



Lithium Based Electrolytes in Electrochemical Energy Storage Devices- A Review

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Abstract

An interesting manifestation with improvising technological development for advanced applications focuses the energy storage systems. The development leads to the initiation of the polymer electrolyte in batteries with high thermal stability. The most commonly used batteries are lithium due to its high compatibility. This includes the introduction of biopolymers as a substitute for synthetic polymers of better properties. The ionic conductivity with increasing voltage is found by doping the salts with the polymers by increasing its conduction for application purpose.

Introduction

Energy conservation has served as a theme of discussion in most of the World Forums since the past few decades. The process of sufficing the increasing energy demand that is prevalent round the globe has many challenges to overcome. The key challenges worth mention are conversion and storage of electrical energy. This scenario has been put to rescue with the invention and commercialization of electrochemical energy storage technologies based on batteries. This technology has gained universal acceptance as a prominent solution to the challenge of rapidly increasing demand for energy. Further, the Li-ion technology in battery systems is yet sophistication in the field, as they exhibit increased viability and integrate the renewable resources that provide intermittent energy to the grid. Lithium based rechargeable batteries are deemed a boon with appealing features that promote efficiency in the usage of devices. This article attempts to explore research in the field of energy storage systems. Interdisciplinary areas of research leading to the development of ionic technologies are known as Solid State Ionics (SSI) which deals with the properties of ionic solids. The demands for thin-film applications clearly differ from that of the conventional batteries. Biopolymers (like cellulose derivatives, chitosan, and starch or natural rubber) have been mainly focused because of their good physical and chemical properties, biodegradability, cost, good performance and low production [1]. The development of polymer electrolytes has different stages with different behavior namely solid polymer, gel polymer, and composite polymer electrolytes. In the former electrolyte the host polymer itself is used as a solvent (solid) along with lithium salt without containing any organic liquids. However, these polymer electrolyte systems present very low ionic conductivity at ambient temperature [2]. With relation to green chemistry very interesting substitutes for synthetic polymers are natural polymers. The polymer hosts in inorganic salts have ease dissolution when the dielectric constant (ϵ) of the polymer is high and the lattice energy of the salt is low [3]. The electrolytes were also tested as ionic conductors in electrochromic devices.

Despite recent exhaustive efforts in rechargeable lithium batteries the development of electrolytes that facilitate commercially possible lithium metal anodes remains challenging. Electrolytes of related composition, however different structure, have been investigated by **Jurng, et al.**, to be aware of input mechanisms for improving the cycling performance. A flexible electrolyte with leakage free is required more importantly for energy devices to increase safety. By asset, a new class of electrolytes, by hybridizing aqueous with non-aqueous solvents, based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ provided a better electrochemical stability from non-aqueous systems by delivering a high energy density to 4.1 V, of 165 Wh/kg [4]. On the other hand, the ionic based electrolyte 1-methylpyridinium 2, 6-dicarboxylate anion in IL matrix (Pyr14TFSI) were stable up to 150 and 200 °C and showed ion conductivities of 2.8 and 3.2 $\text{mS}\cdot\text{cm}^{-1}$ at room temperature [5]. The poly- (vinylidene fluoride) (PVdF) has been identified as a potential host for lithium polymer batteries of the interesting properties. On adding the poly (vinylidene fluoride-hexa fluoropropylene) (PVdF-HFP) as a gel polymer electrolyte which has drawn the attention of many researchers. The composite polymer electrolytes (CPE) alone have offered lithium polymer batteries with improved electrolyte/electrode compatibilities and safety hazards. It has also found that the layered nano composite polymer electrolytes based on PEO offered better electrochemical characteristics because of the apparent synergism between the host and the polymer. Solid polymer electrolytes with considerable ionic conductivity have been paid attention in recent investigations due to its potential applications. However, the crystallinity of polymer below melting point reduces the overall polymer flexibility and offers a low ionic conductivity at ambient temperature. But the ionic conductivity can be increased by the addition of plasticizer or nano particles. The polymer electrolyte with legible ionic conductivity can be obtained by using ionic liquid based electrolyte. Ionic liquids, typically consisting of bulky, asymmetric organic cations and in-organic anions, offer many favorable conditions such as good thermal and electrochemical stability, high ionic conductivity, negligible vapor pressure and non-flammability.

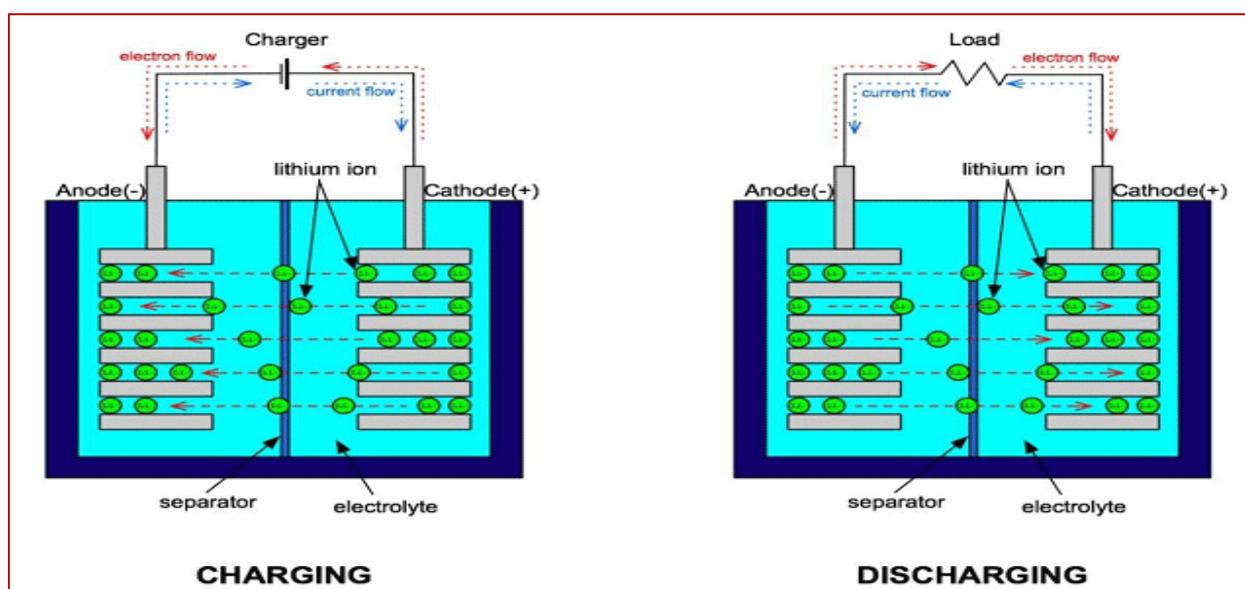


Figure1. Schematic Diagram of the charge- discharge mechanism of a Li-ion Battery

Also polymer electrolytes play a major role in all the other electrochemical devices. A sulfonated poly(arylene ether benzimidazole) copolymer membrane doped with sulfuric acid resulted with highest power density of 23.7mWcm^{-2} for fuel cell [6]. In super capacitors, electrolyte comprising of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide immobilized in (PVDF- HFP) showed high ionic conductivity of $3.81 \times 10^{-3} \text{ S cm}^{-1}$, high specific energy and power (~ 26.1 and 18 kw kg^{-1} , respectively) [7]. GPE containing PVA/PEO blend in sodium salt mixture (CH_3COONa)/ (Na_2SO_4), resulted with energy density of 3.25 Wh kg^{-1} and power density of $586.166 \text{ W kg}^{-1}$ at current density of 1 Ag^{-1} [8]. With the addition of cross linker and plasticizer to PEO with LiClO_4 , the power density and energy density has been found to be increased to 6.91 kW kg^{-1} and 27.62 Wh kg^{-1} at a high current density of 5 A g^{-1} for the membrane [9]. A relevant number of interfaces and interfacial regions are created especially when nanosized materials are introduced in electrochemical cells, thus opening up to some

opportunities for enhanced electrochemical performances provided that the current manufacturing methods are updated. Possible solutions include surface coating the AMPs with the solid electrolyte; homogeneous embedding in SLICs or SPEs, with electronic wiring provided by carbon additives or electro active polymers. As compared to systems with binary LEs, CE with single ion conductor solid electrolytes, such as SIEs and single Li⁺ ion conductors in principle, able to deliver larger specific capacity at higher current densities despite a lower conductivity or a higher thickness [10].

Table 1: Reviews based on biopolymers doped with lithium salts as a promising electrolyte in electrochromic devices and proton batteries

Ref. No	Title of the paper	Electrolyte	Method	Ratio	Ionic Conductivity	Reference
11	'Gellan Gum-LiI Gel Polymer Electrolytes'	Gellan gum, Lithium iodide, Glycerol	Solution casting technique	LiI (10–50 wt %), glycerol (10–50 wt %)	1.7×10^{-3} S/cm	N. F. A. Halim, <i>et al.</i> , <i>Mol. Cryst. Liq. Cryst.</i> , (2012)
12	'Plasticized pectin-based gel electrolytes'	Pectin, Glycerol, LiClO ₄	Plasticization technique	68 wt.% glycerol	4.7×10^{-4} S/cm	Juliana R, <i>et al.</i> , <i>Electrochimica Acta</i> , (2009)
13	'Characteristics of gellan gum–LiCF ₃ SO ₃ polymer electrolytes'	Gellan, LiCF ₃ SO ₃	Solution casting technique	40 wt.% LiCF ₃ SO ₃	5.4×10^{-4} S/cm	I.S.M. Noor, <i>et al.</i> , <i>Solid State Ionics</i> , (2012)
14	'Morphology and Ion-Conductivity of Gelatin–LiClO ₄ Films: Fractional Diffusion Analysis'	Gelatin, LiClO ₄ , Glycerol	Solution cast technique	2.70% LiClO ₄	-	Tania Basu, <i>et al.</i> , <i>J. Phys. Chem. B</i> (2012)
15	'Amylopectin-rich starch plasticized with glycerol for polymer electrolyte application'	Amylopectin-rich Starch, LiClO ₄ , Glycerol	Solution casting technique	30–35 wt.% glycerol	1.1×10^{-4} Scm ⁻¹	Rozely F.M.S. Marcondes, <i>et al.</i> , <i>Solid State Ionics</i> , (2010)
16	'Lithium ion conduction in corn starch based solid polymer Electrolytes'	Corn starch, LiClO ₄	Solution casting technique	40 wt.% LiClO ₄ 60 wt.% corn starch	1.28×10^{-4} S/cm	K.H. Teoh, <i>et al.</i> , <i>Measurement</i> , (2014)

Electrolyte progress

State of art of liquid electrolytes

To allow ion transport in the electrolyte of lithium batteries, a suitable lithium salt is dissolved in the organic solvent mixture. The addition of such a salt results in increased complexity of the system and modifications of the physico- and electrochemical properties of pure solvents and their mixtures. State-of-the-art electrolyte solvents usually consist of a mixture of two kinds of aliphatic carbonates: cyclic carbonates (e.g., ethylene and propylene carbonates (EC, PC)), which possess high dielectric constants [8]. It may be stated that organic carbonate mixtures are certainly very suitable ion-conducting media with respect to their characteristics [17]. It was also reported that electrolytes comprising LiPF₆ as a conducting salt and Dimethyl Carbonate (DMC) as a cosolvent (in combination with EC) showed higher decomposition temperatures than those of electrolyte mixtures containing other linear carbonates, such as Diethyl Carbonate (DEC). Lithium hexafluorophosphate (LiPF₆) is practically the only conducting salt used in commercial state-of-the-art LIBs. To enhance the safety of state-of-the-art LIBs, considerable research efforts were and are still being undertaken to replace organic carbonates (at least partially) by alternative solvents to provide comparable ionic conductivities, One of the most studied compounds is fluorinated ethylene carbonate (FEC), which was first proposed by McMillan et al.

Solid electrolytes

The electrolytes investigated comprise LiPF₆, lithium bis(oxalato)borate (LiBOB), LiBF₄, and lithium difluoro(oxalato)borate (LiDFOB) in a mixture of (EC) ethylene carbonate and (EMC) ethyl methyl carbonate showed a notable difference in the cycling performance despite the effectual equivalent chemical composition of

LiDFOB (1.2 M) in the mixture of EC: EMC (3:7) when compared to 0.6M LiBOB + 0.6 M LiBF₄ in EC: EMC (3:7). The electrolyte LiDFOB compared to the other salts significantly provided a remarkable improvement in electrochemical performance [18]. A garnet-type Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO) solid electrolyte tube showed that the assembled Li||LLZTO||Sn–Pb and Li||LLZTO||Bi–Pb cells can stably cycle at an intermediate temperature of 240 °C for about one month at current densities of 50 mA cm⁻² and 100 mAcm⁻² respectively. The cells showed a theoretical volumetric energy density as high as 570 Wh l⁻¹ and 940 Wh l⁻¹, respectively. [19].The mechanical properties of the PVDF-HFP film electrolyte in terms of flexibility and elasticity were better than with PVDF [20]. The developed highly promising solid polymer electrolytes (SPEs) based on a novel cross-linker containing star-shaped phosphazene with poly (ethylene oxide) (PEO) branches with very high ionic conductivity (7.6×10⁻⁴ S cm⁻¹), improved mechanical stability, and good electrochemical stability for all solid- state lithium batteries. In particular, allyl groups were introduced at the ends of the cross-linker in order to overcome the easy self-polymerization of existing cross-linking acrylate end groups showed initial discharge capacity of 147mAh/g at 0.1°C and 132mAh/g at 0.5°C, and 97% of the capacity was retained at the 100th cycle. [21] Plasticized starch with N, N-dimethylacetamide (DMAc) and certain concentration ranges of lithium chloride (LiCl) by melting extrusion showed conductance of 10^{-0.5} Scm⁻¹. [22]. Compared to polymeric lithium salts, lithium polyperfluorobutylene-1, 4-bis-sulfonylimide (LiPBSI) and lithium polyperfluorohexylene-1, 6-bissulfonylimide (LiPHSI), with different CF₂ backbone lengths in toluene showed that LiPBSI/PEO electrolyte had higher ionic conductivity. Furthermore, the lithium ion transference number of both LiPBSI/PEO and LiPHSI/PEO films were close to 0.4 and the ionic conductivity of LiPBSI/PEO film was close to 1×10⁻⁴ S/cm at 60 °C [23]. Solid polymer electrolytes composed of the polycarbonate-based polyurethanes and LiTFSI exhibited a high ionic conductivity of 1.12×10⁻⁴ S cm⁻¹ at 80 °C and showed excellent mechanical strength. It also delivers an initial discharge capacity of 134 mAh g⁻¹ with 91% capacity retention after 600 cycles at 80 °C at 1 C, which showed an outstanding cycling performance. [24].The electrolyte comprising cellulose phthalate (CP) and LiClO₄ Li⁺ cation formed not only ionic-bond with carboxyl group but also the coordination with carbonyl and ether groups in CP at the low LiClO₄ concentration, while it formed only the ionic-bond at the high concentration. This behavior of the CP/LiClO₄ increased the conductivity [25]. An inexpensive H⁺ transporting SP membrane (HPEOP) is formulated using perchloric acid (HClO₄) as the proton source with a poly(ethylene oxide) (PEO) and polydimethylsiloxane blend. HPEOP600 membrane's ionic conductivity at 30°C is found to systematically vary from 0.01 Scm⁻¹ to 0.1 Scm⁻¹. [26].

Polymer electrolytes

Surface modification of LiCoO₂ with the ultrathin film of solid state electrolyte of Li_{1.4}Al_{0.4}Ti_{1.6}(PO₄)₃ (LATP) were prepared. The coated LiCoO₂ reveals enhanced structural and electrochemical stability at high voltage (4.5 V) in half-cell with liquid electrolyte. The cell exhibits 93% discharge capacity retention of the initial discharge capacity after 50 cycles at the charging cut-off voltage of 4.2 V, suggesting that the LATP coating layer is effective to suppress the oxidation of PEO at high voltage. PEO-based polymer electrolyte was also assembled, and 0.5 wt% LATP modified LiCoO₂ showed high capacity retention (93.2% after 50 cycles) to improve interface stability between the electrode and the electrolyte [27]. Polyvinylidene difluoride (PVDF) or poly(vinylidene fluoride-co-hexafluoropropene) (PVDF-HFP) was added to an ionic liquid electrolyte, in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, to produce either soft gels or free-standing films depending on the polymer content. As a potential electrolyte for lithium-ion batteries, a porous polymer electrolyte membrane based on poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP) membranes possess good pore structure and pore size for a high electrolyte uptake [28]. (PVDF/PSF) blend microporous matrix of polymer electrolyte was found that the addition of PSF not only increases ionic conductivity and electrochemical stable window of polymer electrolyte, but also markedly enhances charge discharge performances of coin cell. The maximum ionic conductivity was 2.03×10⁻³ S cm⁻¹ at 20°C. Blend polymer electrolyte showed higher charge discharge capacity and better discharge performance at 200 mA cm⁻² current density [29]. Hydroxyethylcellulose (HEC) with different quantities of glycerol and addition of lithium trifluoromethane sulfonate (LiCF₃SO₃) prepared samples of transparent films

exhibited very good adhesion properties. The sample containing HEC plasticized with 48% of glycerol showed the conductivity values of $1.07 \times 10^{-5} \text{ S/cm}$ at 30°C and $1.06 \times 10^{-4} \text{ S/cm}$ at 83°C [30].

Biopolymer electrolytes

The lithium triflate was added to chitosan to form a film of chitosan acetate salt complex. There occurred changes that the carbonyl band was observed to shift to as low as 1645 cm^{-1} and the amine band to as low as 1540 cm^{-1} . When chitosan and ethylene carbonate (EC) were dissolved in acetic acid to form a film of plasticized chitosan acetate, EC- LiCF_3SO_3 interactions were indicated by the shifting of the C=O bending band from 718 cm^{-1} in the spectrum of EC to 725 cm^{-1} in the EC-salt spectrum. [31]. The LiFePO_4 electrode with the chitosan binder was observed to have a high ionic conductivity compared to the LiFePO_4 electrode with the PVDF binder. The electrode with the chitosan binder also attained a higher discharge capacity of 159.4 mAh g^{-1} with an excellent capacity retention ratio of 98.38% compared to the electrode with the PVDF binder, which had a discharge capacity of 127.9 mAh g^{-1} and a capacity retention ratio of 85.13% [32].

In order to insight the importance of the polymer electrolytes, literature review is done for moving the research forward. It is presented in a table format sorted and recognized neatly which makes easy inclusion of the most important and relevant data in the following

Table2: Reviews based on biopolymers doped with lithium salts as a promising electrolyte in lithium ion batteries

Ref. No	Title of the paper	Electrolyte	Method	Ratio	Ionic Conductivity	Reference
[33]	'Carboxymethyl Carrageenan Based Biopolymer Electrolytes'	Carboxymethyl kappa carrageenan and carboxymethyl iota carrageenan, LiNO_3	Solution casting technique	20 wt.% LiNO_3	$5.85 \times 10^{-3} \text{ S cm}^{-1}$	N.N. Mobarak, <i>et al.</i> , <i>Electrochimica Acta</i> (2015)
[34]	'Electrical characterization of corn starch-LiOAc electrolytes and application in electrochemical double layer capacitor'	Corn starch, Lithium acetate, Glycerol	Solution casting technique	5 wt.% starch, 25 wt.% LiOAc 30 wt.% glycerol	$(1.04 \pm 0.10) \times 10^{-3} \text{ S cm}^{-1}$	M.F. Shukur, <i>et al.</i> , <i>Electrochimica Acta</i> , (2014)
[35]	'From seaweeds to biopolymeric electrolytes for third generation solar cells: An intriguing Approach'	k-carrageenan, Eucheuma cottonii seaweeds	Multivariate - based preparation	45 wt% NaI, 30 wt.% EC	$5.53 \times 10^{-2} \text{ S cm}^{-1}$	Federico Bella, <i>et al.</i> , <i>Electrochimica Acta</i> , (2015)
[36]	'Studies on lithium acetate doped chitosan conducting polymer system'	Chitosan, Lithium acetate	Solution casting technique	-	10^{-6} S/cm	M.Z.A. Yahya, <i>et al.</i> , <i>European Polymer J.</i> , (2002)
[37]	'Electrochemical studies on epoxidised natural rubber-based gel polymer electrolytes for lithium-air cells'	ENR-50, THF, LiCF_3SO_3	Solution casting technique	35 wt.% LiCF_3SO_3	$4.92 \times 10^{-4} \text{ Scm}^{-1}$	S.N. Mohamed, <i>et al.</i> , <i>Journal of Power Sources</i> , (2008)
[38]	'Plastic crystal- solid biopolymer electrolytes for rechargeable lithium batteries'	Chitosan, lithium bis(trifluoromethylsulfonyle) imide (LiTFSI)	Solution casting technique	50 wt.% Succinonitrile	$0.4 \times 10^{-3} \text{ S cm}^{-1}$	NurUmiraTaib, <i>et al.</i> , <i>J. Membrane Science</i> (2014)

Gel polymer electrolytes

Initially gel polymer electrolytes of alkylene oxide, ethylene oxide, propylene oxide, 20%, were prepared by mixing GBL- $\text{LiBF}_4/\text{LiCoO}_2$ and an initiator in which the ionic conductivity reached over 2.5 mScm^{-1} . The highest discharge capacity (1.3 mAh) was attained [39]. A poly (vinylidene difluoride-co-hexafluoropropylene) (PVdF-HFP)-based gel polymer electrolyte (GPE) containing propylene carbonate (PC)-based liquid electrolyte has been developed to enhance the safety performance of $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ /graphite lithium ion batteries [40]. Another poly (vinylidene difluoride) (PVdF)-based dry-gel due to the presence of crystallized EC-solvent within its matrix that avoids structural collapse and cycling tests were carried out using lithium half-cells using (LiFePO_4 , LFP) and graphite, respectively [41]. The polyphosphazene versus lithium metal in combination with a liquid

electrolyte, consisting of 0.7 mol L^{-1} LiBOB in EC/DMC, a high ionic conductivity of $9 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C has been achieved. The electrochemical stability window ranges between 0 V and 4.4 V. The gel polymer was drop coated onto the electrode materials and cross-linked to achieve high mechanical stability [42]. Poly (ethylene oxide), poly (vinyl pyrrolidone) (PEO/PVP), lithium perchlorate salt (LiClO_4) and different plasticizer based showed that the crystallinity decreases with the addition of different plasticizers. PEO (72%)/PVP (8%)/ LiClO_4 (8%)/EC (12%) has the maximum ionic conductivity value which was supported by the lowest optical band gap and lowest intensity in photoluminescence spectroscopy near 400–450 nm [43]. Cross-linked trimethylolpropane, trimethylacrylate-based gel polymer electrolytes showed the ionic conductivity $>10^{-3} \text{ S cm}^{-1}$ at 25°C , and continuously increased with the increase of liquid electrolyte content with excellent electrochemical stability up to 5.0 V. The LiCoO_2 /TMPTMA-based GPE| graphite cells exhibit an initial discharge capacity of 129 mAh g^{-1} at the 0.2°C and good cycling stability with around 83% capacity retention after 100 cycles [44]. By the plasticization of gelatin with LiBF_4 , and mixture of glycerol and LiBF_4 was developed. It has been found that the effect of glycerol as a plasticizer was more important on the ionic conductivity results than the effect obtained by varying the lithium salt content. The ionic conductivity results showed that the samples were stable up to 160°C [45].

A biodegradable GPE using guar gum (GG) as the polymer matrix, LiClO_4 as the doping salt and glycerol as the plasticizer showed an unusual tubular array type surface morphology. Highest ionic conductivity and lowest activation energy values were $2.2 \times 10^{-3} \text{ S cm}^{-1}$ and 0.18 eV, respectively [46].

Composite electrolytes

The scalable ceramic-polymer composite electrolytes composed of $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$, poly (ethylene oxide), lithium bis(trifluoromethane)sulfonimide, and solid plasticizer succinonitrile presented a maximum conductivity of $1.22 \times 10^{-4} \text{ S cm}^{-1}$ at 30°C exhibiting a broadened electrochemical stability window of 5.5 V [47]. A new kind of nanofibrous composite polymer electrolyte with lithium bis(oxalate)borate succinonitrile polyethylene oxide (LiBOB-SN-PEO) exhibited improved ionic transference number to 0.41. Excellent cycling and rate performance of the Li/LiFePO₄ cells are resulted delivering a discharge specific capacity of $151.1 \text{ mAh} \cdot \text{g}^{-1}$ after 200 cycles under 60°C and $124.1 \text{ mAh} \cdot \text{g}^{-1}$ after 70 cycles at 0.5 C. The cells achieved a superior high temperature-tolerance characteristic up to 170°C which is much higher than that (ca. 100°C) of traditional PEO-based electrolytes [48].

Hybrid electrolytes

A different technique of blending functionalized ceramic particles into the polymer matrix was adopted to synthesize a homogeneous TiO_2 -grafted NHPE with a cross-linked branching structure comprised of ion-conducting poly (ethylene glycol) methyl ether methacrylate (PEGMEM) and non-polar stearyl methacrylate (SMA) demonstrated good C-rate performance, as well as excellent cycling stability with an initial discharge capacity of 153.5 mAh g^{-1} and a capacity retention of 96% after 300 cycles [49]. Hybrid and Nanohybrid polymer electrolytes (NHPE) with ceramic particles have attracted significant attention owing to their improvement in electrochemical performance. The synthesis and the properties of a series of polymer electrolytes, composed of a hybrid inorganic-organic matrix doped with LiTFSI based on ring-like oligo-siloxane clusters, showed good thermo-mechanical and electrochemical stabilities, with conductivities reaching, at best, $8 \times 10^{-5} \text{ S cm}^{-1}$ at 30°C . The cell performances of one representative sample were shown. [50]. Poly (vinylidene fluoride-hexafluoropropylene) (P(VDF-HFP))-based composite polymer electrolyte (CPE) membranes doped with the organic-inorganic hybrid particles poly(methyl methacrylate) - ZrO_2 (PMMA- ZrO_2) deliver excellent rate and cycling performance [51].

Proton conducting electrolyte

A proton conducting polymer electrolyte based on poly (ϵ -caprolactone) (PCL) complexed with different concentrations of ammonium thiocyanate (NH_4SCN) salt with the ionic conductivity of $1.01 \times 10^{-4} \text{ S cm}^{-1}$. The correlation between free ions, ion aggregates and conductivity are obvious [23]. Carboxymethyl chitosan (C-CTS) was a water soluble binder for LiFePO_4 cathode in Li-ion batteries. The electrochemical performances of LiFePO_4 cathode with C-CTS binder was investigated and compared with the conventional water-soluble sodium

carboxymethyl cellulose (CMC) and the commercial non-aqueous polyvinylidene difluoride (PVDF). LiFePO₄ cathode with C-CTS exhibited a comparable cycling performance, but better rate capability than that of CMC and PVDF, retaining 65% capacity of C/5 at 5°C rates as compared with 55.9% and 39.4% for CMC and PVDF, respectively. In addition, LiFePO₄ cathode with C-CTS exhibited excellent cycling performance at 60°C, retaining 91.8%/ 62.1% capacity after 80 cycles at 1 C/ 10 C, respectively [53].

Table 3: Reviews regarding different types of electrolyte, anode, cathode, separator used are categorized in this table

Ref . No	Title of the paper	Components				Reference
		Electrolyte	Anode	Cathode	Separator	
54]	Carboxylated polyimide separator with excellent lithium ion transport properties for a high-power density lithium – ion battery	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate	Graphite	LiCoO ₂	Carboxylated polyimide	Chun-Er Lin, <i>et al J. Mater. Chem A</i> , 2018, 6, 991
55]	Eco-friendly cellulose nanofiber paper – derived separator membranes featuring tunable nanoporous network channels for lithium-ion batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate-diethyl carbonate	Graphite	LiCoO ₂	CNP Separator	Sang-Jin Chun, <i>et al J. Mater. Chem.</i> , 2012, 22, 16618
56]	Composite membrane with ultra-thin ion exchangeable functional layer: a new separator choice for manganese – based cathode material in lithium ion batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate-dimethyl carbonate	Graphite	Manganese – based cathode materials such as spinel LiMn ₂ O ₂	Ion exchangeable composite separator(Nf-PP-Li)	Junli Shi, <i>et al J. Mater. Chem A</i> , 2015, 3, 7006
57]	An environmentally friendly and economic membrane based on cellulose as a gel polymer electrolyte for lithium ion Batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate	Graphite	LiFePO ₄	Methyl cellulose (MC), a gel polymer electrolyte	Shiying Xiao, <i>et al RSC Adv.</i> , 2014, 4, 76
58]	A trilayer poly (vinylidene fluoride)/ polyborate/ poly(vinylidene fluoride) gel polymer electrolyte ,with good performance for lithium ion batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate	Graphite	LiFePO ₄	Poly(vinylidene fluoride) (PVDF) and lithium polyacrylic acid oxalate borate (LiPAAOB)	Yusong zhu, <i>et al J. Mater. Chem A</i> , 2013, 1, 7790
59]	A macro-porous graphene oxide-based membrane as a separator with enhanced thermal stability for high – safety lithium ion batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate	Graphite	LiFePO ₄	Graphene oxide grafted hyper-branched poly ether (GO-g-HBPE) macro – porous membrane	Haiyang Liao, <i>et al RSC Adv.</i> , 2017, 7, 22112
60]	Nanocomposite polymer membrane derived from nano TiO ₂ – PMMA and glass fiber nonwoven: high thermal endurance and cycle stability in lithium ion battery applications	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate	Graphite	LiCoO ₂ / Li	Nano-composite polymer electrolyte membrane (NCPE)	Sen Zhang, <i>et al J. Mater. Chem A</i> , 2015, 3, 17697

61]	Particle size – dependent, tunable porous structure of a SiO ₂ / poly(vinylidene fluoride – hexafluoropropylene) – coated poly (ethylene terephthalate) non woven composite separator for a lithium ion battery	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate	Graphite	LiCoO ₂	Silica (SiO ₂) nanoparticle/ polyvinylidene fluoride – hexa fluoropropylene (PVdF – HFP) – coated polyethylene terephthalate (PET) nonwoven composite membrane	Eun-Sun Choi and Sang-Young Lee <i>J. Mater. Chem.</i> , 2011, 21, 14747
62]	Novel aramid nanofibres – coated polypropylene separators for lithium ion batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/propylene carbonate	Li anode	Lithium manganese oxide (LMO/Li)	Aramid nanofiber – coated polypropylene separators	Shengyu Hu, <i>et al J. Mater. Chem A</i> , 2016, 4, 3513
63]	A rational design of separator with substantially enhanced thermal features for lithium-ion batteries by the polydopamine–ceramic composite modification of polyolefin membranes	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate	Li – metal anode	LiMn ₂ O ₄	PDA – treated SiO ₂ – coated PE separators	Jianhui Dai, <i>et al Energy Environ. Sci.</i> , 2016, 9, 3252
64]	Polyethylene-supported ultra-thin polyvinylidene fluoride/ hydroxyethyl cellulose blended polymer electrolyte for 5v high voltage lithium ion batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate	Li – metal anode	LiNi _{0.5} Mn _{1.5} O ₄	Polyvinylidene fluoride/hydroxyethyl (PVDF/HEC) = 3:1 coated polyolefin separator	Xiangdong Ma, <i>et al J. Mater. Chem A</i> , 2018, 6, 1496
65]	Polyimide matrix-enhanced cross-linked gel separator with three-dimensional heat-resistance skeleton for high-safety and high-power lithium ion batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/propylene carbonate/dimethyl carbonate/ethyl acetate	Li anode	LiFePO ₄	Polyimide matrix-enhanced cross-linked gel separator	Junli Shi, <i>et al J. Mater. Chem A</i> , 2014, 2, 9134
66]	Pyrogallic acid coated polypropylene membranes as separators for lithium ion batteries	Liquid electrolyte of 1M LiPF ₆ in ethylene carbonate/dimethyl carbonate	Li anode	LiMn ₂ O ₄	Pyrogallic acid coated polypropylene membranes	Haibin Wang, <i>et al J. Mater. Chem A</i> , 2015, 3, 20535
67]	Composite of a nonwoven fabric with poly(vinylidene fluoride) as a gel membrane of high safety for lithium ion battery	LiPF ₆ electrolyte	Graphite	LiFePO ₄	Composite membrane of a nonwoven fabric with poly(vinylidene fluoride)	Yusong Zhu, <i>et al Energy Environ. Sci.</i> , 2013, 6, 618-624

Backbone of electrodes

Blended Electrodes

Charge and discharge of lithium ion battery electrodes has been accompanied by severe volume changes. In a confined space, the volume cannot expand, leading to significant pressures induced by local micro structural changes within the battery. While volume changes appear to be less critical in batteries with liquid electrolytes, they will be more critical in the case of lithium ion batteries with solid electrolytes and they will be even more critical and detrimental in the case of all-solid-state batteries with a lithium metal electrode. Comparing and analyzing the volume changes occurring in state of the art electrode materials, based on crystallographic studies quantitatively followed that it was based on the evaluation of the partial molar volume of lithium as a function of the degree of lithiation for different electrode materials [68]. The electrochemical property of LiFeS in a Li ion

conductive glass showed two potential plateaus within the range $0 \leq x \leq 4$, and is reversible. The reduction of FeS_2 by $4e^-$ or LiFeS_2 by $2e^-$ did not proceed to form Fe metal acting as an electrode active material in a solid state lithium battery [69]. Carboxymethyl cellulose (CMC), a green and low-cost binder, has used to make lithium-ion battery composite electrodes containing the high voltage cathode material $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$. It indicated that CMC operates well at very high voltages (4.8 V) with an improved cycling stability as well as a very promising rate capability compared to the PVDF binder [70]. The binder based on natural cellulose as a binder in ionic solvent making volatile solvent-free slurries which are then coated on typical battery current collectors showed a stable specific capacity of 123 mAh per gram of LiFePO_4 at room temperature [71]. The binders with two types of galactomannan gum derived from plant seeds, guar gum (GG) tara gum (TG), for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) negative electrodes were compared to typical carboxymethyl cellulose (CMC) binder. It exhibited better transport of lithium ions in LTO electrodes than CMC binder, a cellulose (linear polysaccharide) derivative, even though their binding capability was not as strong as CMC. It was found that the GG-containing LTO electrode resulted a high reversible capacity of 160.0 mAh g^{-1} at the 100th cycle with 1 C current rate, whereas the CMC-containing LTO electrode had a reversible capacity of 150.1 mAh g^{-1} [72].

Special cathodes

A strategy for obtaining optimized compositions within this class of materials, exhibiting high capacity and energy density as well as good reversibility, by using a combination of low-valence transition metal redox and a high-valence redox active charge compensator, as well as fluorine substitution for oxygen. Furthermore, a new constraint on high-performance compositions by demonstrating the necessity of excess Li capacity as a means of counteracting high-voltage tetrahedral Li formation, Li-binding by fluorine and the associated irreversibility was identified. A 10–12% of Li capacity was lost due to tetrahedral Li formation, and 0.4–0.8 Li per F dopant was made inaccessible at moderate voltages due to Li–F binding. A series of high-performance disordered oxyfluoride cathode materials based on $\text{Mn}^{2+/4+}$ and $\text{V}^{4+/5+}$ redox was succeeded [73]. Layered Ni-rich oxides ($\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$) exhibited high discharge capacity, high Li^+ ion deintercalation/intercalation potential, and low cobalt content. Ni-rich cathodes often suffer from poor cycling stability because of the serious cation mixing, and the poor interfacial/structural stability during the electrochemical process. It delivered a reversible discharge capacity as high as 197.4 mA h g^{-1} at C/10, and exhibits a capacity retention of 95.9%, 90.2% and 83.5% at C/3, 1°C and 3°C after 200 cycles at cut-off voltages of 2.7–4.4 V, respectively [74]. A nanoscopically ordered architecture of calcite-type MnCO_3 nanocrystals mimicking hierarchical structures of biological CaCO_3 in an organic gel matrix with a highly porous structure of spinel-type LiMn_2O_4 was produced as a cathode material consisting of connected LiMn_2O_4 nanoparticles provided high durability in a lithium insertion/extraction process at a high current density due to a high porosity for the electrochemical reaction and three-dimensional channels for ion diffusion. It has been reported that alginate which was extracted from brown seaweed as a polymeric binder for spinel LiMn_2O_4 resolved the chronic issue upholding the feasibility and hence could be for emerging large-scale applications including electric vehicles [75].

Conclusion

The in-depth review on the research carried out in the field of Li-ion battery has facilitated a comprehensive understanding into the concepts, especially, with reference to energy storage and meeting energy demands, with an eye on environmental consciousness. It has given the authors insight and motivation to indicate on identification of the research gap. This manuscript may serve as a ready reference for the future researchers to acquaint themselves on notable works in the area of renewable energy.

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