

A.C. Impedance, XRD, DSC, SEM and Charge/Discharge Studies on Al₂O₃, TiO₂, SiO₂ dispersoid LiPF₆/PVC/PVdF-co-HFP Composite Polymer Electrolytes by Phase Inversion

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Abstract. The PVC/PVdF-co-HFP composite polymer electrolyte membranes (CPEMs) by varying blend ratios 1:1, 1:2, and 2:1 with fixed content of Al₂O₃, TiO₂ and SiO₂ having soaked in 0.5 M LiPF₆ in EC/DEC (1:1) v/v) have been prepared by phase inversion. CPEMs of higher ionic conductivity (not dependent on electrolyte uptake as observed in our study) ASA4 ($3.61 \times 10^{-4} \text{ Scm}^{-1}$), TSA3 ($1.53 \times 10^{-4} \text{ Scm}^{-1}$), and SSA3 ($4.81 \times 10^{-4} \text{ Scm}^{-1}$) have been only chosen for XRD, DSC, SEM and electrochemical studies. In XRD, crystalline peaks (phases) of PVdF have been noted with/without change in intensity as well as FWHM which correspond to type of filler interaction with host matrix. In DSC, it is observed that shifts in baseline, melting endotherms, and area under the endotherms indicating the thermal history of PVC (T_g = 82 °C) and melting of VdF crystallites varied with nature of the filler dispersoid. In SEM, the coagulated fibrils of the polymer coiled with the sponge like structure has been mapped. The charge/discharge studies are carried out on these CPEMs at C/10 rate in the voltage range 2.8 V – 4.2 V, and it is noted that the TSA3 showed better cycling performance with good capacity retention i.e., 50 cycles with 66% capacity retention than ASA4 of 28 cycles with 65% and SSA3 of 5 cycles with 56%. In the present study Coulombic efficiency is concerned only for first cycle and it is noted that the TSA3 showed 71% than 66% and 62% respectively for SSA3 and ASA4.

Key words: PVC/PVdF-co-HFP, Phase Inversion, LiPF₆, A.C impedance/Charge-Discharge

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INTRODUCTION

Exploration of polymer electrolytes has been an active research for lithium rechargeable batteries. The PVdF-co-HFP based polymer electrolytes have their immense use as a separator cum electrolyte for fabricating Li ion batteries were reported by researchers [1-2]. Among the casting techniques employed for preparing polymer electrolytes, the phase inversion technique [3-7] seems to be a versatile technique to achieve the desired characteristics without sacrificing the basic requisites. Hee Rhoo et al., emphasized blending of polymers to achieve some desired properties [8]. i.e, blending of two polymers is a simple, versatile and cost effective technique. Since the inherent nature of PVdF-co-HFP appears to be a best candidate such as its high dielectric constant, anodic stability, owing to its high electron withdrawing nature [9], in the present study the aforesaid polymer is blended to high molecular weight Polyvinyl chloride (PVC) so as to safeguard the membrane during redox process, So PVC/PVdF-co-HFP blend based polymer electrolytes have been attempted. Since the addition of ceramic oxides as fillers Al₂O₃, SiO₂, and TiO₂ has been reported by many researchers [10-22] for enhancing the ionic conductivity, mechanical, thermal stability and electrochemical performance by way of improvising the polymer surface to exhibit to have either as acidic /basic or mixture of both [16], and thereby preventing reorientation of the host, which eventually resulting in more amorphous to the host [9 – 22]. So in the present study the aforesaid fillers have been dispersoid with PVC/PVdF-co-HFP hosts Among lithium salts [23-30], lithium hexafluorophosphate (LiPF₆) remains to be one of best candidates, as it is the most stable at room temperature in practical lithium ion batteries [28-30]. So this salt has been used as an electrolyte [29,30]. The 0.5 M LiPF₆ eletrolyte solution is prepared using ethylene carbonate (EC)/diethyl carbonate(DEC) mixture in 1:1 (v:v) ratio The AC impedance studies has been

carried out for three polymer blend (PVC/PVdF-co-HFP) ratios 1:1, 1:2, and 2:1 with three different fillers. The electrochemical studies have been performed only for the best ionic conductivity membranes in Al_2O_3 (ASA4), in TiO_2 (TSA3) and in SiO_2 (SSA3). In the present study, the lithium foil is selected as an anode due to its appealing electrochemical stability and an excellent compatibility with CPEMs [31]. LiFePO_4 is used as a cathode material due to its salient characteristics. Since many researchers [21-23,32] reported that ceramic filler coated polymer electrolytes showed good charge/discharge cycling and the interfacial resistance of the electrolyte prepared by phase inversion process which is well augmenting with solid electrolyte interphase (SEI), the objective is thus framed w.r.t the salient glimpses of materials.

MATERIALS AND INSTRUMENTATIONS

Materials

PVdF-co-HFP with 12 mol% of HFP (Solvay Solexis, Italy, $\text{MW} = 5.34 \times 10^5$). Polyvinylchloride (PVC) ($\text{MW} = 5 \times 10^5$), ethylene carbonate (EC), diethyl carbonate (DEC) LiPF_6 and Al_2O_3 , TiO_2 and SiO_2 were purchased from Sigma Aldrich USA and used without further purification. The Coin cell 2032 was fabricated in argon atmosphere using glove box M Braun, Germany with Li foil as an anode and lithium iron phosphate (LiFePO_4) as a cathode purchased from MIT Corporation, USA.

Instrumentation

Ionic conductivities of selected CPEMs were studied by a.c. impedance spectroscopy in the frequency range 100 Hz - 1 MHz by using a Bio-Logic SP-150 impedance analyzer. XRD diffractograms were recorded between 3° - 80° using Bruker Axs D8 Advance using $\text{Cu-K}\alpha$ ($\lambda = 1.54060 \text{ \AA}$) radiation as source with operating voltage and current of 40kV and 30mA respectively. Differential scanning calorimetry (DSC) traces were recorded using Mettler Toledo DSC 822e from 130°C to 450°C at the scanning rate of $10^\circ \text{C}/\text{min}$. Morphological features imaged using a Hitachi- S-3000H Scanning Electron Microscope (SEM). Coin cells were assembled using glove box in an argon atmosphere and the cycling test was performed out using WonaTech model WBS – 3000s battery tester at Advanced Lithium Battery Division, CECRI, Karaikudi.

Preparation of composite polymer electrolyte membranes (CPEMs)

In phase inversion technique, PVC and PVdF-co-HFP in 1:1, 1:2 and 2:1 weight ratios and fixed content (10 wt%) of fillers X ($\text{X} = \text{Al}_2\text{O}_3$, TiO_2 and SiO_2) were dissolved in a mixture of acetone (solvent) and ethanol (non-solvent) in 5:1 volume ratio in such way that non-solvent was low enough to allow dissociation and high enough to allow phase separation during evaporation. The non-solvent was to be fixed in such a way that it would have better porosity during the solvent evaporation process. The prepared solution was formed into thin films on a glass substrate, and the solvent was allowed to evaporate. The prepared films were kept under vacuum for 12 h at 100°C to remove the traces of non-solvent.

Polymer blend in different weight ratios with fillers (DryCPMs) were labeled as ASA3, ASA4 and ASA5 for Al_2O_3 , TSA3, TSA4 and TSA5 for TiO_2 , and for SiO_2 , SSA3, SSA4 and SSA5. These Dry CPMs were soaked in electrolyte i.e., EC/DEC in 1:1 v/v is mixed with 0.5M LiPF_6 , (CPEMs). The weights of CPEMs have been measured after and before soaking and their electrolyte uptakes were calculated.

Coin cell assembly

The cathode LiFePO_4 for coin cell assembly 2032 was prepared by a slurry coating process over the aluminium foil using doctor blade comprising of LiFePO_4 (80%), acetylene black (10%), PVdF binder (10%), and N-methyl pyrrolidone (NMP) as a slurring agent. The coated aluminium foil was dried in an oven at 110°C for 2 h and pressed and 16 mm diameter blanks were punched out from the coated area and used as cathode, and lithium foil was used as an anode. Using CPEMs with higher ionic conductivity as a separator cum electrolyte, lithium foil anode, LiFePO_4 cathode and other assemblage, coin cells of 2032 configuration were assembled using glove box (M Braun, Germany) in an argon atmosphere. The cells as assembled were subjected to charge/discharge studies in galvanostatic mode in a computerized battery cycling unit at C/10 rate in the potential window 2.8 V - 4.2 V.

RESULT AND DISCUSSION

Ionic Conductivity

The ionic conductivity studies on CPEMs with three different fillers Al_2O_3 , TiO_2 , and SiO_2 in three blend 1:1, 1:2 and 2:1 weight ratio for the samples ASA3, ASA4, ASA5 (for Al_2O_3), TSA3, TSA4, TSA5 (for TiO_2), SSA3, SSA4, SSA5 (for SiO_2) (Figure.1) have been carried out in the frequency range 100 Hz - 1 MHz using an impedance analyzer at 30, 40, 50, 60 and 70°C . The bulk resistances R_b , of CPEMs noted from their Nyquist

impedance plots, their respective thickness (L) and the area of cross section ($A = \pi r^2$) are used to determine the ionic conductivities of the membranes using the standard relation $\sigma = \frac{AL}{Rb}$.

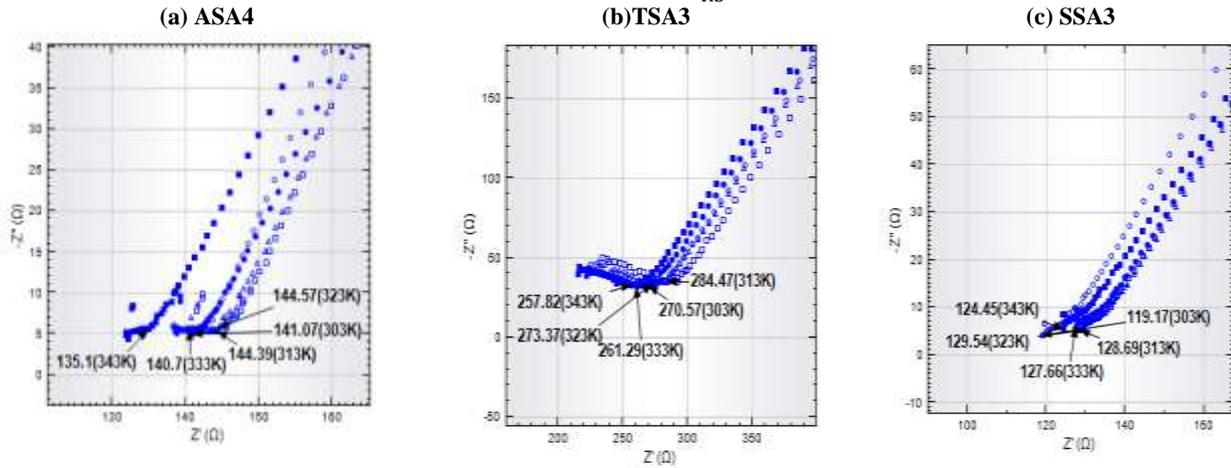


FIGURE.1 AC Impedance studies of CPiEMs, for Al_2O_3 (a) ASA4; for TiO_2 (b) TSA3; for SiO_2 (c) SSA3

The conductivities of PVdF-co-HFP rich phase (1:2) containing samples showed enhanced conductivities irrespective of electrolyte uptake (EUT) for Al_2O_3 (ASA4) $3.61 \times 10^{-4} \text{ Scm}^{-1}$; (**101.48%**), for TiO_2 (TSA4) $8.42 \times 10^{-4} \text{ Scm}^{-1}$; (**104.76%**), and for SiO_2 (SSA4) $5.24 \times 10^{-4} \text{ Scm}^{-1}$ (**120.78%**) than that of PVdF-co-HFP poor phase (PVC rich phase (2:1)) for Al_2O_3 (ASA5) $1.2 \times 10^{-5} \text{ Scm}^{-1}$; (**427.42%**), for TiO_2 (TSA5) $5.09 \times 10^{-5} \text{ Scm}^{-1}$; (**153.23%**), and for SiO_2 (SSA5) $2.36 \times 10^{-5} \text{ Scm}^{-1}$; (**159.15%**) at room temperature. While blending in 1:1 ratio for Al_2O_3 (ASA3) $5.64 \times 10^{-5} \text{ Scm}^{-1}$ (**154.48%**), for TiO_2 (TSA3) $1.53 \times 10^{-4} \text{ Scm}^{-1}$ (**119.69%**) and for SiO_2 (SSA3) $4.81 \times 10^{-4} \text{ Scm}^{-1}$ (**129.76%**) are noted. The drastic decrease or pronounced enhancement in magnitude of the conductivity may be reasoned to the mobility of charge carriers and the consequent increasing conductivity dependent on the blend ratio (1:2 > 1:1 > 2:1) of the host matrices independent of their performance of electrolyte uptake instead EUT of CPiEMs appears to be facilitating to give flexibility to chain segments fully contoured by the nature of fillers (Al_2O_3 , TiO_2 , SiO_2) [16-20] rather their surface to volume aspect ratio [13,21] to drive Li^+ cation mobility for improved ionic transport.

Among the all CPiEMs investigated, higher ionic conductivity CPiEMs (1:2; ASA4, 1:1; TSA3 and 1:1; SSA3) are only selected for further studies.

XRD studies

The XRD for LiPF_6 based Al_2O_3 , TiO_2 and SiO_2 dispersoid CPiEMs have been recorded between $2\theta = 3^\circ - 80^\circ$ (Figure.2). The characteristics peaks associated with PVdF are noted between $2\theta = 25^\circ$ to 35° and at 42° [33-35]. The characteristics peaks of PVdF (α -phase) at $2\theta = 18.3^\circ$, 19.2° and 20° [36] are absent in all the CPiEMs due to the dispersoid of the fillers and the blending. This enhances the amorphoucity of the polymer host. The amorphous characteristics peaks of PVC at $2\theta = 13^\circ$ and 16° are completely absent in all the membranes [9] and this induces the change in crystallographic orientation of VdF crystallites and establishing the correlation between degree of crystallinity and peak intensity. This may be due to the complete blending of PVC and PVdF-co-HFP. The Al_2O_3 impregnated membrane ASA4 show the coexistence of phases of PVdF as doublets at $2\theta = 25.82^\circ$, 26.84° , and $2\theta = 30.54^\circ$, 31.08° doublet, and existence as a singlets at $2\theta = 28^\circ$ and 35° [37-38]. While dispersing the TiO_2 (TSA3), the first doublet has become narrower into singlet at 26° , and the complete absence of the second doublet, with the broader hump for $2\theta = 35^\circ$, and new sharp peak appearance at 42° have all shown that the complexation between polymer host and the TiO_2 anatase [9,39-40], is found to be more than that of with the Al_2O_3 . The broader hump of first doublet of ASA4, the drastic reduction in intensity of second doublet and increase in the intensity of peak at $2\theta = 42^\circ$, are all due to addition of SiO_2 (SSA3) suggestive of the added SiO_2 [41] reducing the crystallinity and increased the amorphoucity for Li^+ mobility. Thus XRD characteristics peaks of CPiEMs confirm that the PVdF semi crystalline structure and suppression of few of its characteristic peaks enhanced the amorphoucity due to interaction between the polymer host and the fillers rather increased the path way of Li^+ cation migration

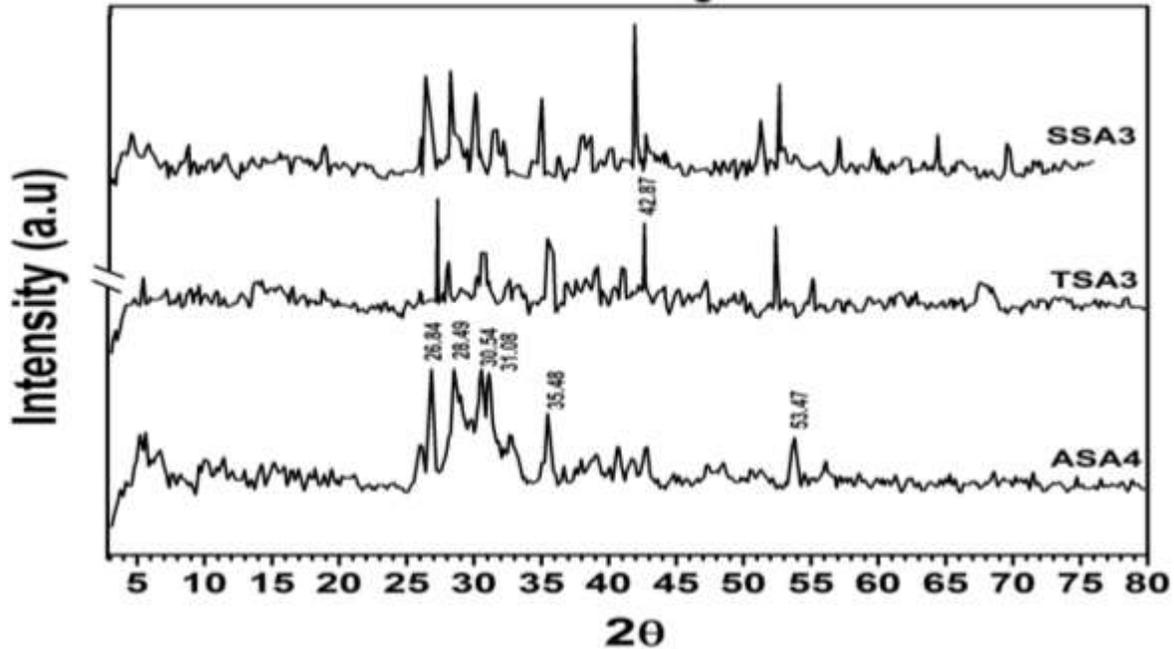


FIGURE.2 XRD profile of identified CPEMs.

DSC studies

DSC studies, in CPEMs with Al_2O_3 (ASA4), TiO_2 (TSA3) and SiO_2 (SSA3) loaded have registered [42] three endothermic events in the temperature range 50°C to 160°C and 250°C to 320°C (Figure.3). The endothermic events have, in general, represented the melting of crystallites of host matrices, in the present case poly vinyl chloride and poly vinylidene flouride in CPEMs. The baseline shift (change in specific heat capacity, but no change in enthalpy) presents the second order phase transition of host matrices. While probing into the sample ASA4, the membrane initiates the endotherm event at 74.27°C with the good shift in baseline with the heat of fusion ($\Delta H_m = 45.92 \text{ J/g}$), stops its event rather restoring by retouching the baseline, and thereafter momentarily undergoes a smallest endothermic event with ΔH_m of 4.42 J/g stops at the end set at 158°C [43-45], and from the endset 158.3°C to 260°C the membrane undergoes no physical changes but thereafter it perturbs by onsetting the melting of certain crystallines domain of VdF evolves with the heat of fusion of 63.29 J/g surrenders its reaction at 208°C . Thus, shifts in baseline and melting endotherms, area under the endotherms have registered the thermal changes of PVC ($T_g = 82^\circ\text{C}$) and melting VdF crystallites. By replacing Al_2O_3 by TiO_2 in the same membrane has shown the typical thermal pattern as that of ASA4 [46] albeit certain shifts in the onsets and endsets and their respective change in area of endotherms or heat of fusion. Noticeably the mitigation of ΔH_m from 45.92 J/g to 21.16 J/g and the complete suppression of the momentary melting of crystallites in the temperature range 150°C to 160°C and the broadening of ΔH_m event shifting the endset to towards lower temperature of 20°C difference and consuming with the higher endotherm, with the extendable endset events **have all present** the thermal stability nature of LiPF_6 based TiO_2 . While examining the same membrane with SiO_2 (SSA3), three distinct thermal events appeared, compared to the TSA3 and ASA4. The endsets recorded in ASA4 and TSA3 in the temperature range $50 - 100^\circ\text{C}$ have registered in between 0°C to 50°C in SSA3 with the ΔH_m of 25.64 J/g , the momentary crystallites melting appeared in 110°C to 130°C has shown its prominence at 80°C to 100°C instead of $100^\circ\text{C} - 193^\circ\text{C}$, and very broaden medium endotherm event with 187.06 J/g with further shifting onset towards lower temperature side with the difference of 5°C and endset of 320°C , **pronounces** the LiPF_6 have allowing the membrane to have distinct thermal events than the former samples TSA3 and ASA4.

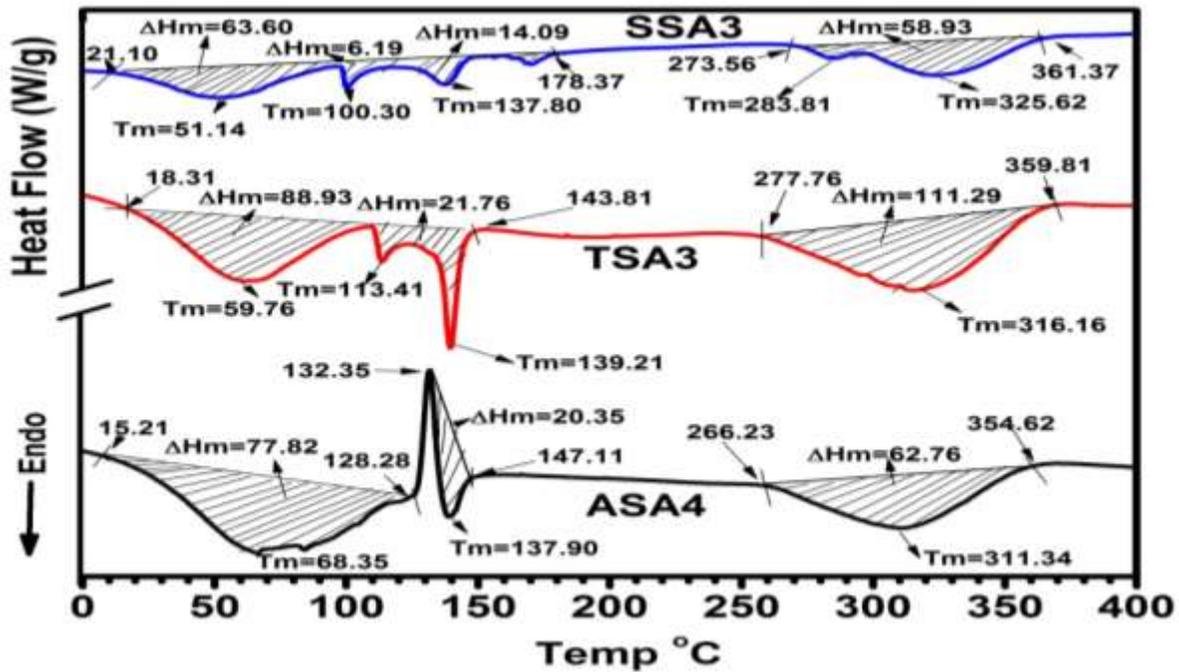


FIGURE 3 DSC studies of identified CP EMs

SEM/EDAX studies

The coagulated fibrils of the polymer coiled with the sponge like structure has been mapped and the corresponding EDAX mapping identify the elements present in the polymer membranes (Figure.4). The degree of complexation of each constituent within the matrix has been shown distinctly either as a sharp or a medium peaks formation. Looking the figuration of (b) with TiO₂ the well connected coordinating centers have shown with the complete folding with ingredients in the same magnification and the factual anomaly has been seen with Cl moiety which flusters the host mapping with the deformed conformation surface. While seeing the surface morphology with the Si, the Cl moiety of PVC has substantially spanned down with smudging intensity profile completely misting. The host structure has been seen.

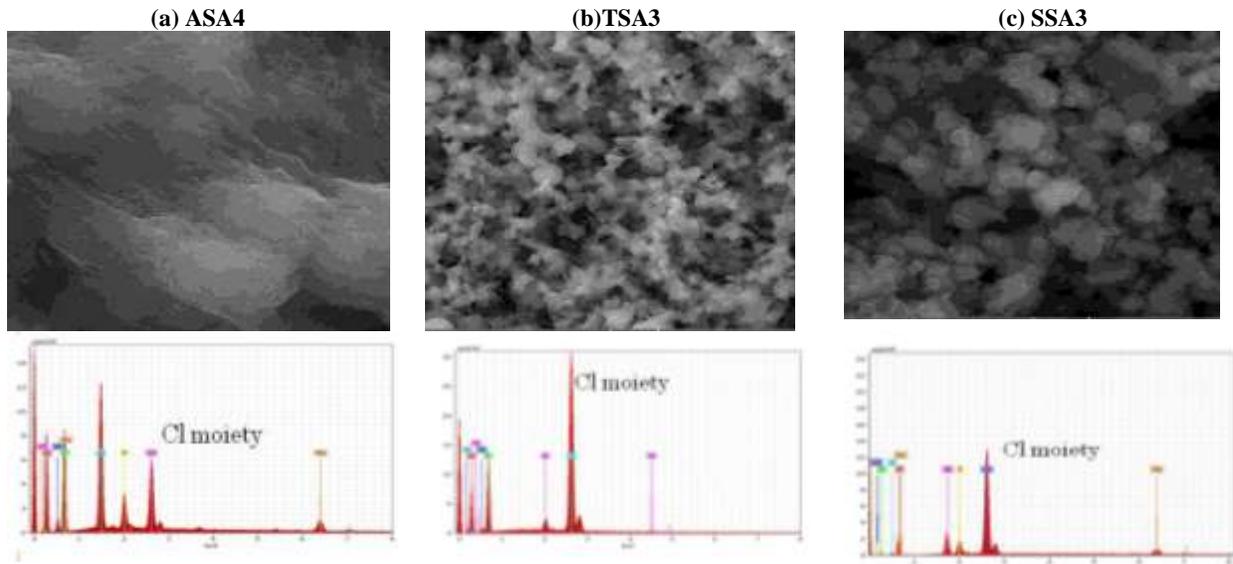


FIGURE.4 SEM/EDAX profile of identified CP EMs

Electrochemical studies

The cells 2032 as-prepared using membranes with higher ionic conductivity found in phase inversion process as a separator cum electrolyte (lithium foil anode, LiFePO₄ cathode) are subjected to charge/discharge studies in galvanostatic mode in a computerized battery cycling unit at C/10 rate in the potential window 2.8V-4.2V.

It is noted that the first charge profile capacity 137 mAhg⁻¹ for both ASA4 (Al₂O₃) and SSA3 (SiO₂), is found to be higher than 117 mAhg⁻¹ of TSA3 (TiO₂) and their corresponding discharges are 90 mAhg⁻¹ and 83 mAhg⁻¹ respectively. While observing the overall charge/discharge performance in the potential plateau, 3.6 V and 3.2 V, (Fig.4) is concerned; it appears to resemble the performance of Cellguard [47]. So, it is conjectured that ASA4, TSA3 and SSA3 are seem to be better electrolytes may be recommended for their end utility for lithium battery applications. While sprouting on the capacity retention, TSA3 is showed 66% with 50 cycles than 65% with 28 cycles for ASA4, and 56% with 5 cycles for SSA3.

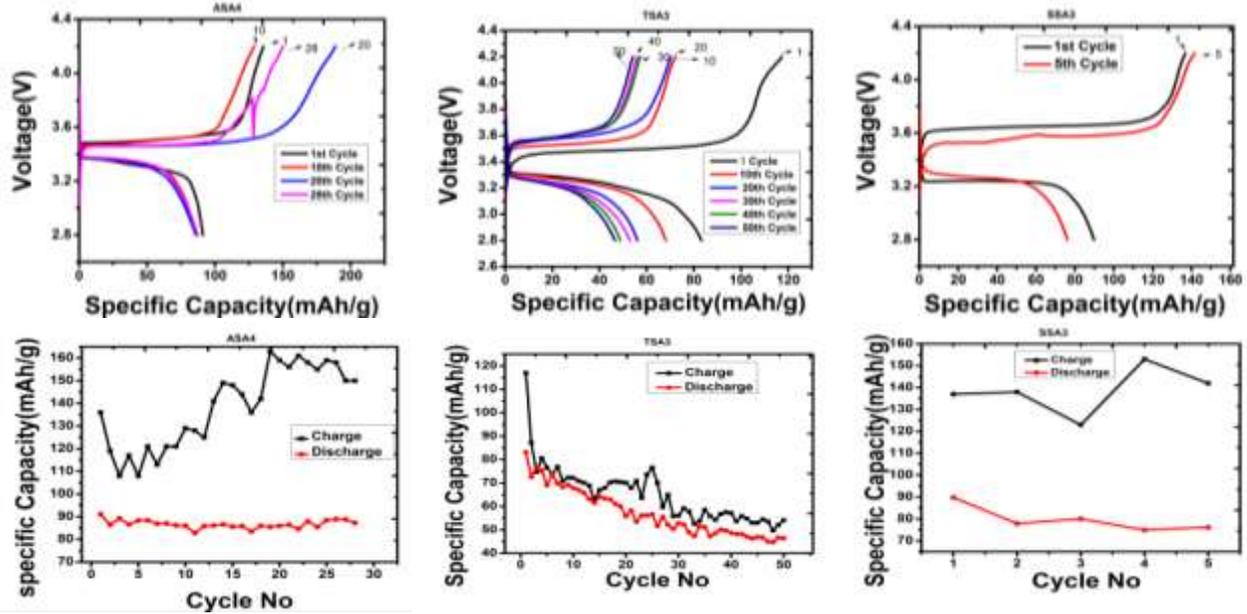


FIGURE.5 Charge – Discharge profile of the coin cell Li/CPEMs/LiFePO₄ (a) ASA4 (b) TSA3 (c)SSA3

Coulombic Efficiency

The perceptible reason for higher cycling efficiency and capacity retention performance may be due to the lower interfacial resistance of TiO₂ dispersoid membrane [32] than Al₂O₃ and SiO₂. As far as the Coulombic Efficiency (CE) is concerned, the relatively low Coulombic efficiency are noted for first few cycles irrespective of the nature of the fillers **may be reasoned to be the formation of SEI** on the electrode surface, and the structural change of the cathode material and the irreversibly oxidative decomposition of the electrolyte solvents [48]. The respective Coulombic Efficiencies 67%, 71% and 66% as calculated for the first cycle for the ASA4, TSA3 and SSA3 started to register a gradual increase and decrease **showing non linearity** with subsequent cycling may be thought of overcharging of coin cell as contented by the authors is reported

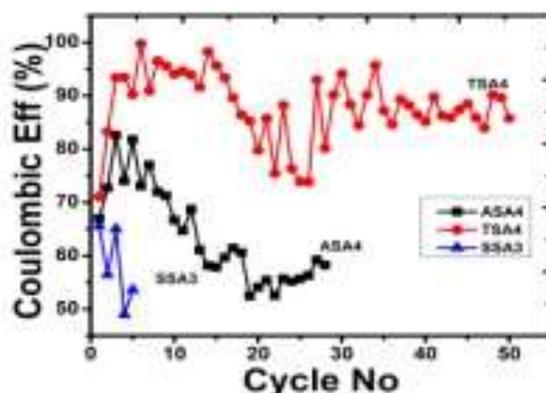


FIGURE.6 Coulombic efficiency of the coin cell Li/CPEMs/LiFePO₄, ASA4, TSA3, SSA3

CONCLUSION

- The study reveals that increasing conductivity is dependent on blend ratio (1:2 > 1:1 > 2:1) of the host matrices but not on EUT .
- The characteristics peaks of VdF crystallites have been noted all the membranes, among them the interaction of the host marice of TiO₂ is higher and enhanced the amorphoucity.
- The endothermic event is highly supported the thermal stability of the as-prepared membrane.
- In SEM, the coagulated fibrils of the polymer coiled with the sponge like structure has been mapped, and the EDAX mapping confirms the elements present in CPEMs.
- Cycling efficiency and capacity retention is noted for TiO₂ dispersoid membrane may be due to the lower interfacial resistance.
- The relatively low coulombic efficiency noted for first few cycles irrespective of the nature of the fillers may be reasoned to be the formation of SEI and the structural changes in cathode material.

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