RECENT DEVELOPMENTS IN SCIENTIFIC RESEARCH II

EDITED BY
Prof. Dr. Ayşegül GÜMÜŞ
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PREFACE

There has been a significant development in science for a century or more, which has been quite accelarated for the past twenty-thirty years. The idea behind the present book lays on presenting a part of the ongoing studies in Faculty of Science and Engineering, Architecture and Design Faculty of Bartin University. This book is a compilation of five chapters relating to chemistry, biochemistry and physical chemistry. In the first chapter of this book, synthesis and theoretical applications on chemosensors obtained by condensation of quinoline carboxaldehyde and aminoanthracene has been reported, in the second chapter, sulfonamide inhibitors have been discussed as potential treatment for acute myeloid leukemia, in the third chapter, a wide information has been reveled in the area of biophotovoltaics, in the fourth chapter, research results from bioactivity of N-substituted cyclic derivatives of thiourea and phenylthiourea has been presented, in the fifth chapter, TADF properties of pyrazine based OLEDs are examined. In the last chapter, nanocomposite and nanohybrid gel polymer electrolytes for safe and high performing lithium metal batteries have been discussed deeply. The efforts of our extreme contributors of this book are highly commendable. We would especially like to express our gratitude to the İKSAD Publishing family, scientific committee, authors and readers who contributed to the preparation, layout and printing of the book.

The editors and authors dedicated this book to the 100th Anniversary of Republic of Türkiye.

Prof.Dr. Ayşegül GÜMÜŞ

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CHAPTER 6

NANOCOMPOSITE AND NANOHYBRID GEL POLYMER ELECTROLYTES FOR SAFE AND HIGH PERFORMING LITHIUM METAL BATTERIES

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1. INTRODUCTION

Lithium-ion batteries (LIBs) have gained widespread popularity in the fields of portable electronics, electric vehicles, and grid storage due to their remarkable characteristics. These include their exceptional energy density, power density, and extended cycle life. The high energy density of LIBs allows them to store a significant amount of energy in a compact size, making them ideal for portable electronic devices. Additionally, their high power density enables them to deliver a substantial amount of power quickly, which is crucial for applications such as electric vehicles. Moreover, LIBs exhibit a long cycle life, meaning they can undergo numerous charge and discharge cycles without significant degradation in performance. This longevity makes them reliable and cost-effective for grid storage systems. Overall, the exceptional features of LIBs have propelled their extensive use in various industries, revolutionizing the way we power our devices and vehicles. The discovery of intercalation electrodes by Whittingham in the 1970s laid the foundation for LIB development. In the subsequent decades, Goodenough and his colleagues played a pivotal role by developing crucial cathode materials such as layered, spinel, and polyanion. Additionally, Yoshino's pioneering work involved the creation of the first safe LIB prototype, which employed $LiCoO_2$ as the positive electrolde and carbon/graphite as the negative electrode. Since then, remarkable advancements have been achieved in increasing energy density, power density, cycle life, cost-effectiveness, and safety of lithium-ion batteries (Liu, 2021).

Sony was the first company to commercialize Yoshino's LIB prototype in 1991 (Yoshio,2009) and according to the Grandview Market Analysis Report (2022), the global lithium-ion battery market was valued at USD 54.4 billion in 2023. Moreover, there are projections indicating a compound annual growth rate (CAGR) of 20.3% from 2024 through 2030.

Considering the pressing reality of the worldwide climate crisis and the diminishing reserves of fossil fuels, the United States and

European Union have devised strategic technology roadmaps to encourage the widespread utilization of electric vehicles (EVs) and gradually phase out conventional fossil fuel vehicles by 2030 and 2050, respectively. This shift towards electric-powered transportation also underscores the imperative requirement for advanced battery technologies that surpass the existing lithium-ion technology (300 Wh/kg) based on intercalation chemistry (Choi, 2016).

One of the main components that will allow for a low-carbon civilization is battery technology. because they efficiently store electricity produced by renewable energy sources and serve as a power supply for electric vehicles, both of which contribute to the reduction of greenhouse gas emissions. Batteries are anticipated to serve as key facilitators, expediting the transition towards sustainable and intelligent mobility. By offering clean, affordable, and secure energy solutions, they have the potential to mobilize the industry towards embracing a cleaner and circular economy (to achieve all significant components of the UN Sustainable Development Goals). If it is possible to achieve all four objectives simultaneously, namely making them more affordable, safe, ultra-high performing, and sustainable, it would be a significant advancement. Put differently, batteries are an essential technological tool in the fight against carbon dioxide emissions from the energy, transportation, and industrial sectors. But in order to meet our sustainability targets, batteries will need to operate at a level well above what they can do now. Ultra-high performance encompasses exceptional longevity and dependability, enhanced safety and environmental sustainability, and energy and power performance that approaches theoretical boundaries. Additionally, for these battery technologies to be commercially viable, they must be scalable in order to allow for large-scale production at a reasonable cost. (Battery 2030+ Roadmap, 2023).

LIBs, or lithium-ion batteries, consist of two electrodes: the cathode, which is the positive electrode, and the anode, which is the negative electrode. These electrodes are separated by a porous separator material. (Armand, 2008). The electrolyte is very important for the cycle life of the battery and it is made up of a lithium salt, such as lithium hexaflorophosphate ($LiPF_6$), lithium perchlorate ($LiClO_4$), lithium triflate ($LiCF_3SO_3$), lithium perbromate ($LiBrO_4$) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), dissolved in an appropriate organic solvent (for example, a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC)). The cathode and anode active materials are coated onto aluminum and copper foil current collectors, respectively. The electrolyte plays a crucial role in enabling the movement of ions between the anode and cathode, thereby maintaining a balanced charge. Additionally, it enables the extraction of electrical energy through the external circuit. On the other hand, the separator serves the purpose of preventing any short circuits between the two electrodes, while it still allows the transfer of lithium ions. Discharging process involves the movement of lithium ions as they migrate from the anode and intercalate into the gaps present between the layers of cathode crystals. This phenomenon is scientifically termed as intercalation. On the other hand, during the charging process, the lithium ions relocate from the cathode, which is situated on the positive side of the battery, and insert themselves into the anode (Ghiji, 2020).

Electrochemical behavior of lithium-ion batteries are heavily dependent on the electrolyte. This is primarily because of the interfacial reactions that take place between the electrodes and the electrolyte. Electrolyte must be compatible with both the positive and negative electrodes, current collectors and separator. An ideal electrolyte should also not undergo any chemical and electrochemical reactions as it comes into contact with electrode surfaces that have strong oxidation/reduction properties. This situation is only achieved by the deposition of a solid electrolyte interface (SEI) on the surface of anode (kinetic protection). Formation of the protective SEI layer depends on the characteristics of the additives, impurities, solvents and dissolved substances present in the electrolyte. Solutes must have high solubility in the solvent and stability over a wide temperature range. Other factors affecting electrolyte selection are cost, safety, health and environmental compatibility (Xing, 2022).

Depending on the composition of the electrolyte solution, in the initial charge carbonate-based electrolytes are reduced against Li/Li^+ at the negative electrode (i.e. graphite electrode) between the voltages from 1.5 to 0.7 V. Therefore, the electrode-electrolyte interface film (SEI) forms on the anode as an electronically insulating but permeable layer to lithium ions. SEI film, as a passivation layer on the anode, is a critical structure for high current efficiency and battery voltage, cycle life and safety. Carbonates such as Li_2CO_3 and $ROCO_2Li$ are indispensable components of the SEI layer due to their acceptable Li^+ conductivity (Wang, 2018).

The rising popularity of electric vehicles and portable/wearable devices has created a growing need for lithium-ion batteries (LIBs) that are both extremely safe and affordable, while also providing high energy density for lasting longer on a single charge. Unfortunately, even conventional LIBs consisting of a graphite anode and lithium cobalt oxide ($LiCoO_2$) cathode, have an average theoretical energy density of only 387 Wh/kg (Cohn,2017). Specific capacity of a battery is greatly influenced by the cathode and anode materials. In the context of anode materials, scientists have been diligently searching for alternatives to the conventional carbon-based anodes in order to enhance the specific capacity. A notable avenue of exploration involves the substitution of lithium metal for traditional carbon-based anodes. This substitution is expected to result in a higher specific capacity, and thus, researchers are actively investigating its feasibility (Qi, 2021). Because it can provide the highest possible capacity of 3860 $mAh.g^{-1}$, lithium metal as an anode material has drawn tremendous research attention of researchers wordwide (Hatzell, 2020). However, lithium is a highly reactive metal that grows dendrites during the cycling of lithium-metal batteries (LMBs) and this may trigger thermal runaway behaviour which is more serious for LMBs. Therefore, it is crucial to acknowledge that the thermal stability and mechanical strength of electrolytes play a vital role in ensuring the safety of LMBs operating under long-term and extreme conditions. Consequently, the pursuit of safe electrolyte technologies to enhance the safety of LMBs has become an area of utmost importance and is considered critically significant in research (Yan, 2014).

Currently, commercial LIBs face certain constraints due to their liquid organic electrolytes. These limitations include flammability, thermal instability, and the tendency of organic solvents to volatilize strongly. Consequently, there is a high risk of fire and explosion in situations of overcharge and short circuit. However, the implementation of all solid-state electrolytes offers notable benefits such as a higher shear modulus, flexibility, and non-inflammability. These advantages have the potential to greatly enhance the safety and energy density of LIBs, making them the most efficient energy storage technology for future generation of emerging energy storage systems (Ji, 2023). However, the successful commercialization of all-solid-state batteries remains a significant obstacle due to several unresolved issues. These include the electrochemical instability caused by high voltage levels exceeding 4.5 V (vs. Li/Li^+), the incompatibility between lithium metal interfaces, and the inadequate ionic conductivity. Overcoming these challenges is crucial for the realization of viable all-solid-state batteries in the future. (Chai, 2016).

Substitution of organic liquid electrolytes by all solid-state electrolytes is a fundamental approach to tackle safety issues, particularly in the context of lithium metal batteries (LMBs). The investigation into solid-state electrolytes, which are composed of polymers, ceramics, or their combinations, has recently progressed towards viable real-world implementations. (Kalhoff, 2015). Certain inorganic electrolytes have been found to exhibit ionic conductivity that is comparable to, or even surpasses, that of commercially available liquid electrolytes. Nevertheless, solid-state batteries (SSBs) incorporating these inorganic electrolytes often exhibit suboptimal performance due to inadequate interfacial contact between the electrolyte and electrode (Wang, 2020). Therefore, broad applications of solid electrolytes are still in its infancy due to their limited performance compared to liquid electrolytes (Ren, 2021). The realm of solid electrolyte technologies has witnessed a significant focus on polymer electrolytes (PEs). This can be attributed to their remarkable ability to maintain a consistent volume throughout the charge and discharge cycle, thereby ensuring stability. Additionally, PEs offer a high level of safety, making them an appealing choice. Furthermore, their ease of manufacturing further enhances their appeal (Gao,2021). Polymer electrolytes find extensive application across a wide range of sectors, encompassing consumer electronics, electric vehicles, and energy storage systems. Moreover, their utilization extends to medical and military domains, where the paramount considerations of safety and dependability hold utmost significance (Chattopadhyay,2023). Utilization of polymer electrolytes holds promise in preventing severe challenges, such as leakage of the electrolyte, flammability, and lithium dendrite formation, thereby bolstering the thermal and electrochemical stabilities of LMBs (Castillo, 2021).

Solid polymer electrolytes (SPEs), which are made up of a lithium salt dispersed in the solid polymer matrix, have better mechanical strength along with chemical, electrochemical, and thermal stability than that of conventional liquid electrolytes. Combination of SPEs and lithium metal anode is attractive for high batteries having long service life but their ionic conductivity at ambient temperature and large electrolyte/electrode interfacial resistance are main drawbacks for their commercial applications (Lee, 2023). Gel polymer electrolytes (GPEs) was introduced to overcome the weaknesses of SPEs by absorbing liquid electrolyte into polymer matrix. As a compromise, gel polymer electrolytes (GPE), which consist of a liquid organic electrolyte containing a polymer matrix and lithium salt, have advantages of both liquid and solid-state electrolytes (Hu,2020). GPEs present distinct advantages over solid electrolytes when it comes to enhancing the connection with electrodes (Li, 2023). Considerable advancements have been achieved in the enhancement of GPEs, resulting in their extensive utilization across diverse battery systems. Similar to liquid electrolytes, GPEs can provide high ionic conductivity, while they have superior electrochemical stability with functional additives, flexible processability, and no leakage (Cui,2017). Within a GPE structure, polymer chains intertwine to create a polymer network characterized by interlinked pores. These pores play a crucial role in enhancing the efficient uptake of the liquid organic electrolyte and facilitating Li^+ mobility . The liquid component plays an important role in enhancing ionic conductivity and interfacial stability, while the polymer matrix provides relatively higher mechanical strength and sufficient shape flexibility. The presence of the liquid component is crucial for improving both ionic conductivity and interfacial stability, whereas the polymer matrix is responsible for imparting greater mechanical strength and shape flexibility. At this stage, GPEs are the most promising electrolytes that can be easily adapted to existing battery technologies. Effective trapping of the liquid component within the polymer matrix can eliminate the leakage problem and enables the use of GPEs in LMBs. Moreover, the remarkable flexibility and elasticity of polymer structures enable them to withstand the adverse effects of electrode volume changes and dendrite puncture-induced short circuits in traditional separators. As a result, the development and production of advanced GPEs are considered a logical approach to achieving both safety and longevity in LMBs (Ren, 2021).

In this review article, state-of-the art polymer electrolytes are discussed with special emphasis of safety issues with conventional liquid electrolytes, gel polymer electrolytes, in situ polymerization method, nanocomposite (NCGPEs) and nanohybrid polymer electrolytes (NHGPEs).

2. SAFETY ISSUES WITH LIQUID ORGANIC ELECTROLYTES

Determination of an appropriate electrolyte is crucial for maintaining high performing and safe LIB, as the electrolyte serves as a critical interfacial component responsible for ion transport and interfacial stability towards the electrodes. Electrolytes utilized in LIBs must fulfill a range of requirements. High boiling point, low vapor pressure and melting point are essential characteristics that allow for a broad range of operating temperatures. Additionally, favorable transport properties that facilitate the rapid movement of lithium ions between the anode and cathode, as well as chemical and electrochemical stability to preserve the integrity of the electrolyte during the charge-discharge process, are vital. Other important properties include high ionic conductivity to achieve high power by facilitating the movement of lithium-ion cations, the ability to form solvates with salts at low temperatures (particularly for low-temperature cells), and the formation of an SEI film to prevent side reactions between anode and electrolyte. The deterioration of the aluminum material, which functions as the current collector, is also a significant aspect to consider. To avoid corrosive pitting of the collector, it is imperative for the electrolyte to passivate the electrolyte-aluminum interface (Piglowska, 2021).

The conventional liquid organic electrolytes consist of carbonate solvents, such as ethylene carbonate (EC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), and propylene carbonate (PC). It is important to note that these solvents are flammable and have the potential to cause a catastrophic failure if subjected to excessive heat, internal short circuits, or battery penetration (Zhou,2021). Cyclic carbonates, primarily PC and EC, exhibit a significantly high dielectric constant. This characteristic increases solubility of lithium salts that possess high viscosity, owing to the strong intermolecular interactions. However, high dielectric constant also hampers the movement of ions. On the other hand, linear carbonates demonstrate lower viscosity due to their linear structure, which increases degree of freedom of solvent molecules (as shown in Table 1). The electrolyte viscosity can be effectively reduced and electrolyte conductivity can be enhanced through incorporating linear carbonates, such as EMC, DMC and DEC. To optimize cell capacity and cycling performance, a combination of linear and cyclic carbonates is frequently used, such as the EC/DMC mixture in a 1:1 weight ratio or EC/EMC in a 3:7 ratio by volume. This mixture positively impacts the cell capacity. Nevertheless, lower viscosity of this mixture is linked to a lower flash point, which raises safety concerns (Piglowska, 2021).

Regrettably, these linear carbonates possess a significant level of volatility and flammability, exhibiting flash points (FPs) within the range of room temperature (approximately 16 to 33°C). When combined with an oxidant and a source of ignition, they have the potential to initiate fires and explosions. To address the fire risk associated with the electrolyte, one approach is to employ non-flammable solvents or incorporate flame-retardant additives into the electrolyte composition (Hess, 2015). Examples of flame-retarding solvents used in the electrolyte include trimethyl phosphate (TMP), triethyl phosphate (TEP), tributyl phosphate (TBP), and triphenyl phosphate (TPP). Among the various options, TMP is especially appealing because can dissolve lithium salts at high concentrations, besides it has high dielectric constant, low viscosity and wide liquid temperature window (- 46 to 197°C). Nevertheless, stability of TMP is compromised in the presence of lithium metal, leading to its decomposition at a potential of 1.2 V versus the Li/Li^+ reference electrode. Moreover, utilization of TMP does not provide a fundamental solution to the dendrite problem as it is unable to form a stable SEI on the surface of lithium metal (Zhou, 2021).

Stability of lithium metal anode is heavily dependent on SEI. However, SEI layer undergoes continuous reforming and consumes electrolyte during cycling. Consequently, Li metal anodes (LMAs) experience significant capacity loss, with Coulombic efficiencies above 95% (Sayavong, 2023). The rational design of a stable SEI has been hindered by the inability to control its structure and stability. In order to improve battery performance of LMBs having liquid electrolyte, Gao et al. designed an SEI by using a reactive polymer composite (RPC) having inorganic nanoparticle and two dimensional (2D) nanomaterial that effectively mitigates electrolyte consumption during SEI formation and maintenance. They coated RPC as the three dimensional host on the lithium metal anode to stabilize SEI layer. The SEI layer in this RPC stabilized lithium metal electrode comprised lithium fluoride nanoparticles, and graphene oxide sheets, a polymeric lithium salt. Notably, this structure displays distinct characteristics compared to the

SEI derived from organic electrolyte and demonstrates exceptional passivation properties, uniformity, and mechanical durability. By utilizing the polymer-inorganic SEI, they achieved efficient lithium deposition, high capacity and and stable cycling of 4 V Li|NMC532 cells. This study revealed that polymer/inorganic composition of the SEI layer with 3D RPC host structure outstandinly stabilized and effectively suppressed electrolyte decomposition. As a result, Li metal batteries can undergo stable cycling even with limited electrolyte, marking a significant advancement in reducing electrolyte consumption. Additionally, this technique was proficiently broadened to devise stable SEI films for sodium and zinc anodes (Gao, 2019). Even though, stabilization of SEI by using this 3 D host of RPC having nanoparticles and nanomaterials is a progress for reducing organic electrolyte loss in LMBs and so obtaining stable discharge profile for 200 cycles, this design is still not sufficient for practical applications of LMBs. In addition, the utilization of ionic liquids (IL) in GPEs holds great promise due to their exceptional electrochemical properties, which set them apart from organic solvents. In contrast to the safety hazards posed by organic solvents, IL offer a safer alternative for various applications (Garaga, 2023).

Table 1: A compilation of carbonate solvents along with their enhanced attributes in comparison to traditional solvent constituents, wherein "+"/"-" denotes a favorable/disfavorable impact on the electrochemical system, while "0" indicates no apparent effects (Pigloska,2021).

Solvent	EC	PC	EMC	DEC	DMC
Melting point	+	-	-	-	0
Boiling point	+	+	-	-	-
Viscosity	+	+	-	-	-
Dielectric constant	+	+	-	-	-
Construction to SEI	+	-	-	-	-
Flash point	+	+	-	-	-
Safety	+	0	-	-	-
Anodic stability	+	+	0	0	0

3. GEL POLYMER ELECTROLYTES

Composition of GPEs allows for their classification into three distinct categories. These categories are comprised of GPEs with plasticizers, GPEs with inorganic fillers, and GPEs that contain both plasticizer and inorganic filler. The presence of lithium salt is essential in the electrolyte as it facilitates the movement of ions within the polymer framework. Additionally, the polymer itself provides the required mechanical strength to accommodate the electrolyte. The utilization of inorganic fillers in GPEs can be traced back to the early 1980s when researchers aimed to increase mechanical stability of the polymer matrix (Huy, 2021). To enhance properties of polymer matrices and achieve high performance in LIBs, blending, copolymerization, and crosslinking techniques are commonly employed. Within GPEs, the liquid electrolyte is securely held by the polymer through physical and chemical cross-linking, resulting in improved stability and functionality (Kim,2010).

Polymer matrices commonly employed in GPEs encompass polyethylene oxide (PEO) (Xue,2015), poly (vinylidene fluoride) (PVDF) (Balakrishnan, 2023), poly(methyl methacrylate) (PMMA) (Hosseinioun, 2019) and polyacrylonitrile (PAN) (Liu, 2016). GPEs can be fabricated by encapsulating liquid electrolytes within various polymer hosts. In this scenario, salt solutions are confined within the polymeric framework, facilitating the process of ionic conduction, while the host polymer imparts mechanical stability. The characteristics and structure of the GPE are contingent upon the specific type and quantity of salt and solvent incorporated within polymer matrix (Tafur, 2014). Preparation of GPEs involves primarily two different techniques, which are determined by inherent characteristics of preparation process. One approach utilizes a porous polymer matrix that enables uptake of the liquid electrolyte by swelling. This objective can be accomplished through two methods: selectively extracting a solvent from a polymer solution or directly creating fibrous structures with inherent porosity within the polymer matrix. Solution casting and phase inversion are the two widely studied processes under this technique. In solution casting process, a polymer, such as PEO and PVDF-HFP or blend of these two is dissolved the liquid electrolyte containing lithium salt and organic solvents. The polymer concentration is usually in the range of 5-20% by weight of the GPE (Song,1999). Since high cycle life cannot be achieved in lithium polymer batteries obtained with this technique, they have not been preferred in recent years. In the second method, polymer membrane with a microporous and channeled morphology is prepared by different methods (mostly by phase inversion approach). This membrane replaces the separator so there is no need to use additional separator. Then, by soaking the polymer membrane in organic electrolyte, which usually contains 1-1.2 M lithium salt ($LiPF_6$, LiTFSI, etc.), the membrane becomes electrochemically active and so the gel polymer electrolyte is obtained (Liu,2016). When compared to polymer membrane obtained by solution casting, GPE membrane by phase inversion method, which has interconnected and open micropores, has a much higher surface area compared to the conventional organic electrolyte/separator system, thus increasing ion storage and Li^+ mobility (high t_{Li+}) (Pu,2006). Although the Li^+ transference number of PVDF-HFP based GPEs is higher than other polymer matrix materials, the ionic conductivities of GPEs are lower than liquid organic electrolytes. When this approach is used, the performance of lithium-ion polymer batteries can be increased by adding ionic liquids (ILs) or nano-sized materials or both into the GPE system. In a 2023 study, blend ethyl-methyl imidazolium bis(trifluoromethanesulfonyl)imide (EMIMTFSI) and PVDF-HFP was combined with 3% Al_2O_3 nanofibers (by weight of GPE), characterized by diameters of 2–6 nm and lengths of 200 - 400 nm. This formulation yielded about 200% increase in the ionic conductivity of GPE (Garaga, 2023).

To summarize, GPEs can be synthesized by means of phase inversion, solution casting and in situ polymerization methods. These techniques have been acknowledged for their energy efficiency, cost-effectiveness, and environmentally friendly attributes when compared to alternative approaches for GPE preparation (Kim, 2019). The application of suitable nanoparticles and nanomaterials in GPEs has recently emerged as a highly promising strategy. This advancement is focused on improving mechanical strength of the membrane, enhancing ionic conductivity, and facilitating efficient transfer of Li^+ ions. Ultimately, it leads to superior performance of GPEs in LIBs (Long,2016).

3.1. Anion receptors and single ion conducting gel polymer electrolytes

SPEs that consist of a polymer matrix and lithium salt are commonly referred to as bi-ionic conductors. In these conductors, the cations form bonds with the polar groups of the polymer electrolyte, leading to a faster movement of anions. As a result, anions contribute more to the overall ionic conductivity compared to cations. However, the migration of anions towards the anode can lead to a significant concentration polarization, which in turn causes a notable decrease in conductivity and an increase in cell impedance over time. The property known as t_{Li+} plays a crucial role in determining whether the conductivity is solely attributed to lithium ions. Typically, lithium ion transport occurs not only with free lithium ions but also with ions of varying sizes that are combined within the system (Jo, 2002). To reduce polarization, two approaches are implemented to limit the movement of anions. The initial approach is to bond anions to the polymer's main chain (backbone), which is a prevalent method for obtaining single ion-conducting polymers. The second approach involves incorporating an anion receptor that exhibits a preference for interacting with anions. The recognition and binding of these receptors to anions are facilitated through hydrogen bond interactions, covalent binding of the anion, or Lewis acid-base interactions. Recently, utilization of boron-based anion receptors as electrolyte additives in lithium-ion batteries and metal-air batteries has gained momentum due to the growing interest in their potential. These receptors, commonly used in biosensors, are being studied for developing high capacity batteries that can operate efficiently at elevated voltages. Boron-based anion receptors have the potential to serve as electrolyte additives in carbonated electrolyte solutions. This potential benefit resides in their capacity to enhance cycling efficiency of lithium-ion, lithium metal and lithium air batteries, while also enhancing the transfer of lithium ions and the conductivity of ions. Furthermore, these anion receptors have been found to have a crucial role in stabilizing SEI layer on the surface of anode (Reddy, 2014). However, presence of insoluble inorganic salts, including LiF, Li_2O_2, and Li_2CO_3, within the SEI layer poses challenges in terms of electron and lithium ion transportation. Consequently, this leads to an increase in impedance and a decline in capacity. To overcome these obstacles, anion receptors within the SEI layer exhibit a specific binding attraction force, which facilitates the dissolution of anions such as F^-, OH^-, and O^{2-}. This dissolution process enables the removal of these anions from the SEI layer, thereby mitigating the impedance increase and capacity loss (Choi, 2013).

Several studies have demonstrated that boron anion receptors, including tris(pentafluorophenyl)borane (TPFPB), have a positive impact on the formation and thermal stability of the solid electrolyte interphase (SEI) on the graphite anode. This effect is particularly observed during the initial galvanostatic cycling of lithium-ion batteries that utilize a carbonaceous meso-carbon microbead (MCMB) anode. The presence of boron anion receptors enhances the SEI formation and improves its resistance to thermal degradation, thereby contributing to the overall performance and longevity of the battery system (Sun, 2003). The research conducted by Amine et al. demonstrated that the incorporation of TPFPB additive at concentrations lower than 3% in $LiPF_6$-based liquid organic electrolytes has a significant impact on the performance of NMC cathode/garaphite anode batteries. Specifically, this additive enables the battery to charge and discharge at high power levels. This improvement can be attributed to the role of TPFPB in breaking down the accumulated LiF within the SEI layer, acting as an anion receptor. Consequently, the impedance decreases, resulting in enhanced lithium ion conductivity (Qin, 2010).

The incorporation of boron anion receptors as additives to the polymer electrolyte has yielded promising results. As a result, recent research efforts have been focused on the development of single-ion-conducting polymer electrolytes. This involves the covalent immobilization of anionic groups on the polymer backbone, which selectively allows the mobility of Li+ cations throughout the polymer matrix. Compared to binary ionic conductors, these ion-selective polymers offer several advantages in battery operation, such as minimizing cell polarization and dendrite growth. These findings underscore the potential of utilizing these polymer electrolytes to enhance the efficiency and performance of batteries (Gao, 2021). Wang et al. successfully synthesized polymeric lithium tartaric acid borate (PLTB) with boron incorporated into the main polymer chain. This synthesis was accomplished in a single step. The researchers then proceeded to create a microporous membrane by combining PVDF-HFP and PLTB, which was subsequently gelled with PC. Despite achieving a high t_{Li+} above 0.90, the resulting ionic conductivity at 20°C was below 0.15 mS/cm. In subsequent experiments, the team tripled the ionic conductivity and obtained a t_{Li+} value above 0.90 by gelling the polymer membrane with a conventional liquid electrolyte. However, the achieved ionic conductivity was still insufficient for the efficient operation of this technology at high charge-discharge rates or low temperatures, such as those required for electric vehicles (Wang, 2013).

In a 2023 study by Wang *et. al*, the successful synthesis of a novel GPE membrane, known as polyethyleneimine (PEI)/PVDF-HFP cross-linked membrane and electrolyte (PPCM GPE), has been reported. The presence of PEI molecular chains, which contain amine groups, played a significant role in the formation of this membrane. These amine groups acted as abundant anion receptors and effectively immobilized the anions present in the electrolytes. The unique cross-linked structure of PPCM, combined with the utilization of its amine groups, resulted in a high t_{Li+} value of 0.70. By incorporating PPCM GPE into the assembled cells, the battery performance was significantly improved due to the enhanced ionic conductivity and Li^+ transference number. This highlights the potential practical application of

Li/PPCM/LFP full cells in the field of LMBs. To further enhance the safety and rate capabilities of LMBs, a feasible approach involves the development of porous polymer membranes that possess a gradient distribution of pores and are rich in anion receptors (Wang, 2023).

3.2. *In situ* polymerized gel polymer electrolytes

The conventional manufacturing methods for polymer electrolytes are commonly known as ex situ processes. In these processes, the polymer electrolytes are prepared as separate films and then assembled into the battery. However, this approach often leads to inadequate physical contact between the ex situ polymer electrolytes and the electrodes due to the presence of voids within the electrodes. As a result, the polymer electrolyte films prepared in this manner are unable to fully penetrate the porous cathodes in ex situ processes, resulting in a significant decrease in the utilization of active materials and achievable energy density. To address this issue and enhance the interfacial contact between the electrolytes and electrodes, an alternative method called in situ polymerization of polymer electrolytes has been proposed. This approach involves the polymerization of electrolytes directly within the battery. In situ polymerization has emerged as a highly promising technique for reducing interfacial resistance and improving interfacial compatibility, thereby enabling the production of commercial lithium-based batteries. In comparison to ex situ processes, the in situ polymerization process is compatible with the production of existing liquid-based batteries. This eliminates the need for additional preparation of electrolyte films or the evaporation of solvents. This compatibility further emphasizes the potential of in situ polymerization as a viable manufacturing method for various types of batteries (Xiao,2023). Moreover, in addition to the advantages stated earlier, it has the ability to enhance the overall design of bare cells. This is achieved by injecting the precursor material before the polymerization process, enabling the desired shapes to solidify and improving the form factor. The enhancement of mechanical performance without the need to increase the thickness of the glassy polymer electrolyte (GPE) can be achieved through the utilization of in situ polymerization in conjunction with the cross-linked network design flexibility (Shim,2017). Additionally, it is a method that is scalable, easy to produce, and fast (Ren,2021).

In the *in situ* polymerization, a lithium-ion cell is fabricated by assembling the liquid precursor solution consisting of lithium salt, organic solvent composition, monomer(s), reaction initiator and electrolyte additives with an anode, separator and cathode. The resulting battery is then heated at 60-80 ^{o}C or exposed to UV light, and gelation occurs through *in situ* polymerization within the battery. This technique is called *in situ* polymerization. The obtained GPEs by this method has a higher viscosity than liquid electrolyte and consists of homogeneously dispersed lithium solution within a cross-linked based polymer network (e.g. poly-acrylate, polyamide, etc.) and thus the *insitu* formation of GPE results in the development of a superior electrode/electrolyte interface. This interface exhibits enhanced receptivity towards Li+ ion migration, thereby promoting homogeneous Li^+ dispersion and preventing the formation of Li dendrites in the LMBs (Chen,2021). This method allowes rapid preparation of GPE films in the battery and improvement of their electrochemical compatibility. Chemical cross-linking results in an irreversible gel. Therefore, chemically cross-linked GPEs have superior thermal and dimensional stability at high temperatures compared to physically cross-linked GPEs. The structure and properties of polymer chains are significantly influenced by monomers. In the synthesis of chemically cross-linked GPEs, acrylate cross-linkers are commonly used due to their fast cross-linking reaction (Choi,2009).

Preparation of GPEs by thermal *in situ* method in batteries is based on free radical polymerization and cross-linking (Park,2023). For this purpose, free radical initiator, liquid electrolyte, vinyl monomers (acrylate, methacrylate, acrylonitrile, carbonate derivatives, etc.) and multifunctional cross-linkers (trimethylolpropane triacrylate (DTPA), poly(ethylene glycol) diacrylate (PEGDA), ethoxylated trimethylolpropane triacrylate (ETPTA), etc.) are commonly used (Chae,2023). Acrylate-based polymers are known to provide high ionic conductivity and reduce the interface resistance between the electrode and the gel polymer electrolyte. Moreover, their stability against electrochemical oxidation has made them promising polymer matrices for electrolytes with high electrochemical stability, especially in high energy density lithium battery cells. For example, polyethylcyanoacrylate (PECA), which has strong coordinating and high electrochemical stability due to the nitrile groups in its structure, is one of the promising matrices for polymer electrolytes. Cui *et al.* synthesized PECA-based GPE thanks to a rapid and reproducible in situ polymerization strategy. They obtained PECA-based GPE with high efficiency by anionic polymerization of ethylcyanoacrylate (ECA) with 4 M $LiClO_4$ solution prepared in EC/DMC solvent mixture with volumetric ratio 1:1. Resulting GPE had the ionic conductivity of 2.7 $mScm^{-1}$ at room temperature and it was electrochemically stable up to 4.8 V. In addition, $LiFePO_4$/PECA-GPE/Li and $LiNi_{1.5}Mn_{0.5}O_4$/PECA-GPE/Li batteries produced with this electrolyte had a stable charge/discharge profile as well as high C-rate and battery cycle performances. By this study, high electrochemical stability was achieved thanks to the nitrile functional groups of the polymer. In addition, the interaction of nitrile and ester functional groups with Li^+ ions contributed to the increase in the solubility of the lithium salt and efficient charge transfer (Cui,2017).

Liu et al. polymerized PEGDA in organic liquid electrolyte by *in situ* thermal polymerization, where PEGDA polymer was the polymer matrix, while cellulose acetate (CA) which has a large number of polar groups was used as an additive. High ionic conductivity (8.81 $mS.cm^{-1}$ at 30°C) and high lithium transference number (0.79) were obtained in GPE and the electrochemical stability window was measured as 4.56 V. Addition of CA increased the ion-dipole interaction, which facilitated the transport of Li^+ ions. With the structural analysis of the GPE, it was observed that as an additive CA improved the electrode/electrolyte interface by reducing the viscosity in the polymerization of PEGDA (Liu,2020).

In another recent study, published in the journal Nature in 2022, which draws attention to the importance of using poly(ethyleneglycol) diacrylate (PEGDA) polymer as a polymer matrix, it was reported that by in situ polymerization of PEGDA and butyl acrylate (BA) in the presence of succinonitrile and LiTFSI, elastomeric solid polymer electrolyte having superior mechanical properties was obtained. Operating at room temperature with a voltage of 4.5 V, the LMB, incorporating a LiNi0.83Mn0.06Co0.11O2 cathode, achieved an energy density surpassing 410 Wh/kg. This exceptional performance was attributed to the presence of an in situ formed elastomer, which facilitated the development of a 3D interconnected crystalline phase consisting of ion conductive plastic crystals. Furthermore, the solid-state PEGDA-co-BA electrolyte employed in this system exhibited a remarkable Coulombic efficiency of 100%, ensuring efficient charge and discharge processes. Additionally, this electrolyte demonstrated excellent adaptability to volume changes, enabling the LMB to endure long-term lithium plating and stripping cycles (Lee,2022).

In GPEs, the solvent is encapsulated within the GPE. When phase inversion method is used along with electrochemical activation of the membrane with the liquid electrolyte, electrolyte uptake is an improtant parameter because high electrolyte uptake of the polymer matrix results in high conductivity. The high electrolyte uptake is closely related to the porosity of the polymer membrane (Zhang, 2014). The polymer electrolytes, which are composed of PVdF/PAN, PVdF-co-HFP/PAN, PEO/PMMA, PEO/Polyurethanes, and P(VdF-co-HFP)/PVAc blends, have been thoroughly examined as the primary material for the polymer electrolyte matrix. In a recent novel study, the miscibility of the PVdF/PMMA blend polymer electrolyte is improved through a unique approach. This involves the in-situ polymerization of methyl methacrylate monomers within the PVdF matrix. The phase inversion membrane composed of PVdF/PMMA blend displayed a uniform microporous structure that boosts a high level of porosity. This unique structure allows for exceptional electrolyte uptake, with an impressive increase of above 400%. Moreover, the membrane exhibits excellent retention capabilities and a reduced contact angle, further enhancing its overall efficiency. The application of the in-situ blend electrolyte proves to be highly advantageous in rechargeable lithium-ion batteries, even under extreme temperature conditions. Its superior performance can be attributed to its unique composition and optimized properties (5.2 $mS.cm^{-1}$ ionic conductivity, electrochemical stability up to 4.8 V vs. Li), enabling enhanced battery performance and stability (Balakrishnan, 2023). The enhanced characteristics of the GPE ensures the benefit of utilizing the in-situ polymerization technique to improve the electrochemical capabilities of the GPE.

3.3. Nanocomposite Gel Polymer Electrolytes

Studies have continuously been done on composite polymer electrolytes (CPEs) to overcome the shortcomings of both the low ionic conductivity of SPEs and the low mechanical strength of GPEs. Although the ionic conductivities of GPEs can reach 10^{-3} $S.cm^{-1}$, their low mechanical strength and poor interfacial properties are obstacles to their practical applications (Long,2016). Thermal, mechanical and electrochemical properties of CPEs depend on the properties of the filler, such as particle size, porosity, concentration, surface area, and interaction between polymer chains and the filler (Kim,2014).

The mechanical strength of polymer electrolytes, especially GPEs, is mainly determined by the polymer matrix. As a result of the combination of the polymer-salt system with the solvent, which is a plasticizer, the solvent reduces the crystalline phase of the polymer matrix. This promotes segmental movement of the polymer matrix and positively affects the ionic conductivity of GPE, while reducing the mechanical strength of the polymer matrix (Hassoun,2015). In this case, dendritic Li can easily pierce GPEs and cause a short circuit between the cathode and anode (An,2022). In order to overcome the shortcomings of both the low ionic conductivity of solid-state polymer electrolytes and the low mechanical strength of GPEs and to improve their ion transport properties, studies on composite polymer electrolytes (CPEs) have been focused on in recent years The addition of inorganic fillers to the polymer/salt system has proven to be a highly effective approach in enhancing the electrochemical performance of gel-state polymer electrolytes (GPEs). This strategy has demonstrated promising results by improving the electrolytic conductance, as well as enhancing the mechanical and thermal stability of the GPEs. The incorporation of these inorganic fillers has shown great potential in advancing the overall performance of GPEs (Huy, 2021).

Lithium-ion transference number (t_{Li+}), which constitutes the share of lithium ion in the total current carried in the electrolyte, is another critical parameter in achieving good cycling performance in lithium-ion batteries. Although, ideally the t_{Li+} value is desired to be close to 1, most electrolytes having high conductivities may have a t_{Li+} value less than 0.5 due to the concentration polarization of ions that occurs during repeated charge/discharge cycles. This causes long cycle performance to deteriorate. The t_{Li+} value of lithium-ion batteries can be increased by adding single-ion conductors and Lewis acids, such as ceramic fillers (SiO_2, Al_2O_3 and TiO_2) and boron-based anion receptors to the electrolyte. When boron anion receptors are used, this improvement is due to the ability to effectively trap anions of lithium salts, thanks to the Lewis acid-base interaction between the empty p orbital of boron and the basic anion of the lithium salt. By improving the electrochemical properties of the electrolyte, the performance and cycle life of the battery increases (Reddy, 2014). The addition of fillers can interfere with the arrangement of polymer chains, reducing the crystallinity of the polymer matrix and thus increasing the amorphous region for better Li^+ migration. Additionally, thermal stability, mechanical durability and electrochemical stability can be improved because all of these three properties are closely dependent on the structure of the polymer electrolyte (Boaretto,2020). For example, Cho *et al.* synthesized GPE from PAN-PEGDA, $LiPF_6/LiCF_3SO_3$ salt mixture and nano-structured inorganic filler materials (e.g., TiO_2, Al_2O_3, $CaCO_3$, $CaTiO_3$, $BaTiO_3$) and improved the discharge capacity and cycle life of the LMB (Huy, 2021) . Higher ionic conductivity and lower interface resistance between Li metal and GPE were obtained in all three polymer nanocomposite GPEs having added nanostructured inorganic fillers, compared to GPEs without added nanostructured inorganic fillers. The reason behind this better Li^+ transport is the fact that the high surface area of nanoparticles improves chemical stability by affecting cross-linking in the polymer electrolyte (Cho, 2007). Boron compounds, which are used as Lewis acids especially in lithium ion batteries, improve the electrochemical properties of the electrolyte by acting as anion receptors. This improvement is due to boron's ability to effectively retain anions of lithium salts, thanks to the Lewis acid-base interaction between the empty p orbital and the basic anion of the lithium salt. By improving the electrochemical properties of the electrolyte, the performance and cycle life of the battery increases (Reddy,2014).

Wang *et al.* prepared a polymer nanocomposite membrane consisting of poly(acrylonitrile-co-vinylacetate), PMMA and TiO_2 nanoparticles by blending and gelled it with 1 M $LiPF_6$ electrolyte solution to obtain GPE-PAVM:TiO_2. The ionic conductivity of this electrolyte was found to be approximately 10 times that of the liquid electrolyte prepared with a commercial separator. In addition, thanks to the interaction with TiO_2, the t_{Li}^+ value of GPE-PAVM:TiO_2 was 0.7 by fixing PF_6^- ions and the suppression of PF_6^- degradation enabled high electrochemical stability up to 6.5 V (vs. Li/Li^+). The immobilization of $PF6^-$ ions also resulted in the formation of a stable solid electrolyte interface and 71% capacity retention of the $LiPO_4$/GPE-PAVM:TiO_2/graphite battery after 1000 charge/discharge cycles at 20^{o}C (Wang,2016).

Liu *et al.* conducted a study in which they synthesized a cross-linked GPE through thermal *in situ* polymerization. Synthesized GPE was composed of cellulose acetate (CA) as the matrix, cross-linker PEGDA, and layered hexagonal boron nitride (BN). The polymerization process occurred in a single step at a temperature of 70°C. When CA and BN were combined using the azobisisobutyronitrile (AIBN) polymer initiator, the presence of polar groups in CA and the Lewis acid properties of BN contributed to an increase in the ionic conductivity of the gel polymer electrolyte. The interaction between the Lewis acid-base properties of GPE and BN resulted in a reduction of ion pairing, thereby enabling the efficient transportation of Li^+ ions. The incorporation of 1% BN into the GPE demonstrated a synergistic effect with the CA matrix, leading to a GPE with remarkable properties. This included a high ionic conductivity of 8.9 $mS.cm^{-1}$ at 30°C, electrochemical stability up to 5.5 V, and excellent thermal stability. results of this study emphasize the considerable potential of boron nitride as a valuable additive in improving the efficiency of GPEs (Liu,2021).

3.4. Nanohybrid Gel Polymer Electrolytes

In order to successfully commercialize LMBs, it is crucial to optimize not only the high ionic conductivity values achieved in GPEs but also their t_{Li+} values and mechanical properties. While GPEs may exhibit favorable ionic conductivity, it is imperative to concurrently enhance the t_{Li+} values and mechanical properties to ensure their viability in the market. In light of recent advancements in research, the integration of nanoparticles or nanomaterials with chemical bonding into a polymer matrix through in situ polymerization has proven to be a successful approach in improving the mechanical and electrochemical properties of GPEs. By this method, uniform dispersion nanomaterial in polymer matrix is ensured. Based on scientific research findings, thermal *in-situ* polymerization of surface-functionalized nanomaterials and crosslinking monomers is a promising method because nanohybrid GPEs (NHGPEs) having high mechanical strength, ionic conductivity and t_{Li+} can be synthesized for high-performance and safe LMBs (Shin,2016). Numerous studies have provided evidence that inorganic materials have the potential to enhance both mechanical strength and electrochemical stability. However, the inherent characteristics of inorganic nanoparticles, such as high surface energy and low zeta potential, often result in particle agglomeration and inadequate contact between fillers and polymers. This, in turn, compromises the conduction of Li^+ ions. To address the challenges faced by LMBs, it is imperative to explore methods that can enhance the affinity of fillers for the polymer matrix and establish a uniform pathway for Li^+

transport. This can be achieved by developing composite polymer electrolytes (CPEs) with high ionic conductivity. Recent research has shown that surface modification of inorganic particles has yielded significant advancements in improving both ionic conductivity and interface contact in CPEs. By functionalizing the particles with organic groups, the surface energy difference between fillers and the polymer matrix can be minimized, leading to improved interfacial adhesive strength. This chemical bonding enhances the compatibility between organic and inorganic materials, facilitating the homogenization of lithium-ion flow. Moreover, grafting functional groups onto particle surfaces can introduce new properties to nanoparticles. The performance of CPEs is greatly influenced by the properties of the filler, including particle size, porosity, concentration, surface area, and the interaction between polymer chains and inorganic fillers. Despite the performance enhancement achieved through the addition of inorganic fillers, effectively dispersing these materials within the polymer electrolyte matrix remains a challenge that requires further investigation. Particularly, the homogeneous dispersion of nano-sized inorganic filler materials with high surface area in the polymer matrix is difficult to achieve, often resulting in agglomeration and the formation of crystal structures (phase separation) in CPEs (Wu, 2023).

During the production of nanocomposites, one of the ways to improve the interaction between the polymer and the synthesized nanoparticles (NPs) is to make chemical crosslinking through in-situ polymerization by using polymerizable active nanoparticles and nanomaterials (Zhai,2017). When fillers are physically blended with polymers without any covalent bonding, agglomeration of fillers and poor polymer-ceramic interaction are inevitable and the ionic conductivity of the electrolyte is restricted, thus shortening battery life (Wu,2023). In situ polymerization can effectively solve the problems of inadequate interface between electrode and electrolyte, which is the main reason behind the poor cycling performance due to high interfacial resistance. For this purpose, polymerizable functional groups are used as cross-linkers and nanohybrid composite polymer electrolytes with a polymeric network with high shear modulus and conductivity can be obtained as a result of in-situ polymerization with surface-functionalized nano-fillers (Chae,2023). As a proof-of-concept example of the fact that chemical bonding increases the interface compatibility between inorganic and organic materials and facilitates the homogenization of lithium-ion flow, Shin et al. effectively synthesized stringy PAN membranes through the integration of mesoporous SiO_2 nanoparticles that were modified with methacrylate groups (MA-SiO_2). Subsequently, a nanocomposite GPE, which was cross-linked in-situ, was fabricated by utilizing a composite membrane, mesoporous MA-SiO_2 nanoparticles, and electrolyte solution containing a limited amount of tri(ethylene glycol) diacrylate (TEGDA). By effectively encapsulating the electrolyte solution, this cross-linked nanocomposite GPE ensured the absence of solvent leakage and exhibited desirable interfacial properties. Utilization of mesoporous SiO_2 nanoparticles in the in-situ chemical cross-linking process proved to be more effective than non-porous SiO_2 nanoparticles in achieving superior battery performance including discharge capacity, rate capability, capacity retention, and stability during cycling tests at high temperature (Shin,2016).

In another study using PEGDA crosslinker, Zhan et al. developed a partially cross-linked PEO-based composite solid electrolyte (p-V-SiO_2/PEO CPE) containing silica NPs functionalized with porous vinyl group (p-V-SiO_2) as inorganic filler and PEGDA as cross-linker. The electrochemical performance of p-V-SiO_2/PEO CPE containing p-V-SiO_2 cross-linked to PEGDA is much higher than that of p-SiO_2/PEO CPE containing only inactive porous SiO_2 NPs (p-SiO_2) added as filler. While ionic conductivity quadrupled, thermal stability and mechanical strength were also higher. In addition, while only below 10% capacity loss was observed after 300 cycles at 60°C and 0.5C cycle rate, the capacity decay was lost at a much faster rate in p-SiO_2/PEO CPE without polymer cross-linking and complete capacity loss was observed before the 200th cycle (Zhan,2021).

4. CONCLUSIONS

In conclusion, the limited energy density and high cost of lithium-ion batteries are the primary reasons why they have not yet become prevalent in electric vehicles and grid-scale energy storage systems. Overcoming the two challenges is of utmost significance for widespread adoption of lithium-ion batteries in these applications. These are battery safety and energy density per unit mass and volume. The safety problem that manifests itself with explosions and fires in the battery is caused by the formation of lithium dendrite that occurs with the use of existing liquid electrolyte. The problem of dendrite formation can be comprehensively eliminated with solid-state electrolytes, but in the current situation, the ionic conductivity of solid-state electrolytes is very low at room temperature. On the other hand, by using GPE technology, in which liquid electrolyte is trapped inside polymer matrix, it is possible to prevent lithium dendrite formation without compromising ionic conductivity. With GPEs, the electrochemical stability of the electrolyte can be improved, and so it is possible to make electrolytes currently suitable for 4 V systems operable at 5 V levels. Thus, the energy density in the battery can be increased. If these developments are achieved, it will be possible to produce batteries with energy density beyond 500 Wh/kg.

Main goal of this review was to gather recent literature on gel polymer electrolytes, with a particular focus on the in situ polymerization technique and the utilization of anion receptor groups within the polymer structure, inorganic fillers, nanofillers, and nanomaterials. The research findings suggest that the thermal in situ polymerization of acrylate monomers, in conjunction with surface-functionalized nano-fillers and nanomaterials, offers a considerable potential for the production of GPEs. These electrolytes possess desirable attributes including enhanced ionic conductivity, selective lithium ion mobility (high t_{Li+}), extensive electrochemical stability, and superior mechanical properties. By this method, versatile nanostructured nanocomposite and nanohybrid gel polymer electrolytes can be developed for safe and high-performing LMBs. For this reason, further research efforts focusing on use of surface functionalized nanomaterials chemically cross-linked to the polymer matrix for safe and affordable LMBs is necessary. This will not only boost manufacturing of robust lithium-metal batteries but also have impact on the implementation of non-lithium-metal based battery technologies by employing similar nanostructured polymer electrolytes.

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