

SOLID POLYMER ELECTROLYTE FOR LITHIUM-ION BATTERIES FOR THERMAL JACKETS

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Abstract

The batteries used in thermal jackets are typically conventional liquid electrolyte types. Still, they face several challenges, such as liquid electrolyte leakage and freezing when exposed to extreme cold weather conditions. Although lithium-ion batteries are engineered for use in freezing climates and are crucial for powering the heating elements that provide warmth, they often employ liquid lithium nitrate electrolytes. These electrolytes are chosen due to high energy density, longevity, and efficiency. However, when exposed to extremely low temperatures, the batteries suffer from reduced ion portability and decreased efficiency. In severe cases, freezing the liquid electrolyte can hinder battery operation and potentially lead to shutdown. Furthermore, at sub-zero temperatures, the transfer of electrons is severely restricted, leading to sluggish battery response, impaired power delivery, or even complete failure. To overcome these limitations, extensive research is being conducted on solid polymer electrolytes, which offer enhanced stability and safety compared to their liquid counterparts. Solid polymer electrolytes eliminate the risk of leakage and maintain performance even in frigid conditions, making them a promising solution for next-generation lithium-ion batteries in thermal jackets. The challenges described are common in liquid lithium-ion batteries. Solid polymer electrolytes have emerged as a promising alternative to handle these issues, offering enhanced safety and stability. Solid polymer batteries have several advantages and pave the way for innovative designs in wearable electronics, flexible displays, and other cutting-edge technologies. This review article discusses the current research in solid polymer electrolyte and their efficacy in working and design.

Keywords: Solid polymer electrolyte, Lithium Batteries, ionic conductivity.

Introduction

Thermal jackets are a very crucial piece of personal protective clothing for extreme cold conditions. These jackets integrate battery-powered heating elements to regulate temperature, ensuring user comfort and preventing cold-related injuries like frostbite and hypothermia. Conventional lithium-ion batteries use liquid electrolytes to facilitate the movement of lithium ions between the anode and cathode during the charge and discharge of ions. These liquid electrolytes are prone to freezing and crystallization at sub-zero conditions. These solid polymer electrolytes are composed of a polymer binders doped with lithium salts, which provides a stable medium for ion conduction without the need for a liquid phase. This solid state prevents freezing and crystallisation. The solid polymer electrolyte has emerged as a promising solution for low-temperature battery applications. The solid polymer electrolyte maintains its stability and ionic conductivity even at low temperatures. This characteristic makes them suitable for powering thermal jackets in harsh environments, where maintaining consistent battery performance for both comfort and safety. The solid polymer electrolyte aims to achieve a uniform and interconnected ion-conduction pathway, which mitigates the limitations of conventional solid polymer electrolytes, and it ensures optimal performance under varying temperature conditions.

Factors Influencing

Ionic conductivity

the Li⁺ cations are dissolved in the polymer solvents and are moved by the motion of the polymer chains. The number of free Li⁺ cations and the moving ability of the chains significantly affects the Li⁺-transport ability within the SPE, in turn, influencing the performance of the batteries^[8]. A good understanding of the conducting mechanisms is favourable for the design and selection of polymer structures for the room temperature operation of solid polymer lithium batteries^[9].

Glass transition temperature (T_g)

The glass transition temperature (T_g) is one of the most important properties of polymers. It is the temperature at which the chain segments start to move while the molecular chains do not move. Below their T_g, there only exist the vibrations of molecule atoms or groups in their respective equilibrium positions^[10]. The polymers are rigid and brittle, and the molecules have very little mobility. At the T_g, a dramatic change occurs in the physical properties of the polymer host, including the density, specific heat, mechanical modulus, mechanical energy absorption, their dielectric and acoustical equivalents, and rate of gas or liquid diffusion through the polymer^[11].

Degree of crystallinity

Crystallinity is the extent of long-range order in a material and has a significant impact on the material properties. The crystallization of polymers is a process associated with the partial alignment of their molecular chains^[12]. The crystallization process involves nucleation and crystal growth. Nucleation starts with small, nanometer-sized areas where some chains or their segments align. These nucleation seeds can either dissociate or grow further depending on the conditions. Apart from the thermal mechanism, nucleation is strongly affected by impurities, plasticizers, fillers, and other additives in the polymer. For this reason, the crystallinity can be reduced by the addition of inorganic particles or plasticizers into the polymer^[13].

Dissolution of polymer

The dissolution of solid polymer electrolytes (SPEs) in lithium-ion battery is fundamentally influenced by the dissolution behaviour of the polymer host with the lithium salt. In contrast, for wearable thermal jackets, flexibility, thermal stability, and low-temperature operation are critical and electrochemical performance. The dissolution of a polymer in an SPE system refers to its ability to solvate and dissociate lithium salts within its polymeric matrix. Polymers such as PEO, due to their polar ether groups, interact strongly with lithium ions. The PVDF-HFP (Kynar™ 2801, Elf Atochem) was dissolved in a mixture of a solvent and a non-solvent (the ratio of solvent and polymer is 9-12, and the ratio of non-solvent and polymer is 0.25-0.5). The dissolution took place at 50-60°C for about 2 hours under continuous stirring. Stoichiometric quantities of PVA, PVP, and LiNO₃ are dissolved in DMSO and then stirred until a homogeneous solution is obtained, and the final solution is poured into polypropylene dishes and dried in an oven at 70°C for 6 days to ensure the removal of solvent traces. Smooth, uniform, thin films, which are transparent to visible light with good mechanical properties, have been obtained. To prepare the polymer electrolyte film, 2.8 g of PEO and 1.2 g of ENR50 were dissolved separately and were continuously stirred with a magnetic bar for 24 hours. These two solutions were mixed and continuously stirred with a magnetic bar for 24 hours. These two solutions were continuously stirred for another 24 hours to obtain a homogeneous mixture. The solution was cast on a Teflon mold and allowed to evaporate completely in a fumed hood at room temperature to produce a film. The film was then kept in a vacuum oven at 60°C for 24 hours to remove the residual solvent. Samples were stored in a desiccator until further usage. This procedure provided mechanically stable, free-standing, and flexible films of thickness from 150 to 250 μm. The preparation of SPE was done in an open atmosphere condition at room temperature. Required amounts of PMMA (Aldrich), with an average molecular weight of 996,000 g/mol, PEO (Aldrich), with an average molecular weight of 1,000,000 g/mol, and EC (Merck) were dissolved. The mixture was stirred with a magnetic stirrer at room temperature. LiCF₃SO₃ (Aldrich) and SiO₂ fillers (Aldrich) were added according to the appropriate weight percent into the mixture. The composition for 5 wt% PMMA and 95 wt% PEO-blend solid polymer electrolytes (5 PMMA: 95 PEO) consists of PMMA, 0.0827 g; PEO, 1.5711 g; EC, 0.5513 g; SiO₂, 0.06 g; and LiCF₃SO₃, 0.735 g. An appropriate stoichiometric ratio of PMMA was dissolved in acetonitrile (Merck), and the solution was stirred for 12 hours. Subsequently, the calculated amount of LiClO₄ was added and stirred for 12 hours to facilitate homogeneous mixing and complexation. The resulting final polymer-salt complex solution for each salt concentration was cast into films in polypropylene dishes, and the solvent was allowed to evaporate slowly at room temperature (27°C). An optimized PVDF 19% polymer solution was prepared by dissolving in 10 ml of DMSO solution. PVDF and LiNO₃ composite membranes were prepared with different LiNO₃ dispersions.

S.No	Polymer	Electrolyte	Type	Ionic conductivity ($S\text{ Cm}^{-1}$)	Electrochemical window	DSC		Ref
						T _g	T _m	
1	PEO	LiCF ₃ SO ₃ (25%)	FILM	9.1×10^{-5} (25°C)			49°C	[1]
2	P (STFSI Li)-PEO-P(STFSI Li)		FILM	1.3×10^{-5} (60°C)	5V			[2]
3	PMMA & PEO, EC	LiCF ₃ SO ₃ (Filler-SiO ₂)	MEMBRANE	2.6301×10^{-4} (25°C)			86°C	[3]
4	PMMA	LiClO ₄	FILM	9.95×10^{-11}				[4]
5	PVDF	LiNO ₃	MEMBRANE	1.61×10^{-3} (28°C)	240 Ohm.Cm ²			[5]
6	PVDF-HFP	TiO ₂ (6.5%)	MEMBRANE	1.66×10^{-3} (25°C)	4.7V			[6]
7	PVA	KI-I ₂	MEMBRANE	8.41×10^{-3}				[7]
8	PVA/PPVP	LiNO ₃ (30%)	FILM	9.917×10^{-5}		82°C		[8]

Table 1 : Comparative Data of Ionic Conductivity, electrochemical, DSC, T_g, and T_m of Polymer Electrolytes

Conclusion

This review explores more on advancements and potential of solid polymer electrolytes for lithium-ion batteries. This type of SPE provide more advantages compared to liquid electrolytes, including higher safety, good thermal stability and flexibility in battery design to use in thermal jackets. However, the SPEs have good properties; some challenges are still there to overcome. The ionic conductivity of SPEs at room temperature remains an important obstacle to their pervasive adoption. Also, there is a need for further optimization of the mechanical properties of the polymers to ensure long term performance in extreme weather conditions.

In the future, research should focus on improving the manufacturing methods for large production of SPEs. It will be more important for their practical application in lithium-ion batteries.

In conclusion, the SPEs have good potential for innovative lithium ion battery technology; further development and research are needed to realize the SPE's performance and abilities, particularly in the area of thermal jackets.

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