

## Chapter 7

### Conclusions and Future Scope

This chapter presents some closing thoughts on the important findings covered in the preceding chapters. The objectives defined in the first chapter are reviewed and important outcomes are addressed. Possible propositions for future work indicated by this research work are also suggested.

#### 7.1 CONCLUSIONS

In the last two decades, various approaches have been adopted to develop highly ion conducting solid polymer electrolytes. Very recently, dispersion of conductive (active) fillers into the polymer matrix has been a widely accepted approach to developed fast ionic CSPEs for the development of all-solid-state devices, in particular ASSBs.

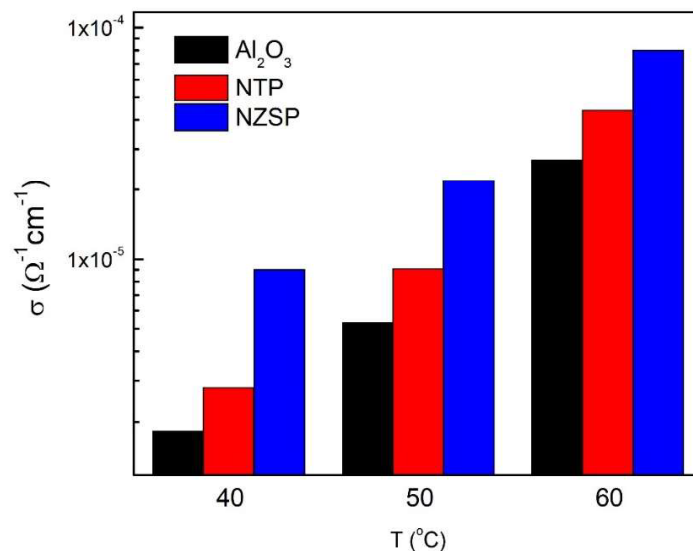
Considering the high bulk conductivity, synthesis of polymer composites was planned using fast ionic solids based on the NASICON framework, e.g.  $\text{LiTi}_2(\text{PO}_4)_3$  (LTP),  $\text{Li}_{1.3}\text{Ti}_{0.7}\text{Al}_{0.3}(\text{PO}_4)_3$ ,  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ , etc. Given their novelty, thorough characterization was also one of the important objectives. In the last few years, some work was done on polymers reinforced with NASICONs. However, a detailed investigation on electrical transport and its mechanism was missing. Further, the compositions were reported in a very narrow range. A wide compositional variation in  $\text{Na}^+$  and  $\text{Li}^+$  ion systems was also required to be carried out in view of ‘ceramic in polymer’ and ‘polymer in ceramic’ approaches. Thus, the present work was also focussed on establishing the merit of these hybrid polymer-NASICON nanocomposites as an electrolyte in all-solid-state supercapacitors. Work on ASSCs still has a strongly dependence on gel electrolytes. We found very less work on ASSCs based on SPEs (solvent-free) in the literature. Hence, while planning a systematic study on polymer-NASICON composites, we pondered around the following questions to define the proposed objectives (chapter 1) of the thesis.

- i. Whether conductive fillers ( $\text{LiTi}_2(\text{PO}_4)_3$  (LTP),  $\text{Li}_{1.3}\text{Ti}_{0.7}\text{Al}_{0.3}(\text{PO}_4)_3$ ,  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ) can enhance the conductivity of composite similar to that of insulating nano-fillers ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ , etc.)?
- ii. What is the limit to which the conductivity can be enhanced? Is it possible to work on a wide composition range and explore new types of composites based on approaches, viz. “polymer in ceramic” and “ceramic in polymer”?
- iii. What is the role of different constituents of the composite namely salt, polymer, size of active filler, and volume fraction in the electrical transport?
- iv. Whether such a dispersion affects uniquely to a particular cation based composites? Can it be applicable to  $\text{Li}^+$  as well as  $\text{Na}^+$  ion systems? In other words, whether conductivity rise is a consistent and general phenomenon?
- v. Can a generalized ion transport mechanism (at least for  $\text{Li}^+$  and  $\text{Na}^+$ ) be proposed using sophisticated techniques, e.g. X-ray absorption spectroscopy or x-ray photoelectron spectroscopy? Is it possible to correlate conductivity with the structure of the composites?
- vi. How high the ionic conductivity can be achieved for  $\text{Li}^+$  and  $\text{Na}^+$  systems in solid state? Whether it is also possible to alter the ionic transport number due to such a reinforcement?
- vii. Whether such a substitution affects thermal stability/thermal cycling of the composites? How the PEO melting event (which is a known hindrance for its application to high temperature devices) can be suppressed due to the formation of such hybrids?
- viii. Due to high ionic conductivity at ambient temperatures, can these composites be treated as potential candidates for solid ionic energy storage devices? Are they stable under electrochemical conditions?
- ix. Due to the high ionic conductivity of the  $\text{Na}^+$  ion conducting systems, can these be applied as electrolytes in all-solid-state supercapacitors? what is the role of reinforced NASICON crystallites in the performance?
- x. What is the stability of these hybrid composites with time?.

Although a huge amount of work is required to be done on each of these defined questions, the present thesis attempted to answer most of the questions. It could at least address major issues.

In the wake of the above questions, present work was planned and methodology was designed for a thorough understanding of these novel composites. It was planned to concentrate on  $\text{Li}^+$  ion as well as  $\text{Na}^+$  ion based NASICON polymer hybrid systems. To understand the role of NASICON in enhancing the ionic conductivity, basic NASICON structures viz. NTP and LTP were chosen for their reinforcement in a wide composition range. Further, to study the role of bulk conductivity of NASICON in enhancing the ionic conductivity of the composites, highly conducting NASICON viz. LATP and NZSP were also chosen for dispersion in the polymer matrix. To propose a mechanism of ion transport in these composite, synchrotron-based x-ray absorption spectroscopy and x-ray photoelectron spectroscopy were explored to correlate the structural findings with conductivity. Further, to explore the potential of these electrolytes in all-solid-state devices, using locally developed electrodes viz. activated carbon and MWCNT- $\text{MnO}_2$ , all-solid-state supercapacitors were fabricated in 2032 type cells. The following points conclude the results obtained as a direct consequence of meeting the defined objectives :

**(i) Role of active fillers:** Incorporation of conducting fillers in polymer matrix leads to a huge conductivity enhancement in both  $\text{Li}^+$  and  $\text{Na}^+$  ion conducting CSPEs. Fig. 7.1 highlights the importance of the conductivity of the fillers in enhancing the ionic conductivity of the CSPEs.



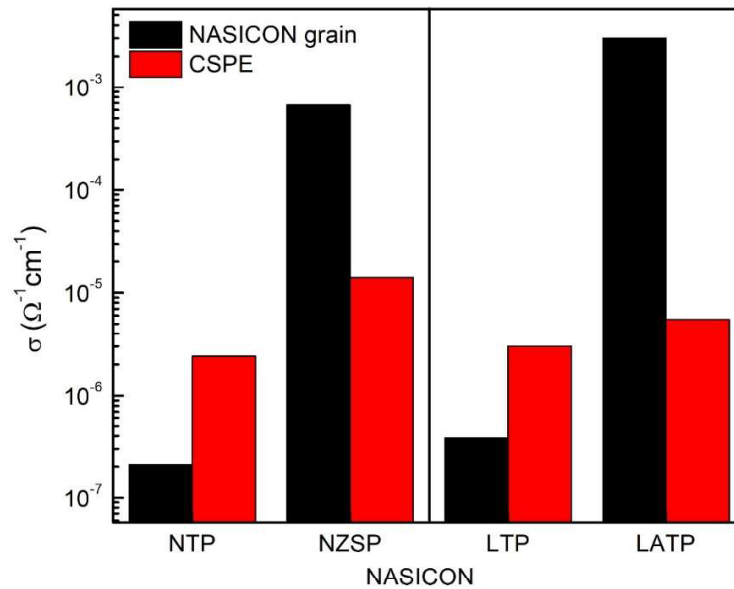
**Figure 7.1** Conductivity of 10NaI-90(60PEO40M) at three different temperatures, where M corresponds to dispersoids NTP,  $\text{Al}_2\text{O}_3$ , and NZSP ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ) of almost same crystallite size of ~ 30 nm

Polymer matrix with the same O/Na ratios is dispersed with different fillers ( $\text{Al}_2\text{O}_3$ ; insulating, NTP; moderate conductor and NZSP; highly conducting). As evident, the conducting nature

of the fillers affects the ionic conductivity of the composites. Even for the moderate content of fillers, enhancement is found to be more significant for active fillers than the insulating nanoparticles. Importantly, this is found to be a general phenomenon. Conductivity increases for all types of ion conducting fillers. How high the rise will be, depends on filler conductivity.

**(ii) Wide composition range:** Active fillers give the flexibility of synthesis in a very wide composition range. Thus, composites could be prepared using both approaches viz. “polymer in ceramic” or “ceramic in polymer”. Composite with lower NASICON content was in a thin film form of 150-250  $\mu\text{m}$  thickness, while the composite with higher NASICON content ( up to 63 wt%) were in pellet shape or sheets of thickness  $\sim 450 \mu\text{m}$ .

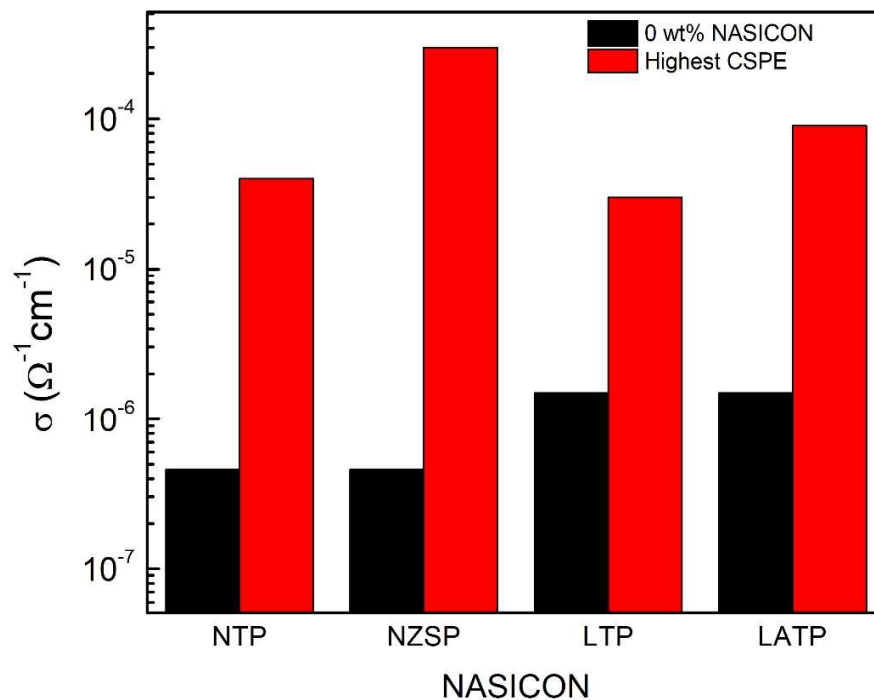
**(iii) Role of in-grain/bulk conductivity of the NASICON:** Grain interior/bulk conductivity of the NASICON plays a major role in the enhancement of ionic conductivity of the composites in both  $\text{Li}^+$  and  $\text{Na}^+$  ion conducting systems. The composites dispersed with highly conducting NASICON such as NZSP and LATP exhibit a greater ion conductivity as compared to CSPEs dispersed with basic NASICON structures such as NTP and LTP respectively. To highlight such an effect, a comparative ionic conductivity of CSPEs for  $\text{Li}^+$  and  $\text{Na}^+$  ion conducting systems at the same NASICON content (36 wt %) ratio is shown in Fig. 7.2.



**Figure 7.2.** Effect of grain conductivity in CSPEs at 40°C for same NASICON content (36 wt %).

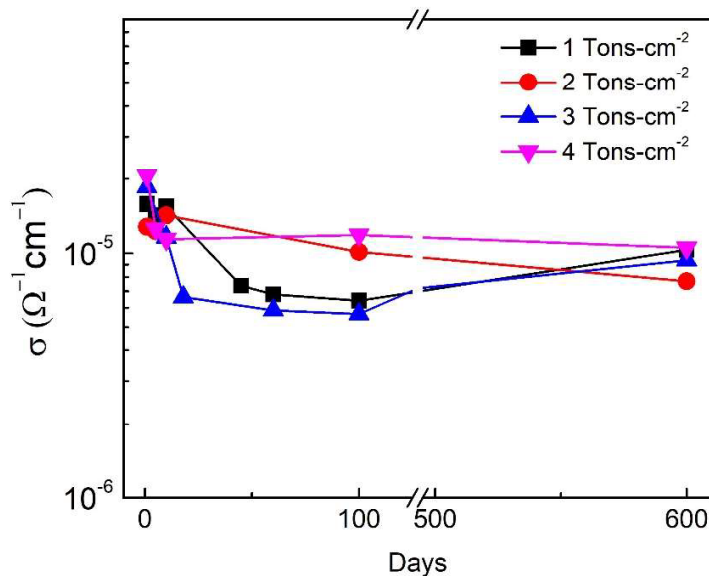
**(iv) Cation transport number and Mobility:** Dispersion of NASICON is found to be an effective method to tailor cation transport number. An interesting observation in the present work is a substantial enhancement in cation transport number due to NASICON addition. This is indeed encouraging as high  $t_+$  would finally lead to localization of anions. A uni-ion device can be realized using this approach. Current work is an important step towards it. Moreover, active filler reinforcement also leads to enhancement in ionic mobility by several orders of magnitudes. Enhanced mobility in the composites, i.e. improvement in the response to electric field readily suggests their strong candidature for the device applications.

**(v) Maximum ionic conductivity achieved:** Dispersion of such highly conducting NASICON provides a maximum room temperature ionic conductivity of  $\sim 10^{-4} \Omega^{-1}\text{cm}^{-1}$  for  $\text{Na}^+$  and  $\text{Li}^+$  ion systems as can be seen again in Fig. 7.3. These are the highest conductivity values reported so far for such CSPEs at room temperature. To highlight the huge enhancement in ionic conductivity with NASICON dispersion, a comparison of ionic conductivity of composites with their host polymer systems is shown in Fig. 7.3.



*Figure 7.3. Highest conducting CSPEs compared with their host polymer salt complex at 40°C.*

(vi) **Thermal stability:** The critical issue of the PEO based polymer electrolyte is the melting event near room temperature. It is important to again emphasize that the dispersion of NASICON not only enhances the ionic conductivity but also provides excellent thermal stability at least up to 100°C for a higher concentration of NASICONs. The  $\sigma$ -T cycles for composites with adequate NASICONs are highly reproducible. This readily suggests the applicability of these polymer-NASICON composites as an electrolyte in energy storage devices that require a wide operating temperature range. If used in devices, it will help in exceeding the current limit of  $\sim 60^\circ\text{C}$  for the devices. Apart from thermal stability, the electrical conductivity of the composites is also stable with time as shown in Fig. 7.4.



*Figure 7.4. Ionic conductivity of the CSPEs in pellet form at 40°C with days.*

(vii) **Ion transport mechanism:** This is for the first time that a conductivity-structure correlation is demonstrated in polymer using soft X-ray absorption. XAS is found to be suitable for investigating polymer composites. A thorough investigation of the chemical charge state of the ether oxygen of polymer with NASICON content using synchrotron based XANES and XPS technique quite accurately provide cation interaction with ether oxygen of polymer. Results from both techniques complement each other. These sophisticated techniques provide strong evidence of cation decoupling from ether oxygen of polymer at higher NASICON content in the CSPEs. Using these, a generalized ion transport mechanism in  $\text{Li}^+$  and  $\text{Na}^+$  ion

conducting polymer-NASICON hybrid composites could be proposed. The mechanism is consistent for  $\text{Li}^+$  as well as  $\text{Na}^+$  ion composites.

**(viii) Potential of these CSPEs in ASSC:** Using the well optimized and highly conducting  $\text{Na}^+$  ion conducting composites, ASSCs in EDLC and pseudo-type configuration could be developed. These ASSCs exhibit an appreciable energy storage capacity. It was observed that the electrolyte conductivity, i.e. the NASICON content plays important role in improving energy storage. ASSCs with  $\text{Na}^+$  ion conducting CSPEs provide an excellent discharge capacity of  $104\text{F}\cdot\text{g}^{-1}$  and suitable cycling performance up to 400 in EDLC configuration. Apart from high discharge capacitance, the ASSCs also provide a high operating voltage of 2V. Also, with the similar composites, the ASSCs in pseudo type exhibits a maximum discharge capacity of  $\sim 205\text{F}\cdot\text{g}^{-1}$  at a discharge current density of  $0.08\text{A}\cdot\text{g}^{-1}$ . Results further suggest that these composites are potential solid electrolytes for future all-solid-state devices.

## 7.2 FUTURE SCOPE

- (i) In the current work, composite polymer solid electrolyte were developed using NASICON based fillers. However, to further enhance the ionic conductivity of the CSPEs, there is a need to explore better conducting fillers such as garnets which exhibit even higher in grain ionic conductivity  $\sim 10^{-3} \Omega^{-1}\text{cm}^{-1}$  at room temperature. As compared to NASICON, these materials not only exhibit higher conductivity but also provide good stability against Li metal along with a wide electrochemical stability window. Such composite would provide a better ionic conductivity in CSPEs. Also, ion transport mechanism proposed in the thesis should be examined for such composites using sophisticated techniques e.g. XANES, XPS, or solid state NMR.
- (ii) In the current work, the ion transport mechanism was explored using sophisticated techniques such as XPS, XANES, and Impedance spectroscopy. However, electrical transport especially impedance spectroscopy can further be explored in GHz region for a better understanding of the electrical response. Also, since XPS is limited to surface studies, nevertheless we have taken proper precautions in interpreting results in the present thesis. It would now be nice to look for depth profiling studies using XPS technique essentially to understand the bulk. Theoretical studies may also be carried out to complement the proposed mechanism.

- (iii) In the present work, the potential of the developed CSPEs was explored as an electrolyte for Na<sup>+</sup> ion conducting EDLCs fabrication. Also, preliminary investigations on applications of these composites electrolytes in pseudocapacitors are encouraging. However, there is a need to study systematically the effect of NASICON content on the charge transfer mechanism. In view of the high ionic conductivity of the LATP dispersed Li<sup>+</sup> ion systems, these are also required to be explored for their use in all-solid-state supercapacitors. A systematic variation of active filler content and its effect on supercapacitance is a way forward to develop ASSCs of desired capacitance.
- (iv) In the present work, the fabrication of ASSCs were carried out in 2032 button cell. The present composites can also be developed in flexible thin film form. Thus studies on flexible ASSCs based on these composites can be a good future work.
- (v) The cell performance of the CSPEs was studied using some standard electrodes, viz. activated carbon and MWCNT-MnO<sub>2</sub> composite. However, to achieve a good storage capacity device, a systematic study using different electrodes for Na<sup>+</sup>/Li<sup>+</sup> ion conducting composites should be attempted. Also, further high surface area (1000-2500 m<sup>2</sup>g<sup>-1</sup>) may lead to better capacitance. Symmetric pseudo, EDLCs, and asymmetric pseudocapacitors can be explored in the future.
- (vi) In the present study, the possibility of these CSPEs in all-solid-state supercapacitor was explored. However, a detailed understanding on the charge transport mechanism at the electrode-electrolyte interface in ASSCs also needs to be explored using in-situ techniques e.g. in-situ XAS, XRD etc.
- (vii) In fact, with a relatively poor conductive active filler, one can find conductivity enhancement by altering the host polymer network. The use of plasticizers and active fillers together may lead to better conductivity enhancement. Efforts are required in this direction.
- (viii) These composites are electrochemically stable, thus are potential candidates for all-solid-state batteries. Particularly high ionic conductivity achieved is encouraging. These composites should be examined for Na<sup>+</sup> ion and Li<sup>+</sup> ion ASSBs.