phase composite electrolyte systems have been investigated and their applications in various All-Solid-State electrochemical devices viz. batteries have been tested [1,3-10]. The reason for σ-enhancement that is the 'creation of a double-layer space-charge region' at the dispersoid-host interface boundary where ion defects get accumulated in relatively larger proportion and subsequently, resulting into an increase in mobile ion concentration 'n'. Further,

different space charge regions may get interconnected leading to creation of high conducting paths, as a result the ionic mobility (μ) get increased. Both these phenomenon eventually lead to an overall increase in σ.

The two phase inorganic composite electrolyte [93NaA: 7NaI] exhibited room temperature conductivity σ_{rt} ~1.38 x 10⁻⁶ S/cm, where Sodium Acetate (NaA): NaCOOCH₃ acted as Iˢᵗ-phase host and active filler material NaI as IIⁿᵈ-phase dispersoid. This paper reports the work in which to achieve additional enhancement in σ_{rt}, dry powder mixture of, Sodium Acetate (NaA) and NaI Optimum Conducting Composition (OCC): [93NaA: 7NaI], was subjected to high energy ball-milling. This consequently increased σ_{rt} further as a consequence of introducing nano-ionic effect at the 2-phase boundaries [11-14]. And for synthesis of CPEs the optimum conducting milled (93NaA: 7NaI) powder mixture was then mixed with polymeric host PEO in appropriate wt.(%). All the optimum conducting CE/CPEs compositions obtained above were then subjected to different experimental studies to characterize the ion-transport and materials properties, in order to examine their utility in All-Solid-State battery application.

2. EXPERIMENTAL

Synthesis of 2-phase composite solid electrolyte systems: [93 NaCOOCH₃: 7 NaI] precursor chemicals viz. Sodium Acetate (NaA≡NaCOOCH₃) anhydrous (purity >99%,

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Merck) and Sodium Iodide (NaI) (purity >99%, Molychem, India) have been used as supplied. For synthesis of Milled Composite electrolyte system the dry powder mixture of NaA and NaI was subjected to high energy ball-milling for different durations viz. 2, 4, 6, 8, 10, 12, 14, 16 hrs, then pellets were formed. The Composite electrolyte prepared by 14 hour milled chemical was identified as optimum conducting system at room temperature.

For synthesis of Composite Polymer Electrolyte the 14 hour milled (93NaA: 7NaI) powder mixture was then mixed with polymeric host PEO in appropriate wt.(%) then mixed physically for about~ 30- 60 minutes. The homogeneously mixed powder was then heated close to the melting/softening point of PEO i.e. ~ 70˚C, with mixing continued for ~ 30-40 minutes. This resulted into a soft lump/slurry which was then pressed (~ 1-2 ton /cm2) between two Stainless Steel (SS) cold blocks to form SPE film of uniform thickness ~ 100-200 μm. The 14 hour milled (93NaA:7NaI) concentration dependent conductivity study at room temperature (27^0C) revealed CPE film composition: [85PEO:15(93NaA:7NaI)] having optimum conductivity (σ_{rt}), which has been referred to as CPE OCC film, as mentioned.

In order to understand ion-transport mechanism, conductivity measurements on optimum conducting CE/CPEs samples were carried out as a function of temperature and the activation energy (Ea) was computed from 'log σ -1/T' Arrhenius plots. The total ionic transference number (t_{ion}) was evaluated by dc polarization Transient Ionic Current (TIC) technique [15, 16]. The materials properties were characterized by XRD (D2 Phaser model: 08 discover, Bruker).

3. ION TRANSPORT CHARACTERIZATION STUDIES

Conductivity Measurement— Fig. 1 shows milling hour dependent conductivity plot for composite electrolyte. It can be clearly noticed that as milling time increased, σ_{rt} increased, attained a maxima then decreased rapidly. Milled CE: [93 NaA: 7NaI], prepared with 14 hr milled
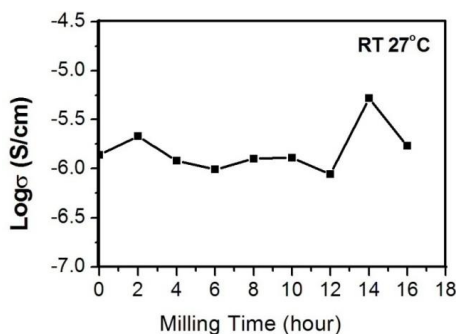

Fig. 1: σ_{rt} as a function of milling hour for Composite Electrolyte System: [93NaA:7NaI].

(NaA+NaI) powder, exhibited highest σ_{rt} ~5.21 x10^{-6} S/cm, which is nearly 4-fold larger than that of physically mixed [93NaA: 7NaI] (previously reported [1]). σ_{rt} increase in milled CE can be directly attributed to nano-ionic effect introduced at the two phase boundaries as a consequence of high energy ball milling [11-14].

Fig. 2 shows the 14 hour milled (93 NaA:7NaI) concentration dependent conductivity of Composite Polymer electrolyte film: [(1-x) PEO: x (93NaA: 7NaI)]. CPE film: [85PEO: 15 (93NaA: 7NaI)] identified as OCC with room temperature conductivity σ_{rt} ~ 3.32 x10^{-7} S/cm, which is two orders of magnitude from that of pure polymeric host (σ_{rt} ~ 3.20 x 10^{-9} S/cm).
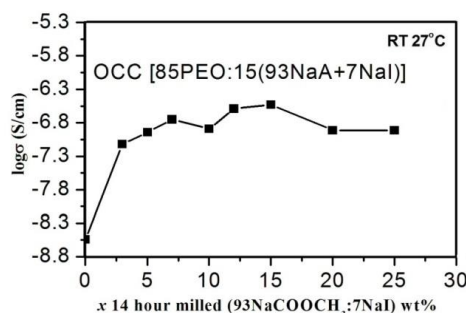

Fig. 2: σ_{rt} as a function of 14 hour milled (93 NaA:7NaI) concentration for Composite Polymer electrolyte film: [(1-x) PEO: x (93NaA: 7NaI)].
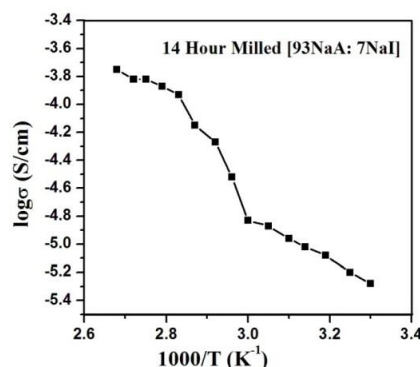

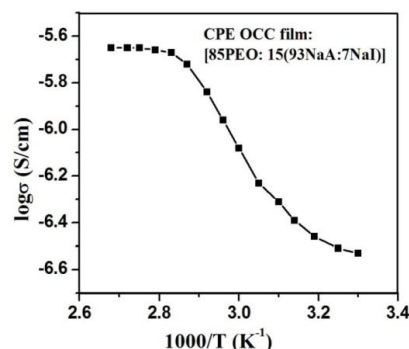**Fig. 3: (a) Shows temperature dependent conductivity variation for 14 hour Milled [93NaA:7NaI]**

Fig. 3: (b) For Composite Polymer Electrolyte OCC film: [85PEO: 15 (93NaA:7NaI)].

Fig.3(a) shows temperature dependent conductivity variation for Milled OCC and Fig.3(b) for Composite Polymer Electrolyte OCC. One can note that 'logσ -1/T' plots for the systems follow Arrhenius type behavior in the lower temperature region and can be expressed by following equation:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$

where 'σ₀' is the pre-exponential factor, 'Ea' is activation energy, which has been computed by least square linear fitting of 'logσ -1/T' plot in the lower temperature region and found to be ~0.32 eV. Fig.4 shows temperature dependent conductivity variation for CPE film [85PEO: 15 (93NaA:7NaI)] and activation energy found to be ~ 0.19eV.

Total ionic transference number (t_{ion}) was determined by dc polarization Transient Ionic Current (TIC) Technique [11, 12], as mentioned in Section 2. Typical TIC plots for both CE OCC and CPE OCC are shown in Fig. 4(a) and (b). t_{ion} was evaluated with the help of following equation:

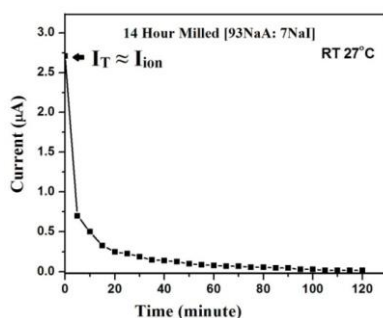$$t_{ion} = \frac{\sigma_{ion}}{\sigma_T} = \frac{I_{ion}}{I_T}$$

Fig. 4: (a) Shows 'Current v/s time' plot for 14 hour Milled [93NaA:7NaI]
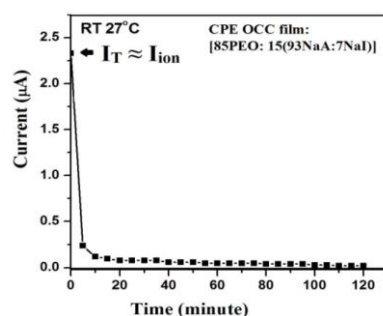

Fig. 4: (b) For Composite Polymer Electrolyte OCC film: [85PEO: 15 (93NaA:7NaI)].

The value of tion, for both Milled CE OCC: [93NaA:7NaI] and CPE OCC: [85PEO:15(93NaA:7NaI)] when polarized for 160 min, was found to be ~0.98 which is very close to unity. This clearly indicates the fact that these solid state ionic materials are pure ionic conducting

systems. In polymer electrolytes, both cations and anions move. However, cation transport is more relevant as far as good/stable performance of the battery is concerned. Hence, cation (Na+) transport number (t+) was evaluated separately in both the SPE OCC films using combined ac/dc technique, as mentioned in Section 2. The values of I0/IS & R0/RS obtained from 'current-time' and 'Z'-Z'' impedance plots (not shown here) respectively, were substituted in equation (1) and t+ was found to be ~ 0.28.

4. MATERIAL CHARACTERIZATION STUDY

Fig.5 shows XRD pattern for pure salts: NaA and NaI as well as physically-mixed OCC: [93NaA:7NaI] and 14 hour milled OCC: [93NaA:7NaI]. Both the salts show well-defined sharp XRD peaks which are indicative of their crystalline/polycrystalline nature. However, as a consequence of dispersal of IInd-phase filler material into Ist-phase and after the formation of 2-phase inorganic composite electrolytes, it can be noticed that all the peaks of both the salts exists in the XRD patterns of both the OCCs with slight overlapping /shifting in position. This is indicative of formation of 2-phase systems. However, the intensity of these peaks' have been suppressed considerably which is indicative of increase in degree of amorphousity in the system.
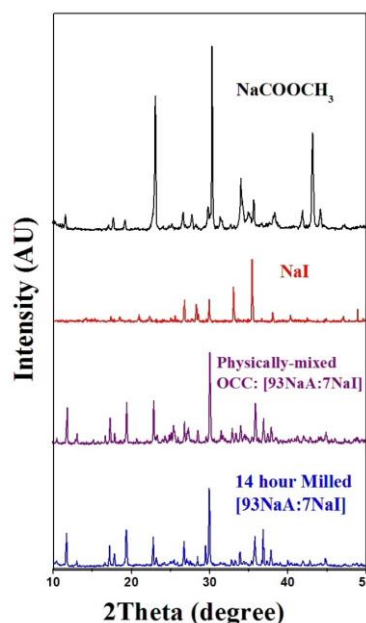

Fig. 5: XRD pattern for (a) pure salts: NaA (b) NaI (c) physically-mixed OCC: [93NaA:7NaI] and (d) 14 hour milled OCC: [93NaA:7NaI].

Fig.6 illustrates XRD patterns for pure polymeric host: PEO, and CPE OCC film: [85PEO: 15(93NaA:7NaI)]. On comparing pattern (a) with pattern (b), one can notice that the intensity of characteristic peak of PEO at 2θ ~ 24°, XRD pattern (a) appeared suppressed considerably. This is indicative of increase in the degree of amorphousity in PEO host as a consequence of salt complexation.
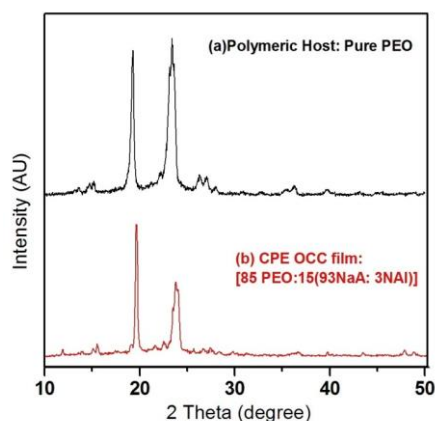
Fig. 6: XRD patterns for (a) pure polymeric host: PEO, and (b) CPE OCC film: [85PEO: 15(93NaA:7NaI)].

5. CONCLUSION

Na^+-ion conducting 2-phase inorganic composite electrolyte systems: [93NaA:7NaI] (14 hour milled) and Composite Electrolyte Film: [85PEO: 15(93NaA:7NaI)] have been synthesized. The materials and ion transport properties have been characterized. As a consequence of ball milling achieved 4times enhanced room temperature conductivity in composite electrolyte with the physically mixed CE. The total ionic transference number measurements indicated clearly that both the systems are purely ionic, hence, can be potentially exploited to fabricate All-Solid-State batteries. This work is currently being pursed in the present laboratory.

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