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SOLID POLYMER ELECTROLYTES BASED ON IONIC LIQUID FOR LITHIUM SECONDARY BATTERY

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Abstract

This paper discusses the development of SPEs, ionic liquids as electrolytes in lithium-ion batteries, and focuses on the benefits related to using them over liquid electrolytes. PEO-based SPEs increase ionic conductivity, improve thermal stability, and ensure safety without leakage and combustion hazards. Ionic liquids enhance lithium-ion mobility and mechanical stability within the high energy density application in electric vehicles and consumer electronics. The study puts forward an additional role of thermal and electrochemical stability that impacts performance and life span of batteries. The different approaches through modification of ionic conductivity at ambient temperature are explored, including the introducing plasticizers and inorganic fillers. In general, the ionic liquid-based SPEs represent a significant step forward in the battery technology landscape with more promising efficient, safer energy storage solutions on the cards.

Keywords: Solid Polymer Electrolytes, Ionic Liquids, Lithium-Ion Batteries, Polyethylene Oxide, Thermal Stability, Electrochemical Stability.

1. INTRODUCTION

Solid polymer electrolytes containing ionic liquids have emerged as advantageous materials for lithium battery backups owing to their improved ionic conductivity, thermal resistance, and safety characteristics. These electrolytes often consist of a polymer matrix, such as a polyethylene oxide, combined with an ionic liquid that functions as a plasticizer to enhance ion transport. In contrast to traditional liquid electrolytes, SPE including ionic liquids mitigate the hazards of leaking and combustibility which are essential for battery safety. The ionic liquids promote lithium-ion mobility within the polymer, sustaining elevated conductivity of ionic substances, even at ambient temperature. Furthermore, these materials exhibit chemical stability and compatibility with the metal lithium anodes, rendering them suitable for high-energy-density applications. SPE derived from ionic liquids have the potential to enhance the safety and efficiency of lithium batteries, hence enhancing energy storage in electric vehicles and handheld electronics.

The advancement of ionic liquid-based lithium-ion conduction polymer electrolytes is a cutting-edge technology for the production of diverse high-performance electromechanical devices, including hybrid automobiles, rechargeable batteries, and super capacitors.

Rising energy consumption, skyrocketing refined fossil fuel prices, and associated environmental problems have elevated energy storage to the status of a major worldwide issue in the last few decades.

As a solution that meets most of the basic requirements for rechargeable battery technology, IL-based Li-ion conductive “polymer electrolytes” have emerged as a viable alternative to lithium-ion batteries”, which are extensively utilized in different portable electronic devices.

The use of the metal lithium as an “anode for lithium batteries” is attributed to its substantial theoretical the gravimetric method capacity of 3861 milliampere-hours per gram mass, which is over tenfold greater than that of the commonly utilized graphite electrode (372 milliampere-hours per gram mass), and its minimal redox potential. Organic liquid electrolytes typically utilized in lithium-ion batteries exhibit significant reactivity with lithium metal, leading to the formation of detrimental dendrites at the anodes, hence impairing battery performance.

The utilization of liquid electrolytes in lithium-ion batteries presents significant safety hazards, including spontaneous explosion, potential leakage of corrosive substances. Consequently, “Li-ion” conducting SPEs may serve as a superior remedy to the aforementioned issues. In comparison to alternative solid electrolytes, polymer electrolyte membranes represent a superior choice for the development of various electromechanical devices, including batteries that are “rechargeable, supercapacitors, fuel cells, and actuators”.

The “lithium-ion batteries” carrying out solid electrolyte made of polymer derived from polyethylene dioxide (PEO) is a highly promising and extensively researched solid polymer matrix, attributed to its advantageous characteristics including superior shape and flexibility, excellent conductivity of ions, effective film-forming capability, high solvation characteristics, and diminished reactivity with electrodes. The current study utilized IL-assisted, PEO-based solid polymer electrolytes for lithium-ion batteries that are rechargeable.

Solid polymer electrolytes (SPEs) augmented with ionized liquids are attracting interest as a safer, outstanding performance substitute for traditional electrolytes that are liquid in lithium-ion batteries. These electrolytes comprise a polymer host, such as “poly (ethylene oxide) (PEO)”, integrated with ionic liquids that function as both plasticizing agents and ionic conductivity. Ionic liquids in solid polymer electrolytes promote ionic conductivity, augment mechanical stability, and reduce flammability risks, so improving the general safety of batteries made from lithium. Ionic liquids, owing to their permanent memories and thermally resilient characteristics, facilitate the retention of ion mobility inside the polymer matrix, even at reduced temperatures. Furthermore, solid polymer electrolytes (SPEs) exhibit chemical compatibility with the mineral lithium anodes, which may enhance battery longevity and increase energy density. Solid polymer electrolytes including ionic liquids constitute a significant advancement, facilitating the creation of safer and more dependable battery packs with lithium for electric automobiles and consumer electronics.

1.1 Thermal and Electrochemical Stability of Ionic Liquid-Based Spes

It is a crucial determinant in the efficacy and safety of lithium-ion secondary batteries. Ionic liquids provide non-volatile, non-flammable characteristics and exhibit great thermal stability, hence improving the safety profile of solid polymer electrolytes by mitigating the risk of burning or leaking. When integrated into a matrix of polymers, these characteristics enable the electrolyte to sustain stability at high temperatures, hence facilitating the dependable functioning of batteries in challenging conditions.

Ionic liquids facilitate the establishment of a stable contact between the solution of electrolytes and the lithium-ion metal anode, hence diminishing the likelihood of side reactions and prolonging battery longevity. Numerous ionic liquids exhibit resistance to electrochemical breakdown, enabling their successful operation across an extensive voltage range, crucial for high-energy-density applications. By improving thermal and electrochemical stability, ionic liquid-based solid polymer electrolytes reduce battery degradation, enhance charge/discharge cycles, and diminish lithium dendrite development. The amalgamation of stability variables renders ionic liquid-based solid polymer electrolytes a compelling option for safer, more durable lithium batteries, particularly in high-temperature and high-performance contexts such as electric vehicles. Previously investigated solid polymer electrolytes (SPEs) created by complexing polyethylene oxide with diverse alkali metal salts exhibit low ionic conductivities at ambient temperature, hence constraining their utility in the production of various electrochemical devices. The diminished ionic conductivity results from the multiphasic characteristics of polymer electrolytes, which have a predominant crystalline phase and a lesser amorphous phase, hence obstructing ion mobility inside the polymeric matrix. To achieve elevated ionic conductivity at ambient temperature, various strategies have been suggested, including (a) the incorporation of low-molecular- weight synthetic plasticizers or organic carbonates into polymers such as the “carbonates ethylene carbonate (EC), the carbonate of propylene (PC), and diethyl carbonate (DEC)”, (b) the formation of composites by dispersing inorganic fillers in them (including “ZrO_2, $BaTiO_3$, Sb_2O_3, SiO_2, Al_2O_3, CNT, and TiO_2”), and integrating ionic liquids into lithium-ion conducting systems made of polymers [12–15]. The incorporation of ionic liquids (IL) in polymers and polymer electrolytes is a multifaceted strategy due to the several advantages IL provides, including enhanced conductivity of ions, non-flammability, low pressure in the vapor, excellent thermal stability, and an extensive electrochemical window.

Incorporating ionic liquids into electrochemical systems, such lithium-ion batteries, enhances electrophysiological performance and thermal stability while also satisfying the need for plasticizing salts. Potential plasticizers for use in batteries and capacitors have been explored using a variety of ionic liquids, such as piperidinium, quaternary ammonium, morpholinium, and compounds based on pyrrolidinium. As an example, Shin et al. shown that “PYR13TFSI”, an ionic liquid based on “pyrrolidinium cations and bis(trifluoromethanesulfonylimide)”, is suitable for use in lithium rechargeable batteries. Ionic liquids (ILs) based on 1-butyl-3-methylimidazolium (BMIM+) cations exhibit interesting electrolyte characteristics, although they have been largely unexplored. The compound known as “1-butyl-3-methylimidazolium bis(trifluoromethyl sulfonyl)imide (BMIMTFSI)” has a number of positive qualities: with a cathodic limit of -2 Volt, an anodic limit of 2.6 Volt, a high stability electrochemical window of 4.6 V, a viscosity of 52 constant pressure at 20 degree Celsius, and a temperature-dependent ionic conductivity of 3.9 mS/cm at 20 degree Celsius, compared to 1.4 mS/cm at 25 degree Celsius, in comparison to pyrrolidinium-based ionic liquids, which have a cathodic limit of -1.5 Volt. When contrasted with pyrrolidinium-based ionic liquids, BMIMTFSI exhibits much superior characteristics, making them a promising material for use in electrochemical devices and future research.

1.1.1 Incorporating ionic liquids and lithium salts into a poly (ethylene oxide) (PEO) matrix to improve compatibility for lithium-ion applications in batteries.

1.1.2 Polymer electrolyte system aimed at enhancing lithium-ion transportation effectiveness at environmental temperature.

1.1.3 Liquid-based electrolytes made of solid polymer to assess their efficacy in sustaining performances at extreme temperatures in batteries made of lithium ion.

This paper presents the production and comprehensive characterization of a polymer electrolyte membrane consisting of the ionic liquid “BMIMTFSI, lithium salt (lithium bis(trifluoromethanesulfonic)imide, LiTFSI)”, and the polymer. Poly (ethylene oxide) (PEO). We have analyzed the impact of BMIMTFSI on the physicochemical parameters of the “PEO-LiTFSI system”, emphasizing critical performance factors like conductivity of ions, structural strength, and the shape of the surface. Structural study elucidates the influence of the ionized liquid on association within the membrane, with phase transition characteristics and enhanced thermal stability. The research evaluates the transfer capacity number, electrochemical equilibrium window, and charge-discharge properties of the electrolyte, offering insights into the viability of the system for lithium applications in batteries. This work seeks to ascertain the degree to which the ionic liquid enhances the conductivity, stability, and overall electromechanical performance of PEO-based electrolytes composed of polymers for safer, high-efficiency battery packs with lithium.

2. RELATED WORKS

He, et. al, (2024) characterized by inherent safety and elevated energy density. The energy density, quick charging capabilities, and safety of ASSLBs are greatly affected by the solid electrolyte, which is positioned between the anode and cathode and is crucial for the conduction of lithium ions. The research found that the only way to achieve energy-dense properties and high-rate efficiency with the cathode and anode material arrangement was to drastically reduce the amount of solid polymeric electrolytes. The most likely material for commercial applications is "ultra-thin solid polymeric electrolytes (SPEs)" because to its many advantages in processing capabilities, cost-effectiveness, and scalability. Improving the ultra-thin solid polymer electrolyte's mechanical characteristics and increasing its ion conductivity necessitated designing a suitable structure and controlling the electrolyte components.

Alandur Ramesh, et.al, (2024) discovered the ionic conductivity of polyethylene oxide–alkaline metal ion combination. Nonetheless, SPE study has experienced significant advancement, with conductivity levels increasing from "1 × 10–7 S•cm−1 to 1 × 10–1 S•cm−1", The development of “solid polymer electrolytes (SPEs)” originates from the necessity to provide design flexibility in battery architectures, alongside the demand for waterproof electrolytes, enhanced operating safety, increased energy population density, and other factors. The advantages of SPEs were clear; yet, inadequate interfacial contact significantly restricts their application. It also seeks to present a comprehensive overview of the progression and variety of study advancements in the production of more sustainable solid polymer electrolytes via additive manufacturing technology.

Zhang, et. a l, (2024) stated that Solid polymers represent a potential class of electrolytes for lithium-metal batteries; yet, they have constraints in concurrently attaining high conductivity of ions, robust durability, and tolerance with high-voltage cathodes, and suppression of lithium dendrites. We develop a category of solid polymer electrolytes with high local concentration, derived from polymer blends, referred to as "(LPIFD)”. The Li-polymer (polymer-in-salt) facilitates uninterrupted Li-ion conducting channels and aids in the growth of the interphase between solid electrolytes (SEI), while the F diluter enhances mechanical strength. Study indicated that one-phase LPIFD, derived from a miscible copolymer blend, is devoid of phase boundaries and generated an organic-free, LiF-dominant SEI, effectively inhibiting lithium dendrite formation. The single-phase LPIFD exhibits an ionic conductivity of 3.0 × 10−4 S per centimeter, facilitating the lithium anode to achieve a high coulombic efficiency of 99.1 percent and a critical current density of 3.7 mA per centimeter square. The formation of an F-rich anode electrolyte interphase enabled “LiNi0.8Co0.1Mn0.1O2||Li cells” to attain a cycle life of 450 cycles at a high voltage that operates of 4.5 V. This approach will motivate initiatives that will market electrolytes made from polymer for high-energy lithium-metal batteries.

Zhou, et. al, (2023) emerged as the focal point for “next-generation high-safety lithium batteries” owing to their three-dimensional, thermal, and electrochemical durability. In order to facilitate the growth of solid batteries, it was vital to improve solid electrolytes with appropriate overall performance. There is a great deal of interest in studying "Poly (vinylidene fluoride) (PVDF)" solid polymer electrolytes (SPEs) because of its remarkable mechanical qualities, electrically produced thermal stability, and possible use in solid-state lithium batteries. On the other hand, there aren't many reactive sites, the PVDF solid polymer electrolytes are very crystallin, and the ionic conductivity is minimal. Composite solid polymer electrolytes (CSPEs) based on photovoltaic diode technology have shown to be an efficient method for improving electrolyte performance. Focussing on the methods of ionic conductivity enhancement and interface control via altered fillers, based on diverse design strategies, the research offered a complete assessment of current developments in PVDF-based solid polymer electrolytes (SPEs). We also review the possible applications of solid polymer electrolytes based on PVDF in lithium-sulfur and lithium-oxygen battery systems. The research paved the way for better solid polymer electrolytes based on PVDF with exceptional durability.

Nguyen, et. al, (2023) employed organic electrolytes that were liquid are perceived as a significant impediment to the swift proliferation of batteries in electric vehicles as well as large-scale energy storage systems. Solid-state batteries (SSBs) utilized solid-state electrolytes are developing as viable alternatives to tradition (LIBs) due to their enhanced energy density and stability. In this context, solid electrolytes are essential for the advancement of solid-state batteries (SSBs). (CSPEs) were particularly noteworthy among solid-state electrolytes since they integrate the benefits of both inorganic solids and solid polymer electrolytes. The implementation of CSPEs is constrained by their inherent deficiencies. This review examines the thorough comprehension of the current advancements in CSPEs, primarily concentrating on the basics, design tactics, and synthesis techniques aimed at enhancing ionic conductivity and establishing stable interfaces with electrodes. Furthermore, prospective tactics and viewpoints are presented, outlining potential avenues to expedite the advancement of CSPEs.

Xie, et. al, (2023) explained that in all-solid-state (ASS) batteries, the use of solid polymer electrolytes (SPEs) is limited due to their smaller electrochemical window and reduced Li+-conductivity. Specifically, this study looked into “poly-carbonate (PCE), poly-oxalate (POE), and poly-malonate (PME) F-modified SPE families”. The improved asymmetry and flexibility of these pentanediol-prepared SPEs result in a greater Li+-conductivity compared to their butanediol-prepared counterparts. The Li+-conductivity of PME and POE is approximately 10 and 5 times that of PCE, respectively, due to their greater chelating coordination with Li+. During the in-situ passivation of Li-metal, the trifluoro acetyl-units are found to be more effective than the “$-O-CH_2-CF_2-CF_2-CH_2-O-$ “units.

Wang, et. al, (2023) stated that the limited ionic conductivity and brief lifespan of solid polymer electrolytes (SPEs) constrain the use of ambient-temperature polymer lithium metal batteries, likely due to the intrinsic restricted segment mobility of the polymer at room temperature. A dual-layer solid electrolyte made of polymers for ambient temperature is produced, and its operational principles are examined innovatively. Subsequent density functional theory simulations indicate that these patterns facilitate the fast transit of Li ions across polymer segments. The results were corroborated by infrared spectroscopy used the Fourier transformation and nuclear magnetic resonance. Consequently, the lithium-ion transport system for ambient-temperature solid polymer electrolytes may be adequately elucidated. Qin, et. al, (2023) presented a straightforward separator-free dual-curing approach that integrates UV-curing externally and subsequently thermal-curing internally, wherein the latter polymerization process enhances interfacial characteristics while maintaining ionic conductivity. The resultant DC-SPEs exhibit elevated "ionic conductivity" an extensive electrochemical stability window, and enhanced interfacial characteristics. The in situ-formed DC-SPE can efficiently inhibit the proliferation of lithium dendrites and attain stable cycling performance in lithium symmetric cells at elevated current densities utilized $LiFePO_4$ exhibit exceptional coulombic efficiency and remarkable cycling stability (900 cycles) at a 1C rate at 40 °C. The dual-curing strategy offers an innovative in situ processing technique that eliminates the need for costly and inert separators, applicable to the advancement of all-solid-state lithium metal batteries.

Lin, et. al, (2023) summarized the methods and sophisticated characterization methodologies of ASSLMBs to correlate microstructures and characteristics. Initially, we outline the difficulties encountered by solid polymer electrolytes in all-solid-state lithium metal batteries (ASSLMBs), included low ion mobility at ambient temperature and inadequate interface stability. Secondly, various conventional enhancement techniques for polymer ASSLMBs are examined, such as compound "SPEs, ultra-thin SPEs, SPE" surface modification, and lithium anode surface modification. Recent study have shown an improved understanding of battery microstructures. We propose that in situ assessment, noninvasive identification, and sub-angstrom resolution are essential technologies for enhancing our understanding of battery microstructures and advancing battery development. Potential investigations were anticipated to elucidate the evolution of microstructures and the behavior of batteries, intending to provide further theoretical direction for the layout of ASSLMBs with optimal performance.

Wu, et. al (2014) utilized "solid polymer electrolytes (SPEs)" to supplant conventional flammable fluid electrolytes, is considered one of the most promising approaches in the pursuit of high-energy-density battery systems. Specialized polymeric elastomers (SPEs) exhibiting exceptional thermal stability, favorable processability, and elevated mechanical modulus are garnering growing attention. Nonetheless, SPE-based batteries are not invulnerable, as they decompose and are combustible under extreme conditions. study asserted that the integration of suitable flame-retardant chemicals, solvents, or shards into solid polymer electrolytes (SPEs) can inherently diminish their flammability, addressing battery safety concerns. This study summarizes recent research advancements in incombustible solid polymer electrolytes (SPEs), with a particular focus on flame-retardant structural design. This text emphasizes a concise introduction to the flame-retardant mechanism, safety evaluation indices for solid polymer electrolytes (SPEs), and a comprehensive review of recent advancements in various types of SPEs across different battery systems. A profound understanding of the heat-runaway process, the development of free-standing incombustible gel polymer electrolytes, and the strategic design of pouch cell architectures may be essential in advancing next-generation safety reactors.

3. MATERIALS AND METHODOLOGY

3.1 Preparation of Li-Ion Conducting Solid Polymer Electrolyte Membranes

The lithium-ion conduction "solid polymer electrolyte (SPE)" membrane were synthesized utilizing poly (ethylene oxide) (PEO) as the polymer matrix, in conjunction with lithium bis(trifluoromethanesulfonic) imide (LiTFSI) salt and differing quantities of the ionizing fluid, BMIMTFSI. The foundational composition of the SPE membranes comprised PEO with 20 weight percent (wt.%) of LiTFSI, whereas the concentration of BMIMTFSI was adjusted to 0, 5, 10, 15, and 20 wt.% to investigate its impact on the membrane's characteristics. The SPE screens were fabricated using a solution-casting method. Prior to utilization, LiTFSI salt and BMIMTFSI were subjected to under vacuum drying at 120 °C for 24 hours to eliminate remaining moisture, and thus guarantee stable and predictable electrochemical characteristics. The components were housed in a glovebox sealed with argon to avert moisture or oxygen damage. The ultimate thickness of the produced SPE films varied from around 150 to 300 micrometers (µm).

3.2 Cathode Preparation

"The cathode material for the battery cell" was synthesized utilizing a slurry castings technique. The active material utilized was lithium manganese oxide ($LiMn_2O_4$), constituting 80 wt.% of the mixture, to attain maximum electrochemical performance. Carbon black was used as a conducting addition (10 wt.%) to augment the electrode's electrical efficiency, while polyvinylidene fluoride (PVDF) functioned as a binder (10 wt.%) to bolster the structural integrity of the cathode. The various parts were combined with 1-methyl-2-pyrrolidinone (NMP), serving as a solvent to guarantee equal dispersion and adherence.

The different parts were meticulously combined under an argon (Ar) environment and agitated for 24 hours. Subsequently, the slurry was applied onto an aluminum foil current collector with a doctor's blade for accurate thickness regulation and allowed to dry at room temperature. The electrode then subsequently baked in a sealed chamber at 110 °C for 8 hours to eliminate any residual NMP. The desiccated cathode film then subsequently compressed at an atmosphere of 1 ton utilizing a hydraulic press, and disk-shaped electrodes with an inner diameter of 2 cm were excised for installation.

4. CELL ASSEMBLY

The complete cell structure comprised a lithium metal anode and a cathode constructed from $LiMn_2O_4$, utilizing the manufactured "solid polymer electrolyte (SPE)" membrane. Assembly occurred within a glovebox containing an argon environment, and H_2O and O_2 concentrations kept at 0.5 ppm to avert any detrimental reactions during the process.

Characterization and Measurements

4.1 Ionic Conductivity Measurements:

"Electrochemical impedance spectroscopy (EIS)" with an Alpha analyzer (NoVo control) was used to assess the ionic conductivity of the SPE membranes. The experiments were performed over a frequency spectrum of 1 Hz to 40 MHz Bulk resistance (Rb) was derived from the Nyquist plot generated by impedance analysis. The ionic conductivity (σ) of the substrates was determined using the subsequent equation

$$\sigma = \frac{l}{Rb.A}$$

Where:

- l is the membrane thickness,
- A is the cross-sectional area of the sample,
- Rb is the bulk resistance from the Nyquist plot".

In temperature-dependent investigations, the polymer membranes were interposed between two stainless steel electrodes and positioned in a temperature-regulated the oven, wherein conductivity was assessed as an indicator of temperature utilizing a Novotherm Alpha analyzer.

4.2. Structural Analysis (XRD)

An analysis utilizing X-ray diffraction (XRD) was performed to elucidate the structural features of the polymer electrolytes.

The XRD images were acquired utilizing an “X’Pert PRO diffractometer (PANalytical)” employing “Cu-Kα radiation” across a scanned frequency of 2θ about 10° to 50°.

4.3. Morphological Examination (SEM)

The examination of the surface shape of the cell membranes was conducted utilizing a Quanta C-200 scanning electron microscope (SEM). This examination offered a deeper understanding of the membrane's the microstructure along with its possible phase shipping.

4.4. Thermal Analysis

The thermal characteristics of the SPE substrates were examined utilizing “differential scanning calorimetry (DSC) as well as thermogravimetric analysis (TGA)”.

DSC was conducted using a Mettler DSC1 apparatus over a temperature range of −100-to-100-degree Celsius, with a heating rate of 10 10-degree Celsius per minute inside a nitrogen atmosphere to examine thermal transition.

TGA was conducted with a Mettler TGA/DSC1 device, ranging from 30 to 600-degree Celsius at an average temperature rise of 10 degrees Celsius per minute in nitrogen to assess thermal stability. The thermal analysis was computed using the subsequent equation:

$$\Delta H = \int \Delta T . Heat\ Flow\ (mW) dt$$

Where:

- ΔH= Enthalpy change (J/g)
- ΔT= Change in temperature (°C)
- $eat\ Flow\ (mW)$= Power required to maintain the sample at a constant temperature during heating”.

4.5. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the SPE membrane were collected employing a Perkin-Elmer FTIR spectrometer (model RX1) within a temperature range of 3500 to 400 cm^{-1} to ascertain chemical connections and modifications to structure in the polymer matrix.

4.6. Electrochemical Stability and Performance Testing

The electrochemical stability window of the SPE was evaluated by cyclic voltammetry (CV) utilizing an “AUTOLAB PGSTAT 302 N” electrochemical analyzer operated with NOVA 1.10.4 software. The ionic as well as cationic transduction coefficients of the solid polymer electrolytes were ascertained using the methods of AC impedance spectrum and timing amplifier measurements ($\Delta t < 1$ ms). “Linear sweep voltammetry (LSV) and cyclic voltammetry (CV)” of the constructed Li | solid polymer electrolyte | $LiMn_2O_4$ cell were conducted at ambient temperature (about 30 °C) with a scan rate of 0.01 Voltas per second, covering a voltage range that ranged from 0–4.5 V for LSV and 2.8–4.4 V for CV. The two-electrode cell configuration (Li | SPE | $LiMn_2O_4$) was subjected to charges and discharges testing by cycling between 4.5 and 2.8 V at a 0.2 C rate to assess electrochemical performance, including stability as well as energy retention throughout cycles. 2 C rate to evaluate electrochemical performance, such as stability and capacity retention over cycles.

5. RESULTS

5.1 Ionic Liquid-Based Solid Polymer Electrolytes for Lithium-Ion Secondary Batteries

The polymer PEO is characterized by its polar and semi-crystalline form. The polar group in PEO, namely the C-O-C link, is recognized for forming complexes with various alkali metal salts, hence enhancing its conductivity to ions. In addition to conductance, a level of crystallization is another crucial factor that governs ionic transport in polymer electrolytes. The incorporation of IL into the “PEO-LiTFSI” complex system markedly alters the amount of crystallinity, as evidenced by “XRD and DSC” analyses.

5.2 Ionic Transport Properties

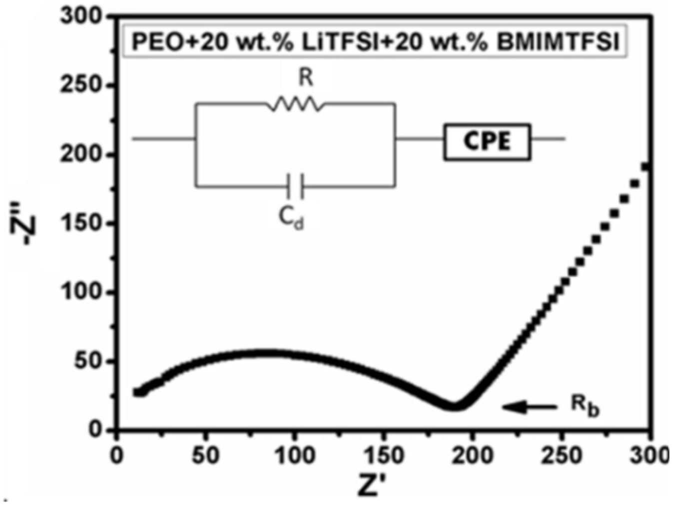

Figure 1: Typical Nyquist plots of (“PEO +20% LiTFSI) + 20% [BMIM][TFSI”] at room temperature and its equivalent circuit

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Figure 1 shows the ionic conductivity which is dependent on composition of the (“PEO + 20 wt% LiTFSI) + x wt.% [BMIM][TFSI”] system at room temperature for x = 0, 5, 10, 15, and 20. The ionic conductivity in the PEO + 20 wt. LiTFSI system rises with increasing IL concentration, according to the results.

At roughly 30 °C, with a 20 wt.% IL loading in the solid polymer electrolyte (SPE), the ionic conductivity peaks at around 1.5à10^-4 S.cm^-1. Because of the plasticizing impact of [BMIM][TFSI], the amorphous phase in the polymer electrolytes increases, leading to an increase in ionic conductivity with increasing IL concentration. Shalu et al. demonstrated that at room temperature (~30 °C), the ionic conductivity (σ) of pure [BMIM][TFSI] is about 5.8×10^-3 S.cm^-1. At increasing temperatures, the ionic mobility (µ) of the charge carriers in ionic liquids improves and the conductivity grows as a result of reduced viscosity, which allows for better ionic transport.

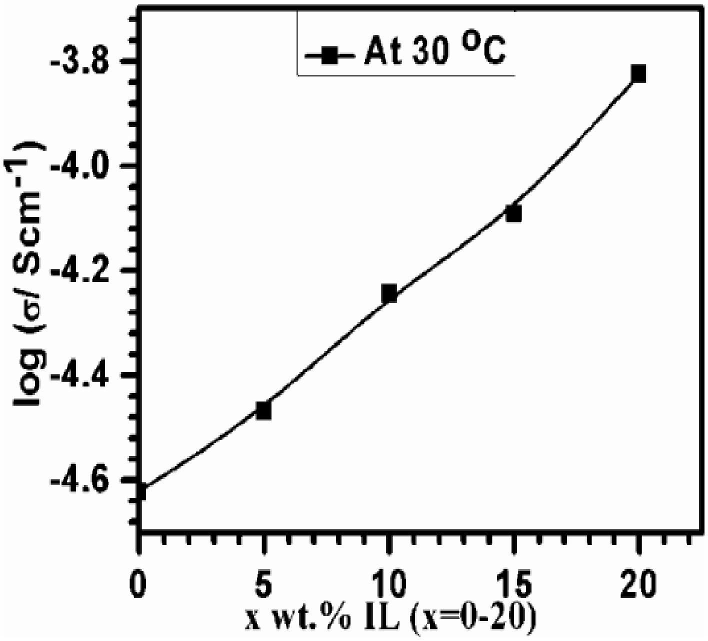

Figure 2: Polymer electrolyte membranes with ionic conductivity that varies with composition (“PEO + 20 wt. LiTFSI + x wt.% of [BMIM][TFSI]”) at 30 °C for x = 0, 5, 10, 15, and 20

Figure 2 displays the temperature-dependent ionic conductivity of PEO, 20 wt.% LiTFSI, and various concentrations of BMIMTFSI solid polymer electrolytes (SPEs) across the temperature range of 30-70 °C at x = 0, 5, 10, 15, and 20. The following demonstrates that the ionic conductivity continuously and linearly increases with temperature, which is a hallmark of thermally stimulated processes:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{kT}\right)$$

The activation energy is represented by Ea, the pre-exponential factor is the symbol σ, and the Boltzmann constant is the symbol k. Equation has been used to calculate the activation energy of all polymer electrolytes. As the amount of [BMIM][TFSI] increases, the activation energy (Ea) for the PEO+20 wt.% LiTFSI polymer electrolyte drops from about 0.49 eV to a low of about 0.17 eV at the highest ionic liquid loading of 20 wt.%.

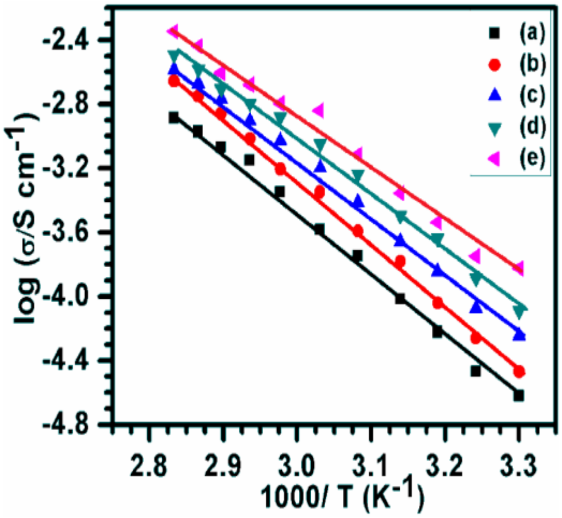

Figure 3: The polymer electrolyte membranes' ionic conductivity varies with temperature. The two samples in question are "(a) PEO + 20 wt. LiTFSI and (PEO + 20 wt.% LiTFSI) + x wt.% [BMIM][TFSI], where x ranges from 5 to 20, on the one hand, and 10 to 15 on the other"

An increase in the number of mobile charge carriers and enhanced ionic transport may explain why solid polymer electrolytes (SPE) have a lower activation energy (Ea). As shown in Figure 3, a phenomenological model has been put out to elucidate the behavior of ionic transport in SPE.

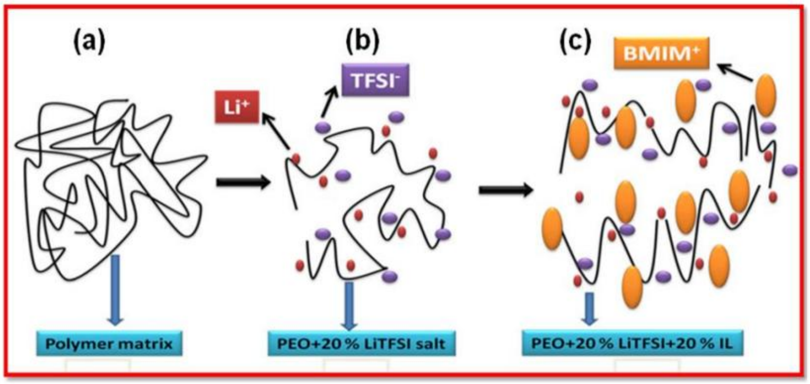

Figure 4: Visualisation aid for comprehending the ionic transport properties of "(a) pure PEO and SPEs the mixture of (b) PEO with 20 weight percent LiTFSI and (c) PEO with 20 weight percent LiTFSI and 20 weight percent [BMIM][TFSI] at ambient temperature (~30 °C)"

The semi-crystalline structure of the polymer PEO matrix is seen in Figure 4(a). As can be shown in Figure 4(b), the polymer chains exhibit enhanced flexibility after introducing 20 wt.% LiTFSI salt. Figure 4.23(c) shows that the solid polymer electrolyte membrane becomes more flexible and conductivity increases when 20 wt.% [BMIM][TFSI] ionic liquid is added to the polymer-salt system.

5.2.1 Transference number

As shown in Figure 5, the total ionic transference number of the solid polymer electrolyte that was created and evaluated using the DC polarisation approach is shown. Two stainless steel electrodes support the SPE, and the current fluctuation is recorded as time progresses.

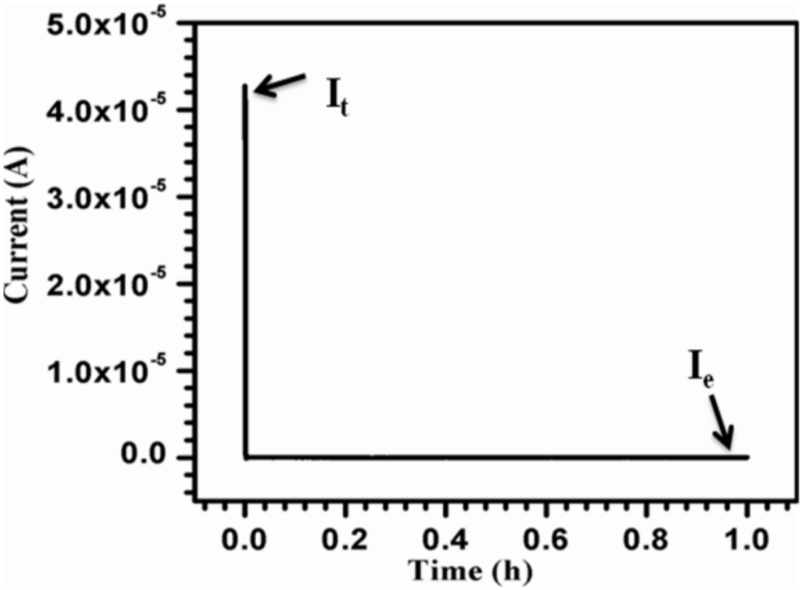

Figure 5A: chronoamperometric curve of the cell SS | SPE | SS with a voltage applied of 10 mV

Here is the formula that was used to compute the total ionic transference number (ion t):

$$t_{ion} = 1 - \frac{I_e}{I_t}$$

The total current is denoted by t I, whereas the steady state current is represented by e I. The ion t of SPE was determined to be around 0.99. The total conductivity is mostly caused by the ions, as seen by this assessed value of ion t. However, the cationic transference number () is a crucial metric for evaluating the cell's effectiveness from an application standpoint. A mixed ac/dc approach is used to compute the of the SPE PEO+20 wt.% LiTFSI+20 wt.% [BMIM][TFSI]. A common current-versus-time diagram for the symmetrical cell is shown in Figure 6 Li compounded with SPE and/or Li. The inset of Figure 6 displays the cell's resistance both before to and after polarisation.

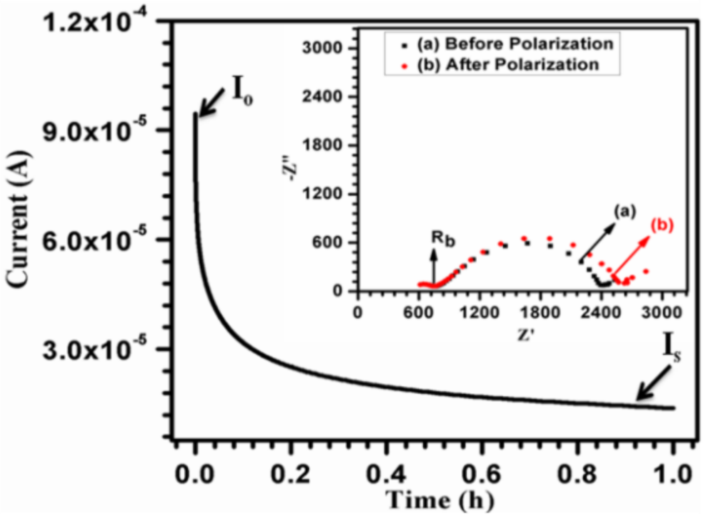

Figure 6: Chronoamperometric curve at an applied voltage of “10 mVof the cell Li | SPE | Li at room temperature (~30 °C)”

The Li-cationic transference number is calculated by using the following equation

$$t_{Li^+} = \frac{I_S(\Delta V - R_0 I_0)}{I_0(\Delta V - R_S I_S)}$$

“Where, o I and s I are the initial and steady state currents respectively, Ro and Rs are the cell resistances before and after polarization respectively. From the equation it has been calculated ~0.27”.

5.3 Electrochemical Performance

5.3.1 Electrochemical Stability

To examine the electrochemical characteristics of the optimized solid polymer electrolyte (SPE), it is positioned between a lithium anode and a lithium manganese oxide cathode (Li | SPE | $LiMn_2O_4$, as illustrated in Figure 7).

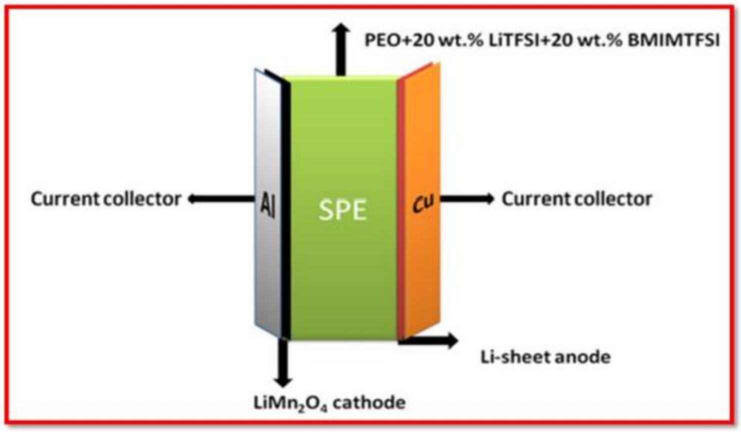

Figure 7: Schematic illustration of prepared cell Li | SPE | $LiMn_2O_4$

Researchers used cyclic voltammetry and linear sweep voltammetry to find the electrochemical potential window of the ideal concentration of an "IL-based Li-ion" conducting solid polymer electrolyte. Li metal acts as the reference and counter electrode in this arrangement, with $LiMn_2O_4$ acting as the working electrode. Figure 8 displays the results of the linear sweep voltammetry analysis of the electrochemical stability of the built cell. It is shown in Figure 8 that the cell is electrochemically stable up to around 4.4 V. Lithium rechargeable batteries are thought to be a good fit for this wide electrochemical window.

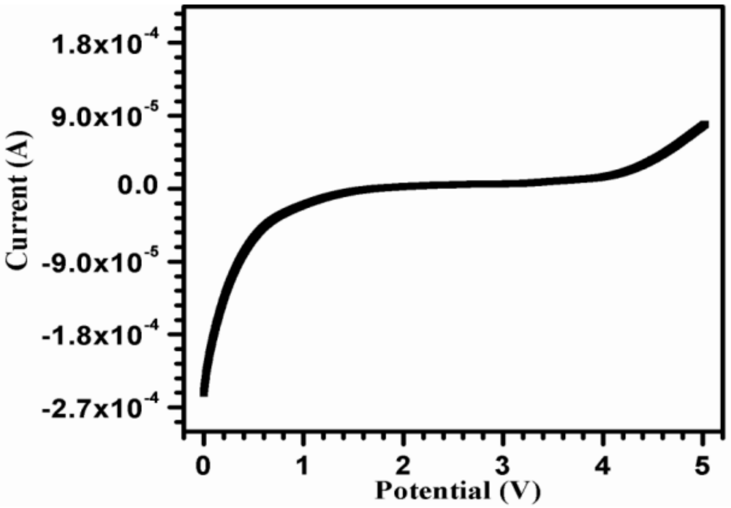

Figure 8: LSV of assembled cell "Li | SPE | $LiMn_2O_4$" at scan rate of 0.01 Voltage per second

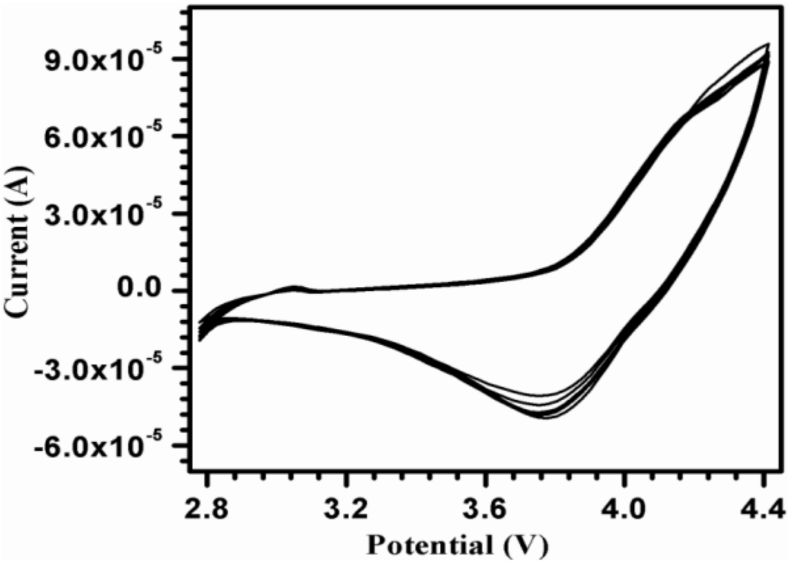

Figure 9: "CV profiles of Li | SPE | $LiMn_2O_4$ battery at scan rate of 0.01 V/s in the range of 4.4 to 2.8 V"

Figure 9 illustrates the “cyclic voltammetry curve of the Li | SPE | LiMn$_2$O$_4$ cell” throughout a voltage range of 2.8 to 4.4 V at ambient temperature, employing scan speeds of 0.01 Voltage per second.

Figure 9 illustrates that each cyclic voltammetry curve of the constructed cell indicates the intercalation and deintercalation of Li+ from the LiMn$_2$O$_4$ cathode occurs at voltages of 3.8 V and 4.1 V, respectively.

5.3.2 Galvanostatic Charge-Discharge Studies

The electrochemical performance of the cell was documented at room temperature with a 0.2 C rate, as illustrated in Figure 10.

The cell's “lower and higher cutoff potentials” are established at 2.8 and 4.4 V, respectively, to prevent electrolyte breakdown. Flat plateaus have been observed at around 4.1 and 3.8 V, corresponding to the deintercalation/intercalation of Li ions.

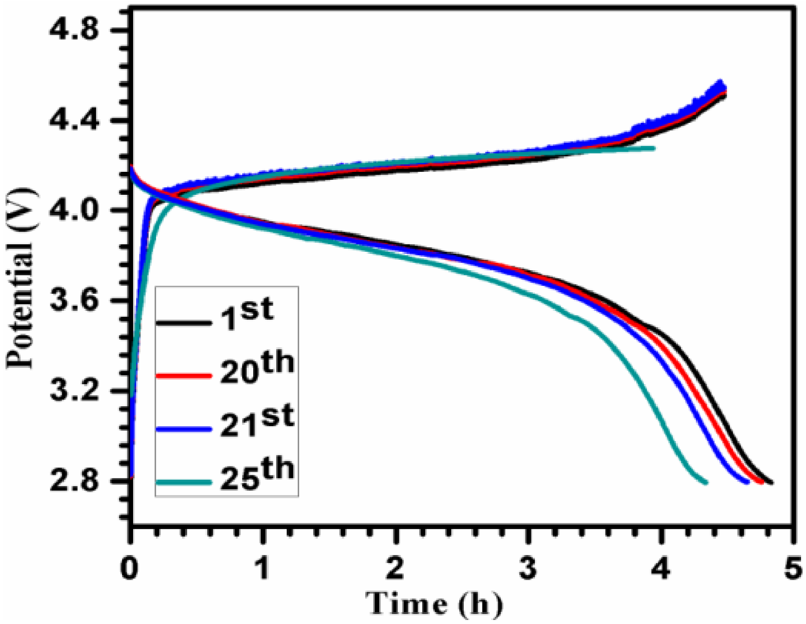

Figure 10: “Charge-discharge characteristics for 1st, 20th, 21st and 25th cycles between ~4.4 and 2.8 V”

The Li~SPE^{L}LiMn$_2$O$_4$ cell's cyclic performance is shown in Figure 11. The results show that even after 20 cycles at room temperature, the area discharge capacity remains at 152 μAh/cm².

The solid electrolyte interface (SEI) is responsible for this stability; it creates a barrier at the electrode-electrolyte contact and blocks capacity loss during the first twenty cycles.

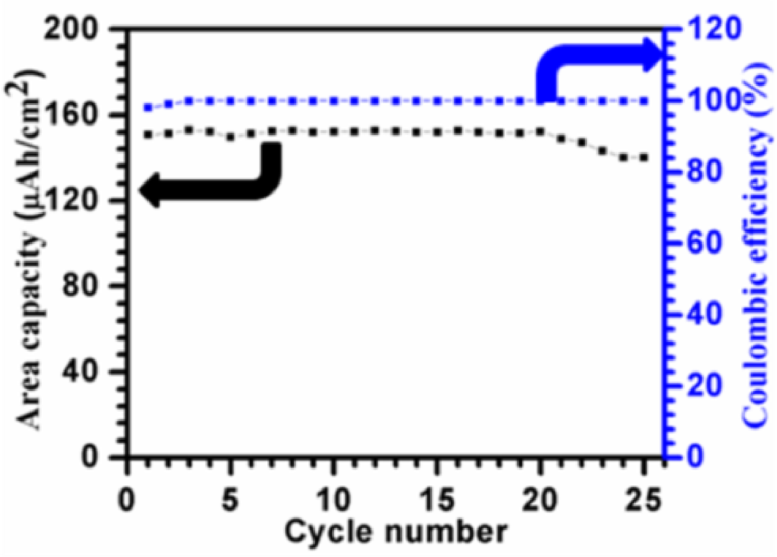

Figure 11: Cyclic performance of “cell Li | SPE | LiMn2O4 during cycling of charge-discharge for 25 cycles”

The area discharge capacity started to degrade after 20 cycles and reached about 140 µAh/cm² by the 25th cycle. As the solid electrolyte interface (SEI) layer forms at the electrode-electrolyte contact during intercalation and deintercalation, it is probable that this deterioration is caused by it. Furthermore, the coulombic efficiency was calculated with the help of the following formula:

$$n = \left(\frac{\Delta Q_d}{\Delta Q_c}\right).100\%$$

$$\Delta Q_d = \left(Q_f - Q_i\right)\ and\ \Delta Q_c = \left(Q_f - Q_i\right)$$

Equation was used to determine the “cell's coulombic efficiency” for the battery across 25 cycles, with the quantities of charge specified for both the charge and discharge cycles.

The coulombic efficiency of the cell “(Li │SPE│LiMn$_2$O$_4$)” approaches 100%, with the exception of the first cycle. The reduced capacity in the first cycle is attributable to the development of a protective solid electrolyte interface coating at the “electrode-electrolyte” boundary.

The cycle performance seen is indicative of their consistent charge-discharge capability. Enhanced interfacial properties with respect to the “lithium metal anode” and improved cycling performance of the cell yield favorable outcomes at ambient temperature.

This optimized high content IL-based solid polymer electrolyte may function as both a separator and electrolyte in lithium rechargeable batteries, indicating favorable cycling behavior for this battery system.

6 CONCLUSIONS

The document, therefore, concludes that with ionic liquid-based SPEs, a significant milestone in lithium-ion battery technology is offered: it elevates safety, efficiency, and performance-related characteristics. One obvious advantage of incorporating ionic liquids into polymer matrices is a priori the enhancement of both ionic conductivity and thermal and electrochemical stability-related prerequisite for high-energy-density applications. It means overcoming some of the disadvantages these materials possess relative to traditional liquid electrolytes, namely leakage and flammability. The data reveal bright prospects for the development of safer and more reliable energy storage systems linked with electric vehicles and portable electronics by ionic liquid-based SPEs. Future studies should be focused on optimizing the composition and structure of these electrolytes to further optimize their performance and applicability for future battery systems. In summary, the work contributes valuable insights on the design of advanced solid polymer electrolytes that are to advance enhanced lithium-ion battery technologies.

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