A Review on Green Polymer Binder-based Electrodes and Electrolytes for All Solid-State Li-ion Batteries

Adhigan Murali[1,], Saravanan Ashok Vallal[1], Mohan Sakar[2], R. Ramesh[3], M. Devendiran[4], N. Suthanthira Vanitha[5]*

It is not an exaggerated fact that the whole world relies on the energy storage systems such as Li-ion batteries (LIBs). Li-ion batteries have been widely used in electric vehicles and electronic devices such as laptops, mobile phones, etc. However, the commercial Li-ion batteries have many issues associated with safety and durability including the thermal runaway and the use of toxic solvents during the construction of batteries. In order to highlight the recent developments towards addressing these issues, we have summarized the major impact in replacing the toxic solvents, which are conventionally used to dissolve the binder in the commercial Li-ion batteries, with the aqueous-based binder called green binders. Further, an emphasis has been given on the importance of shifting from flammable liquid electrolytes to non-flammable solid-electrolytes, which essentially suppress the issues such as leakage problems, mechanical failure and fire explosives in LIBs. Even though considerable works have been performed on the development of green-based solid polymer electrolytes, it still needs more effort to overcome the obstacles towards improving the properties of the solid-polymer matrix, which is their low ionic conductivity at low temperatures. Further research in this direction has been highlighted in this review, which involves improving the interfacial contacts in the solid-polymer electrolytes, where the interfacial interaction and conductive mechanisms are yet to be clearly investigated to have the solid-electrolytes with improved electrochemical property.

Introduction

Energy storage and useful consumption of energy are the mandatory factors for the technological development and social progress. In this technological era, the whole world relies on energy storage devices and it has become a basic necessity for industrial and economic growth [**1**]. Until 20th century, the world's energy consumption was simply dependent on the fossil fuels and other conventional non-renewable sources. This situation led to the emission of greenhouse gases, which significantly affected our environment.

Further, the availability of crude oil on earth is also decreasing rapidly. Hence, this is the ideal time to switch from non-sustainable energy sources to sustainable energy sources [**2-6**]. For this purpose, the energy storage devices such as batteries and supercapacitors [7] are highly used, which store the energy without any significant damages to the environment. Such devices also possess a very high energy density and power densities. Batteries are the devices which transfer the chemical energy stored in the chemical molecules or chemical entities to the desired circuit in the form of electrical energy via the electrochemical redox reactions. Thus, batteries can be an ideal source of energy storage [**8**]. Li-ion batteries possess high energy density properties fundamentally due to the smaller size of the Li-ions. Since LIBs are portable, it is largely used in several electronic devices such as laptops, mobiles, electrical vehicles, smart televisions, Bluetooth and wireless speakers, etc. It is also found in many medical devices such as hearing aids, rechargeable nebulizers, ventricular stimulators as well as in assistors. However,

---

[1]School for Advanced Research in Petrochemicals (SARP)-ARSTPS, Central Institute of Petrochemicals Engineering & Technology (CIPET), Chennai-600 032, Ministry of Chemicals & Fertilizers, Govt. of India.
[2]Centre for Nano and Material Sciences, Jain University, Bangalore 562112, Karnataka, India.
[3]College of Biological and Chemical Engineering, Addis Ababa Science and Technology University, Post Box No16417, Addis Ababa, Ethiopia
[4]Vels Institute of Science Technology and Advanced Studies (VISTAS), Pallavaram, Chennai -117, India
[5]Department of Electrical & Electronics Engineering, Muthayammal Engineering College (Autonomous), Namakkal 637408, Tamilnadu, India

*Corresponding author:
E-mail: precymurali@gmail.com
Tel.: (+91) 44 22254794, Fax: (+91) 44 22254793

DOI: 10.5185/amlett.2021.21111679

LIBs have some safety issues such as the use of toxic solvents during the manufacturing process of the electrodes, which are highly unstable, flammable, and highly explosive [**9**]. This eventually has become a biological threat as well as leads to the environmental degradation. In order to overcome such issues, these toxic organic solvents used as binders for electrodes should be avoided and instead the aqueous-based binders should be used towards constructing the green-based lithium-ion batteries. The schematic representation of the non-solvent-based electrolytes for solid state batteries is given in **Fig. 1**.

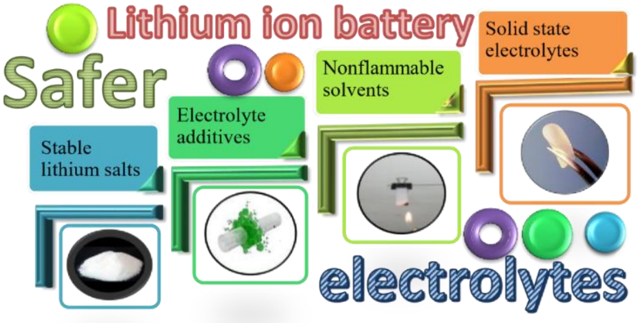

Fig. 1. Schematic representation on the construction of lithium-ion batteries with improved safety and stability [10].

Similarly, the other major safety issue involved in the lithium-ion batteries is associated with their 'liquid'-based electrolytes. In LIBs, the use of liquid electrolytes is leading to the leakage problem (electrolyte spill) and increase the formation of lithium dendrites and damages the separators by making a direct physical contact between anode and cathode, which leads to the short circuit in the system. For instance, the LIBs can easily catch the fire and burst in presence of liquid organic electrolytes, which are easily combustible as shown in **Fig. 2** [**11-14**].

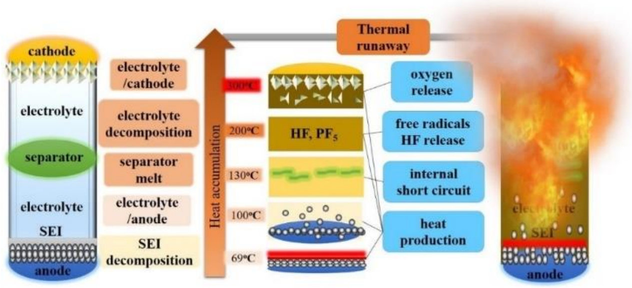

Fig. 2 Schematic depiction of a blast occurring in LIBs by commercial liquid electrolyte [10].

To overcome this problem, researchers are focusing on solid-state electrolytes due to their improved safety. At the same time, the high energy density, ionic conductivity, and electrochemical performance of the electrolytes should also be considered. One of the crucial needs for solid electrolytes is their flexibility and bendability [**15**], which can gradually increase the volumetric energy density of LIBs [**16,17**].

Working principle of Li-ion batteries

Lithium-ion batteries are basically referred to the secondary batteries, which can be reversed (recharged) and reused. The lithium-ion works by the principle of movement of lithium ions to and fro (forward and backward motion) between two electrodes *via* a separating entity [**18**]. The motion of electrons through the outside electrical circuit in the path opposite to that of the movement of Li^+ ions generate an electric current in the circuit. A basic lithium-ion battery is made up of four primary units such as anode, cathode, separator (separating unit for selective separation) and electrolyte in which several materials can be used as different components (see **Fig. 3**) [**19**]. Due to the front and back rocking movement of Li-ions during charging and discharging cycles, such batteries are also called as "Rocking Chair" batteries.

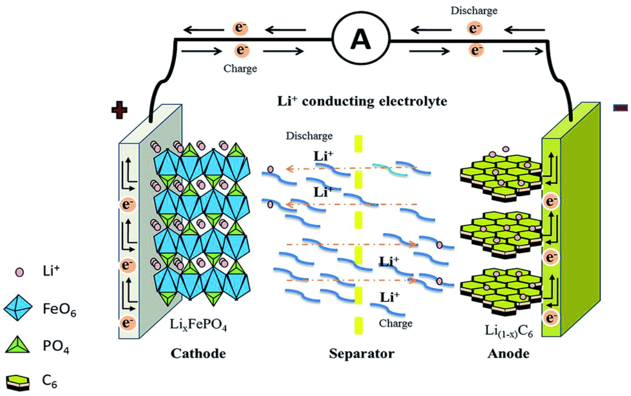

Fig. 3. Working principle of a Li-ion battery during its charging and discharging process [20].

During charging at an anode, the Li^+ ions intercalated at the cathode leave the cathode and passes through a separator which selectively allows the Li ions solely and reach the anodic compartment and get inserted into the anode source such as a graphite entity. This charging-discharging process can be represented by the following equation (1).

$$C + xLi^+ + ne^- \leftrightarrow Li_xC \qquad \text{(Eq. 1)}$$

During discharge at cathode, the lithium-ions which already interposed inside the anode leave the anode as a lithium-ion and an electron is generated at the anode. These lithium-ions travel through the separator, which selectively allow the lithium-ion alone and the electrons pass through the external circuit via anode and lithium ions reach the cathodic compartment and get inserted inside the cathode, which is basically a lithium transition metal oxide.

Binders

Binders are materials accountable for holding the electroactive particles together within the electrode of a battery to maintain a strong assembly between the electrode and the contacts. Usually, materials used as binders are normally inert and play an important role in the design and production of a battery. The binder also plays a major role in preparing the stable electrodes and is crucial for mechanical stabilization and electrical conduction. Notably, their mechanical strength can be improved by modifying the swelling pressure of active materials and adhesion to the conductive network.

Commercial polyvinylidene fluoride (PVDF) based binder

The most used commercial binder for LIBs is PVDF and it possesses high mechanical, thermal and electrochemical stability. Further, it also enhances the adhesion between the active material and current collector with low electrical resistivity. However, PVDF shows adverse effects in presence of moisture. It is highly hygroscopic and absorbs water from the environment and loses its bonding nature. Besides, N-Methyl pyrrolidone (NMP) is conventionally used as a solvent to dissolve PVDF, which is also highly unstable, flammable, explosive, and highly noxious, which ultimately leads to the environmental degradation as well as biological damages [**21-23**].

Importance of aqueous based binders

It is reported that water can be used as a solvent to replace the toxic organic solvent to dissolve the commercial binder (PVDF) in LIB batteries. As compared with the traditional binder such as PVDF, the water-based binders provide significant enhancements in safety, electrochemical performance, and lowering the manufacturing cost. A comparative life cycle assessment (LCA) study shows that switching to water from NMP gradually decreases the releases of CO_2 [**24-28**]. The manufacturing cost of the LIB mainly depends on the usage, dehydrating, and rescue of the organic solvent [**29-31**].

Table 1. Advantages of aqueous binders [30].

Slurry properties	**Electrode properties**	**Electrochemical properties**
Homogenous paste	It has a high adhesive strength	It has low resistance
Stable mixture	Flexible for winding process	Less swelling
Easy to coat	-	Good cycle stability

Numerous effects of aqueous-based binders in the Li-ion batteries

Anode in lithium-ion batteries is basically a negative electrode, which is primarily made up of any carbon materials such as natural graphite, activated graphite, carbon black, activated carbon, titanium dioxide, molybdenum trioxide, vanadium sulphide, etc. The most used carbon source is graphite, which may be coated over a metal foil such as copper and used for battery performance [**30,32**]. These graphite sources have some interlayer spaces, where the lithium ions get intercalated during the redox process.

The reason for employing the graphite is that it is lightweight, highly available, non-toxic, and highly stable. Park *et. al.*, [**33**] have studied in detail about the impact of high molecular weight poly vinyl alcohol (PVA) as the binder for the anodes of Li-ion batteries. Considering the presence of a huge number of -OH groups in the polymer network, a strong hydrogen bonding between the current collector and electroactive substances are achieved, which largely enhances the binding capacity of the electrodes. It is also demonstrated in their study that as compared to polyvinylidene fluoride and polyacrylic acid, the PVA with high molecular weight show very good cyclic performance in carbon/silicon electrodes. Similarly, Song, *et. al.*, [**34**] have used the interpenetrated gel polymer binder-based silicon as an ideal anode material, however, they observed some changes in the volume during the charging and discharging process, where its efficiency faded out very easily during the practical applications.

It is reported that the interpenetrated gel made from water-soluble polyacrylic acid (PAA) and polyvinyl alcohol (PVA) binders with silicon anode adapts itself to the change in volume during lithium-ion transfer. This provided a very high cyclic stability and high columbic electrical efficiency of about 99.3% with very high current density. It also showed about 4.3 Ah cm^{-2} areal current density with water-soluble PAA-PVA gel binder coated on silicon anodes (see **Fig. 4**). Similarly, Lee *et. al.*, [**35**] made comparative studies on the effect of different kinds of polymer binders in the dissolution of manganese and electrochemical characteristics of $LiMn_2O_4$ electrodes (LMO). In the studies on the three most binders such as PVA, PAN, and PAA, they were used as effective binders and compared with commercial binder of polyvinylidene (PVDF).

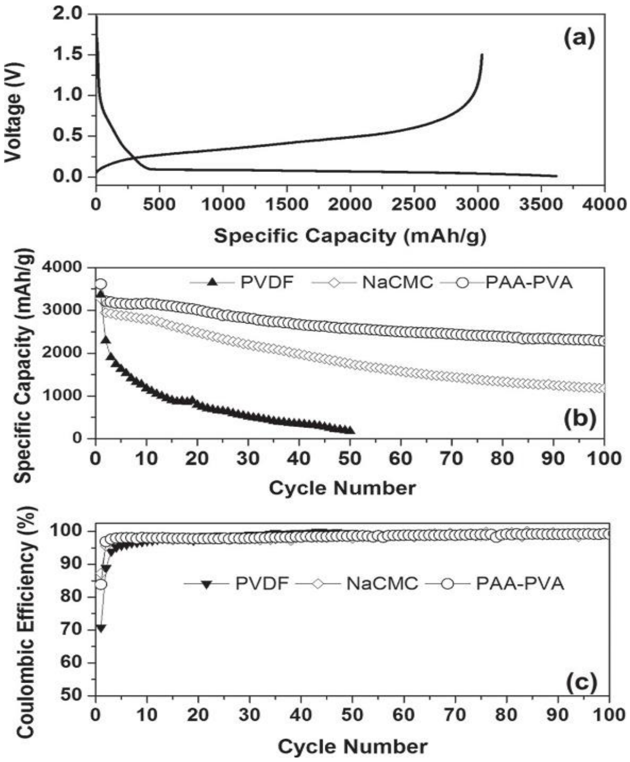

Fig. 4. Comparative studies of coulombic efficiency and cycling stability of the commercial PVDF binder with aqueous-based PAA-PVA, and NaCMC binders [34].

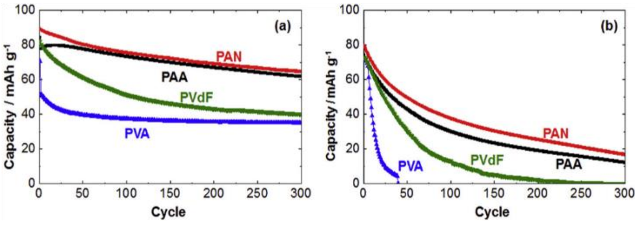

Fig. 5 Comparative electrochemical studies of commercial PVDF binder with aqueous-based PAA, PAN, PVA binders at 25 ºC and 60 ºC [35].

PAN showed excellent good results such as high electrothermal stability and good cycling properties as shown in **Fig. 5**. Studies on eco-friendly aqueous binders [**36**] and carbon coated silica powder electrodes with sodium alginate or styrene-butadiene rubber or carboxymethyl cellulose or polyacrylic acid as binders showed excellent performance and electrochemical stability for Li-ion batteries with the cycling stability of about 940A hg^{-1} per 100 cycles. Similarly, Jiarong *et. al.*, [**37**] have studied the performance of polyvinyl alcohol grafted polyacrylic acid aqueous binders on Si anode and have reported excellent electrochemical efficiency for PVA, PAA, and PAN binders. Zheng *et. al.*, [**38**] and Aslan *et. al.*, [**39**] have proved the excellent electrochemical performance of polyvinyl alcohol, polyacrylic acid, and polyvinylpyrrolidone. Studies on inkjet-printed silicon nano powder thin film as an anode, showed impressive durability and cyclic stability of about 1000 mA hg^{-1} after 1000 cycles [**40**]. Similarly, the binding mechanism between carboxymethyl cellulose and Si anode has also been reported [**41**]. Using CMC, a 4-fold efficiency was achieved under similar experimental conditions. CMC facilitates an efficient networking process among Si particles. Investigation on carboxymethylcellulose as an alternative binder to PVDF for electrochemically stable molybdenum disulphide particles with 2-D nanowall structures as an anode showed excellent performance and a very high specific discharge capacity of almost 800 mA hg^{-1} for about 50 cycles (**Fig. 6(c)**) [**42**].

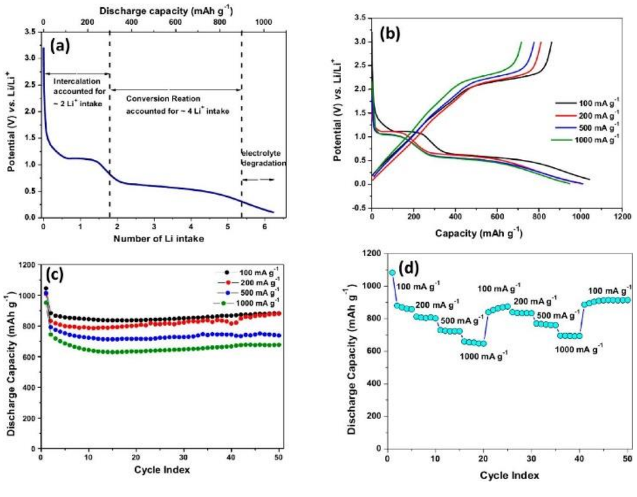

Fig. 6. Electrochemical behaviour of CMC aqueous-based binder [42].

The observed high specific discharge capacity and electrochemical stability were attributed to the nanowall structure of MoS_2 and were used in CMC. Similar results were also observed for MoS_2 nanorods [**43**]. Prosini *et. al.*, [**44**] have designed a lithium-ion battery with water processable electrodes and made a detailed study on the performance of the particular battery. Polystyrene acrylate and polyvinyl acetate were used as binders for anode and cathode, respectively. The advantages of both of these binders are easily dispersible in water, less toxic and no need for organic solvents. When $LiFePO_4$ and MCMB graphite materials are used as electrode active material with these binders, they showed very good efficiency and electrochemical cyclic stability. Studies on hexagonal brucite phase β-$Ni(OH)_2$ nanoflowers and multi-walled carbon nanotubes [**45**] as anode materials exhibited a six times increment in the capacity when 1:1 ratio (by weight) of nickel hydroxide and multi-walled nanotubes were used. The capacitance value reported was about 1416 mAhg^{-1}. The observed capacity increase was attributed to the nickel nanostructures and the easy dissolution of nickel ions in electrolytes.

Electrolytes

Electrolytes used in lithium-ion batteries are basically liquid in state which facilitates the ions transfer between cathodic and anodic compartment. Selection of the electrolyte should be made on a few crucial factors such as high thermal stability, the high solubility of lithium salts, low vapour pressure, suitability with electrode materials used in LIBs. The widely used electrolytes include the salts of lithium such as $LiPF_6$ dissolved in the mixture of organic solvents such as EC (Ethylene Carbonate) and DMC (Dimethyl Carbonate) mixtures.

Solid-state electrolyte

The solid-state electrolyte plays a dual character as electrolyte and separator as well. It acts as a great wall between the anode and cathode to avoid the blast. It plays a major role in the battery, where its properties can directly influence the activity of the batteries [**46-49**]. To enhance the performance of the solid-state battery, it should comply with the following properties (see **Fig. 7**).

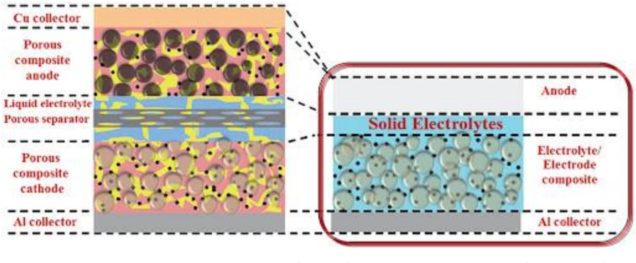

Fig. 7. Representation diagram of the fundamentals needs for a perfect solid-state electrolyte [50].

Ionic conductivity

Ionic conductivity is a major property for determining the capability of ions conduction in the electrolyte arrangements, and it is a crucial factor to measure the electrochemical behaviour of the solid-state batteries [**51**]. The general, ionic conductivity of the commercial organic liquid-based electrolyte is ranging between 10^{-3} and 10^{-5} S cm^{-1} at room temperature. On the other hand, the ionic conductivity of a solid polymer electrolyte is ranging between 10^{-6} and 10^{-5} S cm^{-1}. To enhance the ionic conductivity of the solid-state polymer electrolyte, it is essential to increase the ability of the lithium salt dissociation in the system, which enriches the number of carriers and diminishes the crystallinity behaviour of the polymer matrix *via* enhancing the rate of the carrier transfer. In the battery system, the overall resistance is directly affected by the ionic conductivity. Basically, an ideal solid polymer electrolyte will have an ionic conductivity value larger than 10^{-4} S cm^{-1} to achieve a consistent charging and discharging activities of a battery. Further, the solid-state polymer electrolyte must contain the electronic insulator property, therefore the ion transport makes easier and self-discharge of the battery can be diminished largely [**52**].

Technologies for the development of solid-state polymer electrolyte polymerization

Nowadays, various polymerization methods are used by many researchers to develop novel solid-state electrolytes for a lithium-ion batteries.

Grewal *et. al.*, [**53**] synthesised a solid-state polymer electrolyte membrane containing a bifunctional polyethylene glycol cross-linked structure through a facile one-pot reaction method using the raw materials such as PEMP (pentaerythritol tetrakis 3-mercaptopropionate), LiTFSI (lithium bistrifluoromethane sulfonimide), and PEG (polyethylene glycol) and it also showed excellent mechanical properties. An *in-situ* type of polymerization has also been established in order to decrease the interface impedance (**Fig. 8(a)**) [**54**]. It is demonstrated that this method can be suitable for the large-scale development of solid-state electrolytes. In the manufacturing process of the solid-state electrolyte, the usage of initiators is very crucial, therefore the selection of initiator also plays a major role. Because the unsuitable initiators have the ability to produce side reactions, which cause the formation of poor solid electrolyte interfaces (SEI), which suppresses the overall performance of the batteries [**55**]. Huang *et. al.*, [**56**] described the preparation of polytetrahydrofuran (PTHF)-based polymer electrolyte (PTSPE) using BF_3 (boron trifluoride) as the initiator through the *in-situ* type polymerization of THF (tetrahydrofuran) (**Fig. 8(b)**). Their results clearly explained that the *in-situ* polymerization type of electrolyte can enhance their contact properties and interfacial stabilities.

Many researchers have found that UV polymerization and thermal polymerization techniques are easy to operate, simple to use, environmentally friendly and are appropriate for large-scale development of solid polymer electrolytes [**57-60**]. Nair *et. al.*, [**61**] described a greatly conductive solid polymer electrolyte (**Fig. 8(c)**) synthesized in presence of lithium salt and imidazolinone-based room temperature ionic liquid (RTIL) through free radical photopolymerization. The resulting solid polymer electrolyte showed a large ionic conductivity and decent interface contact with the electrode. Similarly, the cationic ring-opening polymerization (CROP) is also found to be an effective approach to develop the solid polymer electrolytes. Based on particular targets, it can successfully form a novel solid-phase polymer and could also be a better choice to enhance the applicability of industrial polymers such as polysiloxane, polytetrahydrofuran [**62,63**]. Nair and co-worker [**64**] have also described that the thermally tempted and the lithium salt catalysed CROP technology can be used to construct a cross-linked 3D network solid polymer electrolyte without using any solvent or external catalyst of ethylene oxide solid-phase extraction system (**Fig. 8(d)**). The manufactured solid polymer electrolyte showed a great ionic conductivity (>0.1mS cm^{-1}), poor T_g (<-50°C), and outstanding oxidation stability (>5.5 V *vs* Li/Li^+).

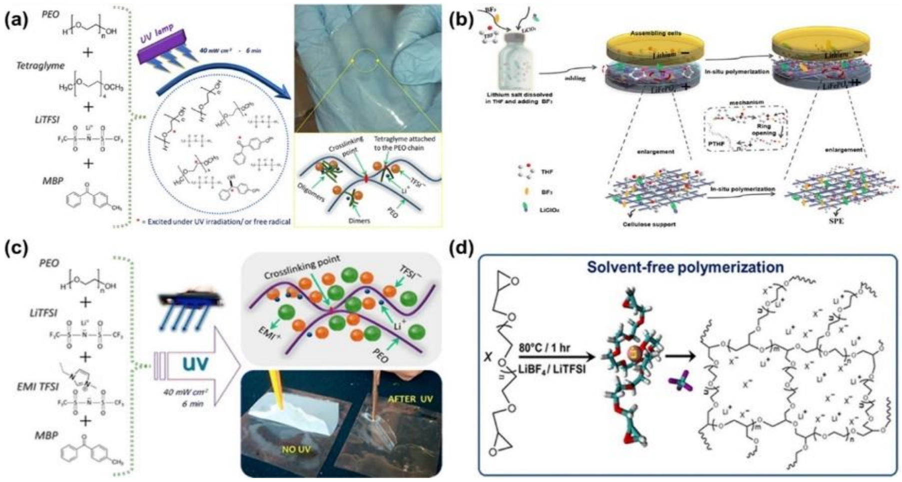

Fig. 8 (a) Outlines of in-situ polymerization and materials used to synthesis electrolytes [54], (b) schematic figure of PTHF electrolyte through in-situ designed polymerization method [56], (c) After the UV-ray polymer electrolyte has non-adhesive, bendable and transparent [61], (d) schematic picture of the manufactured solid polymer electrolyte through thermally tempted and lithium salt-catalysed CROP technology [64].

Alternative approaches for the solid-state polymer electrolytes

It is reported that decreasing the glass-transition temperature (T_g) of the solid-state polymer electrolyte could efficiently enrich the amorphous region and significantly develop the ion transport behaviours in the system. Meanwhile, diminishing the crystallinity of the electrolyte can also support the segmental motion. Jinisha *et. al.*, [**65**] have synthesized a novel solid polymer electrolyte for solid-state lithium batteries. They prepared polyethylene oxide and polyvinylpyrrolidone blend polymer solid electrolyte membrane incorporated with magnesium ions. The amorphous nature of polymer blend is enhanced by the addition of magnesium ions and verified by XRD technique. It also gives the option for neglecting a separator as the electrolyte membrane by itself acts as a separator, which helps to achieve high electrochemical activities [**66-69**].

There are numerous alternation schemes established to increase the electrochemical behaviour of the solid-state polymer electrolytes (SSPEs). While compare the conventional monomeric polymer electrolytes with block co-polymer electrolytes, these block co-polymeric electrolytes show the properties of better controllability and block co-polymers with particular structures normally act like simple linear polymers, besides many random copolymers as well. These numerous properties of the combination of polymers have stimulated a great interest. An individual function of a block copolymer with an electron-rich group in the polymers such as polyethylene oxide (PEO), poly-methyl methacrylate (PMMA), and polyvinyl chloride (PVC), etc is to obtain both great mechanical strength and great ionic conductivity [**70,71**]. Young *et. al.*, [**72**] invented the lithium perchlorate doped PS-b-PEO block copolymer electrolyte. Their results showed that a gradual change of PEO volume fraction from 0.70 to 0.75 can achieve three morphologies such as LAM (lamellae), HEX (Hexagonally packed cylinder), and HPL (Hexagonally Perforated Lamellae) as shown in **Fig. 9(a)**. Aldalur *et. al*., [**73**] fabricated a comb polymer electrolyte through block polymerization using polyethylene oxide and LiFSI (lithium bis(fluorosulfonyl)imide. The electrolyte T_g is as low as about -55°C, and completely amorphous. It has larger ionic conductivity than the conventional polyethylene oxide-based solid polymer electrolyte. Further, it holds an excellent electrochemical behaviour with the anode material. Furthermore, Nguyen *et. al.*, [**74**] fabricated the multi-block aromatic structure that delivered higher ionic conductivity, larger ion mobility, and excellent mechanical stability. The greatest voltage stability window is achieved at 4.9 V and the largest ionic conductivity is about 3.29×10^{-4} S cm^{-1}. The structural strength of polymer electrolytes should be enriched by the hyperbranched star-shaped polymers. Further, it also enhances their topological and physical properties. Accordingly, these materials are considered as an appropriate polymer electrolyte composite for the solid-state Li-ion batteries [**75**]. The crystallization of polymer is prevented by the existence of branch points and also, offers high ionic conductivity by providing extra free volume for the action of the polymer segment [**76-78**]. Further, the presence of individual characteristics of the hyper-branched star polymers is easily alternated to a huge number of functional groups [**79**]. In particular, the rigid segments in the structure have enhanced the excellent mechanical property of the star shaped polymers [**80,81**]. The stability was enriched between the core and outer arm by the covalent bond connection [**82**]. Xu *et. al.*, [**77**] developed a fluorine-carrying star tape hyper-branched polymer (HBPS-PTFEMA-b-PPEGMA) electrolyte through ATRP (Atom Transfer Radical Polymerization) technique. It possessed excellent thermal stability as well as good ionic conductivity (2.4×10^{-5} S cm^{-1} at 25°C) and thermal decomposition temperature. The electrolyte also possessed an extensive electrochemical window (4.9 V) and excellent interface compatibility (**Fig. 9(b)**). Xiao *et al.*, [**83**] have demonstrated the fabrication of star hyper-branched polymer electrolytes by employing the polyethylene glycol di-methacrylate (PEGDMA) as the monomer and ethylene glycol di-methacrylate (EGDMA) as the crosslinking agent. The fabricated electrolyte is very flexible with an excellent strain of about 300% and tensile stress of about 1.7 MPa. It showed an excellent ionic conductivity of about 1.48×10^{-5} S cm^{-1} at 20°C, which is recognized as a favourable topological design that stimulates the fast ion transport. The range of voltage stability window reached about 5.4 V. Hence, these results clearly express that the star polymer electrolyte can be an excellent electrolyte material for energy storage and conversion devices. The structure of the polymer is a crucial element affecting the mechanical and electrochemical behaviour of the polymer electrolytes. Using chemical cross-linking methods to fabricate the polymer structures is a smart strategy for fabrication of new polymer electrolytes. Usually, it is believed that having a host polymer into the cross-linked chemical structure is a powerful step to enhance the thermal stability, electrochemical stability, and mechanical properties of the polymer electrolyte. Chemical crosslinking of the polymer needs steady ionic conductivity and mechanical strength. Lu *et al.*, [**84**] claimed a novel initiator-free single pot synthesis approach based on ring-opening polymerization using (diglycidyl ether of bisphenol-A) as the assistant framework to enrich the mechanical strength of the polymer complex.

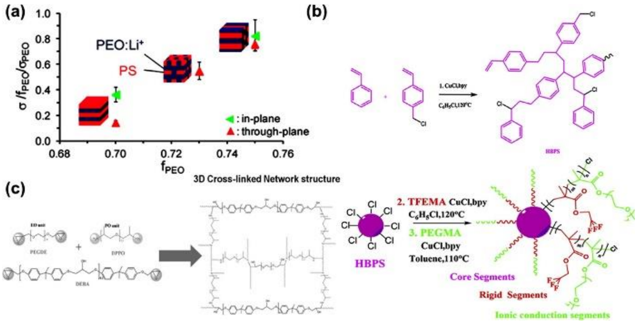

Fig. 9. (a) Morphology of altered PEO f_{PEO} [72], (b) synthesis of star-branched polymer [77], (c) manufacturing method of cross-linked polymer membrane [84].

The polymers such as diamino polypropylene oxide (DPPO) and poly (ethylene glycol) diglycidyl ether) (PEGDE) can act as the cross-linking agent to guaranteeing the fast transport of ions and to avoid the crystallization of the polymer and stimulate faster segment migration (**Fig. 9(c)**). Lin *et al.*, [**85**] projected the new mobile crosslinking strategy by applying polyethylene glycol, which has a cross-link with α-CD (α-cyclodextrin) to yield SPE. PEG section is engaged to transport Li^+ though the cross-linked α-CDs are not chemically attached to the PEG to attain mobile cross-links, which can destroy the crystallization behaviour of the PEO and preserve its segmental mobility even after the crosslinking. The crosslinked structure efficiently boosted the ionic conductivity and durability of SPE. Zhang *et. al.*, [**86**] synthesized a novel free cross-linked hybrid polymer electrolytes using polyhedral oligomeric silsesquioxane (POSS) as a cross-linking agent. The hybrid polymer electrolytes system with the maximum polyhehedral oligomeric silsesquioxane content of 5% weight showed the largest ionic conductivity (3.94×10^{-5} S cm^{-1} at 25°C). Furthermore, the EO chain grafted on the POSS units makes a new ion conduction way. The primary discharge ability of the Li-ion battery accumulated with this polymer electrolyte was about 154 mAh g^{-1}. After 150 cycles, still, the discharge capacity of the battery was high as 152.1 mAh g^{-1}. Zhang *et. al.*, [**87**] demonstrated the synthesis of flexible polymer electrolytes by cross-linking of PEO, tetraethylene glycol dimethacrylate (TEGDMA), and Tetraglyme (TEGDME). Through the UV in-situ double reaction technique to form an electrolyte on the surface of the electrode, the resistance in the interface can be reduced. The ion conductivity of the polymer electrolyte is 30 times larger than the pure PEO polymer electrolyte (0.27 mS cm^{-1}). The number of ion migration is 0.56 and it also supports removing the concentration polarity influence inside the battery and showed some pros and cons with respect to different alteration strategies.

Separators

Separators in LIBs are used to avoid the direct electrical connection between the anodic and cathodic compartments by repelling the electrons and allowing the ions to move between two compartments. The widely used separators include the organic polymers such as polypropylene or polyethylene-modified membranes which offer very good selective permeability. The ideal separator should have very less thickness, should be mechanically strong and able to withstand the mechanical stress. It should also be chemically inert and electrically stable at the range of working potential of the cell. Separators are significant materials within a Li ion battery. It should be mechanically and thermally stranger in order to separate anode and cathode within a cell while allowing high ionic conductivity. The separators should have thickness around 10- 30 µm with a weight of 10-25 g/m^2 and porosities are between 38-45%. During the working procedure of batteries, the ion transport plays significant role in the Li-ion performance. A separator can offer fast ion transport between electrodes to prevent internal short circuit failure, which ultimately causes the explosions. Other hand, due to thermal lethargy the temperature can remain to rise until the separator would melt and short circuit the electrodes, which leading to vicious reaction and generation of heat. This singularity is called separator breakdown, which is one step of thermal runaway process in Li-ion battery. Hence, the separator should have better thermal stability as well as mechanically strong during the charge/discharge process.

Conclusion

The aqueous-based binder for lithium-ion batteries is still an unexplored research area as compared to amount of work done the novel anode and cathode active materials. The significance of aqueous-based binder battery production is being recognized recently and becoming very significant. In the review, various types of aqueous-based binders were highlighted and discussed their modern advances in the field of aqueous-based binders, which is so-called the green binders for lithium-ion batteries and clarified how it could reduce the environmental impact and manufacturing cost, and how it can improve the electrochemical properties and safety of the lithium-ion batteries. Further, another big issue is liquid electrolyte. As comparing the commercial liquid electrolyte with solid-state electrolyte, this solid-state electrolyte shows supreme benefits including large energy density, excellent safety, and stable cycle life towards lithium-ion batteries. Over years of investigations and developments, the solid-state electrolytes have been achieved some successes, but because of their certain limitations and challenges, it is still unable to reach large-scale commercialization. The other focus of this review involved the ionic conduction of the solid-state electrolyte and essential factors required for solid-state electrolyte, as well as the structure and its performance of various types of solid-state electrolytes. These developments in the field clearly show that the solid-state electrolyte-based lithium-ion batteries will emerge as a crucial factor in the energy storage devices in the near future.

Acknowledgement

The author (Dr. A. Murali) thankful to the Department of Science and Technology (DST), Govt. of India, grant no: DST/INSPIRE/4/2018/ 001762 for DST Inspire Faculty scheme.

Keywords

Lithium-ion battery; aqueous binder; green solid-state electrolyte.

References

1. Thackeray, M. M.; Wolverton, C.; Isaacs, E. D.; *Energy Environ. Sci.*, **2012**, *5*, 7863.
2. Tarascon, J. M.; Armand, M.; *Nature.*, **2001,** *414*, 359.
3. Meesala, Y.; Jena, A.; Chang, H.; Liu, R. S.; *ACS Energy Lett.*, **2017**, *2*, 2734.
4. Arya, A.; Sharma, A. L.; *J. Phys. D Appl. Phys.*, **2017**, *50*, 443002.
5. Cheng, X.; Pan, J.; Zhao, Y.; Liao, M.; Peng, H.; *Adv. Energy Mater.*, **2018**, *8*, 1702184.
6. Lin, D.; Liu, Y.; Cui, Y.; *Nat. Nanotechnol.*, **2017**, *12*, 194.

7. Tallner, C.; Lannetoft, S. CODEN: LUTEDX/(TEIE-5194)/1-71 (**2005**).
8. O'Brien, R. U.S. Patent Application No. 11/374,600.
9. Courtel, F. M.; Niketic, S.; Duguay, D.; Abu-Lebdeh, Y.; Davidson, I. J.; *J. Power Sources*, **2011**, *196*, 2128.
10. Wang, Q.; Jiang, L.; Yu, Y.; *Sun, J. Nano Energy.*, **2019**, *55*, 93.
11. Liu, H.; Cheng, X. B.; Huang, J. Q.; Yuan, H.; Lu, Y.; Yan, C.; Zhu, G. L.; Xu, R.; Zhao, C.Z.; Hou, L. P.; He, C. X.; Kaskel, S.; Zhang, Q.; *ACS Energy Lett.*, **2020**, *5*, 833.
12. Li, G.; Monroe, C. W.; *Phys. Chem. Chem. Phys.*, **2019**, *21*, 20354.
13. Zeng, X. X.; Yin, Y. X.; Li, N. W.; Du, W. C.; Guo, Y. G.; Wan, L. J.; *Am. J. Chem. Soc.*, **2016**, *138*, 15825.
14. Li, N. W.; Shi, Y.; Yin, Y. X.; Zeng, X. X.; Li, J. Y.; Li, C. J.; Wan, L. J.; Wen, R.; Guo, Y.G. Angew. Chem. Int. Ed., **2018**, *57*, 1505.
15. Zhou, G. M.; Li, F.; Cheng, H. M.; *Energy Environ. Sci.*, **2014**, *7*, 1307.
16. Gao, Z.; Sun, H.; Fu, L.; Ye, F.; Zhang, Y.; Luo, W.; Huang, Y.; *Adv. Mater.*, **2018**, *30*, 1705702.
17. Yongjin, F.; Xin-Yao, Y.; Xiong Wen (David), L.; *Mater*, **2019**, *1*, 90.
18. Chan, C. K.; Liang, W. U.S. Patent No. 8, **2015**, 968.
19. Kutbee, A T. Integration Strategy for Free-form Lithium Ion Battery: Material, Design to System level Applications. Diss. **2017**.
20. Lee, H.; Yanilmaz, M.; Toprakci, O.; Fu, K.; Zhang, X.; *Energy Environ. Sci.*, **2014**, *7*, 3857.
21. Marshall, J.E.; Zhenova, A.; Roberts, S.; Petchey, T.; Zhu, P.; Dancer, C.E.J.; McElroy, C.R., Kendrick, E.; Goodship, V.; *Polymers*, **2021**, *13*, 1354.
22. Wei, J.; Wang, Z.; Xing, X.; *Sensors*, **2020**, *21*, 193.
23. Bresser, D.; Buchholz, D.; Moretti, A.; Varzi, A.; Passerini, S.; *Energy Environ. Sci.*, **2018**, *11*, 3096.
24. Lee, K. P.; Chromey, N. C.; Culik, R.; Barnes, J. R.; Schneider, P. W.; *Fundam. Appl. Toxicol.*, **1987**, *9*, 222.
25. Malek, D. E.; Malley, L. A.; Slone, T. W.; Elliott, G. S.; Kennedy, G. L.; Mellert, W.; Deckardt, K.; Gembardt, C.; Hildebrand, B.; Murphy, S. R.; Bower, D. B.; Wright, G. A.; *Drug Chem. Toxicol.*, **1997**, *20*, 77.
26. Zhu, W.; Schmehl, D. R.; Mullin C. A.; Frazier, J. L.; *PLoS One*, **2014**, *9*, 77547.
27. Maity, K.; Garain, S.; Henkel, K.; Schmeisser, D.; Mandal, D.; *ACS Appl. Polym. Mater.*, **2020**, *2*, 862.
28. Haufroid, V.; Jaeger, V. K.; Jeggli, S.; Eisenegger, R.; Bernard, A.; Friedli, D.; Lison D.; Hotz, P.; *Int. Arch. Occup. Environ. Health*, **2014**, *87*, 663.
29. Wood Iii, D. L.; Li, J.; Daniel, C.; *J. Power Sources.*, **2015**, *275*, 234.
30. Peng, H.; *Energy. Polym. Rev.*, **2019**, *59*, 739
31. Susarla, N.; Ahmed, S.; Dees, D. W.; *J. Power Sources.*, **2018**, *378*, 660.
32. Perera, S. D.; Patel, B.; Nijem, N.; Roodenko, K.; Seitz, O.; Ferraris, J. P.; Chabal, Y. J.; Balkus Jr, K. J.; *Adv. Energy Mater.*, **2011**, *1*, 936.
33. Park, H. K.; Kong, B. S.; Oh, E. S.; *Electrochem. Commun.*, **2011**, *13*, 1051.
34. Song, J.; Zhou, M.; Yi, R.; Xu, T.; Gordin, M. L.; Tang, D.; Yu, Z.; Regula, M.; Wang, D.; *Adv. Funct. Mater.* **2014**, *24*, 5904.
35. Lee, S.; Kim, EY.; Lee, H.; Oh, ES.; *J. Power Sources.*, **2014**, *269*, 418.
36. Feng, X.; Yang, J.; Yu, X.; Wang, J.; Nuli, Y.; *J. Solid State Electrochem.*, **2013**, *17*, 2461.
37. He, J.; Zhang, L.; *J. Alloys Compd.*, **2018**, *763*, 228.
38. Zheng, M.; Wang, C.; Xu, Y.; Li, K.; Liu, D.; *Electrochim. Acta*, **2019**, *305*, 555.
39. Aslan, M.; Weingarth, D.; Jackel, N.; Atchison, J. S.; Grobelsek, I.; Presser V.; *J. Power Sources*, **2014**, *266*, 374.
40. Lawes, S.; Sun, Q.; Lushington, A.; Xiao, B.; Liu, Y.; Sun, X.; *Nano Energy*, **2017**, *36*, 313.
41. Lestriez, B.; Bahri, S.; Sandu, I.; Roué, L.; Guyomard, D.; *Electrochem. Commun.*, **2007**, *9*, 2801.
42. Sen, U. K.; Mitra, S.; *ACS Appl. Mater. Interfaces.*, **2013,** 5, 1240.
43. Sen, U. K.; Mitra, S.; *J. Solid State Electrochem.*, **2014**, *18*, 2701.
44. Prosini, P. P.; Cento, C.; Carewska, M.; Masci, A.; *Solid State Ion.*, **2015**, *274*, 34.
45. Pramanik, A.; Maiti, S.; Mahanty, S.; *Sci. Lett.*, **2015,** *4*, 104.
46. Meziane, R.; Bonnet, J. P.; Courty, M.; Djellab, K.; Armand, M.; *Electrochim. Acta*, **2011**, *57*, 14.
47. Zhu, Y. S.; Gao, X. W.; Wang, X. J.; Hou, Y. Y.; Liu, L. L.; Wu, Y. P.; *Electrochem. Commun.*, **2012**, *22*, 29.
48. Zhu, Y. S.; Wang, X. J.; Hou, Y. Y.; Gao, X. W.; Liu, L. L.; Wu, Y. P.; Shimizu, M.; *Electrochim. Acta*, **2013**, *87*, 113.
49. Wang, Z.; Tang, Y.; Li, B.; *RSC Adv.*, **2018**, *8*, 25159
50. Yao, X.; Huang, B.; Yin, J.; Peng, G.; Huang, Z.; Gao, C.; Liu, D.; Xu, X.; *Chin. Phys. B*, **2016**, *25*, 018802.
51. Wang, H.; Sheng, L.; G Yasin, G.; Wang, L.; Xu, H.; He, X.; *Energy Storage Mater.*, **2020**, *33*, 188.
52. Mitra, S.; Kulkarni, AR.; *Solid State Ion.*, **2002**, *37*, 154
53. Grewal, M. S.; Tanaka, M.; Kawakami, H.; *Polym. Int.*, **2019**, *68*, 684.
54. Porcarelli, L.; Gerbaldi, C.; Bella, F.; Nair, J. R.; *Sci. Rep.*, **2016**, *6*, 19892.
55. Cui, Y.; Liang, X.; Chai, J.; Cui, Z.; Wang, Q.; He, W.; Liu, X.; Liu, Z.; Cui, G.; Feng, J.; *Adv. Sci.*, **2017**, *4*, 1700174.
56. Huang, S. Q.; Cui, Z. L.; Qiao, L. X.; Xu, G. J.; Zhang, J. J.; Tang, K.; Liu, X. C.; Wang, Q. L.; Zhou, X. H.; Zhang, B. T.; Cui, G. L.; *Electrochim. Acta.*, **2019**, *299*, 820.
57. Nair, J. R.; Colo, F.; Kazzazi, A.; Moreno, M.; Bresser, D.; Lin, R. Y.; Bella, F.; G. Meligrana, G.; Fantini, S.; Simonetti, E.; Appetecchi, G. B.; Passerini, S.; Gerbaldi, C.; *J. Power Sources*, **2019**, *412*, 398.
58. Nair, J. R.; Destro, M.; Bella, F.; Appetecchi, G. B.; Gerbaldi, C.; *J. Power Sources.*, **2016**, *306*, 258.
59. Chunsheng, Wang.; Ying, S. M.; Kang, Xu; *J. Electrochem. Soc.*, **2018**, *166*, A5184.
60. Falco, M.; Simari, C.; Ferrara, C.; Nair, J. R.; Meligrana, G.; Bella, F.; Nicotera, I.; Mustarelli, P.; Winter, M.; Gerbaldi, C.; *Langmuir*, **2019**, *35*, 8210.
61. Nair, J. R.; Porcarelli, L.; Bella, F.; Gerbaldi, C.; *ACS Appl. Mater. Interfaces*, **2015**, *7*, 12961.
62. Ehteshami, N.; Eguia-Barrio, A.; de Meatza, I.; Porcher, W.; Paillard, E.; *J. Power Sources.*, **2018**, *397*, 52.
63. Nuyken, O.; Pask, S. D.; *Polymers*, **2013**, 5, 361.
64. Nair, J. R.; Shaji, I.; Ehteshami, N.; Thum, A.; Diddens, D.; Heuer, A.; Winter, M.; *Chem. Mater.* **2019**, *31*, 3118.
65. Jinisha, B.; Anilkumar, K. M.; Manoj, M.; Pradeep, V. S.; Jayalekshmi, S.; *Electrochim. Acta.*, **2017**, *235*, 210.
66. Gerbaldi, C.; Destro, M.; Jijeesh, R. N.; Ferrari, S.; Quinzeni, I.; Quartarone, E.; *Nano Energy*, **2013**, *2*, 1279.
67. Huang, S. Q.; Cui, Z. L.; Qiao, L. X.; Xu, G. J.; Zhang, J. J.; Tang, K.; Liu, X. C.; Wang, Q. L.; Zhou, X. H.; Zhang, B. T.; Cui, G. L.; *Electrochim. Acta*, **2019**, *299*, 820.
68. Nair, J.R.; Destro, M.; Gerbaldi, C.; Bongiovanni, R.; Penazzi, N. J.; *App. Electrochem.* **2013**, *43*, 137.
69. Nair, J.R.; Gerbaldi, C.; Destro, M.; Bongiovanni, R.; Penazzi, N.; *React. Funct. Polym.*, **2011**, *71*, 409.
70. Young, W. S.; Kuan, W. F.; Epps, T. H.; *J. Polym. Sci., Part B: Polym. Phys.*, **2014**, *52*, 1.
71. Giacomelli, C.; Schmidt, V.; Aissou, K.; Borsali, R.; *Langmuir*, **2010**, *26*, 15734.
72. Young, W. S.; Epps, T. H.; *Macromolecules*, **2012**, *45*, 4689.
73. Aldalur, I.; Martinez-Ibanez, M.; Piszcz, M.; Rodriguez-Martinez, L. M.; Zhang, H.; Armand, M.; *J. Power Sources*, **2018**, *383*, 144.
74. Nguyen, H. D.; Kim, G. T.; Shi, J. L.; Paillard, E.; Judeinstein, P.; Lyonnard, S.; Bresser, D.; Iojoiu, C.; *Energy Environ. Sci.* **2018**, *11*, 3298.
75. Sun, X. Y.; Yang, X. H.; Liu, Y. H.; Wang, X. L.; *J. Polym. Sci. Part A Polym. Chem.*, **2004**, *42*, 2356.
76. Zhang, J. F.; Ma, C.; Liu, J. T.; Chen, L. B.; Pan, A. Q.; Wei, W. F.; *J. Membr. Sci.*, **2016**, *509*, 138.
77. Xu, H.; Wang, A. L.; Liu, X.; Feng, D.; Wang, S.; Chen, J.; An, Y.; Zhang, L. Y.; *Polymer*, **2018,** *146*, 249.
78. Kim, D. G.; Shim, J. M.; Lee, J. H.; Kwon, S. J.; Baik, J. H.; Lee, J. C.; *Polymer*, **2013**, *54*, 5812.

79. Ren, J. M.; McKenzie, T. G.; Fu, Q.; Wong, E. H.; Xu, J.; An, Z.; Shanmugam, S.; Davis, T. P.; Boyer, C.; Qiao, G. G.; *Chem. Rev.*, **2016**, *116*, 6743.
80. Nair, J.R.; Gerbaldi, C.; Chiappone, A.; Zeno, E.; Bongiovanni,R.; Bodoardo, S.; Penazzi, N.; *Electrochem. Commun.*, **2009**, *11*, 1796.
81. Nair, J.R.; Gerbaldi, C.; Meligrana, Bongiovanni, R.; Bodoardo, S.; Penazzi, N.; Reale, P.; Gentili, V.; *J. Power Sources*, **2008**, *178*, 751.
82. Ren, S. T.; Chang, H. F.; He, L. J.; Dang, X. F.; Fang, Y. Y.; Zhang, L. Y.; Li, H. Y.; Hu, Y. Lin, Y. L.; *J. Appl. Polym. Sci.*, **2013**, *129*, 1131.
83. Xiao, Z. L.; Zhou, B. H.; Wang, J. R.; Zuo, C.; He, D.; Xie, X. L.; Xue, Z. G.; *J. Membr. Sci.*, **2019**, *576*, 182.
84. Lu, Q.; He, Y. B.; Yu, Q.; Li, B.; Kaneti, Y. V.; Yao, Y.; Kang, F.; Yang, Q. H.; *Adv. Mater.*, **2017**, *29*, 1604460.
85. Lin, Y. C.; Ito, K.; Yokoyama, H.; *Polymer*, **2018**, *136*, 121.
86. Zhang, J.; Li, X.; Li, Y.; Wang, H.; Ma, C.; Wang, Y.; Hu, S.; Wei, W.; *Front. Chem.*, **2018**, *6*, 186.
87. Zhang, Y. H.; Lu, W.; Cong, L. N.; Liu, J.; Sun, L. Q.; Mauger, A.; Julien, C. M.; Xie, H. M.; Liu, J.; *J. Power Sources*, **2019**, *420*, 63.