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# Effect of Different Lithium Salts on the Structure and Morphology of Polystyrene-co-acrylonitrile Based Composite Solid Polymer Electrolytes

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**Abstract**

*In the present study, a series of poly(styrene-co-acrylonitrile) (SAN) polymer electrolytes and SAN- poly(vinyl alcohol) (PVA) polymer blend electrolytes were prepared with different lithium salts using a solvent casting technique. The morphology of prepared polymer blend electrolytes was studied by XRD studies. FT-IR spectroscopy studies reveal the interaction between polymer host and the lithium salt.*

**Keywords:** Polymer blend electrolytes, FT-IR, Thermal studies, Li ion battery, PVA

**Introduction**

For past two decades, solid polymer electrolytes (SPE) have attracted considerable amount of attention due to growing demand for portable devices and powering these devices. Among them, lithium metal and lithium ion batteries are the most promising ones, due to their very high discharge capacity and high open circuit voltage up to over 4V. Polymer based ion conducting materials

have generated remarkable interest in the field of lithium ion batteries due to their approach as electrolytes<sup>(1)</sup>. As it is well known, solid polymer electrolytes (SPE) have several advantages over the liquid counterpart such as desirable shape mouldability, free from leakage, low self-discharge, elastic relaxation under stress, easy processing, good conductivity and flexibility of design, thereby permitting miniaturization<sup>(2)</sup>. However, a main drawback of this first generation SPE is high degree of crystallization of polymers.

Polymeric materials are rarely used in their pure state. The blending of polymers yields inexpensive method of modifying various properties of a polymer such as tensile strength, conductivity and impact strength. The versatility of polymer blends is reflected in the range of usable end properties that can be achieved through alterations in the composition and/or effective control of the morphology of the polymeric mixture. Numerous works have been carried out to minimize the semi-crystalline nature of PVA. Blending is one of the most relevant techniques that completely redefine the physical and chemical properties of PVA<sup>(3)</sup>. The polymer electrolytes with plasticizers are known as second generation polymer electrolytes<sup>(4)</sup>. The addition of plasticizers may also improve the salt-solvating power and high ion mobility to the polymer electrolytes<sup>(5)</sup>.

In the present work, new plasticized polymer electrolytes composed of the SAN, SAN/PVA blend, propylene carbonate (PC) as a plasticizer, and various lithium salts have been studied.

The polymer electrolytes SAN-PC-LiX and PVA-SAN-PC-LiX, (X=Cl<sup>-</sup>, Br<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) are prepared using a solvent casting technique. The structure and morphology of the prepared polymer electrolyte films are studied using XRD, FT-IR techniques.

## Experimental

All polymer complexes were prepared using solution casting techniques<sup>(6,7)</sup>. The polymers Poly (Styrene-co-acrylonitrile) (SAN) (Sigma-Aldrich) (M<sub>w</sub> = 165000), Polyvinyl alcohol (PVA) (Sigma-Aldrich) (M<sub>w</sub> = 146000), propylene carbonate (Alfa-Aesar) and different lithium salts that include lithium chloride, lithium bromide and lithium carbonate (Alfa-Aesar) were purchased and used as such without any further purification. The polymers were dried at 373 K in vacuum for 12 h before use. The solvent THF/DMF was distilled before use. The plasticizer and the lithium salt (LiX) with X = Br<sup>-</sup>, Cl<sup>-</sup>, and CO<sub>3</sub><sup>2-</sup> in appropriate quantities (wt %) were mixed separately in THF and then transferred to beaker containing SAN in THF. The polymer blends along with plasticizer and lithium salts are stirred at room temperature for 48 h or until slurry of polymer electrolyte is homogenous. The same procedure is repeated for PVA/SAN-PC-LiX in solvent DMF. This homogenous blend of plasticised polymer with lithium salt is cast on to Teflon coated glass plate and dried over vacuum at 60°C for 12 h to remove any traces of solvent.

X-ray diffraction (XRD) analysis was carried out using an X'Pert proPANalytical diffractometer using CuK<sub>α</sub> as source. Fourier Transform Infra Red (FT-IR) measurements were made using BRUKER Optik GmbH spectrometer in 4000 – 500 cm<sup>-1</sup> under transmittance mode.

## Results and Discussion

### X-Ray Diffraction Studies

XRD studies were performed for SAN-PC-LiX (where X=Cl, Br, CO<sub>3</sub><sup>2-</sup>) (Fig.1) and PVA-SAN-PC-LiX (where X= Cl<sup>-</sup>, Br<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) (Fig.2) in order to investigate the amorphous nature of the electrolyte. From the XRD analysis of the PVA / SAN composite film, it can be seen that the film exhibited broad scattering peaks at 2θ value around 21° which suggest that the PVA and SAN composite films are virtually amorphous. XRD pattern for pure PVA exhibit diffraction peaks at 2θ = 19.5 and 47° are assigned to PVA. X-ray diffraction studies show that the broadening peak (at about 2θ = 21°) is characteristic of amorphous nature<sup>(8)</sup>. Furthermore, no distinguishable peak of

SAN is observed up to 2 value of 10. No peaks correspond to pure lithium salts appeared in the complex which indicates the complete dissolution of salt in the polymer electrolytes and no excess salts present in the complex<sup>(9)</sup>. Thus, the XRD studies reveal that the formation of complex in the polymer matrices.

### FT-IR Studies

The structure of the various composite polymer blend electrolytes was analyzed by FT-IR spectroscopy. The FT-IR spectra of composite polymer electrolytes revealed the presence of chemical absorption of SAN-PC-LiX and PVA-SAN-PC-LiX (where X= Cl<sup>-</sup>, Br<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>) and are shown in Fig.3 and 4 and the corresponding peak assignments are shown in Table 1 and 2.

A characteristic peak appears at 2237 cm<sup>-1</sup> corresponding to cyanide (CN) group in all four SAN complexes<sup>(10)</sup>. This indicates that there is no change in acrylonitrile content in the complexes. The peaks around 3027 and 2927 cm<sup>-1</sup> are assigned C-H stretching vibration of styrene component of SAN polymer<sup>(11)</sup>. The signals at 1500-1638 cm<sup>-1</sup> resulting from the unsaturation sites in the benzene ring as well as the peaks at 1492 cm<sup>-1</sup> and 1444 cm<sup>-1</sup> attributing to both of stretching vibration of aromatic ring and the deformation vibration of -CH<sub>2</sub><sup>(12)</sup>. The C-O and C=O stretching vibrations of PC occur around 1177 and 1800 cm<sup>-1</sup> and is largely shifted 1192 and 1728 cm<sup>-1</sup> due to interaction of counter ions with polymer. The bending vibration of PC at 849 cm<sup>-1</sup> is shifted towards 858 cm<sup>-1</sup> in the polymer containing SAN, plasticizer PC and LiCl. Similarly the peak at 712 cm<sup>-1</sup> corresponds to ring breathing deformation of PC shifted to 700 cm<sup>-1</sup> upon the addition of polymer SAN and LiX salt.

The band at 2922 cm<sup>-1</sup> is assigned to C-H stretching of both symmetric and asymmetric vibration of CH<sub>3</sub> group. The large band observed between 3414 cm<sup>-1</sup> – 3450 cm<sup>-1</sup> are linked to the stretching O-H from the intermolecular and intramolecular hydrogen bands. The vibrational band observed at 2865 cm<sup>-1</sup> refers to the stretching C-H from alkyl group of PVA<sup>(13)</sup>. The C-N stretching frequency appears at 2140 cm<sup>-1</sup> in all three complexes (P1 – P3) reveal that the presence of SAN polymer in all four complexes. The above assignments indicate that the presence of polymers PVA and SAN in all three blend complexes (P1–P3).

The very strong C–O stretching vibration (1184 cm<sup>-1</sup>) of PC is considerably broadened to 1177 cm<sup>-1</sup> in PVA / SAN / PC / LiX complex. This peak is also considerably broadened and combined with ring stretching vibration of carbonate (PC) in LiBr and Li<sub>2</sub>CO<sub>3</sub> complexes (P2 and P3). The absence of characteristic peak at 1142 cm<sup>-1</sup> responsible for the crystallinity of PVA explains the effective blending of PVA with SAN leading to amorphous nature of the polymer electrolyte<sup>(14,15)</sup>. The vibration at 850 cm<sup>-1</sup> corresponds to CH<sub>2</sub> asymmetric rocking of PVA is largely shifted to 910 cm<sup>-1</sup> in LiCl salt (P1) complexes. This may further indicate the involvement of PVA in the complexes (P1 – P3). The O–C–C bending vibration at 849 cm<sup>-1</sup> is shifted to 831 cm<sup>-1</sup> with the addition of polymer SAN and PVA and Lithium salts. Further, the combination band of –CH<sub>2</sub> rocking and O-H bending vibration of PVA occurs at 1950 cm<sup>-1</sup> is shifted slightly to 1953 cm<sup>-1</sup> upon the addition of polymer SAN and lithium salts<sup>(16-18)</sup>. Then combination of C–O stretching and C–O–C bending vibration (1895 cm<sup>-1</sup>) is shifted lowering to 1885 cm<sup>-1</sup> with the addition of polymers SAN and Lithium salts and PC. The change in intensity, shape and position of the peaks confirms the complexation of PVA/SAN and SAN blends to different lithium salts (X = Cl, Br, and CO<sub>3</sub><sup>2-</sup>) and plasticizer (PC)<sup>(19,20)</sup>.

### Conclusion

Polymer electrolyte films were prepared using SAN, PVA, PC and lithium salts comprising of chloride, bromide, carbonate as counter anions. FT-IR studies provide strong evidence that there is

a specific interaction between PVA and SAN blends that favours the miscibility of the blends. The amorphous morphology of the polymeric blends with lithium salts and plasticizers is confirmed from the XRD analysis where it shows no distinct sharp crystalline peaks are observed. Thus formation of the amorphous polymeric blend in the above samples suggest application of these polymeric films as electrolytes.

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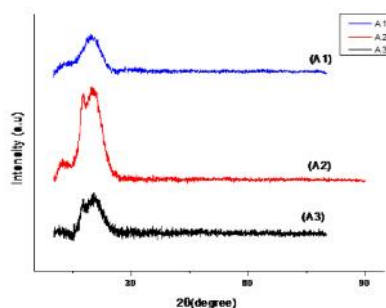
## Figure Captions

1. **Figure 1:** XRD pattern of SAN-PC with LiCl (A1),  $\text{Li}_2\text{CO}_3$  (A2), and LiBr (A3).
2. **Figure 2:** XRD pattern of PVA-SAN-PC with LiCl (P1),  $\text{Li}_2\text{CO}_3$  (P2), and LiBr (P3).
3. **Figure 3:** FT-IR Spectra of SAN+PC with (a) LiCl, (b)  $\text{Li}_2\text{CO}_3$ , (c) LiBr.
4. **Figure 4:** FT-IR Spectra of PVA+SAN+PC with (P1) LiCl, (P2)  $\text{Li}_2\text{CO}_3$ , (P3) LiBr.

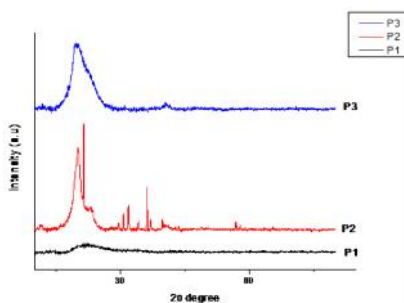
## Tables

**Table 1:** FT-IR Spectral assignment of SAN+PC with LiCl (A1),  $\text{Li}_2\text{CO}_3$  (A2) and LiBr (A3).

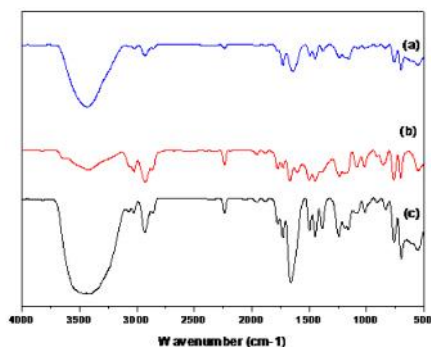
**Table 2:** FT-IR Spectral assignment of PVA+SAN+PC with LiCl (P1),  $\text{Li}_2\text{CO}_3$  (P2) and LiBr (P3).



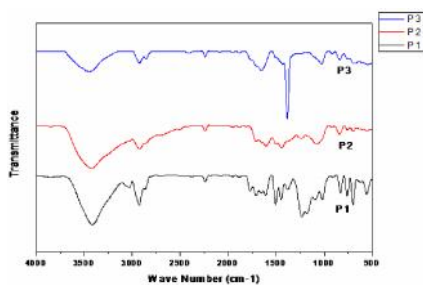
**Figure 1: XRD pattern of SAN-PC with LiCl (A1),  $\text{Li}_2\text{CO}_3$  (A2), and LiBr (A3)**



**Figure 2: XRD pattern of PVA-SAN-PC with LiCl (P1),  $\text{Li}_2\text{CO}_3$  (P2), and LiBr (P3)**



**Figure 3: FT-IR Spectra of SAN+PC with (a) LiCl, (b)  $\text{Li}_2\text{CO}_3$ , (c) LiBr**



**Figure 4: FT-IR Spectra of PVA+SAN+PC with (P1) LiCl, (P2)  $\text{Li}_2\text{CO}_3$ , (P3) LiBr**

**Table 1: FT-IR Spectral assignment of SAN+PC with LiCl (A1), Li<sub>2</sub>CO<sub>3</sub> (A2) and LiBr (A3)**

Sl. No.	Vibrations	A1	A2	A3
1	C-N <sub>str. (SAN)</sub>	2237	2237(s)	2237(m)
2	C-H <sub>aromatic (SAN)</sub>	3027	3026	3026
3	C-H <sub>alkene (styrene)</sub>	2927	2929	2926
4	CH <sub>alkyl (PC)</sub>	2862(sh)	2859(sh)	2859(sh)
5	C-O <sub>Str.</sub>	1192(s)	1190(s)	1163(sh)
6	C = O <sub>Str.</sub>	1728	1773	1773
7	CO <sub>3</sub> <sup>2-</sup> (sym-def)	758	758	758
8	Ring breathing vibration of CO <sub>3</sub> <sup>2-</sup> ion	699	697	697
9	Ring str. vibration CO <sub>3</sub> <sup>2-</sup>	1085	1081	1076
10	O-C-C bending	858	834	834

**Table 2: FT-IR Spectral assignment of PVA+SAN+PC with LiCl (P1), Li<sub>2</sub>CO<sub>3</sub> (P2) and LiBr (P3)**

S. No.	Vibration	P1	P2	P3
1	O-H Stretching vibration (PVA)	3417	3427	3446
2	C-H <sub>aromatic</sub> Stretching vibration (SAN)	3029	3028	3020
3	C-H Stretching alkyl (SAN)	2927	2922	2923
4	C-H alkyl Stretching of PVA	2865	2857	2851
5	C ≡ N Stretching vibration (SAN)	2239	2240	2239
6	Ring breathing vibration of CO <sub>3</sub> <sup>2-</sup>	699	699	695
6a	C-O Stretching of PC	1381	1443	1383
7	O-C-C bending vibration	831	838	837
8	Ring stretching vibration of CO <sub>3</sub> <sup>2-</sup>	1096	1083	1027
9	Symmetric deformation CO <sub>3</sub> <sup>2-</sup>	759	757	-
10	Combination of band of CH <sub>2</sub> – rocking and O-H bending vibration (shouldn't at 1950 (PVA))	1954	1952	1953
11	Combination of C-O stretching C-O-C bend (1895) (PVA)	1885	1884	1882
12	CH <sub>2</sub> – asymmetric rocking of PVA (850)	908	913	913