

Mobility and Number Density of Lithium Ions in Solid Polymer Blend Electrolytes Based on Poly(ethyl methacrylate) and Poly(vinylidene fluoride-co-hexafluoropropylene) Incorporated with Lithium Trifluoromethanesulfonate

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OVERVIEW

- **Introduction**
 - Polymer electrolytes
- **Objectives**
- **Methodology**
 - Preparation of polymer electrolyte films
- **Results and discussion**
 - Conductivity studies (EIS)
 - Structural studies (XRD) & morphology studies (SEM)
 - Infrared studies (FTIR)
 - Calculation of number density and mobility of free ions
- **Conclusions**
- **References**
- **Acknowledgement**

INTRODUCTION:

Potential of polymer electrolytes

Applications in:

- a) Electrical double layer capacitors
- b) Rechargeable Li ion and Li-air batteries
- c) Fuel Cells
- d) Solar cells
- e) Electrochromic devices



rechargeable batteries



battery for laptops



battery for mobile phones



electrochromic window

Advantages over commercial liquid electrolytes:

- ✓ Safe – no leakage
- ✓ Flexible – can be moulded into any shape
- ✓ Thin and Light-weight
- ✓ Mechanically stable
- ✓ Can offer higher energy density

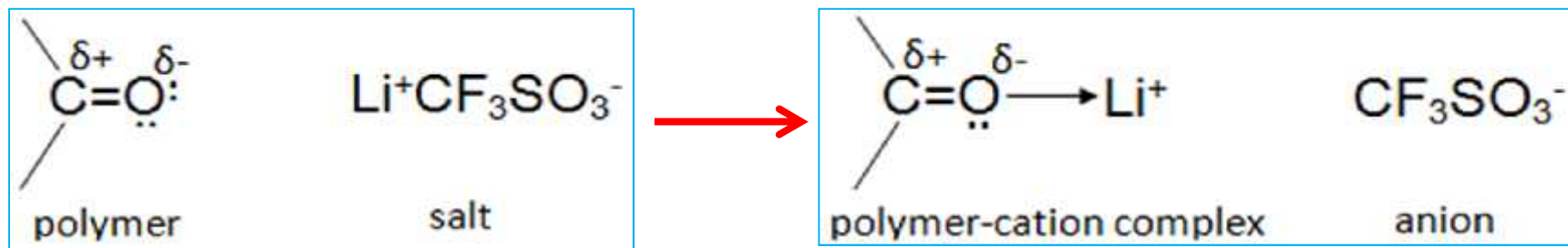
INTRODUCTION : Polymer electrolytes

Polymer serves as a medium for the charge transfer to occur, in which the charges are in the form of ions from salt.

Polymer must contain donor atoms to accept cation from salt.

Fundamentals of ionic conduction:

- 1) electrostatic attraction between negatively charged lone pair electrons on electronegative atom of polymer (i.e. oxygen in C=O, C-O) with positively charged ion (i.e. Li^+ , Na^+ , H^+) from salt

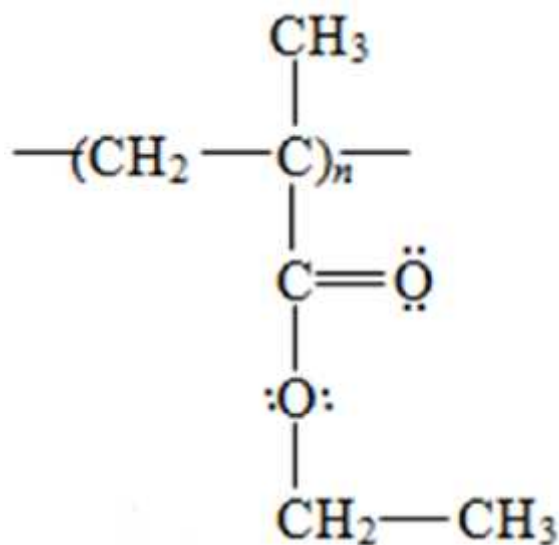


- 2) migration of cation from one coordination site to another
- Coordination must be labile to allow cation mobility.

Polymer hosts

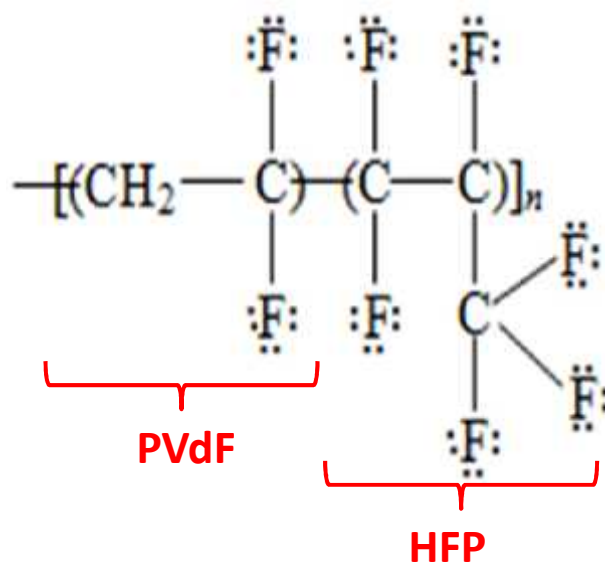
Li⁺ ion salt

Poly(ethyl methacrylate)
(PEMA)



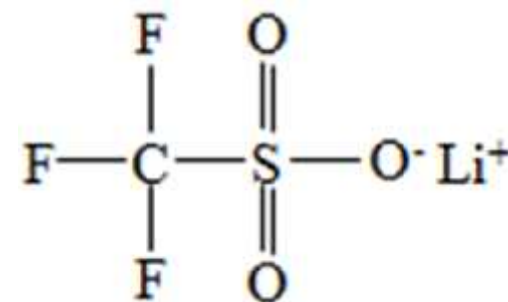
- amorphous polymer
- good transparency
- contains polar O atoms at C=O and C-O groups

Poly(vinylidene fluoride-co-hexafluoropropylene)
(PVdF-HFP)



- semicrystalline polymer
- VdF units – crystalline
- HFP units – amorphous
- contains fluorine atoms at CF₂ and CF₃ groups

Lithium
trifluoromethanesulfonate,
Lithium triflate (LiCF₃SO₃), LiTf



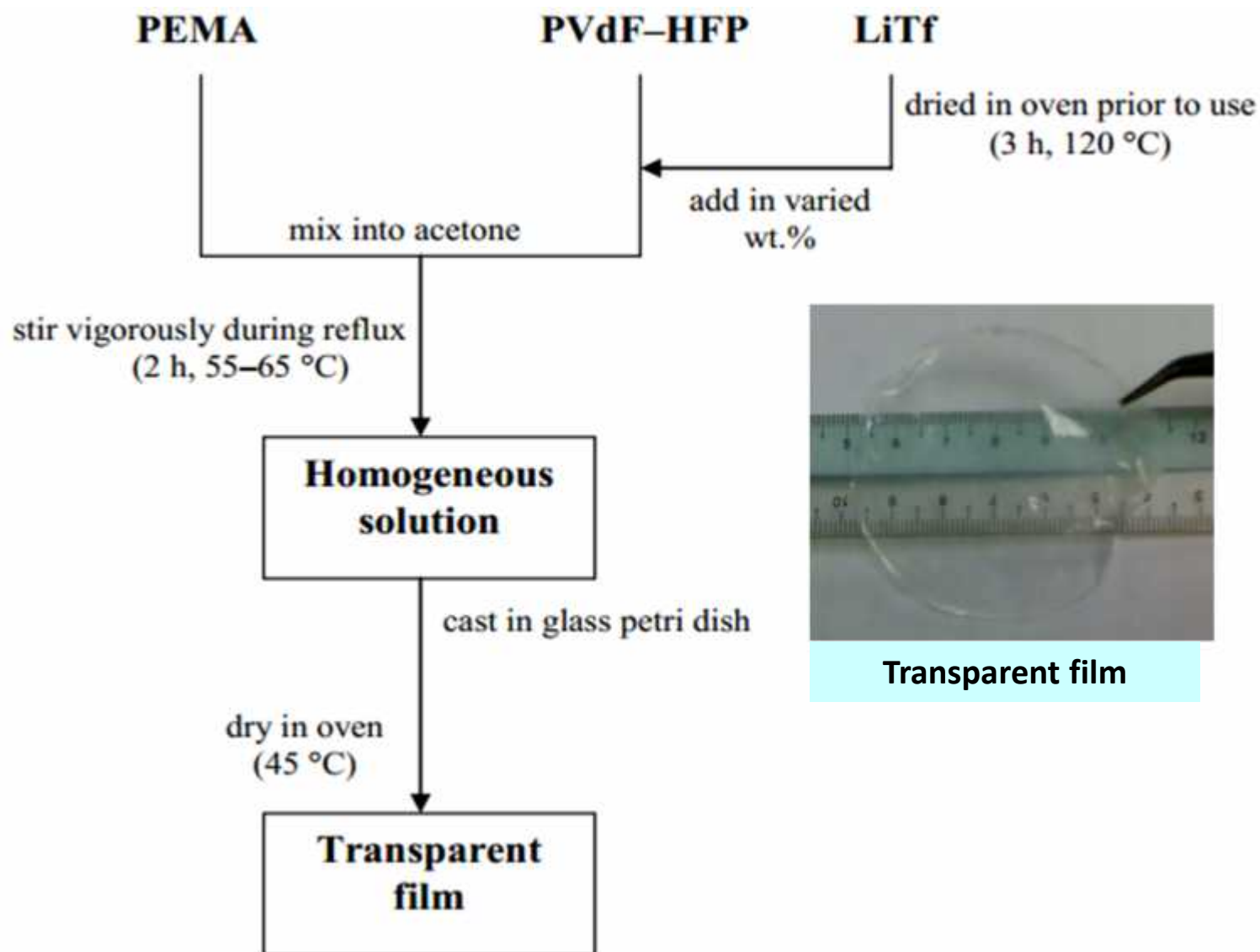
- low lattice energy salt
- large anion
- stable due to delocalized negative charge

OBJECTIVES

1. To study the effect of LiTf variation on ion dissociation and conductivity
2. To study the effect of LiTf on the structure changes of PEMA/PVdF-HFP-LiTf films
3. To investigate the dependence of conductivity on the number density as well as mobility of free ions

METHODOLOGY: PREPARATION OF POLYMER ELECTROLYTE FILMS

System: PEMA/PVdF-HFP blend + LiTf



Compositions of PEMA/PVdF-HFP-LiTf films

Table 1. Compositions of different PEMA/PVdF-HFP-LiTf electrolytes

Designation	PEMA (g)	PVdF-HFP (g)	LiTf (g)	PEMA: PVdF-HFP: LiTf (w:w)
S-10	0.7	0.3	0.1111	63 : 27 : 10
S-20	0.7	0.3	0.2500	56 : 24 : 20
S-30	0.7	0.3	0.4286	49 : 21 : 30
S-40	0.7	0.3	0.6667	42 : 18 : 40

RESULTS & DISCUSSION

IONIC CONDUCTIVITY STUDIES

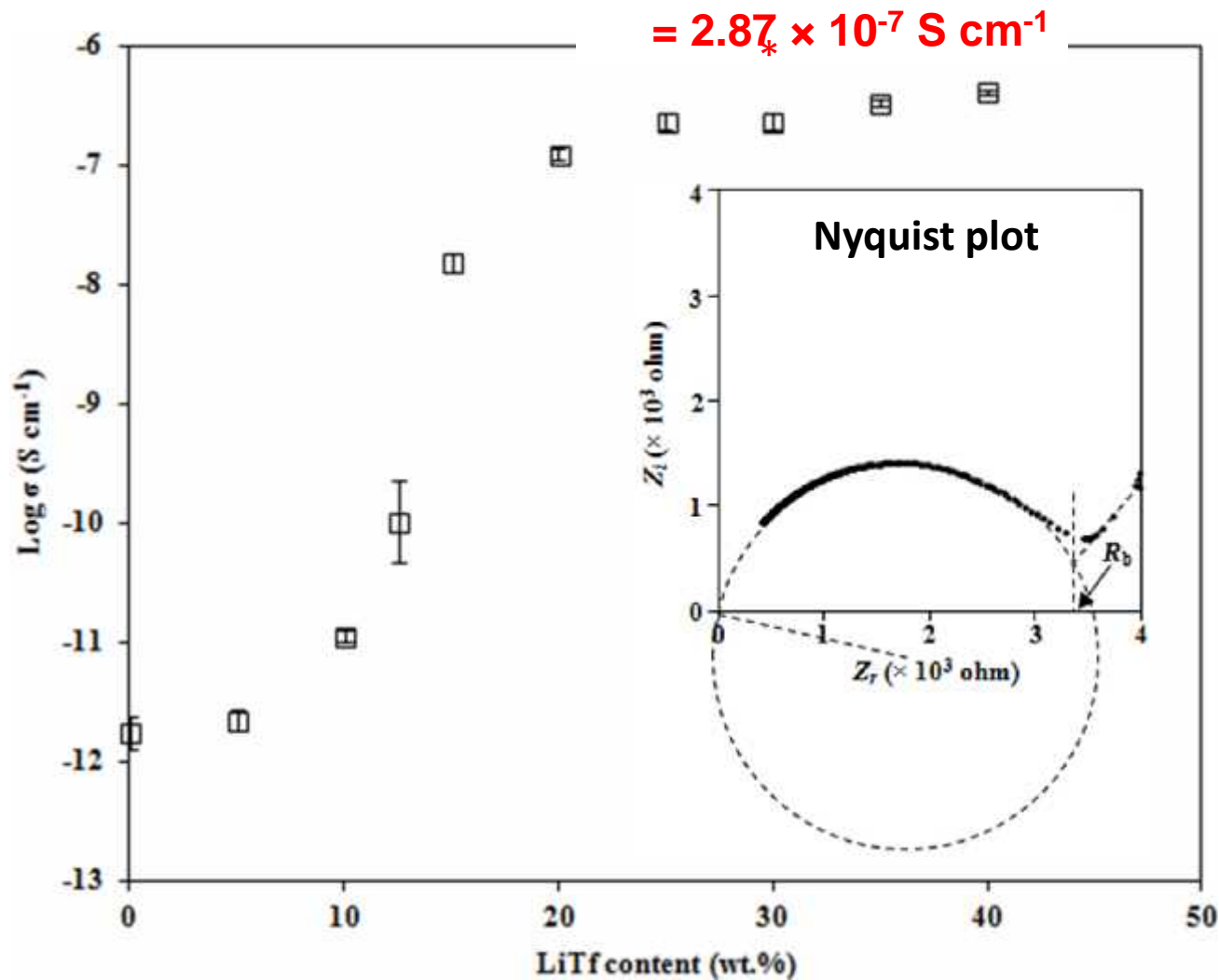


Fig. 1 Log conductivity versus LiTf content

Conductivity,

$$\sigma = \frac{t}{R_b A}$$

t = Thickness of film (cm),
 R_b = Bulk resistance ()
 A = Area of contact
 between electrode and
 electrolyte

TEMPERATURE DEPENDENT IONIC CONDUCTIVITY STUDIES

Table 2. Ionic conductivities of different PEMA/PVdF-HFP-LiTf electrolytes

Sample	Average (S cm⁻¹)
S-10	1.14×10^{-11}
S-20	1.25×10^{-7}
S-30	2.87×10^{-7}
S-40	4.13×10^{-7}

increases with addition of LiTf at room temperature.

However, above 35 wt.% LiTf, polymer electrolyte films loss mechanical stability whereby the films are softer.

Sim et al. (2012)

X-RAY DIFFRACTION (XRD)

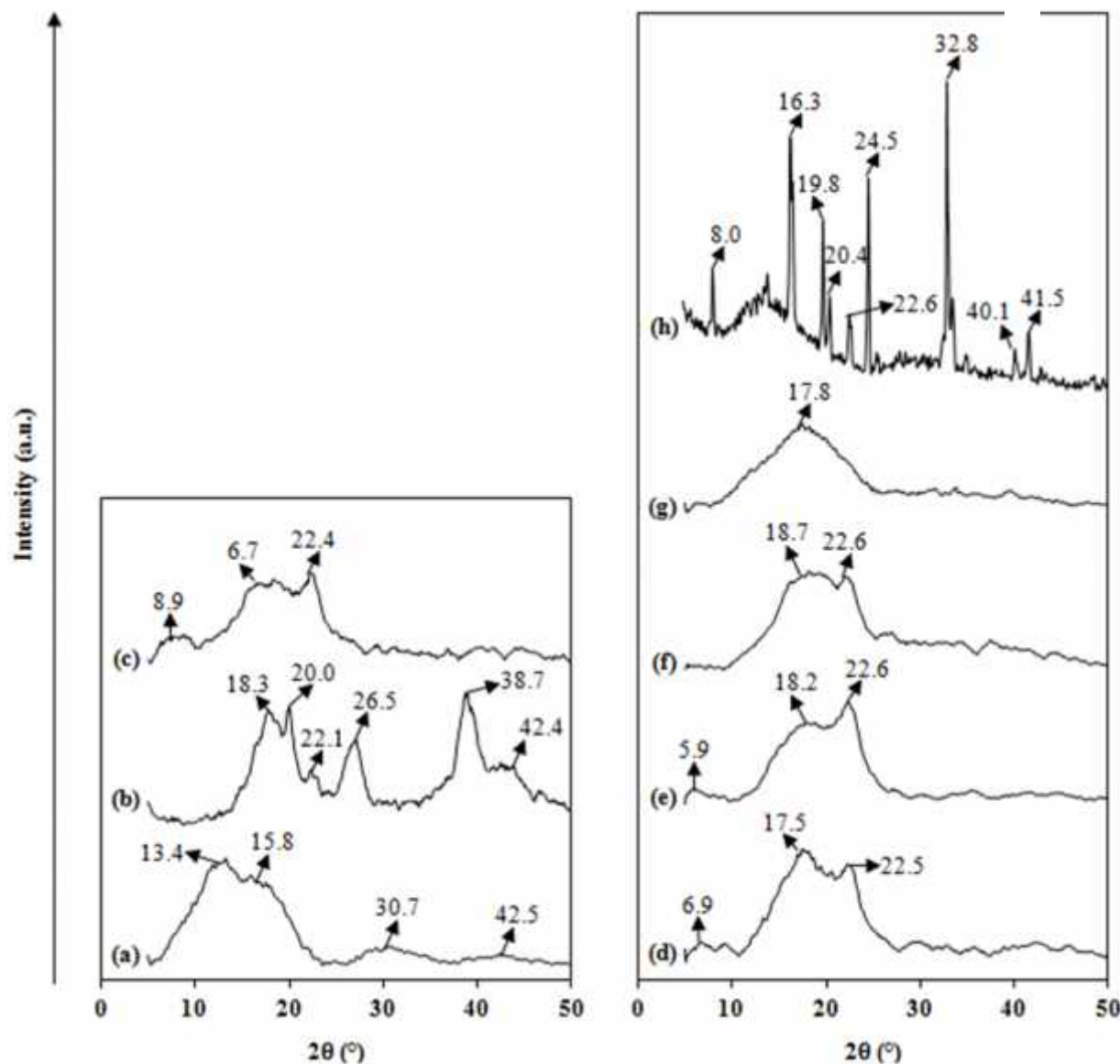


Fig. 9 XRD diffractograms of (a) PEMA, (b) PVdF-HFP, (c) S-0, (d) S-10, (e) S-20, (f) S-30, (g) S-40 and (h) LiTf

- PEMA: amorphous
- PVdF-HFP: semi- crystalline
- PEMA/PVdF-HFP: amorphous
 - Inclusion of PEMA reduces intermolecular interactions between PVdF- HFP chains and increases flexibility of polymer backbone.
- Addition of LiTf, S10 –S40: still amorphous with absence of LiTf peaks.
 - LiTf has dissolved in the polymer matrix and has dissociated into free Li^+ and Tf^- ions.

INFRARED STUDIES

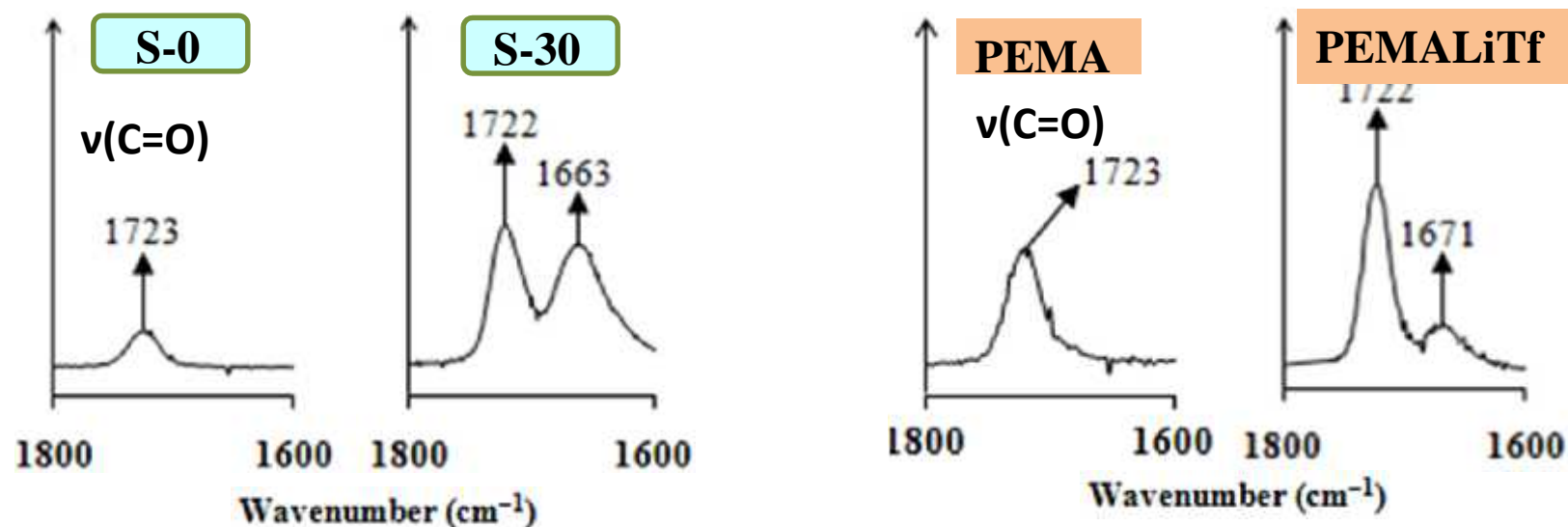


Fig. 3 IR spectra of S-0, S-30, PEMA and PEMA-LiTf samples

Upon addition of 30 wt.% LiTf :

$\nu(\text{C=O})$ of PEMA

- ✓ No significant wavenumber shift
- ✓ Increased intensity of $\nu(\text{C=O})$ band
- ✓ Changes in this band suggests **coordination of Li^+ onto O atom at C=O group of PEMA**

INFRARED STUDIES

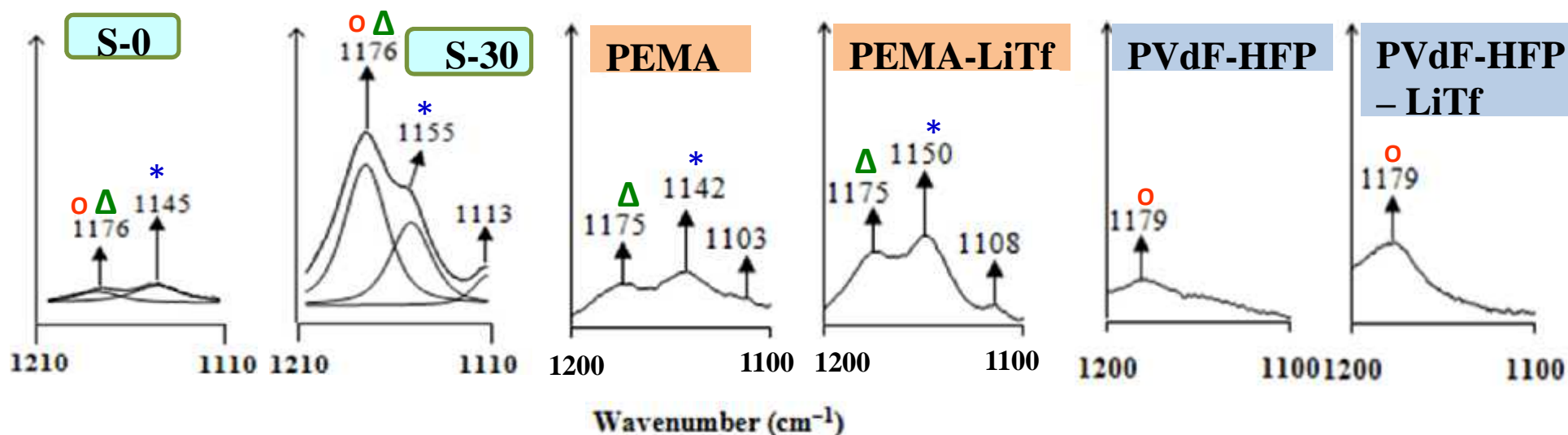


Fig. 4 IR spectra of S-O, S-30, PEMA, PVdF-HFP, PEMA-LiTf and PVdF-HFP-LiTf samples

Upon addition of 30 wt.% LiTf:

$\nu(\text{CO})$ of $\text{O-C}_2\text{H}_5$ group of PEMA, Δ and $\nu_a(\text{CF}_2)$ of PVdF-HFP, o

- ✓ Characteristic growth of intensity of IR band(s) with no change in wavenumber
 - suggests Li^+ ions coordinate to both F atoms in CF_2 group of PVdF-HFP and O atom at C-O-C group of PEMA

$\nu_a(\text{COC})$ band of PEMA, *

- ✓ Increased intensity & large wavenumber shift ($\sim 8\text{-}10 \text{ cm}^{-1}$) of $\nu_a(\text{COC})$ band of PEMA
 - indicates coordination of Li^+ onto O atom of C-O-C group of PEMA

INFRARED STUDIES

Table 3 Comparison between $\nu(\text{C=O})$ and $\nu_a(\text{COC})$ of PEMA

Assignment of bands	Wavenumber (cm^{-1})				
	S-0	S-10	S-20	S-30	S-40
$\nu(\text{C=O})$	1723	1723	1722	1722	1721
			$- = 1 - 2 \text{ cm}^{-1}$		
$\nu_a(\text{COC})$	1145	1148	1153	1155	1153
			$+ = 3 \text{ to } 10 \text{ cm}^{-1}$		

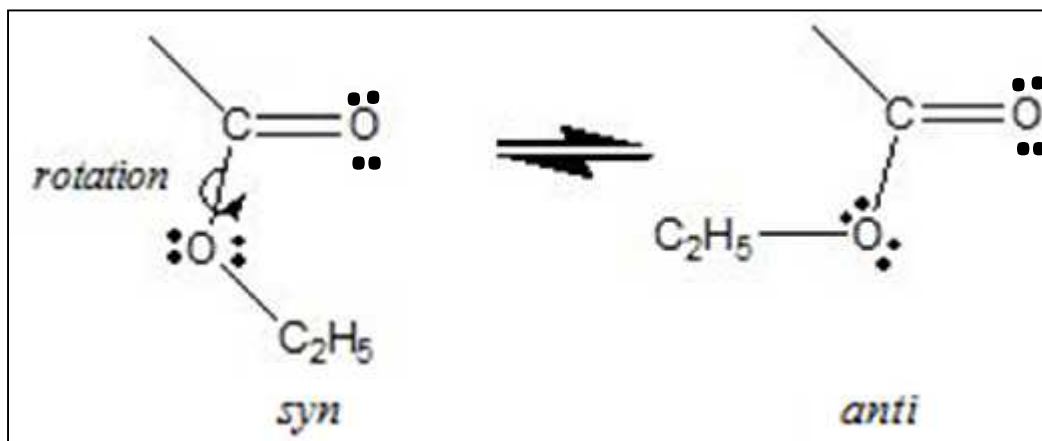


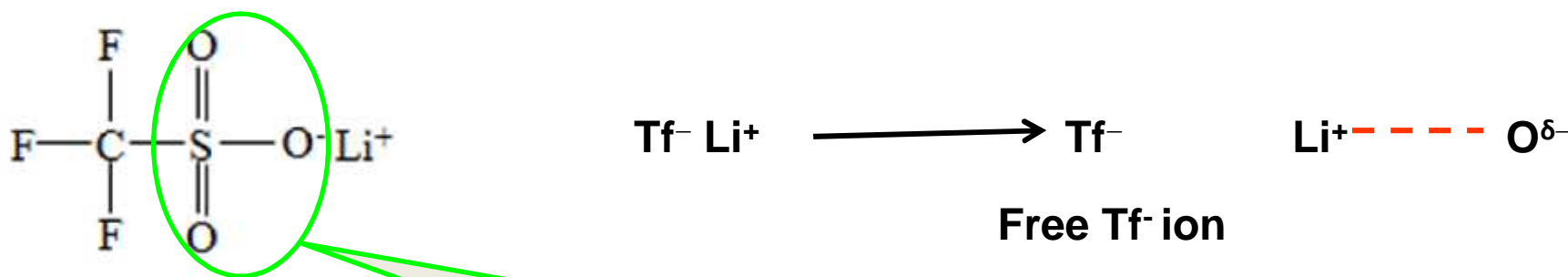
Fig. 5 Schematic diagrams of two possible conformations of the ester group of PEMA.

Sim et al. (2012)

-Ability to rotate about the single bonded COC group

-flexibility to expose lone pair electrons to Li^+ ions

more Li^+ can coordinate at C-O-C group rather than at C=O group 14



**Lithium triflate
(LiTf)**

- Li⁺ cations interact with Tf⁻ anions through the SO₃⁻ end.
- The $\nu_s(\text{SO}_3)$ mode can be used to distinguish between free ions, ion pairs and ion aggregates.

Huang & Frech (1992)

Table 5 Types of ionic species obtained from $\nu_s(\text{SO}_3)$ band of LiTf

Ionic species of Tf⁻	Wavenumber (cm⁻¹)
Free ions	1030 - 1034
Ion pair	1040 - 1045
Ion aggregate	1049 - 1053

NUMBER DENSITY AND MOBILITY OF PEMA/PVDF-HFP-LiTf SYSTEM

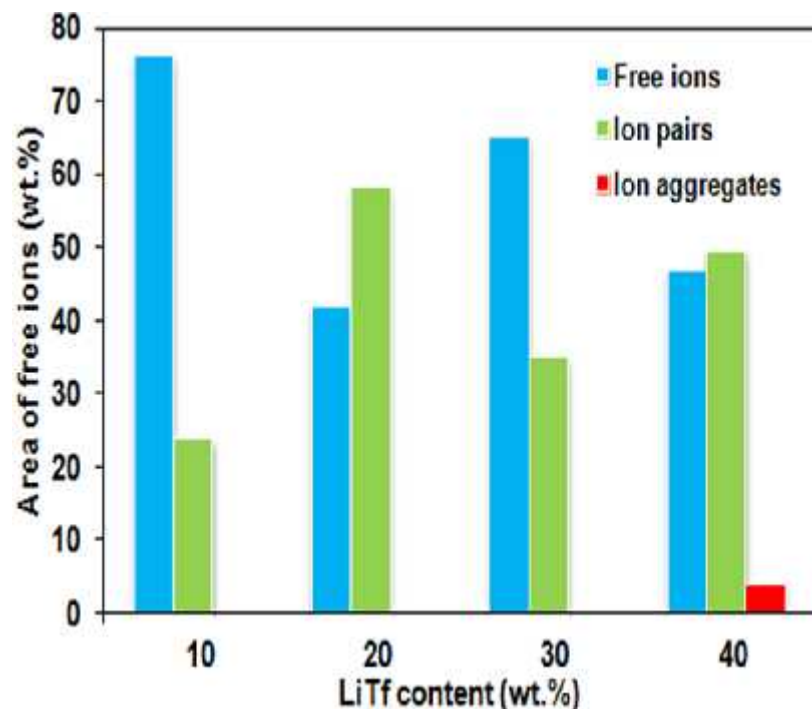
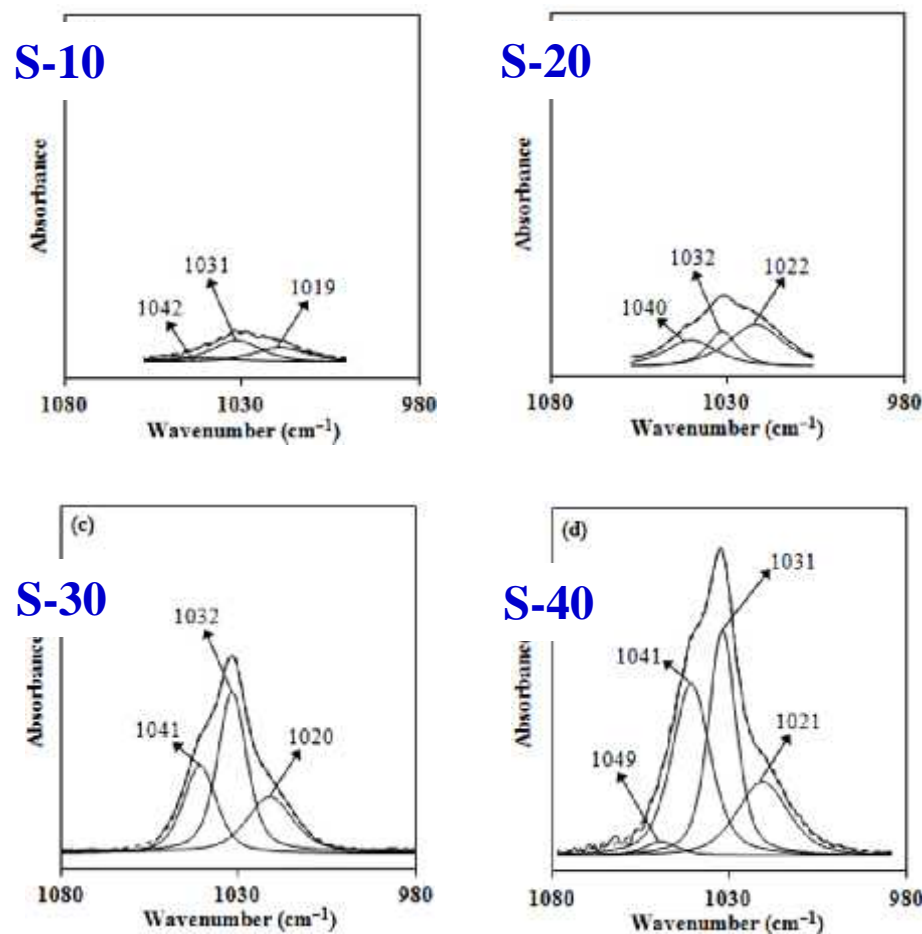


Fig. 6 Plot of area of ionic species versus LiTf contents

IR studies revealed presence of

- free ions and ion pairs for all blends with 10, 20, 30 and 40 wt.% LiTf
- ion aggregates were only formed for that with of 40 wt.% LiTf only

Deconvolution of $\nu_s(\text{SO}_3)$ band of LiTf



1019 – 1022 cm^{-1} : (C-H) of PEMA

Fig. 7 Deconvoluted IR spectra of S-10, S-20, S-30, S-40

CALCULATIONS OF NUMBER DENSITY AND MOBILITY OF FREE IONS

Ionic conductivity, κ , is the most important parameter in determining performance of polymer electrolyte in electrochemical cells.

Generally κ are governed by number density and mobility of the charge carriers

Number density

the amount of charge carriers per unit volume

$$n = \frac{\%FI}{100} \times \frac{m}{M_w} \times \frac{N_A}{V}$$

%FI = Area % of free ions obtained from FTIR deconvolution,

m = mass of LiTf used,

M_w = molecular mass of LiTf (156.01 g mol⁻¹),

N_A = Avogadro's number (6.02×10^{23}),

Mobility

the velocity attained by an ion moving under unit electric field

$$\mu = \frac{\kappa}{n \times e}$$

V = total volume of components present in the sample

κ = conductivity of each sample at 298 K,

e = electron charge (1.60×10^{-19} C),

CALCULATIONS OF NUMBER DENSITY AND MOBILITY OF FREE IONS

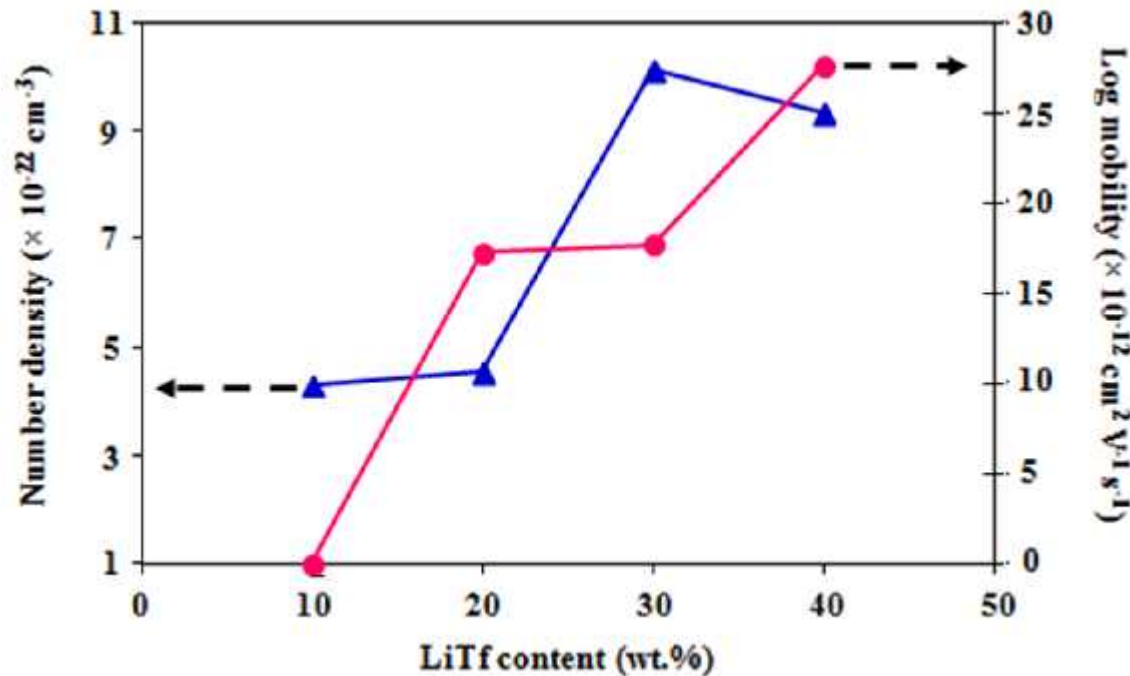


Fig. 8 Effect of LiTf content on the number density and mobility of PEMA/PVdF-HFP-LiTf system

- Both n and μ increase with increasing LiTf which tally with the continual increase of conductivity of PEMA/PVdF-HFP-LiTf system in Table 1
- But n decreases with 40 wt.% LiTf
 - decrease in amount of free ions and formation of more ion pairs and also ion aggregates

CONCLUSIONS

1. The optimized polymer electrolyte is PEMA/PVdF-HFP blend incorporated with 30 wt. % LiTf with ionic conductivity of $2.87 \times 10^{-7} \text{ S cm}^{-1}$.
2. The ionic conductivity increased with LiTf content
3. The ionic conductivity is influenced by both n and μ of free ions with the addition of up to 30 wt. % of LiTf.
4. At 40 wt.% of LiTf, the μ is the dominant factor. that influences the conductivity enhancement.
5. The 70 wt. % [PEMA/PVdF-HFP]-30 wt. % LiTf film shows **porous, amorphous** nature which exhibits the potential to be further enhanced in terms of conductivity using additives.

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Thank you for your attention

