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Review Article

# Effect of incorporation of different plasticizers on structural and ion transport properties of PVA-LiClO<sub>4</sub> based electrolytes

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## Abstract

To date high ionic conducting polymer electrolytes are of great interest because of their potential applications in various electrochemical devices such as batteries, fuel cells, solar cells and super capacitors etc., as electrolytes. Ion conduction through polymer electrolytes can occur mostly in amorphous environment exists above their glass transition temperature ( $T_g$ ). In order to improve ionic conductivity, many approaches such as addition of plasticizer, blending of polymers, nano composite have been employed. This paper reviews the influence of different plasticizers/additives on the ion transport mechanism of Poly(vinyl alcohol) (PVA)-LiClO<sub>4</sub> polymer electrolytes since poly vinyl alcohol is a semi crystalline, synthetic biodegradable polymer and lithium perchlorate is one of the most moisture resistant lithium salts. This review also reveals the relation between dynamical disorder in polymer electrolyte with ionic conductivity.

Keywords: Materials science, Electrochemistry, Materials chemistry

## 1. Introduction

Rechargeable Li ion cells which are the key component as power supply for portable, computing and telecommunication services, consist of two electrodes, a reductant (anode) and oxidant (cathode) which are separated by an electrolyte. Electrolyte plays the major role in transferring ionic components, created during the chemical reaction that occurs inside the cell from cathode to anode and vice-versa [1].

Lithium ion batteries are more attracted than other batteries because of its high operating voltage and high capacity parameters. Most of the commercial Li-ion batteries use liquid electrolytes that have serious issues like leakage, corrosion at electrodes which are to be solved. Solid electrolytes overcome the issues of liquid electrolyte and conduct electricity by the movement of ions with negligible electronic transport. The present focus in lithium ion batteries is to exploit safe polymer electrolytes as solid electrolyte and to finally fabricate batteries with full plastic structure. Such plastic  $\text{Li}^+$  batteries with solid electrolyte are anticipated low cost with mass production than their liquid counterparts. In addition, the presence of solid electrolytes allows packaging in light-weight, less volume plastic containers.

Polymer electrolyte refers to any macromolecular polymer chain with added ionic salt characterized by a significant ionic conductivity approximately of the order of  $10^{-6} \text{ S cm}^{-1}$  [2]. They are having advantages such as natural seal, resistance to shock and vibration, resistance to temperature and pressure variation. Main drawbacks of this type of electrolytes are (i) low ambient conductivity and (ii) high interfacial resistance with electrodes. The above drawbacks are to be rectified by different approaches such as blending of two polymers [3, 4], plasticizing [5, 6] the polymer matrix using liquid additive, incorporation of nano sized fillers [7, 8, 9, 10] into polymer matrix etc.

Among them, addition of some small amount liquid into polymer matrix can plasticize the polymer chain as well as enhances the salt dissociation rate. Non volatile organic solvents or low molecular weight polymers are mostly used as plasticizer. For example, polyethylene glycol (PEG-200, PEG-400, PEG-600), dimethylformamide (DMF), ethylene carbonate (EC), propylene carbonate (PC) etc are reported as good plasticizers.

This short review is devoted to deal with PVA based polymer electrolytes,  $\text{LiClO}_4$  based polymer electrolytes and plasticized PVA- $\text{LiClO}_4$  polymer electrolytes with various plasticizers. Further, discussions are made with two new types of plasticizers called Sulfolane (Tetra Methyl Sulfone) and Triton (Poly ethylene glycol p-tert octyl phenyl ether) in to PVA- $\text{LiClO}_4$  electrolyte.

## 2. Main text

### 2.1. PVA based solid polymer electrolytes (SPEs)

PVA based electrolytes are extensively being studied till now for different applications. These electrolytes really refer solvent-free PVA/salt complexes. Many research investigations have been dedicated to develop proton conducting [11, 12, 13, 14, 15, 16],  $Mg^{2+}$  conducting [17],  $Cu^{2+}$  conducting [18] and  $Li^+$  ion conducting [10, 19, 20, 21] and  $Ag^{2+}$  [22] ion conducting electrolytes using PVA as host polymer. The electrolytes exhibit conductivity in the range of  $10^{-7}$  to  $10^{-3}$  S  $cm^{-1}$  at ambient temperature and are listed in Table 1. But, the membrane with very low conductivity cannot be used in battery applications.

Hema et al [14] prepared proton conducting solid polymer electrolyte using ammonium iodide ( $NH_4I$ ) as ionic salt and Dimethyl Sulfoxide (DMSO) as solvent. They clearly explained the correlation between crystallinity and dc conductivity of electrolyte films. They calculated crystallinity from Differential Scanning Calorimetry (DSC) studies. According to them, the film which contains low crystallinity shows maximum conductivity. This may be due to the reason that increase of amorphous nature reduces the energy barrier for ion movement and there by facilitates the fast ion transport.

PVA is a semi crystalline polymer. In order to prepare high conducting polymer electrolyte using PVA as host polymer, it is essential to reduce its semi-crystalline phase into amorphous using appropriate salts or plasticizers or fillers or blending polymer host. Rathod et al [10] achieved higher ambient temperature conductivity

**Table 1.** Electrolyte composition and dc conductivity values for various ion conducting PVA based solid polymer electrolytes.

S. No	Electrolyte composition	dc conductivity at RT (S $cm^{-1}$ )	References
1.	PVA – $CH_3COONH_4$	$5.62 \times 10^{-6}$	[11]
2.	PVA – $Cu(NO_3)_2$	$1.60 \times 10^{-5}$	[18]
3.	PVA – $AgNO_3$	$7.56 \times 10^{-7}$	[22]
4.	PVA – $NH_4Br$	$5.70 \times 10^{-4}$	[13]
5.	PVA – $NH_4I$	$2.50 \times 10^{-3}$	[14]
6.	PVA – $LiAsF_6$ – $TiO_2$	$5.10 \times 10^{-4}$	[20]
7.	PVA – Poly acrylonitrile (PAN) – $LiClO_4$	$8.64 \times 10^{-6}$	[15]
8.	PVA – $Mg(NO_3)_2$	$7.32 \times 10^{-7}$	[17]
9.	PVA – Poly vinyl pyrrolidone (PVP) – $CH_3COONH_4$	$8.12 \times 10^{-5}$	[19]
10.	PVA – $H_3PO_4$	$2.56 \times 10^{-3}$	[16]
11.	PVA – Chitosan – $LiClO_4$	$3.00 \times 10^{-6}$	[10]
12.	PVA – Starch – $LiBr$	$5.00 \times 10^{-3}$	[21]

of the order of  $10^{-6}$  by incorporating different concentrations of  $\text{LiClO}_4$  into PVA-Chitosan matrix. The complex nature between salt and polymer host was confirmed by FT Raman and UV-Vis studies. It was found that the dielectric properties of the composites followed non-Debye behavior.

Blending the polymer host is other way to improve electrical, thermal, mechanical and electrochemical properties of polymer electrolyte. One of such work was done by Chatterjee et al. [21]. They prepared PVA-Potato starch-LiBr (Lithium bromide) blend polymer electrolytes. They achieved highest ambient temperature conductivity of  $5 \times 10^{-3} \text{ S cm}^{-1}$  for 20% of LiBr into blend matrix. Enhancement of the conductivity upon addition of salt is correlated to the enhancement of amorphous nature of polymer electrolyte and was also confirmed through XRD studies.

In summary, PVA based solid/blend/nano composite polymer electrolytes were studied by various research groups. In all types of polymer electrolytes, enhancement of conductivity is somehow correlated to the increase of amorphous region of polymer matrix.

## 2.2. PVA based plasticized polymer electrolytes

This section focuses the plasticized PVA electrolytes which are available in literature. The incorporation of substantial amount of plasticizer in the polymer electrolytes enhances the ionic conductivity of polymer electrolytes. Plasticizer facilitates the reduction of crystalline nature of the polymer matrix and also increases the polymer segmental mobility. It further results in greater ion dissociation which allows greater number of charge carriers for ion transport in the electrolyte. Many research groups have been working in the field of plasticized polymer electrolytes [23, 24, 25, 26, 27, 28, 29, 30, 31]. They have obtained ambient temperature conductivity values in the range of  $10^{-7} - 10^{-3} \text{ S cm}^{-1}$ . Electrolyte composition and their corresponding dc conductivity values are listed in Table 2.

The effect of plasticizers (sulfolane/triton) on the structural properties of PVA -  $\text{LiClO}_4$  matrix through XRD (Fig. 1) was studied by our group. The characteristic diffraction peak around  $2\theta = 20^\circ$  of PVA which shows its semi-crystalline nature was disrupted upon addition of 20 mol%  $\text{LiClO}_4$  into PVA matrix. The relative degree of crystallinity is calculated using the formula (Eq. 1),

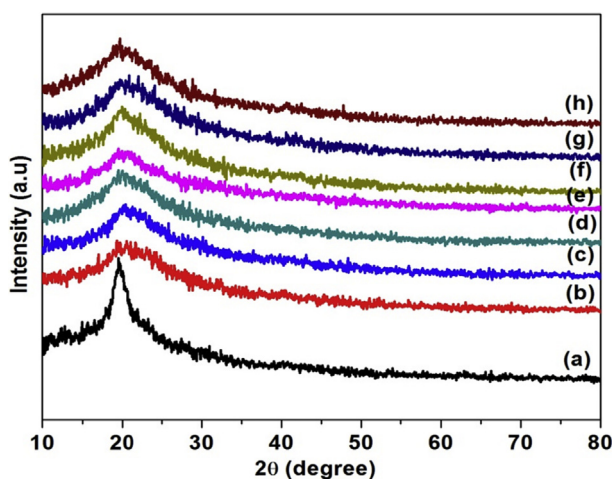
$$\chi_C = \frac{I_C}{I_C + I_a} \times 100\% \quad (1)$$

where,  $I_C$  is integrated intensity of crystalline region.

$I_a$  is integrated intensity of amorphous region.

**Table 2.** Electrolyte composition and dc conductivity values for various ion conducting PVA based plasticized polymer electrolytes.

S.No	Electrolyte composition	dc conductivity at RT ( $S\text{ cm}^{-1}$ )	References
1.	PVA – Chitosan – $\text{NH}_4\text{NO}_3$ – Ethylene Carbonate	$1.60 \times 10^{-3}$	[23]
2.	PVA – KI – N-Methyl Pyrrolidone- $\gamma$ -butyrolactone	$8.41 \times 10^{-3}$	[24]
3.	PVA – PMMA – $\text{LiBF}_4$ – Ethylene Carbonate	$1.28 \times 10^{-6}$	[25]
4.	PVA – PVP – $\text{KClO}_3$ – Dimethyl formamide	$7.4 \times 10^{-7}$	[26]
5.	PVA – PVP – KOH – Propylene Carbonate - Ethylene Carbonate	$1.5 \times 10^{-4}$	[27]
6.	PVA – KOH – $\text{Al}_2\text{O}_3$ -Propylene Carbonate	$\sim 10^{-4}$	[28]
7.	PVA – $\text{LiClO}_4$ -[EMIM][EtSO <sub>4</sub> ]	$1.9 \times 10^{-6}$	[29]
8.	PVA – $\text{NH}_4\text{SCN}$ – Dimethyl sulfoxide	$2.58 \times 10^{-3}$	[30]
9.	PVA – PMMA – $\text{LiClO}_4$ –Dimethyl Phthalate	$6.0 \times 10^{-4}$	[31]
10.	PVA – $\text{LiClO}_4$ – Dimethyl Phthalate	$1.49 \times 10^{-3}$	[32]

**Fig. 1.** XRD diffractogram of (a) Pure PVA (b) 80mol% PVA:20mol%  $\text{LiClO}_4$  (c) 75.3 mol% PVA:20 mol%  $\text{LiClO}_4$ :4.7 mol% sulfolane (d) 69.9 mol% PVA:20 mol%  $\text{LiClO}_4$ :10.1 mol% sulfolane (e) 59.3mol % PVA:20 mol%  $\text{LiClO}_4$ :20.7 mol% sulfolane (f) 78.9 mol% PVA:20 mol%  $\text{LiClO}_4$ :1.1 mol% triton (g) 78 mol% PVA:20 mol%  $\text{LiClO}_4$ :2 mol% triton (h) 76 mol% PVA:20 mol%  $\text{LiClO}_4$ :4 mol% triton electrolytes.

$I_c$  and  $I_a$  values were obtained by deconvoluting the XRD spectra. (deconvoluted spectra are not shown). The calculated relative degree of crystallinity values are listed in Table 3.

While adding various amounts of sulfolane/triton into 80mol%PVA: 20mol% Li- $\text{ClO}_4$  electrolyte (Fig. 1b), amorphous nature of the electrolyte is further increased.

**Table 3.** Relative degree of crystallinity of PVA-LiClO<sub>4</sub>-sulfolane/triton electrolytes.

S.No	Sample designation (mol%)	Relative degree of crystallinity (%)
1.	100:0 (Pure PVA)	19.08 ± 0.33
2.	80PVA:20LiClO <sub>4</sub>	16.86 ± 0.45
3.	75.3 PVA:20 LiClO <sub>4</sub> :4.7sulfolane	13.38 ± 0.35
4.	69.9 PVA:20 LiClO <sub>4</sub> :10.1sulfolane	11.78 ± 0.37
5.	59.3 PVA:20 LiClO <sub>4</sub> :20.7sulfolane	12.99 ± 0.33
6.	78.9 PVA:20 LiClO <sub>4</sub> :1.1triton	14.60 ± 0.46
7.	78 PVA:20 LiClO <sub>4</sub> :2 triton	15.44 ± 0.41
8.	76 PVA:20 LiClO <sub>4</sub> :4 triton	16.23 ± 0.44

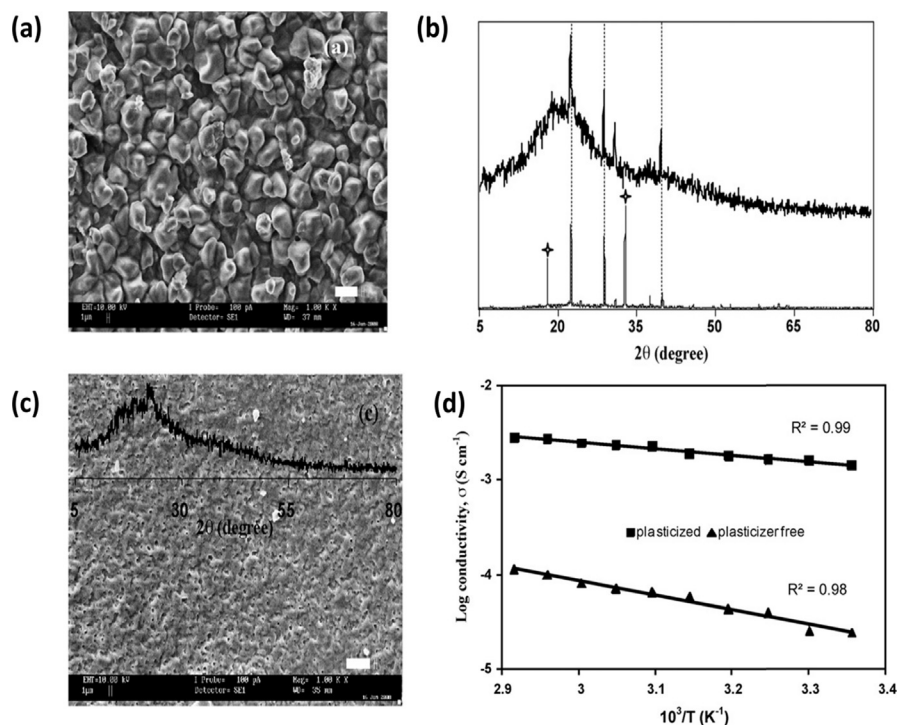
Fig. 1 shows the XRD pattern of PVA-LiClO<sub>4</sub>-Sulfolane (Fig. 1 (c–e)) and PVA-LiClO<sub>4</sub>-Triton (Fig. 1 (f–h)) electrolytes.

From the Table 3, both plasticizers reduced the crystalline phases available in PVA-LiClO<sub>4</sub> matrix and thus it created sophisticated conducting pathways for charge carriers. Another important observation is that sulfolane effectively plasticize the PVA-LiClO<sub>4</sub> matrix than triton which is reflected on degree of crystallinity values. This result is consistent with the results of conductivity study where sulfolane based electrolytes shows higher conductivity than triton based electrolytes.

Kadir et al. [23] plasticized PVA-Chitosan blend matrix using Ethylene carbonate (EC). The conductivity was found to the order of 10<sup>-3</sup> S cm<sup>-1</sup> for the addition of 70 wt% of EC. They calculated that the carrier concentration values are 6.57 × 10<sup>19</sup> cm<sup>-3</sup> and 2.20 × 10<sup>21</sup> cm<sup>-3</sup> for bare and 70 wt% EC incorporated electrolytes respectively and mobility values are 1.97 × 10<sup>-6</sup> and 4.54 × 10<sup>-6</sup> cm<sup>2</sup>V<sup>-1</sup>S<sup>-1</sup> for plasticizer free and plasticizer added electrolytes respectively. Thus the conductivity enhancement is primarily due to carrier concentration enhancement and secondarily due to carrier mobility enhancement. They also observed that EC free electrolyte matrix has some regular arrangement with crystalline phase using Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD) characterization. After the addition of EC, the observed regular arrangement and crystalline phase completely changed into amorphous. Effect of EC on the structural and morphological properties of (PVA-Chitosan) – NH<sub>4</sub>NO<sub>3</sub> electrolyte are given in Fig. 2.

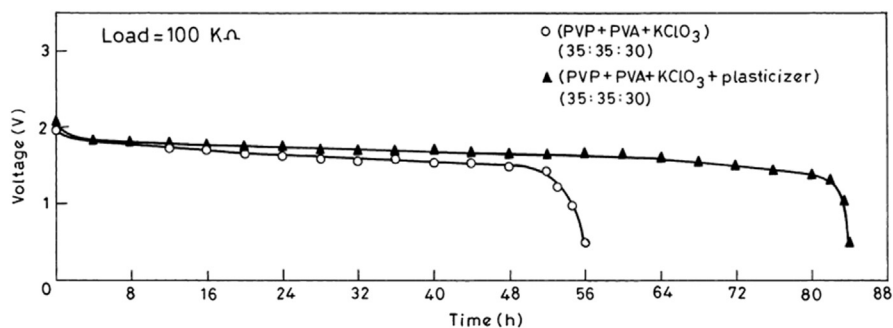
Fig. 2 (d) clearly explained that temperature dependent conductivity obeys Arrhenius rule irrespective of plasticizer addition. It all reveals that plasticizer addition affects the crystallinity and morphological properties and not the conduction mechanism involved.

In some investigations, plasticizer addition did not improve the conductivity in significant manner but it efficiently enhanced the electrochemical properties. One of



**Fig. 2.** (a) SEM image (b) XRD pattern of plasticizer free PVA-Chitosan-  $\text{NH}_4\text{NO}_3$  complex (c) XRD and SEM image of 70 wt % EC (d) Arrhenius plot of plasticizer free and plasticizer added electrolytes [23] "Reprinted from *Electrochimica Acta*, vol.55(4), M.F.Z Kadir, S.R.Majid, A.K.Arof, Plasticized Chitosan-PVA blend polymer electrolyte based proton battery, 1475–1482 copyright (2018) with permission from Elsevier".

such work is reported in [26], in which authors used DMF to plasticize PVA-PVP- $\text{KClO}_3$  electrolyte. The conductivity value of bare electrolyte is reported to be  $4.6 \times 10^{-7} \text{ S cm}^{-1}$  while DMF plasticized electrolyte shows the conductivity value of  $7.4 \times 10^{-7} \text{ S cm}^{-1}$ . It was found that DMF incorporated PVA-PVP- $\text{KClO}_3$  blend polymer electrolyte system shows an increased discharge time and is presented in Fig. 3.



**Fig. 3.** Discharge characteristics of DMF free and DMF plasticized PVA-PVP- $\text{KClO}_3$  matrix [26] "Reprinted from *Journal of Power Sources*, vol.111(2), Ch.V.Subba Reddy, A.K.Sharma, V.V.R.Narasimha Rao, Effect of plasticizer on electrical conductivity and cell parameters of PVP + PVA +  $\text{KClO}_3$ , 357–360 copyright (2018) with permission from Elsevier".

The electrochemical cells were fabricated using the electrolytes that contain plasticizers like EC, PC and the performance of the cells was analyzed through discharge characteristic studies [27]. It was found that the discharge capacity of the cell using PC plasticized electrolyte delivers better capacity of  $145 \text{ mAh g}^{-1}$  than the cell contains EC plasticized electrolyte which delivers capacity of  $125 \text{ mAh g}^{-1}$ . They concluded that PC effectively plasticizes the polymer matrix than EC.

### 2.3. PVA based blend and composite polymer electrolytes

As discussed earlier, in addition to plasticized polymer electrolytes, PVA based blend and composite electrolytes have been reported with large number of applications. Some of them are listed in Table 4.

Qiao et al. [44] reported low-cost proton-conducting semi-interpenetrating polymer (S-IPN) network of PVA/PAMPS blends with the addition of poly(ethylene glycol) bis(carboxymethyl) ether (PEGBCME) as plasticizer. PAMPS, which is ion conducting site is relatively low content in the blend resulting that S-IPN exhibits proton conductivity of  $0.1 \text{ S cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$ . This blend makes higher power density of  $51 \text{ mW cm}^{-2}$  at  $80 \text{ }^\circ\text{C}$ . Composite solid polymer electrolyte (CSPE) based on montmorillonite (MMT) nano-clay fillers was reported [46]. In this report, the effect of MMT on the ionic conductivity and electrochemical properties of the CSPE have been demonstrated. Lithium ions transference number of 0.40 was also reported. Electrochemical performance was evaluated using  $\text{LiFePO}_4$  cathode material and achieved a good electrochemical performance with low capacity fading on charge–discharge cycling.

Thus, it is noticed that irrespective of the types of electrolyte, PVA based electrolytes are extensively studied for the fabrication of various electrochemical and energy storage devices [33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55].

### 2.4. $\text{LiClO}_4$ as ionic dopant

The ionic conductivity of polymer electrolytes is impeded by ion segregation of changed species as ion pairs, or higher ion aggregates called charged multiples of ions. The less ionic conductivity is also observed when the salt with more lattice energy or large inter coulombic interaction is added with polymer host as ionic dopant.

If the solvation energy is strong enough, contact ion pair formation is rather avoided but formation of solvent-separated ion pairs, leading to quasi free ions results significant ionic conduction. Ion dissolution energy by polymer host must be larger than the ion pairing stabilization as marked by the lattice energy of dopant salt. Hence, salt selection is an important parameter in the preparation of polymer electrolytes.



**Table 4.** PVA based blend and composite electrolytes and their ambient temperature conductivity along with applications.

S.No	Electrolyte composition	conductivity (S cm <sup>-1</sup> )	Applications	Reference
1.	PVA – PVP – L-Asparagine doped NH <sub>4</sub> Br	2.34 × 10 <sup>-4</sup>	Proton battery	[33]
2.	PVA – Mg(Tf) <sub>2</sub> -EMITf	2.1 × 10 <sup>-4</sup>	Mg ion battery	[34]
3.	PVA – Poly vinylidene Fluoride -LiCF <sub>3</sub> SO <sub>3</sub> -SiO <sub>2</sub>	9.4 × 10 <sup>-4</sup>	Characterization only	[35]
4.	PVA – Poly vinylidene Fluoride -LiCF <sub>3</sub> SO <sub>3</sub>	2.7 × 10 <sup>-3</sup>	Characterization only	[36]
5.	PVA – Sulfonated Poly(Arylene Ether Ketone Sulfone) copolymers containing carboxylic acid groups	9.4 × 10 <sup>-2</sup>	DMFC	[37]
6.	PVA – PAN-Mg(ClO <sub>4</sub> ) <sub>3</sub>	2.96 × 10 <sup>-4</sup>	Mg ion battery	[38]
7.	PVA/sodium alginate-Glutaraldehyde	9.1 × 10 <sup>-2</sup>	DMFC	[39]
8.	Cyanoethylated polyvinylalcohol – PAN – LiClO <sub>4</sub> -Propylene carbonate	1.46 × 10 <sup>-2</sup>	Characterization only	[40]
9.	PVA – Phosphonic acid grafted bis(4-v-amino propyldiethoxy silyl phenyl) sulfone	4.6 × 10 <sup>-2</sup>	Poly electrolyte/DMFC	[41]
10.	PVA – PAAS-KOH.H <sub>2</sub> O		0.1 Super capacitor	[42]
11.	PVA – LiBr-H <sub>2</sub> SO <sub>4</sub>	1.5 × 10 <sup>-3</sup>	Solid acid PEs/Mg battery	[43]
12.	PVA – Poly(2-Acrylamido2-Methyl-1-Propane Sulfonic acid -Poly(ethylene glycol) bis(carboxymethyl)ether		0.1 DMFC	[44]
13.	PVA – Poly vinylidene -NH <sub>4</sub> SCN	1.09 × 10 <sup>-3</sup>	Characterization only	[45]
14.	PVA – Poly vinylidene -Montmorillonite-LiTFSI	4.31 × 10 <sup>-4</sup>	Lithium ion battery	[46]
15.	PVA – CH <sub>3</sub> COONH <sub>4</sub> - BmImBr	9.29 × 10 <sup>-3</sup>	Characterization only	[47]
16.	PVA – CH <sub>3</sub> COONH <sub>4</sub> - BmImCl	5.74 × 10 <sup>-3</sup>	PEMFC	[48]
17.	PVA – P(MA-co-AHPS)-Al <sub>2</sub> O <sub>3</sub>	1.08 × 10 <sup>-3</sup>	Lithium ion battery	[49]
18.	PVA – Poly vinylidene fluoride-LiCF <sub>3</sub> SO <sub>3</sub> -SiO <sub>2</sub>	3.7 × 10 <sup>-3</sup>	Characterization only	[50]
19.	PVA – Poly(2-Acrylamido2-Methyl-1-Propane Sulfonic acid)- Zeolitic Imidazolate Framework	0.134 at 60 °C	Characterization only	[51]
20.	PVA – Poly(2-Acrylamido2-Methyl-1-Propane Sulfonic acid)-1,2,4 trizole	2 × 10 <sup>-3</sup>	Characterization only	[52]
21.	PVA – LiCF <sub>3</sub> SO <sub>3</sub> -N-methyl pyrrolidone	2 × 10 <sup>-3</sup>	Super capacitor	[53]
22.	PVA – SSA	1.7 × 10 <sup>-4</sup> at 40 °C	DMFC	[54]
23.	PVA – CH <sub>3</sub> COOK	4.57 × 10 <sup>-6</sup>	Potassium battery	[55]

Among all Li salts, LiClO<sub>4</sub> is moisture resistant and thus it eliminates the use of glove box for maintaining inert atmosphere for the preparation of electrolyte. Many investigations on polymer electrolytes are reported based on LiClO<sub>4</sub> as ionic salt such as polymer-LiClO<sub>4</sub> complexes [32, 56, 57, 58] and polymer blend-LiClO<sub>4</sub>

complexes [59, 60]. Table 5 presents the list of electrolytes that use LiClO<sub>4</sub> as ionic dopant with its dc conductivity at ambient temperature.

LiClO<sub>4</sub> addition destructs the crystalline phase which present in Poly ethyl methacrylate (PEMA) [56] and it is confirmed by obtained scherrer length values. LiClO<sub>4</sub> also enhances amorphous phase of polymer matrix and hence decreases the glass transition temperature [60] of the host polymer which lowers the energy barrier for segmental motion. From the Table 5, it is noticed that the polymer-LiClO<sub>4</sub> complexes show the moderate conductivity values. Nano composite polymer electrolytes have also been developed and reported by many researchers [8,73–77] to enhance the mechanical strength as well as the conductivity. Another way to increase the electrical and electrochemical properties of polymer-salt complexes is adding plasticizer within the polymer salt matrix. The works based on plasticized polymer

**Table 5.** Electrolyte composition and obtained dc conductivity values for LiClO<sub>4</sub> incorporated solid polymer electrolytes.

S.No	Electrolyte composition	dc conductivity at RT (S cm <sup>-1</sup> )	References
1.	Thermoplastic Polyurethane-LiClO <sub>4</sub>	$8.89 \times 10^{-5}$	[61]
2.	Poly ethylene oxide-Poly methyl methacrylate- LiClO <sub>4</sub>	$\sim 10^{-5}$	[62]
3.	Poly vinyl chloride- Poly methyl methacrylate - LiClO <sub>4</sub>	$7.17 \times 10^{-3}$	[63]
4.	Poly ethylene oxide –Poly vinyl pyrrolidone - LiClO <sub>4</sub>	$2.3 \times 10^{-6}$	[59]
5.	Gelatin- LiClO <sub>4</sub>	$1.04 \times 10^{-4}$	[64]
6.	Poly ethyl methacrylate – LiClO <sub>4</sub>	$2.34 \times 10^{-6}$	[56]
7.	Poly ethylene oxide – LiClO <sub>4</sub>	$\sim 10^{-6}$	[57]
8.	Poly vinyl pyrrolidone – LiClO <sub>4</sub>	$\sim 5 \times 10^{-5}$	[58]
9.	Poly vinyl acetate/Poly methyl methacrylate – LiClO <sub>4</sub>	$1.76 \times 10^{-3}$	[60]
10.	Poly vinyl pyrrolidone - LiClO <sub>4</sub>	IR only	[65]
11.	Poly vinylidene fluoride- LiClO <sub>4</sub>	$\sim 10^{-5}$	[66]
12.	Poly(bis(pentyl amino phosphazene) - LiClO <sub>4</sub>	$8.1 \times 10^{-3}$	[67]
13.	Poly ethylene oxide -PES- LiClO <sub>4</sub>	$3 \times 10^{-5}$	[68]
14.	Poly propylene oxide-LiClO <sub>4</sub>	$\sim 10^{-5}$ at 70 °C	[69]
15.	Poly ethylene oxide -LiClO <sub>4</sub> - $\alpha$ alumina	$5.2 \times 10^{-4}$	[70]
16.	Poly ethylene oxide - PVDF-HFP-LiClO <sub>4</sub> -TiO <sub>2</sub>	$2.27 \times 10^{-4}$	[71]
17.	Poly ethylene oxide - PVDF-HFP-LiClO <sub>4</sub> -SrTiO <sub>3</sub>	$4.82 \times 10^{-5}$	[72]
18.	Poly ethylene oxide - LiClO <sub>4</sub> -SiO <sub>2</sub>	$2.3 \times 10^{-5}$	[73]
19.	Poly vinyl chloride - LiClO <sub>4</sub> – ZnO	$3.7 \times 10^{-7}$	[74]

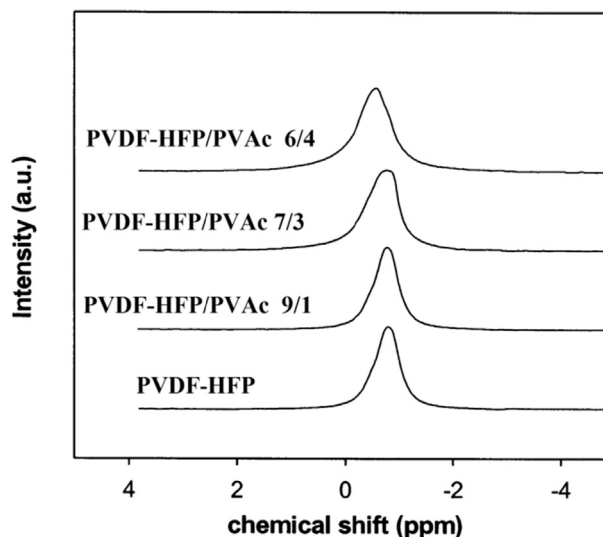
electrolytes with  $\text{LiClO}_4$  as ionic salt, are reported by many researchers [63,66,78–84,89–93,95]. The conductivity values of plasticized polymer electrolytes which contain  $\text{LiClO}_4$  as ionic salt are listed in Table 6.

$^7\text{Li}$  NMR studies confirm [78] that mobility of charge carriers decreases with increasing PVAc content and is presented in Fig. 4. The line width is found to be broader with PVAc increment in the blend that indicates diminution of  $\text{Li}^+$  mobility with PVAc.

In an another investigation, authors [80] prepared plasticized polymer electrolytes by mixing poly vinyl sulfone (PVS) and poly vinylidene fluoride (PVDF) with high conductive solutions of  $\text{LiClO}_4$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$  and  $\text{LiAsF}_6$  which were dissolved in PC, EC and sulfolane mixtures. It has been found that PVS based electrolytes have shown the conductivity of the order of  $10^{-4}$   $\text{S cm}^{-1}$  and PVDF based

**Table 6.** Electrolyte composition and dc conductivity values for plasticized polymer electrolytes which contain  $\text{LiClO}_4$  as ionic salt.

S.No	Electrolyte composition	dc conductivity at RT ( $\text{S cm}^{-1}$ )	References
1.	P(VdF-co-HFP):PVAc – $\text{LiClO}_4$		[78]
2.	P(VDF-co-HFP)/PMMA- $\text{LiClO}_4$		[79]
3.	poly(vinyl sulfone) – and poly(vinylidene fluoride) – $\text{LiClO}_4/\text{LiN}(\text{CF}_3\text{SO}_2)_2/\text{LiAsF}_6$	$10^{-4}$ to $10^{-3}$	[80]
4.	PEO – PVP – $\text{LiClO}_4$ – EC	$2.72 \times 10^{-4}$	[81]
5.	PAN – $\text{LiClO}_4$ – EC	IR only	[82]
6.	PAN – PC – 1,4-butyrolactone – DMSO – $\text{LiClO}_4$	$4.7 \times 10^{-3}$	[83]
7.	PEO – P(VDF-co-HFP) – $\text{LiClO}_4$ – PC	$2.39 \times 10^{-3}$	[63]
8.	PVDF – $\text{LiClO}_4$ – PC	$\sim 10^{-5}$	[66]
9.	Chitosan – Starch – Glycerol – $\text{LiClO}_4$	$3.7 \times 10^{-4}$	[84]
10.	PEO – $\text{LiClO}_4$ – DOP- $\text{vAl}_2\text{O}_3$	$4.29 \times 10^{-4}$	[85]
11.	PMMA – $\text{LiClO}_4$ – DMP- $\text{CeO}_2$	$5.36 \times 10^{-5}$	[86]
12.	PMMA – $\text{LiClO}_4$ – PC- $\text{SiO}_2$	$\sim 10^{-3}$	[87]
13.	P(VDFcoHFP) – PVAc – $\text{LiClO}_4$ – EC-PC	$2.3 \times 10^{-3}$	[78]
14.	PVDFcoHFP – PMMA – $\text{LiClO}_4$ – PC	$\sim 10^{-3}$	[79]
15.	PVP – $\text{LiClO}_4$ – PC- $\text{BaTiO}_3$	$1.2 \times 10^{-3}$	[88]
16.	PVS – PVDF – $\text{LiClO}_4$ – EC-PC-Sulfolane	$\sim 10^{-3}$	[80]
17.	PAN – $\text{LiClO}_4$ -ED4CN-PC	$1.05 \times 10^{-2}$	[89]
18.	PPC – $\text{LiClO}_4$ – BMIMBF <sub>4</sub>	$1.5 \times 10^{-3}$	[90]
19.	PEO – $\text{LiClO}_4$ – d2000	$1.5 \times 10^{-5}$	[91]
20.	PVDF – PVC – $\text{LiClO}_4$ – EC – PC	$4.68 \times 10^{-3}$	[92]
21.	PVC – PAN – $\text{LiClO}_4$ – EC – $\text{TiO}_2$	$4.46 \times 10^{-3}$	[93]
22.	P(VDF-co-HFP) – PVDF – $\text{LiClO}_4$ – PC – DEC	$7.5 \times 10^{-3}$	[94]



**Fig. 4.**  $^7\text{Li}$  NMR spectra of PVDF-HFP/PVAc –  $\text{LiClO}_4$ - EC-PC electrolytes [78] "Reprinted from Electrochimica Acta, vol.46(10–11), Nam-Soon Choi, Young-Gi Lee, Jung-Ki Park, Jang-Myoun Ko, Preparation and electrochemical characteristics of plasticized polymer electrolytes based upon a P(VdF-co-HFP)/PVAc blend, 1581–1586, copyright (2018) with permission from Elsevier".

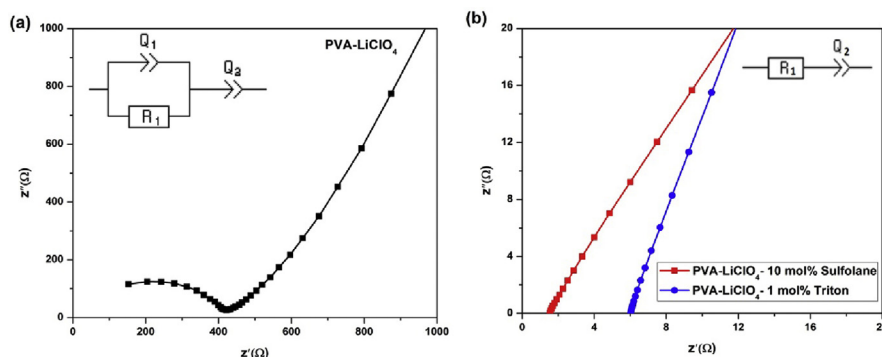
electrolytes have shown the conductivity of the order of  $10^{-3} \text{ S cm}^{-1}$  at  $30^\circ\text{C}$ . But, in the case of electrochemical stability, PVS based electrolytes have shown better stability (4.5–4.8 V vs  $\text{Li/Li}^+$ ) than PVDF based electrolytes (3.9–4.3 V vs  $\text{Li/Li}^+$ ).

In summary, it is concluded from the literature reports and our experimental work that plasticizer incorporation into polymer-salt preferably poly (vinyl alcohol) as host polymer and  $\text{LiClO}_4$  as ionic dopant can have great impact on electrical and electrochemical properties. The enhancement of amorphous nature and disordered morphologies improves the electrochemical performances of the electrolytes.

## 2.5. Ion transport studies of plasticized PVA – $\text{LiClO}_4$ based electrolytes

The effect of plasticizers, sulfolane/triton incorporation on the ion transport properties of PVA- $\text{LiClO}_4$  electrolytes is discussed here. A series of PVA- $\text{LiClO}_4$  electrolytes are prepared and among them 80mol%PVA-20mol% $\text{LiClO}_4$  shows the conductivity of  $5.64 \pm 0.44 \times 10^{-5} \text{ S cm}^{-1}$  at room temperature [95] and its Nyquist plot is given in Fig. 5a. The plot consist two regions: 1) incomplete semicircle at high frequency region and 2) inclined line at low frequency region. Typically, the semicircle part relates ionic conduction due to bulk of the sample and the inclined line is due to the effect of electrode polarization.

From Fig. 5b, it can be seen that (sulfolane/triton) plasticized polymer electrolytes show only slanted line region. That is semi circle region is disappeared.



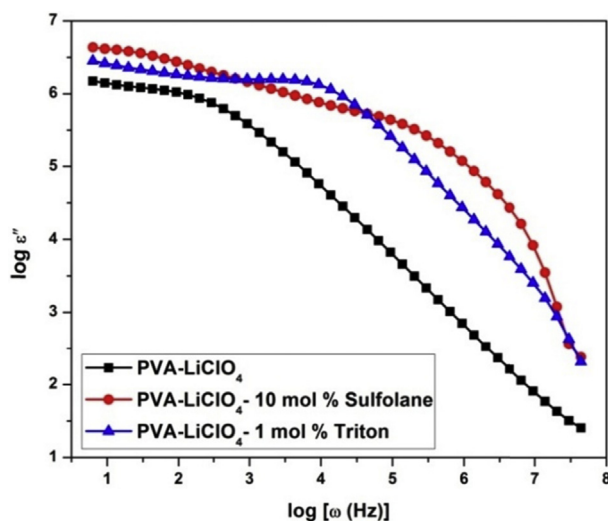
**Fig. 5.** Nyquist plot of (a) PVA-LiClO<sub>4</sub> (b) sulfolane/triton plasticized PVA-LiClO<sub>4</sub> electrolyte.

The representation of equivalent circuit corresponds to Nyquist plot is an easy way to provide complete picture of the system. In the present work, PVA-LiClO<sub>4</sub> and plasticized PVA-LiClO<sub>4</sub> electrolytes are fitted using z-fit software.

The equivalent circuit corresponds to the unplasticized electrolyte (Fig. 5a insert) shows parallel combination of resistance ( $R_1$ ) and constant phase element ( $Q_1$ ) along with another constant phase element ( $Q_2$ ) in series. Conductivity of 80mol%PVA-20mol%LiClO<sub>4</sub> electrolyte is enhanced to  $1.14 \pm 0.20 \times 10^{-2} \text{ S cm}^{-1}$  and  $1.92 \pm 0.23 \times 10^{-3}$  for the addition of 10 mol% sulfolane and 1 mol % triton respectively [95,96]. Plasticized PVA-LiClO<sub>4</sub> electrolytes at room temperature are shown in Fig. 5b. From the Fig. 5b, inclined line alone detected in the frequency range studied. The existence of the inclined line in the region reveals occurrence of polarization of ions at the electrode-electrolyte interface. Hence, the addition of plasticizer (Sulfolane and Triton) causes the enhancement of ion concentration in the PVA- LiClO<sub>4</sub> matrix. The disappearance of semicircle suggests the resistive component of polymer prevails. The angle between the inclined line and X-axis is less than 90° that suggests non-homogenous or roughness nature of electrode-electrolyte interface [97]. The corresponding equivalent circuit is given as insert Fig. 5b which is a series combination of resistance ( $R_1$ ) and constant phase element ( $Q_2$ ). Similar results were found in literatures [3, 31] in which PMMA-PVA LiClO<sub>4</sub> electrolyte doped with Dimethyl Phthalate (DMP) and PVA-LiClO<sub>4</sub> electrolyte doped with same DMP plasticizer depict Nyquist plot as slanted region only. Enhancement of charge carrier concentration is correlated by incorporation of plasticizer. Thus it proves that sulfolane/triton addition enhance the charge carrier concentration.

Fig. 6 shows the dielectric loss spectra for bare and sulfolane/triton plasticized PVA-LiClO<sub>4</sub> electrolytes.

From the Fig. 6, plasticizer free electrolyte does not show any relaxation but shows only polarization. It reveals that PVA chains are rigid and conduction is



**Fig. 6.** Dielectric loss spectra of PVA-LiClO<sub>4</sub> and Sulfolane/Triton plasticized PVA-LiClO<sub>4</sub> electrolytes.

only due to available free charge carriers. Sulfolane plasticized electrolyte shows two types of relaxations such as fast and slow relaxations. Triton plasticized electrolytes show single relaxation process which reveals plasticizer enhances segmental mobility of polymer chains and thus enhances the free volume there by facilitate the ion transport. That is relatively fast segmental motion coupled with mobile ion enhances the ion transport in PVA matrix. It proves that plasticizer addition not only enhances amorphousness of host polymer and carrier concentrations but also improves the segmental mobility of polymer chains. Thus plasticizers create an effective and sophisticated pathway for the transportation of ions. Fig. 7 shows the variation of tangent loss with frequency of PVA-LiClO<sub>4</sub> electrolyte with different plasticizers.

The tangent loss spectra characterized by peak appearing at a characteristic frequency. Relaxation peak is appeared for plasticizer free sample whereas relaxation peak is not observed in the measured frequency range for the plasticized electrolytes. At the same time, the magnitude of loss tangent for plasticized electrolytes is very high than unplasticized one. This is because of the reason that plasticizer increases the amorphousness content in the materials (which was already proven by XRD reports) and mobile dilute molecules (sulfolane and triton) speed up the segmental motion by increasing the available free volume. It is evidenced by shifting of peak maxima towards higher frequency side there by reduces the relaxation time. Similar results have also been observed in literatures [7,98,99]. Thus it is substantiated that plasticizer addition not only affects the structural properties of polymer-salt matrix but also influences on ion transport properties. On the comparison of two plasticizers sulfolane shows better performance than Triton due to availability of strong polar groups.

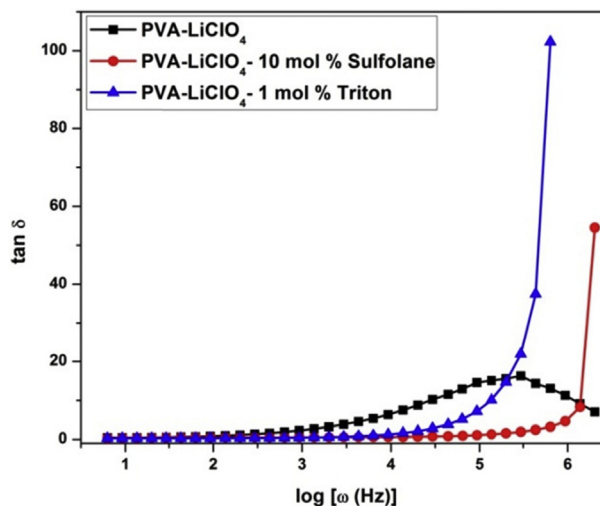


Fig. 7. Loss tangent spectra of PVA-LiClO<sub>4</sub> and Sulfolane/Triton plasticized PVA-LiClO<sub>4</sub> electrolytes.

## 2.6. Static and dynamical disorder, ionic conductivity correlation

The structure and morphology of the polymer chain cause static disorder. Polymer materials normally do not show any crystalline phase in its structure and hence X-ray diffraction or optical microscopy techniques cannot be useful. The dynamic disorder is totally a complicated process than static disorder since the local environment of a particular site of the polymer undergoes considerable change with time due to liquid like motions [100].

Polymer electrolytes are usually studied above glass transition temperature,  $T_g$ , the temperature below which the polymer electrolyte behave as glass like and no flexible chain movement. If the temperature of the polymer electrolyte exceeds glass transition temperature, the local structure is in solid like structure with highly viscous nature along with fast changes in local bond as well as bond angle. It is also important to note that the materials above  $T_g$  can flow easily for a short chain polymer electrolyte and behave as liquid like. In dynamically disordered system, nearest atoms about a specific site will always changes with time.

The decoupling index,  $R_\tau$ , (the ratio between relaxation time corresponding structural relaxation and  $\tau_\sigma$  relaxation time corresponding to conductivity) is normally observed as unity in the polymer electrolytes. Sometimes it occurs below unity for concentrated electrolytes where structural relaxations do not contribute any ion movement. For most of the polymer materials, the temperature dependence of the conductivity can be represented by Vogel-Tamman-Fulcher formula and is given in Eq. (2).

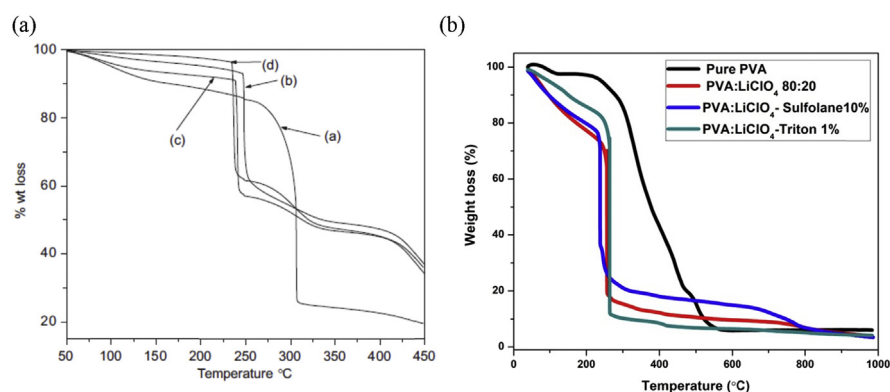
$$\sigma(T) = \sigma_0 \exp \left[ -B/(T - T_0) \right] \quad (2)$$

As the polymer materials are always studied above the glass transition temperature, both static and dynamical disorders occur.

From the above discussions, addition of plasticizer could enhance the amorphous nature polymer-salt complexes. Hence static disorderness is enhanced and thus it reflects in the ionic conductivity values. At the same time incorporation of salt or/ and liquid additive or plasticizer reduces the glass transition temperature ( $T_g$ ) of polymer and hence dynamical disorder also enhances. The glass transition temperature ( $T_g$ ) of PVA-LiClO<sub>4</sub> is found to be 63 °C. On the addition of Ionic Liquid (IL),  $T_g$  is further reduced where as  $T_g$  of pure PVA is 92 °C [29]. Hence above 60 °C, dynamical disorder also arises in addition to static disorder. Hence, addition of different types of plasticizer into polymer-salt matrix improves the static and dynamical disorder of the system and thus enhances the ionic properties.

## 2.7. Drawbacks of plasticized polymer electrolytes

Main drawback of plasticized polymer electrolytes is lower thermal stability while comparing solid polymer electrolytes (SPEs) and Nanocomposite Polymer Electrolytes (NCPes). According to literature report [29], incorporation of Ionic Liquid 1-ethyl-3-methyl imidazolium ethyl sulfate [EMIM] [EtSO<sub>4</sub>] into PVA-LiClO<sub>4</sub> matrix, reduces the thermal stability of bare electrolyte. The TGA curves of IL added PVA-LiClO<sub>4</sub> electrolyte is given in Fig. 8 (a). From Fig. 8 (a), it is clear that addition of IL into PVA-LiClO<sub>4</sub> system reduces the thermal stability. It is possibly due to complexation of EMIM cation of Ionic liquid with the hydroxyl group of the polymer, which destabilizes the adjacent C–H bond soft the PVA backbone. Fig. 8 (b) shows the TGA curves for Pure PVA, PVA-LiClO<sub>4</sub> and PVA-LiClO<sub>4</sub>-Sulfolane/Triton electrolytes. Pure PVA shows thermal stability at 353 °C. Thermal stability is reduced to



**Fig. 8.** TGA curves (a) for (a) 0 (b) 5 (c) 10 and (d) 15 wt % of IL added PVA-LiClO<sub>4</sub> electrolytes [29] "Reprinted from Journal of Physics and Chemistry of Solids, 73(2), A.L.Saroj, R.K.Singh, Thermal, dielectric and conductivity studies of PVA/Ionic liquid[EMIM]{EtSO<sub>4</sub>} based polymer electrolytes, 162–168, copyright (2018) with permission from Elsevier" and (b) for PVA-LiClO<sub>4</sub> Sulfolane/Triton electrolytes.



252 °C for the addition of LiClO<sub>4</sub> into PVA matrix. The thermal stability of PVA-LiClO<sub>4</sub> complex is further reduced for the addition of various plasticizers such as sulfolane/triton.

Hence, while plasticizing the polymer matrix, conductivity and electrochemical properties are improved but thermal properties of polymer electrolytes become reduced. In order to compensate these properties, nano filler incorporation within plasticized polymer electrolytes has been suggested by many researchers [85–88,101]. The combined effect of filler and plasticizer on polymer-salt matrix can lead to better electrical, electrochemical as well as thermal properties.

### 3. Conclusions

Effect of inclusion of plasticizers on structural properties of polymer electrolytes is discussed with aid of literature reports available. It is evidenced from literature reports and from our work that the incorporation of substantial amount of plasticizer has effectively enhanced the amorphous nature, ionic conductivity, electrochemical performance of polymer electrolytes. Ion transport properties of prepared sulfolane/triton plasticized PVA-LiClO<sub>4</sub> are analyzed. It is found that sulfolane performs better than triton as plasticizer on the enhancement of ion transport properties. Incorporation of liquid additive into polymer-salt matrix may affect/reduce the thermal and mechanical stability of electrolyte. In order to balance, incorporation of nano filler (metal oxide) into plasticized polymer-salt complex is suggested. Conductivity enhancement by the addition plasticizer is also correlated with enhancement of static and dynamical disorderness of polymer-salt complexes.

### Declarations

#### Author contribution statement

All authors listed have significantly contributed to the development and the writing of this article.

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#### Competing interest statement

The authors declare no conflict of interest.

## Additional information

No additional information is available for this paper.

## References

- [1] J.B. Goodenough, K.S. Park, The Li-ion rechargeable battery: a perspective, *J. Am. Chem. Soc.* 135 (2013) 1167–1176.
- [2] V.D. Noto, S. Lavina, A. Guinevere, E. Negro, B. Scrosati, Polymer electrolytes: present past future, *Electrochim. Acta* 57 (2011) 4–13.
- [3] S. Rajendran, O. Mahendran, Experimental investigations on plasticized PMMA/PVA polymer blend electrolytes, *Ionics* 7 (2001) 463–468.
- [4] L. Fan, Z. Dang, Ce-Wen Nan, M. Li, Thermal, electrical and mechanical properties of plasticized polymer electrolytes based on PEO/P(VDF-HFP) blends, *Electrochim. Acta* 48 (2002) 205–209.
- [5] M. Imperiyka, A. Ahmad, S.A. Hanifah, M.Y.A. Rahman, Preparation and characterization of polymer electrolyte of glycidyl methacrylate-methyl methacrylate-LiClO<sub>4</sub> plasticized with ethylene carbonate, *Int. J. Polym. Sci.* 2014 (2014), 638279, 7 pages.
- [6] J. Benedict, T. Banumathi, S. Veluchamy, A. Gangadharan, R.Z. Ahamad, A.S. Rajendran, Characterization of plasticized solid polymer electrolyte by XRD and AC impedance methods, *J. Power Sources* 75 (1998) 171–174.
- [7] D.K. Pradhan, B.K. Samantaray, R.N.P. Choudhary, N.K. Karan, R. Thomas, R.S. Katiyar, Effect of plasticizer on structural and electrical properties of polymer nanocomposite electrolytes, *Int. J. Electrochem. Sci.* 2 (2007) 861–871.
- [8] K.H. Teoh, S. Ramesh, A.K. Arof, Investigation on the effect of nano silica towards cornstarch–lithium perchlorate-based polymer electrolytes, *J. Solid State Electrochem.* 16 (2012) 3165–3170.
- [9] S. Tang, P. Zou, H. Xiong, H. Tang, Effect of nano-SiO<sub>2</sub> on the performance of starch/polyvinylalcohol blend films, *Carbohydr. Polym.* 72 (2008) 521–526.
- [10] G.S. Rathod, R.F. Bhajantri, V. Ravindrachary, P.K. Pujari, T. Sheela, Ionic conductivity and dielectric studies of LiClO<sub>4</sub> doped poly (vinylalcohol) (PVA)/chitosan (CS) composites, *J. Adv. Dielect.* 4 (2014), 1450033, 7 pages.

- [11] G. Hirankumar, S. Selvasekarapandian, Kuwata, J. Kawamura, T. Hattori, Thermal, electrical and optical studies on the poly(vinyl alcohol) based polymer electrolytes, *J. Power Sources* 144 (2005) 262–267.
- [12] G. Hirankuamr, S. Selvasekarapandian, M.S. Bhuvaneshwari, R. Baskaran, M.S. Vijayakumar, AC impedance studies on proton conducting polymer electrolyte complexes (PVA-CH<sub>3</sub>COONH<sub>4</sub>), *Ionics* 10 (2004) 135–138.
- [13] M. Hema, S. Selvasekerapandian, G. Hirankumar, Vibrational and impedance spectroscopic analysis of poly(vinyl alcohol)-based solid polymer electrolytes, *Ionics* 13 (2007) 483–487.
- [14] M. Hema, S. Selvasekerapandian, G. Hirankumar, A. Sakunthala, D. Arunkumar, H. Nithya, Structural and thermal studies of PVA:NH<sub>4</sub>I, *J. Phys. Chem. Solid.* 70 (2009) 1098–1103.
- [15] N. Rajeswari, S. Selvasekarapandian, S. Karthikeyan, C. Sanjeeviraja, Y. Iwai, J. Kawamura, Structural, vibrational, thermal, and electrical properties of PVA/PVP biodegradable polymer blend electrolyte with CH<sub>3</sub>COONH<sub>4</sub>, *Ionics* 19 (2013) 1105–1113.
- [16] L. Sa'adu, M.A. Hashim, M bin Baharuddin, Conductivity studies and characterizations of PVA-orthophosphoric electrolytes, *J. Mater. Sci. Res.* 3 (2014) 48–58.
- [17] A.R. Polu, R. Kumar, Preparation and characterization of PVA based solid polymer electrolytes for electrochemical cell applications, *Chin. J. Polym. Sci.* 31 (2013) 641–648.
- [18] C.S. Ramya, T. Savitha, S. Selvasekarapandian, G. Hirankumar, Transport mechanism of Cu ion conducting PVA based solid polymer electrolyte, *Ionics* 11 (2005) 436–441.
- [19] N. Rajeswari, S. Selvasekarapandian, S. Karthikeyan, H. Nithya, C. Sanjeeviraja, Lithium ion conducting polymer electrolyte based on poly (vinyl alcohol) – poly (vinyl pyrrolidone) blend with LiClO<sub>4</sub>, *Int. J. Polym. Mater. Polym. Biomater.* 61 (2012) 1164–1175.
- [20] M.M. Varishetty, W. Qiu, Y. Gao, W. Chen, Structure, electrical and optical properties of (PVA/LiAsF<sub>6</sub>) polymer composite electrolyte films, *Polym. Eng. Sci.* 50 (2010) 878–884.
- [21] B. Chatterjee, N. Kulshrestha, P.N. Gupta, Preparation and Characterization of Lithium ion conducting solid polymer electrolytes from biodegradable polymers Starch and PVA, *Int. J. Engine. Res. Appl.* 5 (2015) 116–131.

- [22] G. Hirankumar, S. Selvasekarapandian, M.S. Bhuvanewari, R. Baskaran, M. Vijayakumar, Ag<sup>+</sup> ion transport studies in a polyvinyl alcohol-based polymer electrolyte system, *J. Solid State Electrochem.* 10 (2006) 193–197.
- [23] M.F.Z. Kadir, S.R. Majid, A.K. Arof, Plasticized chitosan–PVA blend polymer electrolyte based proton battery, *Electrochim. Acta* 55 (2010) 1475–1482.
- [24] S. Cavus, E. Durgun, Poly(vinyl alcohol) based polymer gel electrolytes: investigation on their conductivity and characterization, *Acta Phys. Pol. A* 129 (2016) 612–624.
- [25] S. Rajendran, M. Sivakumar, R. Subadevi, Investigations on the effect of various plasticizers in PVA–PMMA solid polymer blend electrolytes, *Mater. Lett.* 58 (2004) 641–649.
- [26] Ch V. Subba Reddy, A.K. Sharma, V.V.R. Narasimha Rao, Effect of plasticizer on electrical conductivity and cell parameters of PVP + PVA + KClO<sub>3</sub> blend polymer electrolyte system, *J. Power Sources* 111 (2002) 357–360.
- [27] F.F. Hatta, T.I.T. Kudin, R.H.Y. Subban, A.M.M. Ali, M.K. Harun, M.Z.A. Yahya, Plasticized PVA/PVP–KOH alkaline solid polymer blend electrolyte for electrochemical cells, *Func. Mater. Lett.* 2 (2009) 121–125.
- [28] A.A. Mohamad, A.K. Arof, Plasticized alkaline solid polymer electrolyte system, *Mater. Lett.* 61 (2007) 3096–3099.
- [29] A.L. Saroj, R.K. Singh, Thermal, dielectric and conductivity studies on PVA/Ionicliquid [EMIM][EtSO<sub>4</sub>] based polymer electrolytes, *J. Phys. Chem. Solid.* 73 (2012) 162–168.
- [30] S.L. Agrawal, A. Awadhia, DSC and conductivity studies on PVA based proton conducting gel electrolytes, *Bull. Mater. Sci.* 27 (2004) 523–527.
- [31] S. Rajendran, M. Sivakumar, R. Subadevi, Li-ion conduction of plasticized PVA solid polymer electrolytes complexed with various lithium salts, *Solid State Ions* 167 (2004) 335–339.
- [32] K.H. Teoh, C.S. Lim, S. Ramesh, Lithium ion conduction in corn starch based solid polymer electrolytes, *Measurement* 48 (2014) 87–95.
- [33] V. Parameswaran, N. Nallamuthu, P. Devendran, E.R. Nagarajan, A. Manikandan, Electrical conductivity studies on Ammonium bromide incorporated with Zwitterionic polymer blend electrolyte for battery application, *Phys. B Condens. Matter* 515 (2017) 89–98.

- [34] J. Wang, S. Song, M. Ravi, X. Hu, R. Liu, Structural, electrical, and electrochemical properties of PVA-based biodegradable gel polymer electrolyte membranes for Mg-ion battery applications, *Ionics* 23 (1988) 1759–1769.
- [35] M. Hema, P. Tamilselvi, P. Pandaram, Conductivity enhancement in SiO<sub>2</sub> doped PVA:PVDF nanocomposite polymer electrolyte by gamma ray irradiation, *Nucl. Instrum. Methods Phys. Res. B* 403 (2017) 13–20.
- [36] P. Tamilselvi, M. Hema, Structural, thermal, vibrational, and electrochemical behavior of lithium ion conducting solid polymer electrolyte based on poly(vinyl alcohol)/poly (vinylidene fluoride) blend, *Polym. Sci. Ser. A* 58 (2016) 776–784.
- [37] J. Xu, H. Ni, S. Wang, Z. Wang, H. Zhang, Direct polymerization of a novel sulfonated poly(arylene ether ketone sulfone)/sulfonated poly(vinylalcohol) crosslinked membrane for direct methanol fuel cell applications, *J. Membr. Sci.* 492 (2015) 505–517.
- [38] R. Manjuladevi, M. Thamilselvan, S. Selvasekarapandian, R. Mangalam, M. Premalatha, S. Monisha, Mg-ion conducting blend polymer electrolyte based on poly(vinyl alcohol)- poly (acrylonitrile) with magnesium perchlorate, *Solid State Ions* 308 (2017) 90–100.
- [39] Jen-Ming Yang, Nian-Ci Wang, Hsien-Chih Chiu, Preparation and characterization of poly(vinyl alcohol)/sodium alginate blended membrane for alkaline solid polymer electrolytes membrane, *J. Membr. Sci.* 457 (2014) 139–148.
- [40] H. Tsutsumi, T. Kitagawa, High ionic conductive behavior of cyanoethylated polyvinylalcohol and polyacrylonitrile-based electrolytes, *Solid State Ions* 177 (2006) 2683–2686.
- [41] P.B. Tripathi, A. Saxena, V.K. Shahi, Phosphonic acid grafted bis(4 v- aminopropyl diethoxysilylphenyl) sulfone (APDSPS)-poly(vinyl alcohol) cross-linked polyelectrolyte membrane impervious to methanol, *J. Membr. Sci.* 318 (2008) 288–297.
- [42] S. Zihong, Y. Anbao, Electrochemical performance of nickel hydroxide/activated carbon supercapacitors using a modified polyvinyl alcohol based alkaline polymer electrolyte, *Chin. J. Chem. Eng.* 17 (2009) 150–155.
- [43] E. Sheha, Ionic conductivity and dielectric properties of plasticized PVA<sub>0.7</sub> (LiBr)<sub>0.3</sub> (H<sub>2</sub>SO<sub>4</sub>)<sub>2.7</sub>M solid acid membrane and its performance in a magnesium battery, *Solid State Ions* 180 (2009) 1575–1579.
- [44] J. Qiao, S. Ikesaka, M. Saito, J. Kuwano, T. Okada, Life test of DMFC using poly(ethylene glycol)bis(carboxymethyl)ether plasticized PVA/PAMPS proton-conducting semi-IPNs, *Electrochem. Commun.* 9 (2007) 1945–1950.

- [45] M. Muthuvinayagam, C. Gopinathan, Characterization of proton conducting polymer blend electrolytes based on PVdF-PVA, *Polymer* 68 (2015) 122–130.
- [46] Y. Ma, L.B. Li, G.X. Gao, X.Y. Yang, Y. You, Effect of montmorillonite on the ionic conductivity and electrochemical properties of a composite solid polymer electrolyte based on polyvinylidenedifluoride/polyvinyl alcohol matrix for lithium ion batteries, *Electrochim. Acta* 187 (2016) 535–542.
- [47] C.W. Liew, K.H. Arifin, J. Kawamura, Y. Iwai, S. Ramesh, A.K. Arof, Electrical and structural studies of ionic liquid-based poly(vinyl alcohol) proton conductors, *J. Non-Cryst. Solids* 425 (2015) 163–172.
- [48] C.W. Liew, S. Ramesh, A.K. Arof, A novel approach on ionic liquid-based poly(vinyl alcohol) proton conductive polymer electrolytes for fuel cell applications, *Int. J. Hydrogen Energy* 39 (2013) 2917–2928.
- [49] X. Huang, X. Ma, R. Wang, L. Zhang, Z. Deng, Combined effect of surface-charged latex nanoparticle AHPS and Al<sub>2</sub>O<sub>3</sub> nano-fillers on electrochemical performance of the anionic gel polymer electrolytes PVA/P (MA-co-AHPS), *Solid State Ion*s 267 (2014) 54–60.
- [50] M. Hema, P. Tamilselvi, Lithium ion conducting PVA:PVdF polymer electrolytes doped with nano SiO<sub>2</sub> and TiO<sub>2</sub> filler, *J. Phys. Chem. Solid*. 96–97 (2016) 42–48.
- [51] E. Mustafa, H. Usta, M. Citir, U. Sen, Proton conducting poly (vinyl alcohol) (PVA)/poly (2-acrylamido-2-methylpropane sulfonic acid) (PAMPS)/zeolitic imidazolate framework (ZIF) ternary composite membrane, *J. Membr. Sci.* 499 (2016) 156–163.
- [52] E. Mustafa, A. Aslan, U. Erkilic, S. Dadi, O. Yazaydin, H. Usta, U. Sen, Anhydrous proton conducting poly (vinyl alcohol) (PVA)/poly(2-acrylamido-2-methylpropane sulfonic acid) (PAMPS)/1,2,4-triazole composite membrane, *Int. J. Hydrogen Energy* 41 (2016) 11321–11330.
- [53] J. Chatterjee, T. Liu, B. Wang, P.J. Zheng, Highly conductive PVA organogel electrolytes for applications of lithium batteries and electrochemical capacitors, *Solid State Ion*s 181 (2010) 531–535.
- [54] M.S. Boroglu, S.U. Celik, A. Bozkurt, I. Boz, The synthesis and characterization of anhydrous proton conducting membranes based on sulfonated poly(vinyl alcohol) and imidazole, *J. Membr. Sci.* 375 (2011) 157–164.

- [55] S.K. Basha, G.S. Sundari, K. Vijayakumar, Studies on electrical properties of potassium acetate complexed with polyvinyl alcohol for electrochemical cell applications, *Mater. Today Proc.* 3 (2016) 11–20.
- [56] S.N. Amir, R. Othman, R.H.Y. Subban, N.S. Mohamed, Ionic conductivity of PEMA-LiClO<sub>4</sub> polymer electrolytes, *Sains Malays.* 40 (2011) 701–705.
- [57] K Susan Fullerton-Shirey, J.K. Maranas, Effect of LiClO<sub>4</sub> on the structure and mobility of PEO-based solid polymer electrolytes, *Macromolecules* 42 (2009) 2142–2156.
- [58] J. Rodríguez, E. Navarrete, E.A. Dalchiale, L. Sánchez, J Ramón Ramos-Barrado, F. Martín, Polyvinylpyrrolidone - LiClO<sub>4</sub> solid polymer electrolyte and its application in transparent thin film supercapacitors, *J. Power Sources* 237 (2013) 270–276.
- [59] K. Kesavan, M.M. Chithra, C. Subbu, S. Rajendran, Transport and optical studies of PEO/PVP/LiClO<sub>4</sub> based polymer blend electrolytes, *Int. J. Chem-Tech. Res.* 6 (2014) 1810–1812.
- [60] R. Baskaran, S. Selvasekarapandian, N. Kuwata, J. Kawamura, T. Hattori, Conductivity and thermal studies of blend polymer electrolytes based on PVAc–PMMA, *Solid State Ions* 177 (2006) 2679–2682.
- [61] Y. Ran, J.J. Bao, T.T. Chen, B.K. Zou, Z.Y. Wen, X.X. Guo, C.H. Chen, Solid polymer electrolyte based on thermoplastic polyurethane and its application in all-solid-state lithium ion batteries, *Solid State Ions* 309 (2017) 15–21.
- [62] S. Choudhary, R.J. Sengwa, Effects of different inorganic nanoparticles on the structural, dielectric and ion transportation properties of polymers blend based nanocomposite solid polymer electrolytes, *Electrochim. Acta* 247 (2017) 924–941.
- [63] P. Pradeepa, S. Edwinraj, M.R. Prabhu, Effects of ceramic filler in poly (vinylchloride)/poly(ethyl methacrylate) based polymer blend electrolytes, *Chin. Chem. Lett.* 26 (2015) 1191–1196.
- [64] R. Ramadan, H. Kamal, H.M. Hashem, K. Abdel-Hady, Gelatin-based solid electrolyte releasing Li<sup>+</sup> for smart window applications, *Sol. Energy Mater. Sol. Cells* 127 (2014) 147–156.
- [65] H.D. Wu, I.D. Wu, F.C. Chang, The interaction behavior of polymer electrolytes composed of poly(vinyl pyrrolidone) and lithium perchlorate (LiClO<sub>4</sub>), *Polymer* 42 (2001) 555–562.

- [66] K. Tsunemi, H. Ohno, E. Tsuchida, A mechanism of ionic conduction of poly(vinylidene fluoride) lithium perchlorate hybrid films, *Electrochim. Acta* 28 (1983), 883–837.
- [67] Y.W.C. Yang, J.J. Hwang, F.H. Chang, Polyphosphazene Electrolytes. 1. Preparation and conductivities of new polymer electrolytes based on poly[bis(amino)phosphazene] and lithium perchlorate, *Macromolecules* 30 (1997) 3825–3831.
- [68] D.W. Kim, J.K. Park, H.W. Rhee, Conductivity and thermal studies of solid polymer electrolytes prepared by blending poly(ethylene oxide), poly (oligo [oxyethyleneloxo sebacoyl] and lithium perchlorate, *Solid State Ions* 83 (1996) 49–56.
- [69] M. Watanabe, K. Sanui, N. Ogata, T. Kobayashi, Z. Ohtaki, Ionic conductivity and mobility in network polymers from poly (propylene oxide) containing lithium perchlorate, *J. Appl. Phys.* 57 (1985) 123–128.
- [70] J.E. Weston, B.C. H Steele, Effects of inert fillers on the mechanical and electrochemical properties of lithium salt-poly ethylene oxide polymer electrolytes, *Solid State Ions* 7 (1982) 75–79.
- [71] S. Jayanthi, B. Sundaresan, Effect of ultrasonic irradiation and TiO<sub>2</sub> on the determination of electrical and dielectric properties of PEO–P(VdF-HFP)–LiClO<sub>4</sub>-based nanocomposite polymer blend electrolytes, *Ionics* (2014).
- [72] S. Jayanthi, A. Arulsankar, B. Sundaresan, NanoSrTiO<sub>3</sub>-filled PEO–P(VdF-HFP)–LiClO<sub>4</sub> electrolytes with improved electrical and thermal properties, *Appl. Phys. A* 122 (2016) 1–11.
- [73] K.S. Ji, H.S. Moon, J.W. Kim, J.W. Park, Role of functional nano-sized inorganic fillers in poly(ethylene) oxide-based polymer electrolytes, *J. Power Sources* 117 (2003) 124–130.
- [74] A. Ahmad, M.Y.A. Rahman, M.S. Su'ait, Preparation and characterization of PVC–LiClO<sub>4</sub> based composite polymer electrolyte, *Phys. B Condens. Matter* 403 (2008) 4128–4131.
- [75] C. Capiglia, P. Mustarelli, E. Quartarone, C. Tomasi, A. Magistris, Effects of nanoscale SiO on the thermal and transport properties of solvent-free, poly(ethylene oxide) (PEO)-based polymer electrolytes, *Solid State Ions* 118 (1999) 73–79.
- [76] B. Scrosati, F. Croce, L. Persi, Impedance spectroscopy study of PEO-based nanocomposite polymer electrolytes, *J. Electrochem. Soc.* 147 (2000) 1718–1721.



- [77] H.Y. Sun, H.-J. Sohn, O. Yamamoto, Y. Takeda, N. Imanishi, Enhanced lithium-ion transport in PEO-based composite polymer electrolytes with ferroelectric BaTiO<sub>3</sub>, *J. Electrochem. Soc.* 146 (1999) 1672–1676.
- [78] N.S. Choi, Y.G. Lee, J.K. Park, J.M. Ko, Preparation and electrochemical characteristics of plasticized polymer electrolytes based upon a P(VdF-co-HFP):PVAc blend, *Electrochim. Acta* 46 (2001) 1581–1586.
- [79] M. Usharani, R.S. Babu, S. Rajendran, Conductivity study on PVDF-HFP/PMMA electrolytes for lithium battery applications, *Int. J. ChemTech. Res.* 5 (2013) 1724–1732.
- [80] H.S. Choe, J. Giaccari, M. Alamgir, K.M. Abraham, Preparation and characterization of poly(vinyl sulfone)- and poly(vinylidene fluoride)-based electrolytes, *Electrochim. Acta* 40 (1995) 2289–2293.
- [81] K. Kesavan, M. Chithra, S. Rajendran, Lithium ion conduction and ion-polymer interaction in poly(vinyl pyrrolidone) based electrolytes blended with different plasticizers, *Chin. Chem. Lett.* 25 (2014) 1428–1434.
- [82] Z. Wang, B. Huang, H. Huang, L. Chen, R. Xue, F. Wang, Infrared spectroscopic study of the interaction between lithium salt LiClO<sub>4</sub> and the plasticizer ethylene carbonate in the polyacrylonitrile -based electrolyte, *Solid State Ion* 85 (1996) 143–148.
- [83] B. Huang, Z. Wang, G. Li, H. Huang, R. Xue, L. Chen, F. Wang, Lithium ion conduction in polymer electrolytes based on PAN, *Solid State Ion* 85 (1996) 79–84.
- [84] Y.N. Sudhakar, M. Selvakumar, Lithium perchlorate doped plasticized chitosan and starch blend as biodegradable polymer electrolyte for supercapacitors, *Electrochim. Acta* 78 (2012) 398–405.
- [85] M.S. Michael, M.M.E. Jacob, S.R.S. Prabaharan, S. Radhakrishna, Enhanced lithium ion transport in PEO-based solid polymer electrolytes employing a novel class of plasticizers, *Solid State Ion.* 98 (1997) 167–174.
- [86] S. Rajendran, O. Mahendran, K. Kannan, Ionic conductivity studies in composite solid polymer electrolytes based on methylmethacrylate, *J. Phys. Chem. Solid.* 63 (2002) 303–307.
- [87] C.W. Kuo, W.B. Li, P.R. Chen, J.W. Liao, C.G. Tseng, T.Y. Wu, Effect of plasticizer and lithium salt concentration in PMMA-based composite polymer electrolytes, *Int. J. Electrochem. Sci.* 8 (2013) 5007–5021.

- [88] K. Kesavan, S. Rajendran, M. Chithra, Influence of barium titanate on poly(-vinyl pyrrolidone)-based composite polymer blend electrolytes for lithium battery applications, *Polym. Compos.* 36 (2015) 302–311.
- [89] H.Z. Tsutsumi, A. Matsuo, K. Onimura, T. Oishi, Conductivity enhancement of a polyacrylonitrile-based polymerelectrolyte containing cascade nitrile as a plasticizer, *Electrochem. Solid State Lett.* 1 (1998) 244–245.
- [90] D. Zhou, R. Rui, C. Chen, W.A. Yee, J. Kong, G. Ding, X. Lu, Non-volatile polymer electrolyte based on poly(propylene carbonate), ionic liquid, and lithium perchlorate for electrochromic devices, *J. Phys. Chem. B* 117 (2013) 7783–7789.
- [91] H.W. Chen, C.Y. Chiu, H.D. Wu, I.W. Shen, F.C. Chang, Solid-state electrolyte nanocomposites based on poly(ethylene oxide), Poly (oxypropylene) diamine, mineral clay and lithium perchlorate, *Polymer* 43 (2002) 5011–5016.
- [92] S. Rajendran, P. Sivakumar, An investigation of PVdF/PVC-based blend electrolytes with EC/PC as plasticizers in lithium battery applications, *Phys. B Condens. Matter* 403 (2008) 509–516.
- [93] S. Rajendran, R.S. Babu, P. Sivakumar, Investigations on PVC/PAN composite polymer electrolytes, *J. Membr. Sci.* 315 (2008) 67–73.
- [94] D. Saikia, A. Kumar, Ionic conduction in P(VDF-HFP)/PVDF-(PC + DEC)-LiClO<sub>4</sub> polymer gel electrolytes, *Electrochim. Acta* 49 (2004) 2581–2589.
- [95] S. Abarna, G. Hirankumar, Vibrational, electrical and Ion transport properties of PVA-LiClO<sub>4</sub>-Sulfolane electrolyte with high cationic conductivity, *Ionics* 23 (2017) 1733–1743.
- [96] S. Abarna, G. Hirankumar, Vibrational, electrical, dielectric and electrochemical studies on new Li ion conducting solid polymer electrolytes based on poly ethylene glycol p-tert-octylphenyl ether, *Polym. Sci. Ser. A* 59 (2017) 660–668.
- [97] M.F. Shukur, M.F.Z. Kadir, Electrical and transport properties of NH<sub>4</sub>Br doped corn starch-based solid polymer electrolyte, *Ionics* 21 (2015) 111–124.
- [98] M. Marzantowicz, J.R. Dygas, F. Krok, Z. Florjanczyk, E. Zygadlo-Monikowska, Influence of crystallization on dielectric properties of PEO:LiTFSI polymer electrolyte, *J. Non Cryst. Solids* 352 (2006) 5216–5223.

- [99] F. Kremer, A. Schonhals (Eds.), *Broad Band Dielectric Spectroscopy*, Springer-Verlag Berlin Heidelberg, New York, 2003.
- [100] M.A. Ratner, A. Nitzan, Conductivity in polymer ionics- dynamic disorder and correlation, *Faraday Discuss. Chem. Soc.* 88 (1989) 19–42.
- [101] K.H. Lee, Y.G. Lee, J.K. Park, D.Y. Seung, Effect of silica on the electro-chemical characteristics of the plasticized polymer electrolytes based on the P(AN-co-MMA) copolymer, *Solid State Ionics* 133 (2000) 257–263.