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Development of Safe Lithium-Ion Batteries Using Peo and Pvdf in Electrolyte: A Review

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Abstract

Conventional lithium-ion batteries utilize liquid electrolyte which holds several safety issues including electrolyte leakage, internal short circuits, and explosion amongst other problems, which limits their use. Solid-State Electrolytes (SSEs) and Gel-Polymer Electrolytes (GPEs) electrolytes in lithium-ion batteries provide excellent safety efficiency and have been on the rise in the lithium battery industry. Poly Ethylene Oxide (PEO) and Poly Vinylidene Fluoride-Hexafluoropropylene (PVDF-HFP) are commonly used compounds in the electrolyte due to their excellent mechanical and electrochemical properties. This paper reviews the use of PEO and PVDF-HFP, along with other additives, in the electrolyte and assesses the battery performance on the metrics of crystallinity, ionic conductivity, discharge-specific capacity, capacity retention, and coloumbic efficiency. With the addition of boron nitride and polymerized dopamine in PVDF-HFP-based GPEs, the electrochemical metrics show promising results in replacing liquid electrolytes in the near future.

Keywords: Engineered materials, Dielectrics, Plasmas, Engineering profession, Battery manufacturing, Lithium ion battery, Solid state battery

Introduction

A Lithium-Ion Battery (LIB) is a type of rechargeable battery that is charged and discharged by lithium ions moving between the negative (anode) and positive (cathode) electrodes in a medium (electrolyte) that enables the movement of lithium ions. Lithium batteries are much lighter in weight which provides advantages for their applications in devices such as power tools, portable wearables, and electric vehicles. LIB is rechargeable and can also be recycled. More than 90% of the raw materials in LIB are recyclable, making it environmentally friendly [1]. In recent times, renewable sources of energy have received a lot of importance because they help reduce the emission of greenhouse gases from fossil fuels and largely reduce air pollution. Scientists and researchers have been working to diversify energy supply and reduce the dependence on imported fuels [2]. Due to the advantages that LIB offers, they are one of the favored options for renewable energy storage.

Conventional LIBs, displayed in Figure 1, use organic Liquid Electrolyte (LE), which enables fast movement of lithium ions between anode and cathode [3]. However, the usage of liquid electrolytes in LIBs possesses several safety problems, leakage of electrolytes in the process of operation, and the electrolyte may heat up due to overcharging, internal short circuits, and other abnormalities, which could potentially result in spontaneous combustion or explosion. For these very safety reasons, Solid-State Electrolytes (SSEs) and Gel-Polymer Electrolytes (GPEs) are better alternatives to LE.

Solid-state electrolyte has excellent safety efficiency, high energy density, and a wide variety of operating temperatures. However, it holds certain challenges like low mechanical and chemical stability, low ionic conductivity, high crystallinity, stress, cracking, wetting behavior, and lithium dendrite growth [4]. Crystallinity is the structural order in a solid material and lower crystallinity allows greater movement of lithium ions, thereby increasing cell performance. Poly Ethylene Oxide (PEO) is an extensively researched polymer in SSEs, but it displays low cell performance due to high crystallinity. Certain additives like fillers, plasticizers, and polymers like Poly Vinylidene Fluoride-Hexafluoropropylene (PVDF-HFP) can be added to PEO to increase its performance. The amorphous HFP region in PVDF-HFP helps reduce the crystallinity of PVDF and serves as a great host in GPEs.

Gel Polymer Electrolytes (GPE) are formed by the incorporation of liquid electrolytes within a polymer matrix, which combines the advantages of high ionic conductivity of liquid electrolytes with the high safety of solid-state electrolytes. Ideally, the polymer matrix of GPEs should exhibit a high absorption capacity of liquid electrolytes to ensure high ionic conductivity, fire resistance to ensure the safety of LIBs, and the capability to transport Li+ to improve the ion conductivity of the GPE [4]. A review by Zahra Moradi et al. addresses the use of both PEO and PVDF electrolytes in SSEs, among several other potential solutions, however, the authors don't address the use of PVDF in GPEs [4].

In this paper, we will review the use of PEO in SSEs, PVDF-HFP in GPEs, and the combined use of PEO and PVDF-HFP in SSEs. Several metrics were used to assess the electrochemical performance of each electrolyte type. The three metrics relevant to all the papers are (i) Ionic conductivity (S/cm) measured at 25°C, (ii) maximum discharge specific capacity (mAh/g), and (iii) capacity retention. A review by Z. Zhang et al. suggests that controlling the thickness of the electrolyte membrane can help meet the requirement of high energy density in SSEs [5]. However, doing so would reduce the quality of the electrolyte membrane and might decrease the mechanical strength. In this review, several papers are addressed where the mechanical strength of the electrolyte membrane can take the load of cell performance.

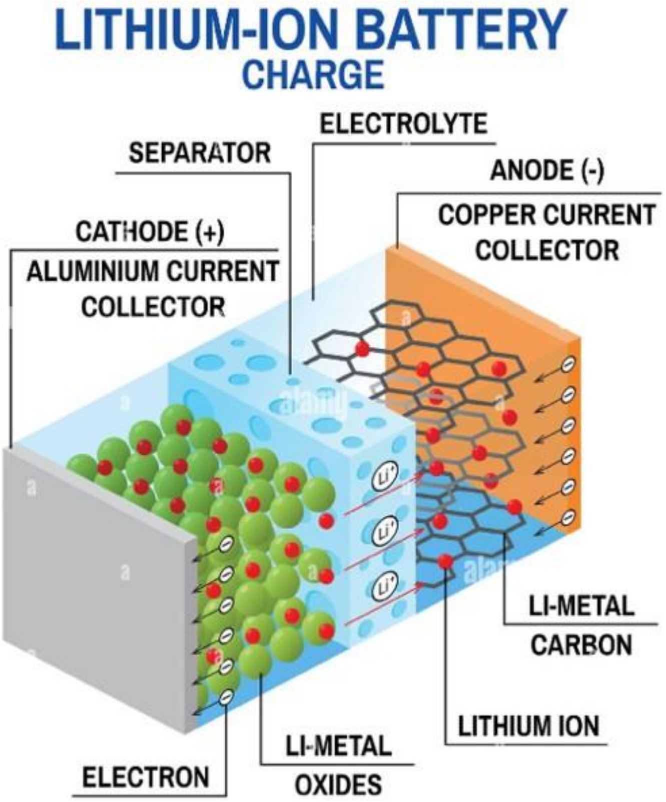

Figure 1: Schematic diagram of the movement of Li-ion in a LIB as adapted from reference [3].

Utilizing poly (ethylene oxide) PEO as a solid-state electrolyte

Solid-state lithium-ion batteries show great safety improvement as compared to liquid electrolytes. A lot of research has been conducted where Poly Ethylene Oxide is used as the host for solid-state electrolytes. The ion conduction mechanism of PEO is due to the high flexibility of the polymer chain. However, the low room temperature conductivity, narrow electrochemical windows, and inferior mechanical properties of PEO are the main obstacles to further development. Blending PEO with certain additives in electrolytes can help overcome this issue. In this section, four different papers are reviewed where PEO is used as a solid-state electrolyte host.

Xiu Shen et al. investigated the effects of adding mesoporous silica SBA-15 in the PEO electrolyte [6]. They postulated that adding fillers into PEO-based electrolytes would reduce the crystallinity of electrolytes and promote lithium-ion migration in the cell, thereby increasing cell performance. To prepare the filler, they used 0.2 M ionic liquid containing lithium-ion (LiIL) and mixed it with SBA-15. The LiIL and SBA-15 were mixed in a 1:1 ratio in the PEO electrolyte and a composite electrolyte PEOLi/SBA-LiIL was formed. As seen in Figure 2, pure PEOLi (d) shows distinct spherulites, and the structures are reduced with the addition of SBA (e). Furthermore, the PEOLi/SBA-LiIL electrolyte membrane with the active filler is relatively very smooth which suggests less crystallization with the addition of the filler.

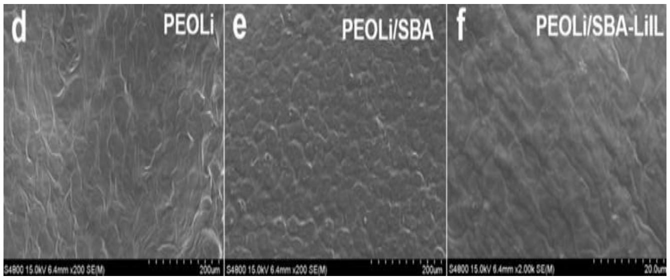

Figure 2: (d) pure PEOLi electrolyte (e) PEOLi/SBA electrolyte (f) PEOLi/SBA-LiIL electrolyte as adapted from reference [6].

The ionic conductivity tends to increase with a decrease in crystallinity [7]. The ionic conductivity of electrolyte was found to be 0.075 x 10^{-4} S/cm at 25°C and 4.3 x 10^{-4} S/cm at 60°C. The results align well with the low glass transition temperature of -48.5°C which is beneficial for ionic transport by thermal motion of the polymer chain. The researchers also investigated how the mechanical strength was affected by the addition of filler. They found an approximate 184% increase in mechanical strength of PEOLi/SBA-LiIL as compared to pure PEOLi electrolyte. These results highlighted the electrolyte's good flexibility and tenacity. The PEOLi/SBA- LiIL showed a higher discharge capacity of 150.3 mAh/g at 0.07 C, and the discharge capacity was maintained at 90.4% after 90 charge-discharge cycles with coloumbic efficiency of 99% throughout the process. The stable cycle performance is attributed to the electrolyte's high ionic conductivity and good mechanical strength. The authors were able to achieve a higher cell performance with the addition of SBA-15 in the PEO electrolyte, which opens further research scope.

Similar to research by Xiu Shen et al., the research by Lin Zhu et al. was motivated by the reduction of crystallization of PEO electrolytes [8]. They studied the effects of adding amorphous salt complexes in PEO-based electrolytes. They blended PEO and poly (propylene carbonate) (PPC) in the electrolyte and used Lithium bis(trifluoromethane)sulfonimide (LiTFSI) as the lithium salt. PPC is an amorphous salt that has high ionic conductivity because it allows easy movement of ions. The authors prepared the electrolyte film by mixing lithium salt solution (LiTFSI) with different mass ratios (10%, 20%, 30%, 40%, 50%) of PPC. As depicted in Figure 3, the addition of PPC decreased the crystallinity of PEO electrolyte. Reduction of crystallinity promoted the diffusion and migration of greater amounts of lithium ions (red dots in Figure 3) which aided in enhanced cell performance.

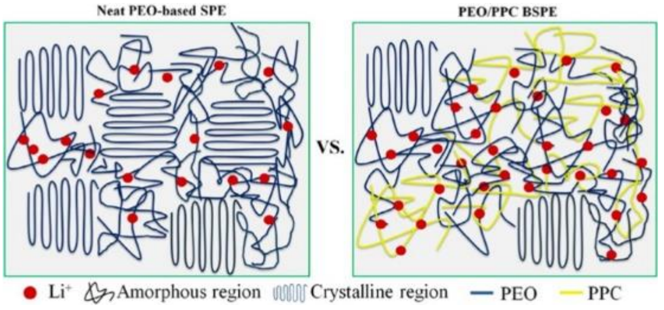

Figure 3: Schematic illustrations of neat PEO-based Solid Polymer Electrolyte (SPE) and PEO/PPC Blended SPE (BSPE) as adapted from reference [8].

The crystallinity reduction was greater with the addition of PPC as compared to silica fillers in PEO electrolytes. Low crystallinity aided in achieving high ionic conductivity of 0.204×10^{-4} at 25°C when the content of PPC was 50% and increased with increasing temperature to 2.82×10^{-4} at 60°C. With the addition of 50% PPC in the PEO electrolyte, the discharge-specific capacity increased from 93 mAh/g to 125 mAh/g at 0.5 C at 60°C after 100 cycles. Its coloumbic efficiency was close to 100%. The addition of an amorphous salt complex like PPC helped increase the cell performance of PEO electrolyte. A lot more similar research has been done where the amorphous phase of the PEO electrolyte is enhanced to achieve greater dissociation of lithium salt in the PEO host.

Ling Xu et al. did one such research where they blended the PEO electrolyte membrane with Poly Oxyphenylene Sulfone (PESf) and Polyvinyl Alcohol (PVA), forming a Composite Polymer Electrolyte (CPE) [9]. PVA and PESf have synergistic effects, thus enhancing the amorphous phase and dissociation of the lithium salt in the PEO host. The authors postulated that this synergistic effect could sustain the high ionic conductivity of CPE. The PEO-PVA-PESf electrolyte was made with 30 wt% PVA and 20 wt% PESf and this system exhibited lower crystallinity and impedance, which enhances its need as a high-potential cathodic material.

The ionic conductivity increased with an increase in temperature from 25ºC to 60ºC from 3.64 x 10-5 S/cm at 25ºC to 8.3 x 10^{-4} S/cm at 60ºC as seen in Figure 4. CPE showed an electrochemical window of 5.38 V which enhanced its need as a high-potential cathodic material. The CPE cell cycled stably for over 200 hours without any indication of the formation of lithium dendrites. The enhanced cell performance and properties display a great potential for research and advancement in the future.

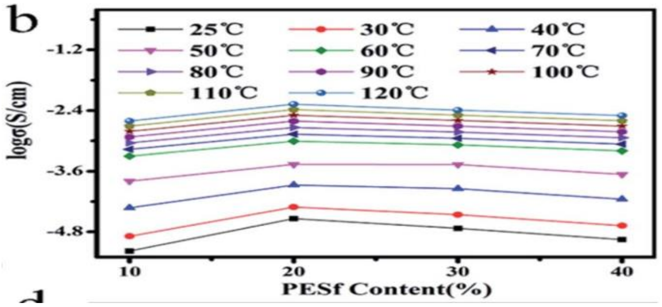

Figure 4: Ionic conductivity measurement as adapted from reference [9].

Wang Lyu et al. used a similar approach as previously discussed papers where the authors tried to improve the cell performance of PEO electrolytes by reducing their crystallinity [10]. Wang Lyu did so by introducing plasticizers which would significantly improve ionic conductivity by providing thermal stability and reducing crystallinity. They prepared a Composite Solid Polymer Electrolyte (CSPE), PEO_{18}--LiTFSI--5% SiO_2--5% SN by solution casting method. The amount of SiO_2 nanospheres and Succinonitrile (SN) added in this experiment was 5% relative to the mass of PEO. As seen in Figure 5b, the SEM figure of the membrane presents wavy folds and no pore structure, which indicates excellent densification of the membrane. The smoothness of the membrane was associated with the nanospheres being well embedded in the PEO matrix (Figure 5).

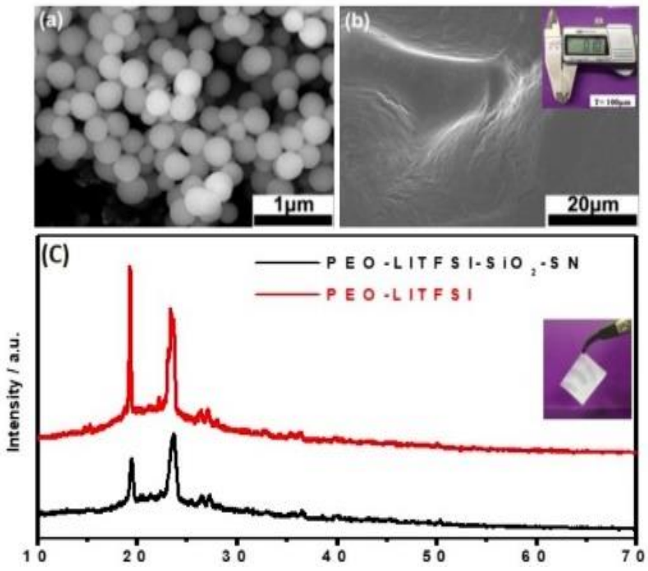

Figure 5: a) SEM images of SiO_2 nanospheres, b) SEM image of CSPE, c) XRD patterns of CSPE as adapted from reference [10].

Solid plasticizer SN and inorganic filler SiO_2 nanospheres were added to increase the amorphous regions of the PEO matrix and to obtain higher conductivity and build excellent conductivity with the electrode material. The crystallinity of Composite Electrolyte (CE) was found to be lower than the regular PEO electrolyte as seen in Figure 5c where the intensity of the diffraction peak was reduced in CE. The ionic conductivity reached 0.8 x 10^{-4} S/cm at 25°C and increased with an increase in temperature. The impedance of CPSE was found to be much lower as the charge-discharge voltage polarization of the system was only 0.06 V. The initial specific discharge capacity was found to be 157.5 mAh/g at 0.5 C and remained at 156 mAh/g after 100 cycles.

The authors were able to achieve better metrics and were able to increase the cell performance of PEO electrolytes. SiO_2 nanospheres along with succinonitrile were the most successful additives in reducing the crystallinity of the PEO matrix, which aided in boosting the cell performance.

Utilizing PEO and poly (vinyl fluoride) Hexafluoropropyl (PVDF-HFP) blend as a solid-state electrolyte

Section 2 summarized how the performance of PEO electrolytes can be increased by the addition of plasticizers and fillers by reducing the crystallinity and thereby increasing the cell performance. Poly Vinylfluoride) (PVDF) is a non-reactive thermoplastic that has been extensively adopted in electrolyte use due to its low cost, low weight, environmental friendliness, and high flexibility. The addition of a Hexafluoropropyl (HFP) to PVDF further decreases the crystallinity of the electrolyte. The composite electrolyte formed by blending PEO and PVDF-HFP provides benefits from both polymers, increasing the mechanical strength from PEO and decreasing crystallinity from PVDF-HFP. The following four papers compare and evaluate the effects of the addition of certain salts and plasticizers to the PEO/PVDF-HFP blend, on the ionic conductivity and electrochemical performance of the cell.

Compared to the research by Wang Lyu et al. in section 2, where they utilized Succinonitrile (SN) alongside other additives in PEO electrolytes; Hao Wang et al. investigated the effects of adding SN and $LiClO_4$ in PEO and PVDF blend [11]. The microporous PVDF film was used as a support layer in the electrolyte and several experimental schemes were made where PVDF and SN content were held constant and $LiClO_4$ and PEO content was varied to form a Composite Electrolyte (CE). As seen in Figure 6, pure PEO and PVDF have high crystallinity. However, as the percentage of $LiClO_4$ increases in the CE the peak intensity decreases which shows low crystallization.

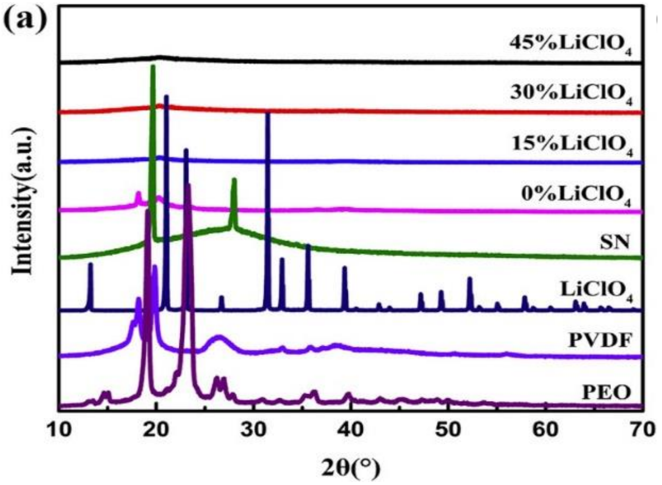

Figure 6: XRD diagrams of PEO, PVDF, $LiClO_4$, SN, and the prepared CE as adapted from reference [11].

The results showed that the addition of $LiClO_4$ reduced the crystallinity of CE which led to high ionic conductivity. CE with 45% $LiClO_4$ showed a lower glass transition temperature leading to a faster segmental mobility of ions and corresponding to a higher ionic conductivity. The prepared electrolyte, with PEO content at 15%, showed an ionic conductivity of 0.13 x 10^{-4} S/cm at 25°C and it further increased with an increase in temperature. CE with 25% $LiClO_4$ and 15% PEO showed an initial discharge capacity of 121 mAh/g with a coloumbic efficiency of 84%. The capacity gradually decreased as the cycle progressed with all coloumbic efficiencies >99%. This method provided insight into how the addition of SN in different host electrolytes can exponentially change cell performance. The prepared CE showed good thermal stability, ionic conductivity, electrochemical stability window, and initial discharge capabilities in cells at ambient temperature, which suggests its great potential in practical application.

In addition to salts and plasticizers, ceramic powders have been popular additives in PEO and PVDF electrolytes due to their high chemical stability to lithium metal, high electrochemical window (> 5V), and high ionic conductivity (> 10^{-4} S/cm) at 25°C. Jun Li et al. investigated the effects of adding a ceramic powder, LLZO ($Li_{6.2}Ga_{0.1}La_3Zr_{1.5}Bi_{0.5}O_{12}$), and LiTFSI in PEO and PVDF electrolyte blend [12]. The PEO/PVDF/LiTFSI weight ratio was fixed at 7:3:2, and the weight percentage of LLZO was varied from 5 to 15 wt% based on the total weight of the composite solid electrolyte (CE). The CE with 10 `wt% LLZO showed the best electrochemical performance. The CSE with 10 wt% LLZO exhibited an ionic conductivity of 4.2 x 10^{-5} S/cm at 30°C and delivered a maximum discharge capacity of the cell remained at 128.3 mAh/g after 100 cycles, which shows that it retained 96.5% of its capacity. Similar to studies discussed in section 2, Figure 7 shows how the crystallinity of the PEO matrix reduces with the addition of PVDF.

Code	Sample	Melting temp., T_m (°C)	Heat of fusion, ΔH_m (J/g)	Crystallinity, χ_c (%)
1	Pure PEO	75.6	154.3	72.2
2	PEO/PVDF = 9:1	73.2	127.2	66.1
3	PEO/PVDF = 8:2	71.9	108.6	63.5
4	PEO/PVDF = 7:3	70.5	91.3	61.0
5	PEO/PVDF = 6:4	69.2	82.9	64.6
6	PEO/PVDF = 5:5	68.7	74.8	70.0

Figure 7: DSC data for pure PEO and PEO/PVDF blends at various compositions as adapted from reference [12].

This study showed an increase of approximately one and a half times enhancement of ionic conductivity with the addition of 10 wt% LLZO as compared to pure PEO/PVDF matrix. The study highlights the use of ceramic powder as a hopeful candidate for next-generation all-solid-state LIBs.

Similar to the study by Jun Li, Jiaxin Huang et al. studied to effects of adding ceramic powder to PEO/PVDF-HFP electrolyte. They used $Li_{6.7}La_3Zr_{1.7}Ta_{0.3}O_{12}$ (LLZTO) and LiTFSI as additives in the PEO and PVDF-HFP matrix [13]. The electrolyte was prepared by mixing PEO and PVDF-HFP in a ratio of 4:1. LiTFSI was then added in a mass ratio of 1:3 against the PEO/PVDF-HFP mix. LLZTO powder was added in mass ratios of 0%, 10%, 15%, and 20% in each of the prepared PEO/PVDF-HFP/LiTFSI Composite Electrolyte (CE) cells. The cell with 10 wt% LLZTO showcased the best electrochemical performance. From XRD analysis of the prepared cells with the addition of LLZTO, the authors found that characteristic peaks of PEO were weakened after the addition of LLZTO. This proves that the addition of the filler promoted the movement of lithium ions by reducing the proportion of the PEO crystallization.

To further confirm the findings, the authors measured the melting temperatures of the electrolyte by DSC. As seen in Figure 8, the melting temperature of the CE reduced from 63.4 C to 53.2 C, indicating that the presence of PVDF-HFP and LLZTO can increase the free volume of PEO, which provides added benefits for the movement of lithium ions. The authors measured the ionic conductivity to be at 1.05 x 10^{-4} S/cm at 35°C with an electrochemical stability window of 5.2 V. Compared to the previous study where authors only added LLZO, the addition of a similar compound, LLZTO, however, increased the cell performance by 120% which highlights the potential and scope of research that the ceramic powders hold.

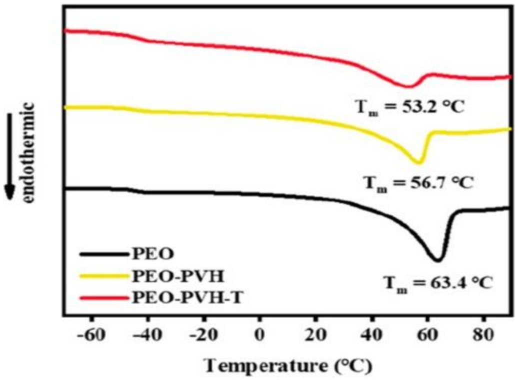

Figure 8: DSC curves highlighting the melting temperature measurements of PEO, PEO-PVH (PEO/PVDF-HFP), and PEO-PVF-T (PEO/PVD- HFP/LLZTO) as adapted from reference [13].

Based on recent studies, it is well known to the researchers that the combined advantages of PEO and PVDF (PEO@PVDF) in the electrolyte provide great potential for future implications. Apart from fillers, plasticizers, and ceramic powders, an inorganic solid-state electrolyte $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$ (LATP) is highly inert against water and oxygen and shows high ionic conductivity of 10^{-3} S/cm at room temperature [14]. To combine the low crystallinity effects of PEO@PVDF and the high ionic conductivity of LATP, Shuhong Yi et al. synthesized a dual polymer matrix with PEO@PVDF with modifications from LATP [15]. The authors prepared electrolytes with various ratios of PEO and PVDF and found that the electrolyte with 10 wt% PEO, 5 wt% LATP, and 5 wt% LiPF6 forming PPLL, showed the best electrochemical performance where the cell cycled steadily for 1000 hours without short circuit. Figure 9 highlights how the combination of PVDF, PEO, LATP, and LiPF6 increases the capacity and cell stability.

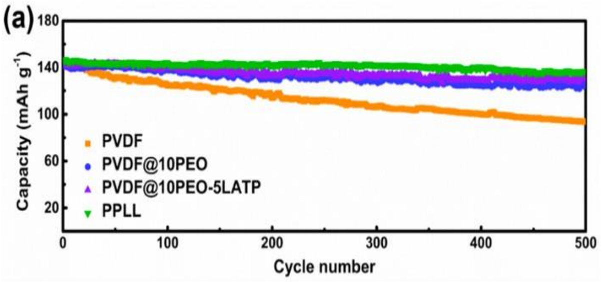

Figure 9: Cycling performance of PPLL in comparison to other cells at 0.1C as adapted from reference [15].

The ionic conductivity was found to be 5.24×10^{-4} S/cm at 25°C and above 10^{-3} S/cm at 50°C. The prepared robust PPLL establishes clear advantages of multi-matrix electrolytes with a combination of both organic and inorganic materials and implies a rewarding avenue to build better all-solid-state lithium-ion batteries.

Compared to ceramic powders like LLZTO and LLZO and plasticizers like SN, the addition of an inorganic substance like LATP enhanced the performance of the dual polymer electrolyte, PEO-PVDF, the most. The presence of HFP in PVDF molecule also enhanced its properties by reducing the crystallinity of the electrolyte. Solid-state electrolytes utilizing PEO and PVDF as electrolyte hosts have been well-researched as they offer the ultimate safety solution to the flammability that liquid electrolytes possess. Based on the papers discussed above, there is still a long way to go to achieve cell performance similar to liquid electrolytes. A lot of scientists have been extensively looking into gel-based electrolytes, which offer advantages of both solid-state and liquid electrolytes. The section below covers the use of PVDF-HFP as a gel-based electrolyte.

Utilizing PVDF-HFP as a host for gel-polymer electrolyte

Gel-Polymer Electrolytes (GPEs) provide the benefits of both solid-state electrolytes and liquid electrolytes, where it overcomes the major challenge of flammability that comes with liquid electrolytes and low ionic conductivity with solid-state electrolytes. PVDF-HFP shows low crystallinity due to the incorporation of the amorphous HFP phase. PVDF-HFP shows high electrochemical stability, and its high dielectric constant is favorable to the dissociation of lithium salts [12]. The following four papers compare and evaluate the effects of certain additives on the performance of PVDF-HFP electrolytes forming Gel-Based Lithium-Ion Batteries (GBLIB).

In sections 2 and 3, the authors, Wang Lyu et al. and Hao Wang et al. used Succinonitrile (SN) to make solid-state electrolytes which effectively reduced crystallinity and glass transition temperature of the electrolyte and helped increase the cell performance. Similarly, Ruling Huang et al. utilized SN and PVDF-HFP to make a gel-based electrolyte [16]. The authors used a general immersion precipitation method to prepare GPE, where they dipped the prepared gel film (PVDF-HFP/SN) in liquid electrolyte for 1 hour. They built a flexible electrolyte film with several weight ratios of PVDF-HFP to SN where the ratio 7:3 showed the best performance. As the SN content increased, the absorptivity of the liquid electrolyte in the electrolyte film also increased to 222%, inferring that SN modulates the porous structure of the polymer membrane, thus increasing its porosity and liquid absorptivity. The XRD spectroscopy also showed that SN helped reduce crystallinity in the PVDF- HFP membranes. Figure 10 shows the effects of SN on ionic conductivity. PSGPE-3 contains the most amount of SN.

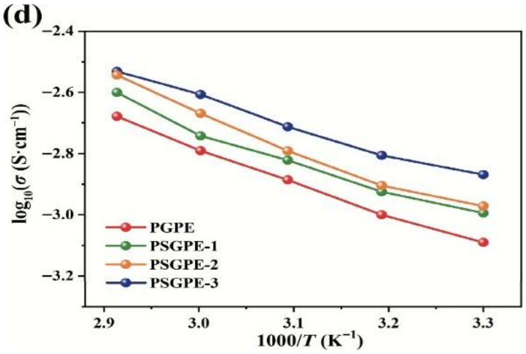

Figure 10: Arrhenius plots of ionic conductivities as adapted from reference [16].

The ionic conductivity at 30°C was 1.35×10^{-3} S/cm, which is significantly higher compared to the solid- state electrolytes' studies in sections 2 and 3. The cell displayed a discharge capacity of 127.3 mAh/g at 0.1 C and cycled steadily for over 250 cycles. The results demonstrate that varying concentrations of SN provide synergistic effects in PVDF-HFP electrolyte membranes. The novel GPE possesses an advantage due to its high liquid electrolyte absorptivity of 222%. Scientists all over have extensively researched and tried to improve liquid electrolyte absorptivity in GPEs, where one such researched additive in PVDF-HFP electrolyte is poly (ionic liquids).

Poly-Ionic Liquids (PILs) are polyelectrolytes that comprise repeating units of ionic liquid species. Zhenyuan Hu et al. created a GPE using PIL called poly(1,2-diethoxyethylimidazolium) bis(trifluoromethanesulfonyl) imide (PDEIm) and PVDF-HFP [17]. The prepared porous electrolyte had a liquid electrolyte absorptivity of 187.2%, which led the authors to measure the crystallinity of the membrane. The crystallinity of PEDIm-40%/PVDF-HFP (PP) was calculated to be 18.2% which is significantly smaller than crystallinity of PVDF-HFP membrane (46.9%). This led to high polymer chain mobility, facilitating the migration of lithium ions and increasing the ionic conductivity. The results showed a high ionic conductivity of 1.78 x 10^{-3} S/cm and lithium-ion transference number of 0.42 at 25°C. The authors also found high thermal stability of PP which demonstrates its potential to enhance the safety of LIB by lowering the risk of short circuits, as displayed in Figure 11. The cell showcased a specific discharge capacity of 157.3 mAh/g at 0.5 C and shows great potential for practical application in advanced lithium-ion batteries with superior electrochemical performances and high safety.

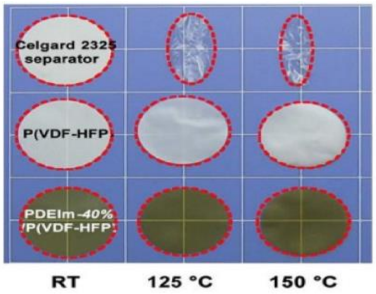

Figure 11: Thermal shrinkage ratio of electrolyte membrane as adapted from reference [17].

Similar to research by Zhenyuan Hu et al, Pei Xu et al. used Ionic Liquids (ILs) as plasticizers in PVDF-HFP GPE [18]. They used 1-ethtyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIM)(TFSI) as a IL plasticizer, due to its wide stability window for lithium batteries, high ionic conductivity, and thermal stability. Different mass ratios of PVDF-HFP, (EMIM)(TFSI), and LiTFSI were mixed and dissolved in DMF. Different amounts of graphene oxide were further dispersed in the solution. The cell with 0.60 g PVDF-HFP, 1.00 g (EMIM)(TFSI), 0.40 g LiTFSI and 0.01 g graphene oxide showcased the best performance. The cell exhibited high thermal stability in TGA analysis, where the thermal decomposition temperature of the GPE increased as the content of IL was increased, as seen in Figure 12.

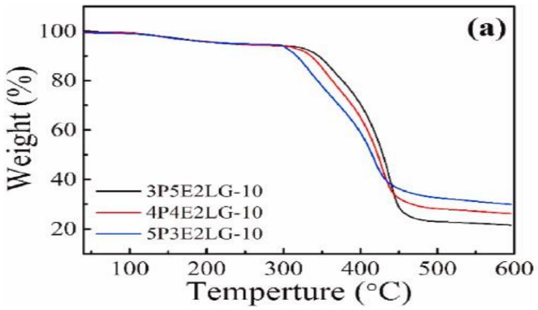

Figure 12: TGA curves of GPEs containing different amounts of ILs as adapted from reference [18].

The results also displayed low crystallinity of the GPE which in turn helped improve ionic conductivity. The cell exhibited maximum ionic conductivity of 2.1 x 10^{-3} S cm-1 at 30°C which suggests a good inhibitory effect on lithium dendrite growth. The cell showed an initial discharge capacity of 163.7 mAh/g at 0.1C. The study doesn't mention if the cell cycled steadily for a larger number of cycles but due to its high electrochemical performance, PVDF-HFP and ILs show great potential for future implications.

More studies have been done where (EMIM)(TFSI) have been used to build GPE. Hanyang Chen et al. created a GPE using (EMIM)(TFSI) [19]. However, the authors also added Boron Nitride (BN) and Polymerized Dopamine (PDA@BN) along with PVDF-HFP, (EMIM)(TFSI), and LiTFSI. Various amounts of PDA@BN were added to the GPE and the cells with 6 wt% PDA@BN showed the best performance. According to the authors, the cell cycled steadily because BN effectively inhibited the growth of lithium dendrites by protecting the lithium metal anode during battery cycling. Figure 13 compares the effect of PDA@BN on cycling stability. The discharge capacity of cell with no PDA@BN tends to go down after 70 cycles while the cell with 6% PDA@BN tends to cycle stably.

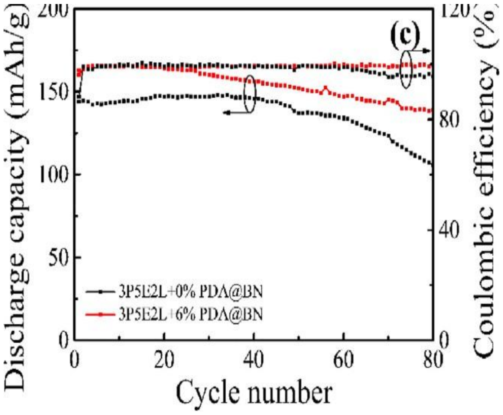

Figure 13: Charge/Discharge curves of GPE as adapted from reference [19].

The cell showed an ionic conductivity of 22.6 x 10^{-3} at room temperature and cycled stably for 300 hours without any short circuits which supports the claim that BN inhibits the growth of lithium dendrites.

Amongst all the twelve papers across three subcategories, the study by Hanyang Chen et al. which utilized Polymerized Dopamine (PDA @BN) and Boron Nitride (BN) as an additive with PVDF-HFP as the host showed the most promising results. The cell with 6% PDA@BN exhibited great electrochemical performance with ionic conductivity at 22.6 x 10^{-4} S/cm and a maximum discharge capacity of 162.9 mAh/g. The performance is exponentially high compared to the solid-state electrolyte batteries utilizing PEO and PVDF as hosts. An in depth discussion and analysis of all the papers is detailed in next section.

Discussion

Table 1 highlights the key metrics and results that were measured in each of the categories of electrolytes. It highlights the effect of each additive on the electrochemical performance of the battery.

Electrolyte	Study	Additive	Ionic conductivity at 25°C (S/cm) 10^{-4}	Discharge specific capacity (mAh/g)	Current density (C)	Capacity retention	Glass transition temperature (°C)	Coloumbic efficiency (%)	Ref
PEO	1	Silica	0.075	150.3	0.07	90.4	-48.5	~100	[6]
	2	PPC	0.204	125	0.5	-	-41.3	~100	[8]
	3	PVA & PESf	0.364	167	0.1	-	-	~98	[9]
				158.4	0.5				
	4	SiO_2, SN	0.8	157.5	0.5	99%	-	~96	[10]
PEO/PVDF	5	$LiClO_4$, SN	0.95	132.2	0.2	-	-75.61	~99	[11]
				105.5	0.5				
	6	LLZO	0.42	133	0.1	96.50%	-	~100	[12]
	7	LLZTO	1.05	133.4	0.5	-	-	-	[14]
	8	LATP	5.24	125	0.5	97.72%	-	-	[15]
PVDF-HFP	9	GPEs, SN	13.5	127.3	0.1	93.10%	-	-	[16]
				119.2	0.5				
	10	PIL	17.8	157.3	0.5	-	-29	~98.50	[17]
	11	EMIM, TFSI, Graphene oxide	21	163.7	0.1	88%	-	99	[18]
	12	BN, PDA@BN	22.6	162.9	0.1	85%	-	99	[19]

Table 1: Comparison table.

In section 2, PEO was used as an electrolyte host for SSE, and certain additives were added across different studies to increase the cell performance. The addition of SiO_2 and SN to the PEO electrolyte increased the cell performance the best by decreasing the crystallinity of the electrolyte. Among studies 2, 3, 4 the electrolyte with PVA and PESf showed the highest discharge capacity at 0.5 C but didn't show as good ionic conductivity as study 4 which is due to higher impedance value as compared to study 4. As the impedance increases, the cell performance decreases [20]. The addition of silica fillers in study 1 showed the least favorable results due to low ionic conductivity and current density. The cells only cycled steadily for ~90 cycles, while the cells in studies 2, 3, and 4 cycled steadily for over 200 cycles. The low cycle stability is not practical for future real-life implications. In addition to lowering the crystallinity, the addition of SiO_2 and SN in study 4 also increased the mechanical strength of the PEO electrolyte by 135% which makes it a great candidate for further research.

Across all three subcategories, SN was used as a plasticizer by several authors. Based on the data in Table 1, SN performed the best in study 9 with PVDF-HFP as a host in GPE. The cell prepared in study 9 showed a high ionic conductivity of 13.5×10^{-4} S/cm at room temperature and it could be credited to high liquid electrolyte absorptivity by GPE. However, the cell in study 9 showed low capacity at 0.5 C compared to studies 4 and 5 at 0.5 C where authors used PEO and PEO/PVDF as electrolyte hosts respectively. The high capacity and capacity retention in study 4 could be credited to the presence of SiO_2 fillers along with SN because the authors found that the mechanical strength of the PEO PEO electrolyte increased by 135% after the addition of fillers. An increase in mechanical strength tends to increase the capacity retention during cycling [21]. In study 5, the presence of 45% $LiClO_4$ decreased the crystallinity of PEO/PVDF electrolyte significantly causing greater segmental mobility of ions and increasing the ionic conductivity by ~17% as compared to study 4. Across all three studies, the cell performance increased by different mechanisms of low crystallinity, high mechanical strength, and high liquid electrolyte absorptivity which shows the SN along with other additives is a great plasticizer that could eventually be used in future implications.

In section 3, both PEO and PVDF were used as electrolyte hosts for SSE, along with certain additives. In studies 6 and 7, an inorganic compound LLZO and LLZTO was added to the PEO/PVDF blend. The cell with LLZTO showed higher ionic conductivity as compared to LLZO. The positive response in LLZTO can be credited to the presence of HFP in PVDF. The presence of HFP further decreases the crystallinity of the electrolyte by increasing the amorphous region in the PEO/PVDF blend [12]. The results also broaden future research scope by incorporating both organic and inorganic materials in the SSE. The cell with LATP showed the most promising results as the cell showed 300 times more ionic conductivity than LLZTO and the electrolyte blend in LATP didn't contain HFP, which demonstrates its strength in increasing cell performance. The cell with LATP shows excelling cycling stability for over 1000 hours (~ 500 cycles), in a high charge density of 1 C, without a short circuit. The results in study 8 are indicative that the addition of LATP in PEO/PVDF SSE could be used for real- life use with further research into advancing its cell performance.

In section 4, PVDF-HFP was used as an electrolyte host for GPE, along with certain additives. The additives in studies 11 and 12 showed very similar results in terms of ionic conductivities, discharge capacities at 0.1 C, capacity retention, and coloumbic efficiency.

However, the mechanisms by which the cell performance increases are different in both studies. In study 11, the addition of (EMIM)(TFSI) and graphene oxide increases the thermal stability of the electrolyte whereas the addition of BN and PDA@BN inhibits the growth of lithium dendrites which allows the cell to cycle steadily for long hours without short circuit. The cell with BN and PDA@BN is relatively better than the rest in its category because the authors reported steady cell cycling for 300 hours. Study 11 shows great results, but no long-term steady cycling data has been reported in the study. Study 10 increases the cell performance by significantly decreasing the electrolyte crystallinity by 88% which hasn't been achieved by any other additive across all three sections where authors tried to increase cell performance by reducing the crystallinity of the electrolyte.

Conclusion

Solid-state electrolytes demonstrate the advantage of good thermal stability, wide electrochemical windows, and high mechanical properties that have attracted more researchers and scientists. GPEs provide the same benefits along with higher ionic conductivity as compared to SSEs. The results show that PVDF-HFP as a host provides better results in both SSEs and GPEs due to its highly amorphous region. Succinonitrile as an additive shows great promise for future industrial use due to its ability to reduce crystallinity in SSE as demonstrated across all three subcategories in this paper. In PEO/PVDF based SSEs, the addition of LATP allowed the cell to steadily operate for over 500 cycles which shows its potential to replace liquid electrolytes with more advancement. GPEs with PVDF-HFP as host showed significantly better performance as compared to SSEs with ionic conductivity of 22.6 x 10^{-4} S/cm with the addition of boron nitride and polymerized dopamine. Due to its ability to cycle steadily with excellent electrochemical performance, GPEs show more promise as compared to SSEs in terms of replacing liquid electrolytes in the near future.

Cell performance can be increased by several mechanisms like reducing the crystallinity of electrolytes, increasing the mechanical strength of electrolytes, reducing lithium dendrite growth, and reducing impedance.

Conflicts of Interest

The authors declare no conflicts of interest in this research. The study was privately funded and independently conducted, with no influence from any external organizations or entities. All findings and conclusions reflect the authors' unbiased scientific efforts, ensuring the integrity and transparency of the research process.

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