



Review

Review on gel polymer electrolytes for lithium batteries

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Abstract

This paper reviews the state-of-art of polymer electrolytes in view of their electrochemical and physical properties for the applications in lithium batteries. This review mainly encompasses on five polymer hosts namely poly(ethylene oxide) (PEO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVdF) and poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP) as electrolytes. Also the ionic conductivity, morphology, porosity and cycling behavior of PVdF-HFP membranes prepared by phase inversion technique with different non-solvents have been presented. The cycling behavior of LiMn_2O_4 /polymer electrolyte (PE)/Li cells is also described.

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Keywords: Polymer electrolytes; Ionic conductivity; Plasticizers; Compatibility; Phase inversion technique

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Abbreviations: DBP, dibutyl phthalate; DEC, diethyl carbonate; DMF, dimethyl formamide; EC, ethylene carbonate; LiClO_4 , lithium perchlorate; LiBF_4 , lithium tetrafluoro borate; LiCF_3SO_3 , lithium trifluoro methane sulfonate; $\text{LiTFSI}(\text{LiNCF}_3\text{SO}_2)_2$, lithium bis(trifluoro methylsulfonyl)imide; $\text{LiBETI}(\text{LiNC}_2\text{F}_5\text{SO}_2)_2$, lithium bis(perfluoro ethylene sulfonyl)imide; LiAsF_6 , lithium hexafluoro arsenide; LiPF_6 , lithium hexafluoro phosphate; PEO, poly(ethylene oxide); PPO, poly(propylene oxide); PAN, poly(acrylonitrile); PMMA, poly(methyl methacrylate); PVC, poly(vinyl chloride); PVdF, poly(vinylidene fluoride); PVdF-HFP, poly(vinylidene fluoride-hexafluoro propylene); PVdF-HFP/PVAc, poly(vinylidene fluoride-hexafluoro propylene)/poly(vinyl acetate).

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1. Introduction

Polymer electrolyte may generally be defined as a membrane that possesses transport properties comparable with that of common liquid ionic solutions. The development of polymer electrolytes has drawn the attention of many researchers in the last three decades as they find applications not only in lithium batteries but also, in other electrochemical devices such as super capacitors and electrochromic devices, etc. These polymer electrolytes have several advantages over their liquid counter parts. The advantages of these electrolytes include such as no internal shorting, leakage of electrolytes and non-combustible reaction products at the electrode surface existing in the liquid electrolytes [1–5].

In principle, a polymer electrolyte battery can be formed by sandwiching the electrolyte between a lithium metal (or a composite carbon) anode and a composite cathode as depicted in Fig. 1 [3]. The charge–discharge profile of the lithium battery and lithium insertion and deinsertion mechanism have already been available elsewhere [6]. The pre-requisites for a polymer electrolyte for lithium batteries

are (i) high ionic conductivity at ambient and sub-ambient temperatures, (ii) good mechanical strength, (iii) appreciable transference number, (iv) thermal and electrochemical stabilities, and (v) better compatibility with electrodes [2–5]. The polymer electrolyte should allow good cycle lives at low temperatures and must withstand with the internal pressure build up during the battery operations [2–5]. Although, the polymer electrolyte was launched in 1973 by Fenton et al. [7], its technological importance was appreciated in early 1980 [8]. The development of polymer electrolytes has gone through three stages (i) dry solid-state polymer, (ii) gel/plasticized polymer electrolyte systems, and (iii) polymer composites.

The very first example of “dry solid” polymer electrolyte is the poly(ethylene oxide) (PEO) based systems that showed very low ambient temperature conductivities of the order of 10^{-8} S cm^{-1} [7]. Since this system does not possess any organic liquid and thus the polymer host is used as solid solvent. However, the cycling performance of this dry solid polymer electrolyte with lithium metal electrodes was not satisfactory and was used as low as 200–300 cycles. The poor performance of the cells was attributed to poor ionic conductivity of the electrolytes.

The second category of polymer electrolyte is called “gel polymer electrolyte” or “plasticized polymer electrolyte” which is neither liquid nor solid or conversely both liquid and solid [8,9]. Gels possess both cohesive properties of solids and the diffusive property liquids. This unique characteristic makes the gel to find various important applications including polymer electrolytes. Composite electrolyte on the other hand, is a subset of polymer electrolytes with an idea of incorporating electrochemically inert fillers in to polymer matrices [10–15]. Generally, high surface area particulate fillers such as ZrO_2 , TiO_2 , Al_2O_3 and hydrophobic fumed silica were incorporated in to the polymer matrices and are called “composite polymer electrolytes” or “composite ceramic electrolytes” [16,17].

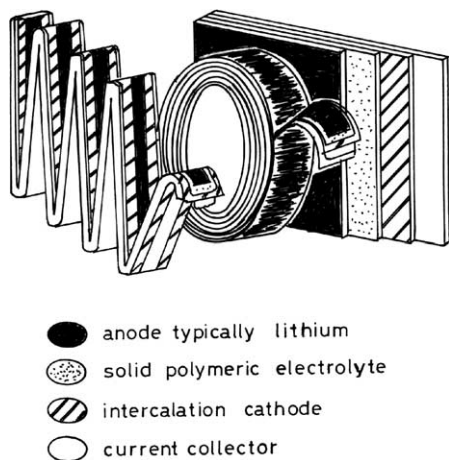


Fig. 1. Schematic diagram of basic construction of polymer-based batteries. The thin membrane composites are flexible and can be arranged into several desired geometries [26].

The advantages of incorporating the fillers are two-fold. One is the enhancement in ionic conductivity at low temperatures and the other one is to improve the stability at the interface with electrodes [18–25].

This article does not intent to review dry and composite polymer electrolytes, but focuses on the gel polymer electrolytes and electrolyte membranes prepared by phase inversion technique/activation processes. To date, several polymer hosts have been developed and characterized that include poly(ethylene oxide) (PEO), poly(propylene oxide) (PPO), poly(acrylonitrile) (PAN), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC), poly(vinylidene fluoride) (PVdF), poly(vinylidene fluoride-hexafluoro propylene) (PVdF-HFP), etc., Tables 1 and 2 display some of the physical properties of polymer hosts and organic solvents commonly used for rechargeable lithium batteries, respectively.

1.1. Poly(ethylene oxide)

Large research efforts have been devoted on PEO-based electrolyte systems in the last two decades. As mentioned earlier, after Wright's discovery of ionic conductivity in alkali metal salt complexes of PEO in 1973, polymer electrolytes were employed as separator in lithium batteries only in 1978. These

electrolytes combine the advantages of solid-state with the ease of casting as thin films. However, PEO-based electrolytes offer very low ionic conductivity that ranges from 10^{-8} to 10^{-4} S cm⁻¹ at temperatures between 40 and 100 °C, which excludes ambient temperature applications [26,27]. The ionic motion of a lithium ion in a PEO-host is displayed in Fig. 2.

Sequeira and Hooper [28] have described the electrochemical properties of solid lithium systems of (PEO)_x-LiCF₃SO₃ in the temperature range 100–170 °C. Later, (PEO)₉-LiCF₃SO₃ solid electrolyte was cycled approximately with 40% capacity at a current density up to 1 mA cm⁻² [29]. In order to improve the room temperature ionic conductivity of PEO complexed with lithium salts, the role of

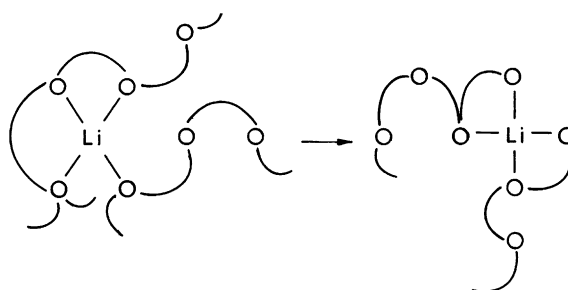


Fig. 2. Cartoon of ion motion in a polymer host [54].

Table 1
Polymer hosts generally studied

Polymer host	Repeat unit	Glass transition temperature, T_g (°C)	Melting point, T_m (°C)
Poly(ethylene oxide)	$-(\text{CH}_2\text{CH}_2\text{O})_n-$	-64	65
Poly(propylene oxide)	$-(\text{CH}(-\text{CH}_3)\text{CH}_2\text{O})_n-$	-60	- ^a
Poly(acrylonitrile)	$-(\text{CH}_2-\text{CH}(-\text{CN}))_n-$	125	317
Poly(methyl methacrylate)	$-(\text{CH}_2\text{C}(-\text{CH}_3)(-\text{COOCH}_3))_n-$	105	-
Poly(vinyl chloride)	$-(\text{CH}_2-\text{CHCl})_n-$	85	-
Poly(vinylidene fluoride)	$-(\text{CH}_2-\text{CF}_2)_n-$	-40	171
Poly(vinylidene fluoride-hexafluoropropylene)	$-(\text{CH}_2-\text{CH})$	-90	135

^a Amorphous.

Table 2
Physical properties of some organic solvents commonly used in rechargeable lithium batteries

	Melting point, MP (°C)	Boiling point, BP (°C)	Density, g (cm ⁻³)	Dielectric constant, ϵ	Molecular weight	Solubility parameter (J cm ⁻³) ^{1/2}
Dimethyl carbonate (DMC)	2.4	90	1.06	3.12	90.08	20.3
Diethyl carbonate (DEC)	-43.0	126	0.9752	2.82	118.13	18.0
γ -Butyrolactone (BL)	-43.3	204	1.1284	39.0	86.09	25.8
Propylene carbonate (PC)	-48.8	242	1.2047	66.14	102.09	27.2
Ethylene carbonate (EC)	36.4	248	1.3214	89.78	88.06	30.1

Source: Ref. [148].

various additives were examined by Kelley et al. [30]. They also found that the partial substitution of high polymer by a PEO of low molecular weight had the effect of increasing the solubility of the crystalline polymer/salt complexes in the liquid polymer as well as lowering the effective melting and glass transition temperature of the polymer. Ito et al. [31], have made ionic conductivity measurements on PEO-LiCF₃SO₃ complexes with poly(ethylene glycol) (PEG) as plasticizer. They observed that the ionic conductivity increases with the increase of PEG content. The increase in conductivity was mainly attributed to the reduction of crystallinity and increasing of free volume of the system. On contrary, the increase in ionic conductivity is adversely accompanied by poor interfacial properties due to the presence of hydroxyl end-groups [31]. In order to avoid this problem few researchers have attempted to replace the hydroxyl end groups of PEG by methoxy one [32]. The crown ethers have also been used as plasticizers to enhance the ionic conductivity of polymer electrolytes. Nagasubramanian and Stefano [33] have achieved the maximum conductivity of the order of $7 \times 10^{-4} \text{ S cm}^{-1}$ for the PEO-LiBF₄ system. Further, the charge-transfer resistance in a cell was considerably reduced upon the addition of 12-crown-4 ether in the system. The cation and anion diffusion coefficient for the amorphous phase of (PEO)₈-LiCF₃SO₃ complexes were measured using pulse-field gradient NMR [34]. The ambiguous determination of the cation (t^+) and anion (t^-) transport numbers for the amorphous electrolyte showed both kinds of ions are mobile in the amorphous phase.

The electrochemical stability and ionic conductivity studies were reported by Fauteaux et al. [35], for high molecular weight PEO based solid polymer electrolytes for electrochemical devices. These electrolytes, however, offered good mechanical property and high lithium ion mobility when they were complexed with LiClO₄ and LiCF₃SO₃. Benedict et al. [36], explored the possibility of using dibutyl phthalate (DBP) as plasticizer in PEO-LiAsF₆ complexes. The activation energy of the system was considerably reduced upon the addition of 0.09 mol of DBP in the system.

The complete phase diagram of PEO-LiCF₃SO₃ was determined by XRD and DSC analysis [37]. The existence of three different molecular adducts involving the polymer and the salt was deduced from the phase diagram and a transition of phase of higher symmetry of salt was identified at 179 °C.

Song et al. [38] have measured the thermal conductivity of PEO for various lithium salt complexes. The thermal conductivity of LiCF₃SO₃ complexes was found to be stable irrespective of the concentration of the salt. However, for the systems the thermal conductivity was found to decrease with increasingly amorphous structure.

The thermal stability of PEO-LiCF₃SO₃ with a combination of plasticizers ethylene carbonate and propylene carbonate was analyzed in air as well as argon atmosphere by Shodai et al. [39]. Their results revealed that the PEO-based electrolytes loses its weight rapidly in air but more gradually in argon gas. These results indicated that the oxygen in the air lowers the decomposition temperature of PEO and accelerates its decomposition rate.

A series of plasticized polymer electrolytes were synthesized based on poly ethylene oxide (PEO), LiN(CF₃SO₂)₂ (LITFSI) as the salt and tetraethylene glycol dimethyl ether (tetraglyme) and EC + PC as plasticizers. The preparation and characterization of the polymer electrolytes were investigated as a function of temperature and various concentrations of LITFSI. The complex of PDMAEMA/PEO/LITFSI/tetraglyme exhibits higher conductivity ($4.74 \times 10^{-4} \text{ S cm}^{-1}$ at 25 °C) than PDMAEMA/PEO/LITFSI/EC + PC [40]. Using Raman and infrared spectroscopy the ionic association in complexes of LiCF₃SO₃ with the low molecular weight PEO dimethyl ethers was reported [41]. The relative concentrations of ion pairs and more highly associated ionic species were found to be dependent on chain length for CF₃ symmetric deformation and the SO₃ symmetric stretching mode.

Appetecchi et al. [42] have described the preparation and characterization of PEO-lithium bis(perfluoro ethylene sulfonyl)imide LiN(C₂F₅SO₂)₂ (LIBETI) polymer electrolytes. The thermal properties of PEO:LIBETI electrolytes investigated using XRD and DSC were correlated with their ionic conductivity measurements. PEO:LIBETI complexes were found to have very high ionic conductivity and was attributed to their amorphous phase.

The ionic conductivity [43], transference number [44,45], DSC and NMR [46], thermal [47], polarization [48] and cycling performance [49,50] of PEO and copolymer of P(EO-MMA)-based electrolytes [51] been reported. A novel poly(ethylene oxide) (PEO) electrolyte was prepared by Egashira et al. [52] with lithium 4,5-dicyano-1,2,3-triazolate as salt. A higher ionic conductivity, electrochemical stability, thermal stability and high transference number

have been achieved with this host than other PEO systems. Very recently, the possibility of using low cost lithium-ion batteries comprising LiFePO_4 /PEO-gel electrolytes/natural graphite system was also explored [53]. This system has shown excellent capacity retention and was found to be more suitable for hybrid electric vehicle applications.

The structure and electrochemistry of polymer electrolytes [54] and review papers also document the development and general characteristics of blend polymer electrolytes [55,56].

The poly(propylene) (PPO) systems were investigated by few researchers in the early 1980's. The spectroscopic [57,58], the thermal stability and high pressure electrical conductivity [59], the interfacial properties with lithium anode [60] and ionic conductivity and NMR of [61,62] of PPO hosts complexed with different lithium salts have been reported.

It is well known fact, that the dissolution of inorganic salts in polymer hosts will be facilitated when the lattice energy of the salt is low and the dielectric constant (ϵ) of the polymer is high. Unfortunately, ionic conductivity of amorphous mixtures of lithium salt with PPO is considerably smaller than the equivalent mixture with PEO because PPO has a lower ϵ and the methyl group hinders the segmental motion of the polymer chain and thus reduces its conductivity [56].

1.2. Poly(acrylonitrile)

Among the polymer hosts studied, so far, the PAN based electrolytes offer a homogenous, hybrid electrolyte films in which the salt and the plasticizer were molecularly dispersed. Watanabe et al. [63,64] used a combination of plasticizers EC and PC to plasticize PAN and complexed with LiClO_4 and they correlated with the mole ratio [plasticizer]/ $[\text{LiClO}_4]$ of the gel electrolytes. The authors concluded that the PAN host is inactive in the ionic transport mechanism but acts as a matrix for structural stability.

Abraham and Alamgir [65,66] found an increase in ionic conductivity of PAN based electrolytes comprising of 38 m/o EC, 33 m/o PC with 8 m/o LiClO_4 and 21 m/o of PAN. According to Appetecchi et al. [67] a fully amorphous gel of PAN- LiClO_4 (1:02) in EC showed room temperature conductivity of the order of $1 \times 10^{-3} \text{ S cm}^{-1}$ at ambient temperature. The PAN-based gels were found to have lithium ion transference numbers more than 0.5 because of the absence of oxygen atoms in the PAN matrix.

Also the transference number was enhanced to 0.7 when the lithium salts like LiTFSI and LiTFSM were used [67].

The conductivity of PAN based lithium salt complexes has been reported for various temperatures ranging from -15 to 55°C by Hong et al. [68]. The room temperature conductivity was of the order of $10^{-4} \text{ S cm}^{-1}$ and the transference number was found to be 0.36. However, the compatibility with metallic lithium was proved to be rather good.

Using ternary solvent mixtures consisting of EC, PC and 3-methyl-2-oxazolodion (MEOX) the low temperature conductivity of PAN based gel electrolytes has been improved [69].

The PAN based electrolytes were prepared by encapsulating Li-salt solutions obtained by dissolving $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, LiAsF_6 , LiCF_3SO_3 and LiPF_6 in a plasticizer mixture of EC and PC [70]. Cyclic voltammetry studies revealed that the electrolytes have an inherent oxidation stability window exceeding 5 V vs Li^+/Li .

Croce et al. [71] examined the electrochemical properties of gel electrolytes by immobilization of PAN matrix with different lithium salts (LiClO_4 , LiAsF_6 , $\text{Li}(\text{CF}_3\text{SO}_2)_2$). These electrolytes exhibited high ionic conductivity and high lithium transference number. However, their application in rechargeable lithium polymer batteries is hindered and is attributed to the instability of lithium electrode interface.

Appetecchi et al. [72] have prepared two classes of gel electrolytes with PAN as host. A combination of plasticizers, EC and DMC has been used with LiPF_6 or LiCF_3SO_3 as salt. These membranes were found to have to high ionic conductivity, electrochemical stability window. These unique characteristics make the membranes suitable for lithium battery applications.

The Raman and IR spectra studies on EC containing various concentrations of LiClO_4 revealed that the vibrational frequencies and the relative intensities of the bands related to the ring structure and C=O group of the EC molecule change with the concentration of LiClO_4 in the solution. A rather strong interaction between Li^+ ions and EC molecules has been identified [73].

The Raman spectra of PAN and/or LiClO_4 complex containing plasticizer EC and the infrared spectra of the polymer electrolytes with different mass ratios of PAN to LiClO_4 have been studied by the same authors [74]. It has been found that the lithium ions strongly interact with the $\text{C}\equiv\text{N}$ groups of

PAN. At a concentration as low as 5% of Li^+ ions, because of the high intensity of the characteristic vibration of the $\text{C}\equiv\text{N}$ group of PAN, it is very difficult to observe the interaction between the ions and the molecules.

The Raman and IR spectra of the systems of plasticizer/ LiClO_4 and plasticizer/PAN/ LiClO_4 have been recorded by Wang et al. [75]. The plasticizers include dimethyl formamide (DMF) and PC. By comparing the spectra, it was found that the association of Li^+ ion is more competitive with DMF than with PC in the liquid or gel electrolytes. Moreover, the addition of PAN into DMF/ LiClO_4 solution has less influence on the Li^+ -solvent association than into PC/ LiClO_4 solution.

Starkey and Frech [76] have undertaken a comparative infrared spectroscopic study for a system of PAN-PC-lithium triflate to examine the plasticizer interactions with the polymer and salt as well as ionic association. It was reported that lithium triflate is highly associated and the lithium ion interaction is stronger with PC than with PAN. The study revealed that the local structure about the lithium ion is characterized by coordination with the three oxygen atoms of the PC molecule and a triflate

anion oxygen, with a weak interaction with the $\text{C}\equiv\text{N}$ group of PAN.

A solid-state Li/ LiMn_2O_4 and C/ LiNiO_2 batteries employing Li^+ -conductive PAN-based electrolytes with room temperature conductivities of the order of $2 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ were fabricated and tested. These batteries have been shown room temperature performance reminiscent of their liquid electrolyte counterparts [77]. The ionic conductivity of PAN based polymer electrolytes and MEEP based polymer electrolytes are depicted in Tables 3 and 4, respectively.

A novel fire-retardant gel electrolyte based on PAN was introduced by Akashi et al. [78] by optimizing the ratio of the polymer, with a combination of ethylene carbonate and propylene carbonate and lithium salt LiPF_6 . The incorporation of LiPF_6 significantly reduces the carbonizing point of the gel electrolytes and increases the residue of carbonaceous materials after burning.

A typical polymer electrolyte comprising of PAN (12%), EC (40%), PC (40%) and LiClO_4 (8%) was prepared by Sun and Jin [79]. The conductivity of the polymer electrolyte was found as high as 2×10^{-3} at room temperature and this polymer elec-

Table 3
PAN-based electrolytes with improved low temperature conductivities [77]

Electrolyte	Conductivity ($\Omega^{-1} \text{cm}^{-1}$) 10^{-3}			
	-40 °C	-20 °C	0 °C	20 °C
21PAN-33PC-38BL-8LiClO ₄	0.30	0.98	1.94	3.71
21PAN-33PC-10EC-18BL-10NMP-8LiClO ₄	0.20	0.74	1.93	2.57
21PAN-33PC-20EC-18BL-8LiAsF ₆	0.28	1.15	1.73	3.87

Table 4
Conductivity of MEEP-based polymer electrolytes [77]

Electrolyte	Conductivity ($\Omega^{-1} \text{cm}^{-1}$)		
	20 °C	50 °C	80 °C
1. MEEP-(LiClO ₄) _{0.25}	1.7×10^{-5}	7.0×10^{-5}	
2. MEEP-(LiBF ₄) _{0.25}	1.5×10^{-5}	5.0×10^{-5}	1.4×10^{-4}
3. MEEP-Li(CF ₃ SO ₃) _{0.25}	1.5×10^{-5}	3.8×10^{-5}	
4. MEEP-[LiN(CF ₃ SO ₂) ₂] _{0.13}	6.5×10^{-5}	1.6×10^{-4}	
5. 55 ^a MEEP/45PEO-(LiClO ₄) _{0.13}	1.3×10^{-6}	9.0×10^{-6}	2.7×10^{-4}
6. 55 ^a MEEP/45PEO-(LiBF ₄) _{0.13}	2.4×10^{-6}	2.0×10^{-6}	3.5×10^{-4}
7. 55 ^a MEEP/45PEO-(LiCF ₃ SO ₃) _{0.13}	1.0×10^{-6}	6.0×10^{-6}	3.5×10^{-5}
8. 55 ^a MEEP/45PEO-(LiNCF ₃ SO ₂) _{0.13}	6.7×10^{-5}	9.0×10^{-4}	
9. 55 ^a MEEP/45PEO-(LiAsF ₆) _{0.13}	1.9×10^{-7}	1.2×10^{-6}	1.5×10^{-5}
10. 87 ^a MEEP/13PEGDA-(LiClO ₄) _{0.13}	1.2×10^{-6}	7.2×10^{-6}	3.8×10^{-4}
11. 87 ^a MEEP/13PVP-(LiClO ₄) _{0.13}	4.0×10^{-6}	2.3×10^{-6}	4.0×10^{-4}

^a Dimensionally-stable composite electrolytes; all ratios are in wt%.

trolyte was employed in $\text{LiMn}_2\text{O}_4/\text{PE}/\text{Li}$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{PE}/\text{Li}$ cells. Better capacity retention and cycling profile were obtained for the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{PE}/\text{Li}$ cells than LiMn_2O_4 cells (Fig. 3) and were attributed to the stabilization of spinel structure by doping.

Ferry et al. [80] reported the spectroscopic and NMR studies on PAN complexed with LiCF_3SO_3 . Significant ionic motion was found at temperatures close to the glass transition temperature. FT-Raman spectroscopy was used to directly probe the local chemical anionic environment as well as the Li^+ -PAN interaction.

Positron annihilation life time spectroscopy was used to estimate the free volume behavior of PAN based electrolyte complexed with LiCF_3SO_3 by Forsyth et al. [81]. The relative free volume cavity size at room temperature was shown to decrease with increase in salt concentration.

Despite the several advantages of PAN-based electrolytes, like high ionic conductivity of the order of $10^{-3} \text{ S cm}^{-1}$ at 20°C , good electrochemical stability of 4.5 V and a lithium-transference number around 0.6, its poor compatibility with lithium metal anode offsets from practical applications. Other studies clearly revealed that the lithium electrode undergoes serious passivation when in contact with PAN-based electrodes and affects cyclability and eventually leads to safety hazards [82].

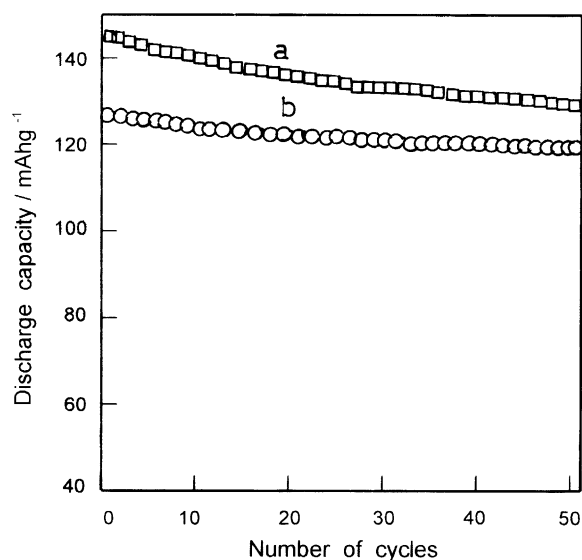


Fig. 3. Variation of discharge capacity with the number of cycles of (a) $\text{Li}/\text{polymer electrolyte}/\text{LiMn}_2\text{O}_4$ and $\text{LiMn}_{1.95}\text{Ni}_{0.05}\text{O}_4$ cells [79].

1.3. Poly(methyl methacrylate)

In 1985, Iijima and Toyoguchi [83] found that poly(methyl methacrylate) could be used as gelating agent. Later, Appetecchi et al. [84] focused their attention on gel PMMA electrolytes with different plasticizers. The authors concluded that the electrochemical stability window depends on the polymer host and lithium salt complexed. Although better scalability has been obtained with PMMA when compared with PAN, the voltammetric results and the efficiency tests revealed a consistent fraction of lithium is lost upon cycling and thus a large excess of lithium would be required eventually to assure an acceptable life to the battery. The lithium ion transport number t_{Li}^+ is displayed for few polymer hosts in Table 5.

The rheological and electrochemical properties of PMMA- LiClO_4/PC membrane were obtained by Bohnke et al. [85]. The addition of PMMA in various proportions increased the viscosity of the macromolecule solution. On contrary, the conductivity was considerably reduced upon the addition of PMMA. However, the room temperature conductivity remained unvaried and closely to the conductivity of the liquid electrolytes. DSC data established the thermal stability of these membranes between -110 and 240°C .

Also the influence of concentration of polymer in the gelled electrolytes and the conductivity and viscosity of gel electrolytes comprising of PMMA- LiClO_4 and PC have been measured [86]. At ambient temperature the ionic conductivity was found to decrease with increasing amount of polymer and was in the range of 5×10^{-3} – $5 \times 10^{-5} \text{ S cm}^{-1}$. In low concentrations of PMMA, the gelatinized electrolyte was considered as a liquid electrolyte encaged in a polymer matrix. However, the decrease in ionic conductivity and an increase in activation energy at high concentration were attributed to

Table 5
The lithium ion-transport number, t_{Li}^+ , of different electrolytes [84]

Electrolyte	Solvent/solution ratio	t_{Li}^+
1. PC/ LiClO_4	Liquid	0.4
2. PEO/ LiClO_4	Polymer	0.2
3. LiClO_4 -PC-EC-PAN	17.6:1	0.6
4. LiAsF_6 -PC-EC-PAN	17.6:1	0.7
5. $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -PC-EC-PAN	17.6:1	0.8
6. LiClO_4 -BL-PAN	17.6:1	0.7
7. $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ -BL-EC-PAN	17.6:1	0.6

some interactions created between the polymer chain and the conducting electrolytes.

A model that emphasized the importance of PC and/or PMMA lithium solvation effect of ion-pairing and the cross linking action of cations at high PMMA concentration have also been reported [87]. The 20 w/o of PMMA gels were considered as a liquid electrolyte encaged in an inert polymer matrix. On the other hand, a very strong interaction between the polymeric chains and the ionic species was observed when the concentration of PMMA was increased to 45 w/o the gel.

The DSC, NMR, electrical conductivity studies have been made by Stallworth et al. [88] for the gel electrolytes synthesized from PMMA, EC, PC and various lithium salts (LiClO_4 , LiAsF_6 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2$). DSC analysis revealed that the gel electrolytes exhibit single glass transition temperature and by dramatic changes in NMR line width, which occur in the vicinity of glass transition. Figs. 4 and 5 show the NMR central line widths vs T for the PMMA and PMMA- LiAsF_6 and PPO_8 LiAsF_6 , respectively. These results are in accordance with those reported for PMMA electrolytes [89].

Vondrak et al. [90] prepared PMMA gel electrolytes with propylene carbonate as plasticizer and complexed with salts of various perchlorates of different cation sizes including lithium. The gel electrolyte, which possesses lithium as cation exhibited maximum conductivity and was attributed to smaller ionic radii. The ionic conductivity of elastic and

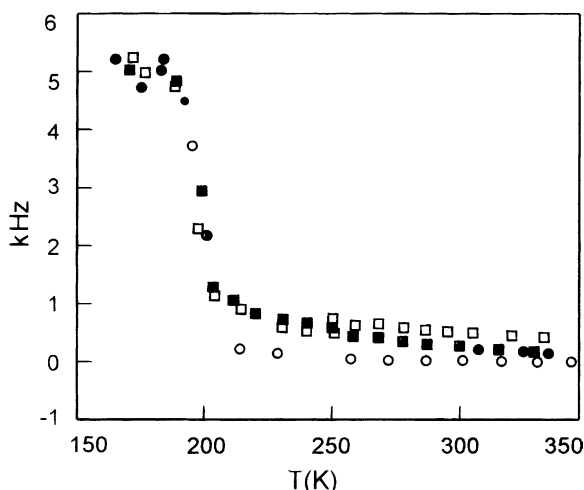


Fig. 4. Lithium-7 NMR central line widths vs T for the PMMA Gels and the reference liquid electrolyte [88]. (○) $\text{LiClO}_4/\text{EC}/\text{PC}$, (□) IMIDE/PMMA , (●) $\text{LiClO}_4/\text{PMMA}$, and (■) $\text{LiAsF}_6/\text{PMMA}$.

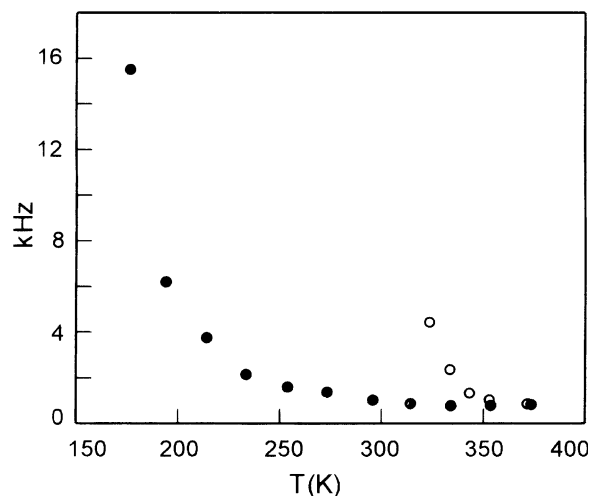


Fig. 5. Fluorine-19 NMR line widths vs T for the LiAsF_6 PMMA gel and for PPO_8 LiAsF_6 [88]. (●) PMMA and (○) PPO.

sticky polymer electrolytes prepared by polymerization of methacrylate solution containing LiBF_4 in propylene carbonate as plasticizer has also been reported [91].

1.4. Poly(vinyl chloride)

Sukeshini et al. [92] complexed poly(vinyl chloride) (PVC) with lithium bis(trimethyl sulfonyl)imide (LiTFSI) and plasticized with dibutyl phthalate (DBP) and dioctyl adipate (DOA). The ionic conductivity of the membranes was increased considerably when PVC content was decreased. Temperature-dependence of ionic conductivity for ternary polymer electrolytes containing PVC-DBP- LiTFSI is depicted in Fig. 6. The electrochemical stability domains close to 4.0 V at 60 °C, established by cyclic voltammetry using Ni-ultra microelectrodes was limited in the cathodic side by lithium deposition and stripping processes and in the anodic side by the oxidation of the polymer. The efficiency of the lithium stripping followed by the deposition was found to be poor and was attributed to the reaction DBP or DOA with lithium.

The cycling behavior of PVC-based electrolytes with LiMn_2O_4 cells were demonstrated by Alamgir and Abraham [93]. Fig. 7(a) shows the temperature dependence of the ionic conductivity of the electrolyte with and (b) shows the cycling data of a $\text{Li}/\text{SPE}/\text{LiMn}_2\text{O}_4$ cell at 20 °C. The film with 10 w/o PVC, 80 w/o PC, 5 w/o $\text{Li}(\text{NSO}_2\text{CF}_3)_2$ compositions exhibited ionic conductivity of

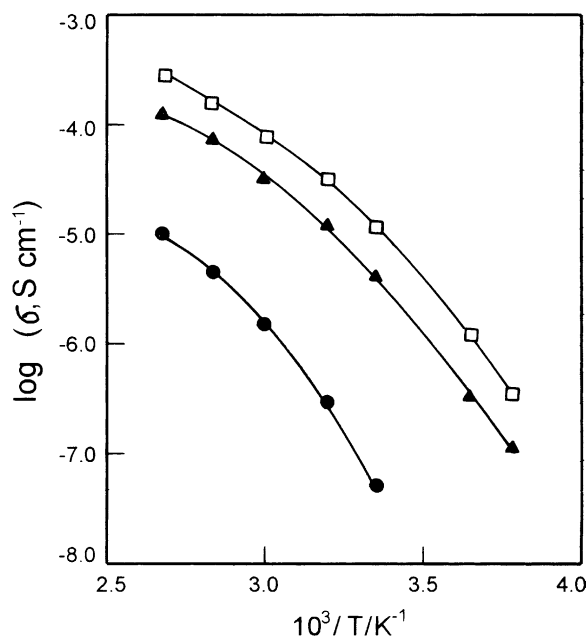


Fig. 6. Temperature dependence of ionic conductivity for ternary polymer electrolytes containing PVC-DBP-LiTFSI [92]. (□) 0.33PVC + 0.55DBP + 0.12LiTFSI, (▲) 0.33PVC + 0.41DBP + 0.09LiTFSI, and (●) 0.67PVC + 0.27DBP + 0.06LiTFSI.

$1.1 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C. Table 6 also displays the conductivity of polymer electrolytes.

1.4.1. Poly(vinyl chloride)/poly(methyl methacrylate) blend

In this juncture the possibility of using PVC-PMMA blend electrolytes was explored also by Rhoo et al. [94] and also by us [95–97]. The problem of poor mechanical strength was circumvented by blending PMMA with a polymer such as PVC, which because of its poor solubility in the plasticizer medium manifests itself in a phase separated morphology providing rather rigid frame work in the polymer electrolyte film. A 7:3 PMMA/PVC blend electrolyte at 70% plasticizer content was found to be optimal in mechanical strength and conductivity points of view. Although, the mechanical strength

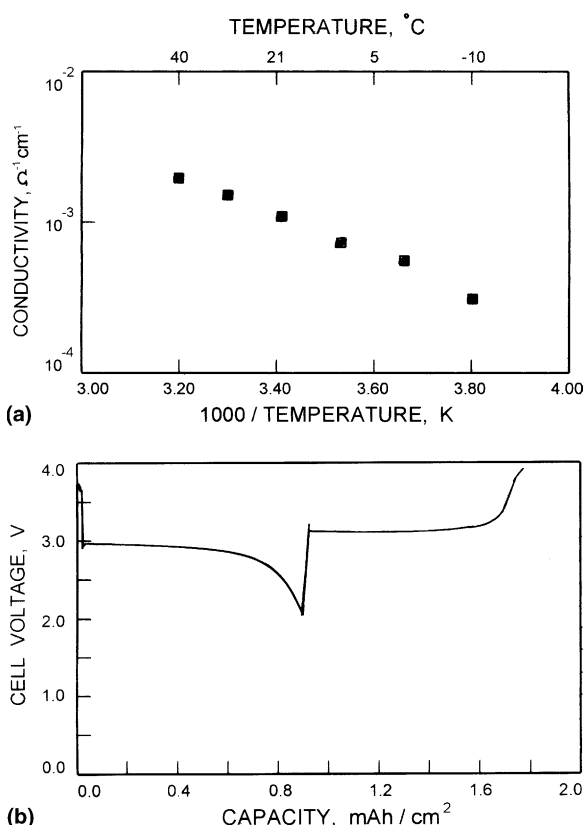


Fig. 7. (a) Temperature dependence of the conductivity of electrolyte with (b) cycling data for a Li/SPE/LiMn₂O₄ cell at 20 °C [93].

was increased upon the addition of PVC in the blend it leads to poor interfacial properties and thus poor cycling. Among the three salts LiClO₄, LiBF₄ and LiCF₃SO₃ examined the films, which possess LiBF₄ offered maximum conductivity and was attributed to the presence of fluorinated compound in the salt.

1.5. Poly(vinylidene fluoride)

By virtue of its attractive properties PVdF has been chosen as a polymer host for lithium battery applications. PVdF based polymer electrolytes are

Table 6
Li⁺-Conductive solid polymer electrolyte with liquid-like conductivity [93]

Electrolyte	Conductivity (S cm ⁻¹)			
	-10 °C	0 °C	20 °C	50 °C
1. 38%EC/33PC/21PAN/8%LiClO ₄	1.1×10^{-3}	1.2×10^{-3}	1.7×10^{-3}	3.5×10^{-3}
2. 42%EC/36PC/15PAN/7LiCF ₃ SO ₃	4.0×10^{-4}	6.0×10^{-4}	1.4×10^{-3}	2.2×10^{-3}
3. 63%EC/13PC/16PAN1PEGDA/8LiClO ₄	4.0×10^{-4}	6.0×10^{-4}	1.2×10^{-3}	3.0×10^{-3}
4. 68%EC/15PC/3PEGDA/14LiClO ₄	1.2×10^{-3}	2.1×10^{-3}	4.1×10^{-3}	8.0×10^{-3}
5. 35%EC/31PC/24PVP10LiCF ₃ SO ₃	4.0×10^{-5}	1.3×10^{-4}	5.0×10^{-4}	1.0×10^{-3}

highly anodically stable due to the presence of strong electron-withdrawing functional group ($-C-F$) and the polymer itself has a dielectric constant ($\epsilon = 8.4$) which helps for greater dissolution of lithium salts and subsequently supports high concentration of charge carriers. The earlier report indicates that a homogenous hybrid film can be obtained with PVdF when EC and or PC with lithium salt of proper proportions [98].

Tsuchida et al. [99,100] examined the plasticized PVdF with 30 mol% of $LiClO_4$ in which they found that the viscosity plays a major role in the conductivity rather than the dielectric constant of the plasticizer. However, these electrolytes exhibited low ionic conductivity of the order of $10^{-5} S cm^{-1}$ at elevated temperatures and were attributed to inhomogeneity of the membrane at or below ambient temperature.

Choe et al. [101] reported PVdF-based electrolytes plasticized with a solution of $LiN(CF_3SO_2)_2$ in PC that offered conductivity of $1.74 \times 10^{-3} S cm^{-1}$ at 30 °C and oxidation potential limits between 3.9 and 4.3 V vs Li^+/Li . Finally, they suggested that the ionic mobility can be increased up to two to four orders upon the incorporation of plasticizers into the solid polymer electrolyte.

A novel polymer electrolyte comprising of PVdF-EC-PC and a lithium salt ($LiCF_3SO_3$, $LiPF_6$ or $LiN(SO_2CF_3)_2$) was prepared by thermal extrusion method [102]. The mechanical strength of the polymer electrolyte film varied widely and depended on the PVdF content. The viscosity of the medium and concentration of the charge carriers, which are directly related to the weight ratio of PVdF-EC-PC and the kind of lithium salt studied, mainly influenced the conductivity of the electrolyte. The Li-electrolyte interface stability under static conduction was found to be more suitable for the system PVdF-EC-PC- $LiN(SO_2CF_3)_2$ electrolytes than the systems studied (Fig. 8). Although, the PVdF-based electrolytes offer excellent electrochemical properties, this fluorinated polymer is not stable towards lithium leading to poor interfacial properties between lithium and fluorine. Fig. 8 shows the impedance plots of a Li/30 w/o PVdF 2822-60 EC/PC-10 imide/Li cell stored at room temperature. This fluorinated polymer forms LiF upon cycling. The compatibility study of lithium metal anode with PVdF-EC-PC-imide polymer electrolyte reveals that these electrolytes may have good shelf life at room temperature. Also the cyclic voltammetry studies suggested PVdF electrolytes are more suitable for

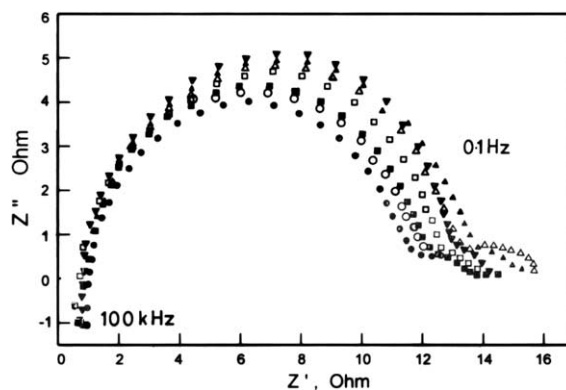


Fig. 8. The impedance plots of a Li/30 w/o PVdF 2822-60 EC/PC-10 imide/Li cell stored at room temperature [102]. (●) Fresh, (○) after 1 day, (■) after 8 days, (□) after 24 days, (▲) after 48 days, (▼) after 72 days, and (∇) after 20 days.

primary than secondary batteries when lithium metal is employed as anode [102].

A rechargeable all-plastic battery was fabricated with PVdF-PC- $LiClO_4$ membrane as electrolyte using poly acetylene film as an active electrode material. This battery system has been found to be feasible for small power source for low current electronic devices. However, the problems associated with ionic conductivity polymer electrolyte and the degradation of battery performance and adhesion between the acetylene films and polymer electrolyte are to be rectified [103].

Shiao et al. [104] have found that the ionic conductivity of new ternary and quaternary solvent mixtures containing significant amount of toluene was reduced upon the addition of PVdF host matrices. However, the ionic conductivity remained sufficiently high yielding down at least -40 °C. Their results revealed that the addition of toluene in the quaternary mixture solvents not only increased the stability of the anodic (solid electrolyte interface) film but also reduces the solubility and swelling of PVdF. The capacity retention of cells using PVdF-mixed quaternary solvent at -40 °C is 50% of nominal capacity at ambient temperatures. Very recently, the electrochemical and dielectric properties of PVdF polymer hosts have been reported [105].

1.6. Poly(vinylidene fluoride-hexafluoro propylene)

Gel polymer electrolytes based on a copolymer of PVdF/HFP and a solution of ethylene carbonate (EC), diethyl carbonate (DEC) and $LiN(CF_3SO_2)_2$

as salt were prepared by Capiglia et al. [106], by changing the content of the polymer. The change in salt concentration was reflected in the conductivity change in the range of 10^{-2} – 10^{-8} S cm $^{-1}$. Figs. 9 and 10 show the variation of ionic conductivity as a function of concentrations of 1 and 0.5 M of LiBETI, respectively. Both diffusion coefficients of lithium (D_{Li}^+) and fluoride species (D_F^-) decrease with increase of polymer content.

The ionic conductivity, thermal stability and compatibility of PVdF-HFP gel electrolytes with a combination of EC and PC as plasticizers and three different lithium salts (LiCF $_3$ SO $_3$, LiBF $_4$, LiClO $_4$) have been examined by us [107]. The ionic conductivity of the gel electrolytes was increased upon the addition of polymer in the gel. Among the salts studied, the film, which possesses LiBF $_4$ as salt exhibited maximum conductivity and was attributed to the low lattice energy of the salt. On contrary, the films, which possess LiBF $_4$ exhibited poor compatibility with lithium metal anode and were identified due to the formation of LiF in the layer.

Saika and Kumar [108] have made systematic studies on the ionic conductivity and transport properties polymer electrolytes comprising of the copolymer of PVdF-HFP + PC + DEC + LiClO $_4$ and PVdF + PC + DEC + LiClO $_4$ separately. The

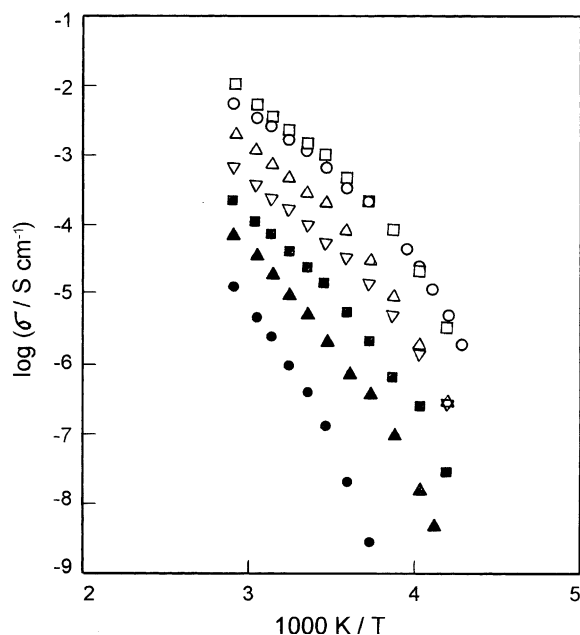


Fig. 9. Arrhenius plots of the conductivity for the samples PVdF-HFP-(EC/DEC/BETI 1 M) [106]. (□) 20:80, (○) 30:70, (△) 40:60, (▽) 50:50, (■) 60:40, (▲) 70:30, and (●) 80:20.

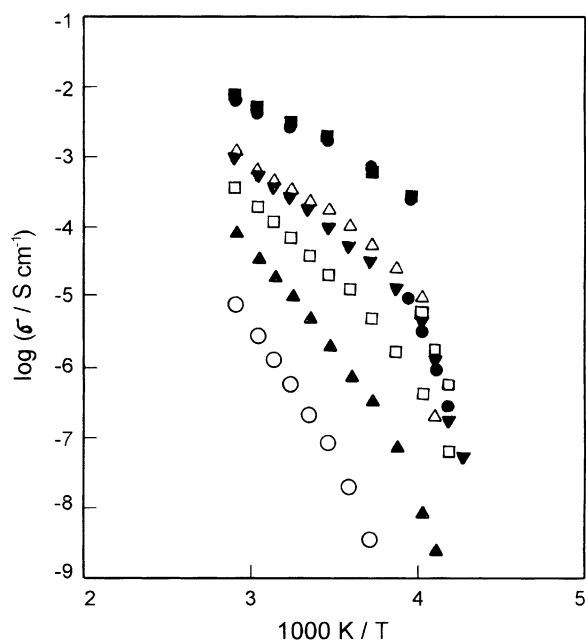


Fig. 10. Arrhenius plots of the conductivity for the samples PVdF-HFP-(EC/DEC/BETI 1 M) [106]. (■) 20:80, (●) 30:70, (□) 40:60, (△) 60:40, (▲) 70:30, (▼) 50:50, and (○) 80:20.

film which possess PVdF-HFP host exhibited higher conductivity and transport number than the film with PVdF. The films were also subjected to FTIR and XRD analysis. The higher conductivity of PVdF-HFP films was attributed to the higher amorphocity as there are two randomly mixed monomers providing the mobile Li $^+$ ion more free (Fig. 11). On the other hand, PVdF has higher degree of crystallinity, which results in lower conductivity.

The electrochemical and cycling profile of LiCoO $_2$ /Li and LiCoO $_2$ /MCMB cells comprising gel polymer electrolyte (PVdF-HFP (25%), EC-PC (65%) and LiN(CF $_3$ SO $_3$) $_2$) have been reported by Kim and Moon [109]. The cells comprising LiCoO $_2$ /GPE/MCMB cells are found to deliver higher capacity and columbic efficiency than the LiCoO $_2$ /GPE/Li cells.

1.6.1. Other polymer hosts

Many researchers discussed physical and electrochemical properties of other polymer host systems. The phase changes with respect to the dissolution of lithium salt in linear poly(ethylene imine) has been investigated by Chiang et al. [110]. Also studies have been made on copolymer of EO-PO [111], poly(ethers) [112], poly(methoxy, ethoxy ethyl methacrylate) poly(MEEMA) [113] and ter-polymer of MMA-EO-PO [114].

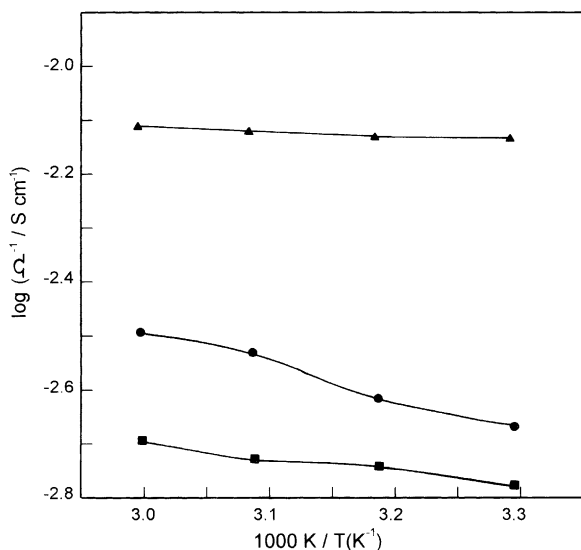


Fig. 11. The dependence of ionic conductivity of P(VdF-HFP)-(PC + DEC)-LiClO₄ polymer complexes: (▲) 25:70:5, (●) 25:70:5, and (■) 25:60:15 [108].

Song et al. reported [115] that PVC based electrolytes suffer from solvent exudation and they suggested two strategies are involving the replacement of PVC with PVAC-copolymer and other, the direct utilization of solvents for PVC or PVAC instead of using an auxiliary carrier solvent THF.

High molecular weight comb polymers P(EO-MEEGE) have also been analyzed by Nishimoto et al. [116], as matrices for polymer electrolyte. An apparent decrease in crystallinity was observed when the content of MEEGE in the copolymer was increased and subsequently, an increase in conductivity was found. The interfacial properties of P(EO-MEEGE) matrices with lithium metal anode were reported by Watanabe et al. [117].

The comb-shaped high molecular weight poly(oxy ethylene) with tri(oxy ethylene) side chains as solid polymer electrolyte was synthesized and characterized by Ikeda et al. [118]. The presence of tri(oxy ethylene) side chains were found to decrease the crystallinity of oxyethane segments.

Polymer electrolytes of poly(acrylonitrile-co-lithium methacrylate), ethylene carbonate and LiClO₄ were prepared and their ionic conductivity studies were reported by Lee et al. [119]. The interfacial resistance behavior between the lithium electrode and PAN ionomer based polymer electrolyte has also been investigated and were compared with that of lithium and PAN based electrolytes.

Anne et al. [120], developed a new type of high performance polymer electrolytes. Polymers composed of interconnecting networks of boronine rings were investigated as suitable hosts B₃O₃ [O(CH₂CH₂O)_nCH₃]₃.

A hyper branched poly[bis(hexathylene glycol)benzoate] with terminal acetyl groups was prepared and ionic conductivity, thermal property and electrochemical stability of the polymer electrolyte with LiN(CF₃SO₃)₂ were investigated by Itoh et al. [121]. Furthermore, the addition of a hyper branched polymer to a PEO/LiN(CF₃SO₃)₂ electrolyte was found to be considerably effective in improving the over all ionic conductivity. The ionic conductivity of terminal-acetylated hyperbranched poly ethylene glycol derivatives containing diethylene and triethylene glycols and 3,5-dioxybenzoate branching units complexed with lithium metal salts such as LiCF₃SO₃ and LiN(CF₃SO₂)₂ have also been reported [122].

A new copolymer poly(acrylonitrile-co-bis[2-(2-methoxy ethoxy) ethyl]itaconate) (PANI) was synthesized and its ionic conductivity and DSC thermogram were reported by Kim et al. [123]. The PAN-PANI blend gel electrolyte as compared with pristine PAN-based electrolytes had better electrochemical stability and was more stable towards lithium electrode, though it exhibited slightly less mechanical rigidity caused by the amorphization of the PAN matrix.

Muranaga and coworkers [124] have developed the interfacial characteristics between the cathode and electrolyte by making thin film of cross linked polymer electrolyte P(EO/MEEGE/AGE), i.e., poly(ethylene oxide) 2-(2-methoxy ethoxy) ethyl glycidyl ether and with and without allyl glycidyl ether (AGE) complexed in LiN(CF₃SO₃)₂ as salt. The charge-discharge and cycle life capability have also been presented.

Kuratomi et al. [125], have developed a long-life lithium battery using LiCoO₂/Li electrode system with cross-linked random copolymer of ethylene oxide and propylene oxide with two different lithium salts namely LiBF₄ and LiN(CF₃SO₂)₂. The battery cyclability was significantly better in the LiN(CF₃SO₂)₂ system compared to LiBF₄ electrolyte system. The battery performance was found to depend on species and concentration of the lithium salts used.

Lee et al. [126] have studied cross-linked polymer electrolytes prepared by polymerization of poly ethylene glycol dimethylacrylate (PEGDMA) and alkyl

monomer in the presence of liquid electrolyte 1.3 M LiPF_6/EC . Flexibility and ionic conductivity of the electrolyte was improved when the monomer content was varied. The electrical performance and cycling behavior of $\text{Li}/\text{PE}/\text{LiCoO}_2$ solid-state cell has also been studied.

The thermal transition, ionic association and ionic conductivity have been measured as a function of LiCF_3SO_3 concentration in poly dioxolane based electrolytes by Silva et al. [127]. The complex formation of the polymer and LiCF_3SO_3 salt system has been suitably identified using Raman spectroscopy. A linear increase of “ T_g ” was observed between 12 and 58 wt% of salt concentration.

York et al. [128], have reported the Raman and IR studies on poly(ethylene imine) (LPEI) complexed with LiCF_3SO_3 and NaCF_3SO_3 . It has been reported that in LPEI/ LiCF_3SO_3 system, free ions, contact ion pairs and triple cation [$\text{Li}_2\text{CF}_3\text{SO}_3$] become dominant species whereas contact pairs appear to be dominant ionic species for the same concentration of LPEI- NaCF_3SO_3 system.

Gel polymer electrolytes composed of acrylonitrile-methyl methacrylate (AM) copolymer and $\text{LiClO}_4\text{-EC/PC}$ were prepared by Kim et al. [129]. The system shows no solvent exudation from the matrix polymer due to enhanced compatibility between AM copolymer and organic liquid electrolyte.

A comparative vibrational spectroscopy study on a series of polymer electrolytes composed of poly(oligoethyleneoxy phosphazane) containing dissolved lithium triflate was done by York et al. [130]. Raman vibrational spectroscopy has been used to examine ionic association and local changes of the polymer and salt concentration and the length of ethylene oxide side chains. The degree of ionic association of the triflate ion was found to increase with increasing salt concentration. The electrochemical behavior of lithium aromatic sulfonyl imide salts in amorphous poly(oxyethylene)network [131], a blend of poly(vinylidene fluoride-co-hexafluoro propylene)/poly(vinyl acetate) [132] and the behavior of lithium ion in comb-like polymer structure have also been reported [133]. A novel gel comprising methyl methacrylate-acrylonitrile-styrene ter-polymer with a combination of plasticizers ethylene carbonate and diethyl carbonate and LiClO_4 as salt was synthesized [134]. The prepared gel polymer electrolytes (GPE) were employed as separators in $\text{Li}/\text{LiNi}_{0.83}\text{Co}_{0.7}\text{O}_2$ and carbon/ $\text{LiNi}_{0.83}\text{Co}_{0.7}\text{O}_2$ cells and their cycling behavior was analyzed. The results revealed

that the cell comprising $\text{Li}/\text{GPE}/\text{LiNi}_{0.83}\text{Co}_{0.7}\text{O}_2$ delivered higher discharge capacity than carbon/ $\text{GPE}/\text{LiNi}_{0.83}\text{Co}_{0.7}\text{O}_2$ cell. A similar study was made by Kim et al. [135] where they employed pseudo-inter penetrating system for the preparation of poly methyl methacrylate-methacrylate gel systems and made cycling studies with composite LiCoO_2 cathode material. A very recent review [136] also documents on the interfacial properties of polymer electrolytes with lithium metal anode.

1.7. Phase inversion technique

Large research efforts have been devoted to obtain polymer electrolytes with high ionic conductivity at ambient temperature, good mechanical and thermal stabilities. Generally, two methods of preparation have been employed. The most common approach has been that of adding liquid plasticizers, such as low-molecular-weight plasticizers like ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, etc. Upon the addition of plasticizers the gain in ionic conductivity is accompanied by a loss of mechanical strength of the polymer electrolyte, which prevented their use in practical cells. Other studies [84] and our earlier studies [95–97] have clearly indicated that these polymer hosts lose their mechanical strength when they are plasticized. Further more the prepared films have to be hardened either by chemical or physical (high energy radiation) curing and that resulted in high processing costs.

On the other hand, the second process involves activation process in which a polymer membrane is soaked in electrolyte solution. Gozdz et al. [137] successfully launched a reliable and practical rechargeable lithium-ion plastic batteries with a copolymer of PVdF-HFP. As mentioned earlier this copolymer consists of two phases; the amorphous domain helps for trapping large amount of liquid electrolyte whereas the crystalline phase acts as a mechanical support for the processing of free-standing films and thereby eliminated the need for a cross-linking step. Using PVdF-HFP polymer, a lithium salt, plasticizer-free membrane was prepared by Gozdz and coworkers [138] and then substituted by the liquid electrolyte during the final stage of cell processing through extraction/activation step. This system, more specifically can be described a heterogeneous, phase separated, plasticizer-free polymer separator. Compared with the solution casting/solvent casting technique, this process requires the

critical moisture control only at the time of assembling the cells and its mechanical strength is retained.

Very recently several reports are available on the development of polymer membranes using phase inversion technique [139–157]. The ionic conductivity and NMR studies on PVdF-HFP polymer membranes prepared by phase inversion technique have also been reported by us [141–143]. In the present study an attempt has been made to prepare PVdF-HFP polymer membrane with different non-solvents and their ionic conductivity and their cycling behavior of LiMn_2O_4 /polymer membrane/Li cells are discussed.

2. Experimental

Microporous polymer films were obtained by a phase inversion technique as described elsewhere. Briefly, PVdF-HFP copolymer (Elf Atochem, Japan) was dissolved in a mixture of acetone (a volatile solvent) and a non-solvent (cyclohexanol, toluene, *n*-pentane, *n*-hexane, 1-butanol and methanol) such that the amount of the non-solvent was low enough to allow solubilization and high enough to allow phase separation upon evaporation. The resulting solution was spread as a film on a glass substrate and the solvent was allowed to evaporate at ambient temperature.

Traces, if any, of non-solvents were removed by vacuum drying for 12 h at 115 °C. All experiments were performed in a dry room. Morphological examination of the films was made by a JSM-5410LV scanning electron microscope under vacuum (10^{-1} Pa) after sputtering gold on one side of the films. The BET surface area and pore-size distribution were determined by a continuous-flow nitrogen gas adsorption/desorption apparatus (BELSORP 28, Japan).

Ionic conductivity was measured with films soaked in a 1 M solution of LiPF_6 in a 1:1 (v/v) mixture of ethylene carbonate and diethyl carbonate for 2 h. Details of ionic conductivity measurements and charge–discharge studies on Li/ LiMn_2O_4 cells assembled with these membranes are available elsewhere [143,144].

3. Results and discussion

Fig. 12(a)–(f) reveals the morphology of the membranes prepared with different non-solvents, toluene, cyclohexanol, 1-butanol, methanol, *n*-pen-

tane and hexane, respectively. A flacky surface with unevenly sized pores was developed when cyclohexanol was used as non-solvent. A similar morphology was obtained for the films prepared with toluene, 1-butanol and methanol. More interestingly, on the other hand, a homogenous phase with uniformly sized pores is seen on the image of the films when *n*-hexane or *n*-pentane was used.

The films, which were prepared with toluene and cyclohexanol exhibited higher pore diameter with minimum surface area. Table 7 shows the average pore diameter and weight ratio of the electrolyte solutions to polymer membrane after gelation for 24 h in 1 M LiPF_6 in EC/DMC of (1:1, v/v). It is seen from the table that only polymer membranes that have bigger pore size as evidenced by SEM and nitrogen adsorption/desorption studies were able to hold large amount electrolyte solutions taking advantages of their cavities.

Generally, the conductivity in conventional battery separator is achieved due to the continuous pathways developed the absorbed liquid electrolyte within the interconnected pores of the membranes. The porous structure is one of the important factors in determining the ionic properties of an electrolyte in a separator. Also of importance the ionic conductivity of a porous membrane undoubtedly, depends on the conductivity of the electrolyte embedded in the pores of the membrane. Therefore, the conductivity is affected by the membranes porosity, tortuosity of the pores, the conductivity of the liquid electrolyte, the thickness of the membrane and the extent to which the electrolyte wets the pores of the membrane.

As we suggested, the ionic conductivity of the membrane is determined by the amount of solution entrapped by the membranes [147,148]. Although, the SEM pictures reveal the surface morphology of the membranes the parameters like pore diameter and distribution of pores cannot be determined even when they are magnified as large as 35,000 times. The polymeric specimen are prone to damage by electron beam when they are magnified [148]. Table 7 displays the pore-size distribution and the amount of liquid electrolyte entrapped in the pores of the PVdF-HFP membranes prepared by phase inversion method using different non-solvents. As indicated in [144,148], the average pore diameter and BET surface area of the commercially available celgard 2400 are 26 nm and $41.79 \text{ m}^2 \text{ g}^{-1}$, respectively. The present study reveals that the films prepared with toluene and cyclohexanol are more or less the

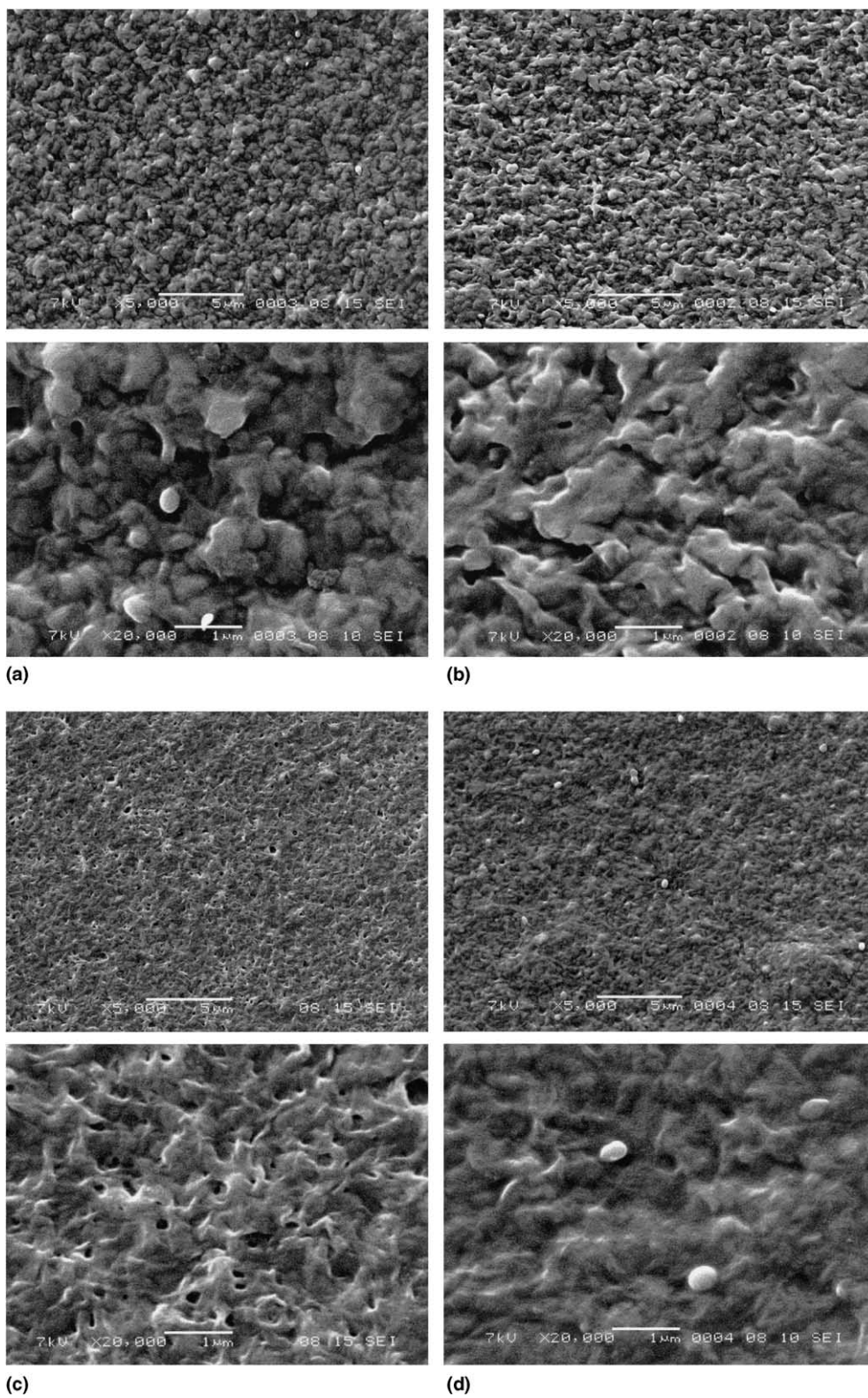


Fig. 12. SEM pictures of PVdF-HFP membranes prepared with different non-solvents: (a) toluene, (b) cyclohexanol, (c) *n*-hexane, (d) *n*-pentane, (e) 1-butanol, and (f) methanol.

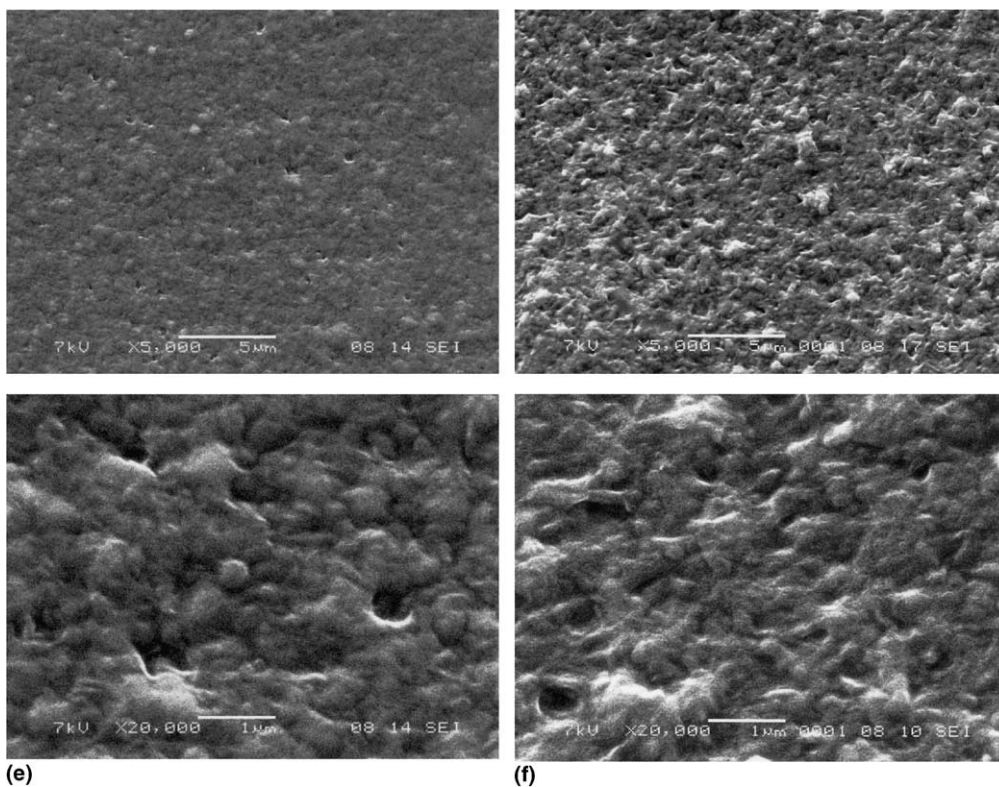


Fig. 12 (continued)

Table 7

Pore diameter, BET surface area and electrolyte intake of PVdF-HFP membranes prepared by phase inversion technique

Non-solvent	Pore diameter (nm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Electrolyte intake (%)
Toluene	28	34	72
Cyclohexanol	27	42	69
1-Butanol	23	68	58
Methanol	22	69	56
<i>n</i> -Pentane	7	181	50
<i>n</i> -Hexane	2	200	49

same as that of commercially available one. But on the other hand, the film prepared with *n*-hexane or *n*-pentane exhibits BET surface area of 5–6 times higher than that of Celgard 2400. In other words, its average pore diameter is minimum. In phase inversion method, the membrane was formed by polymer precipitation, which occurs as a consequence of concentration variation following diffusive interchange between the solvent and non-solvent. The amount of uptake of electrolyte solution was increased when the porosity of the membrane was increased using the non-solvent. Consequently, it increases the ionic conductivity as

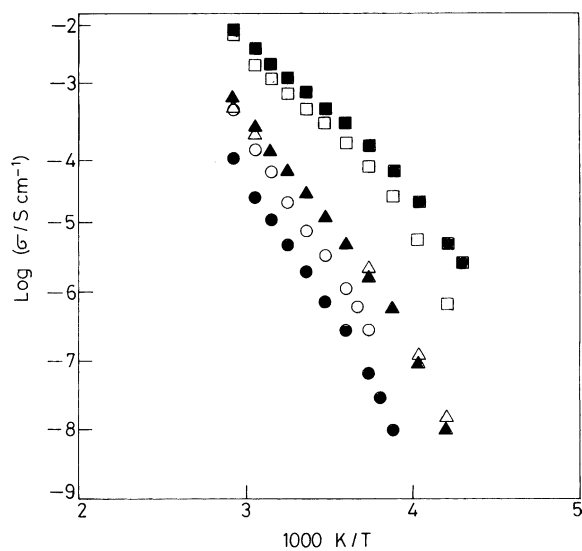


Fig. 13. Temperature dependence of ionic conductivity of PVdF-HFP membranes prepared with different non-solvents: (■) cyclohexanol, (□) toluene, (▲) 1-butanol, (△) methanol, (○) *n*-pentane, and (●) *n*-hexane.

evidenced in Fig. 13. More interestingly, it is obvious from the figure that the films prepared with tol-

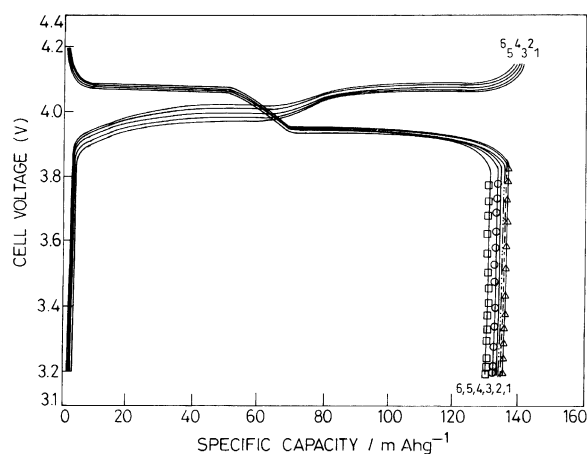


Fig. 14. Cycling profile of cells comprising of $\text{LiMn}_2\text{O}_4/\text{PVdF-HFP}$ membranes/Li. Membranes prepared with (1) toluene, (2) cyclohexanol, (3) methanol, (4) 1-butanol, (5) *n*-pentane, and (6) *n*-hexane as non-solvents.

uene, cyclohexanol, 1-butanol and methanol exhibited higher conductivity than those prepared with *n*-hexane and pentane. The conductivity of the membranes ranging from 10^{-5} to 10^{-3} S cm^{-1} for the temperatures between -30 and 70 $^\circ\text{C}$ when hexane or pentane was used as non-solvent. On the other hand, the ionic conductivity of the membrane vary from 10^{-7} to 10^{-4} S cm^{-1} for the same temperatures studied when hexane and pentane was used as non-solvent.

High ionic conductivity although, a desirable property is not sufficient to make a membrane completely useful in practical terms. Cyclability with the electrode materials is also an important parameter to guarantee acceptable performance in electrochemical devices when reliability and safety are concerned. Fig. 14 shows the cycling profile of $\text{LiMn}_2\text{O}_4/\text{PM}/\text{Li}$ cells between 3.2 and 4.2 V at a $C/20$ rate at 50 $^\circ\text{C}$. The membrane prepared with toluene as non-solvent in which the pore diameter and intake of electrolyte solution was maximum is found to have excellent cyclability when compared to other membranes. For the remaining films although, varied in morphology, BET surface area with the nature of the non-solvent any discernible changes could not be seen in the charge–discharge characteristics up to 25 cycles under the conditions of the experiment. In the cycling behavior two stages of oxidation and reduction are seen which is a characteristic feature of LiMn_2O_4 [79]. However, a small fade in capacity could be attributed to Jahn–Teller effect, which causes severe structural distortion, leading to a decrease in vacant sites as

well as the increase in interfacial resistance between the polymer membrane and electrodes (i.e., lithium and oxide electrode) [79].

4. Conclusions

In general, the ionic conductivity of the polymer host increases when they are plasticized. Among the polymer hosts generally studied, PEO, PAN, PMMA, PVC, PVdF and PVdF-HFP each polymer host has its own advantages and limitations. However, the problems associated with these electrolytes, like compatibility, mechanical strength are to be rectified. The preparation of polymer membrane by phase inversion method has also been identified as a promising method and the morphology of the membrane can be tailored with different non-solvents. In the present study, although the physical properties of the membranes are varied, not much discernible changes could be seen in the charge–discharge studies.

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