

SOLID ELECTROLYTES IN LITHIUM BATTERIES: THE ROLE OF METAL OXIDES IN PERFORMANCE OPTIMIZATION

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ABSTRACT

Because of the rapid development and spread of lithium-ion batteries, there has been an increase in the number of concerns regarding the potential dangers that are associated with the utilization of volatile organic electrolytes. As a result of this, solid-state electrolytes have attracted the interest of both the scientific and industrial communities due to the fact that they are more energy dense and safer than other substances. Solid-state electrolytes confront substantial hurdles that inhibit commercialization, such as poor lithium-ion conductivity and high transfer impedance at the interface between solid-state electrolytes and electrodes. Despite these exciting potential, solid-state electrolytes continue to face these challenges. This review will provide an introduction to typical lithium-ion conductors, which will include inorganic, organic, and hybrid electrolytes that include inorganic and organic elements. Additionally, the mechanics of lithium-ion conduction and the parameters that influence performance will be discussed. Furthermore, this review will present strategies to increase ionic conduction, as well as future development trends, and will undertake an in-depth examination of both advanced and current approaches for characterizing materials.

Keywords: Lithium-ion battery ;Solid polymer electrolyte membrane; Thermal runaway

INTRODUCTION

In today's world, the storage of energy is an extremely important concern, and lithium-ion batteries (LIBs) are playing a crucial part in this regard. The use of lithium-ion batteries can be found in a wide variety of applications, such as electric vehicles, electronic devices, toys, portable power tools, appliances, and conventional energy storage systems. 1991 was the year that Sony made a lithium-ion battery available for commercial use. A report by Fortune Business Insights estimated that the value of the LIB market in the year 2020 was 36.9 billion US dollars. The market was estimated to be worth 48.19 billion in 2022, and it is anticipated to increase at a compound annual growth rate (CAGR) of 18.9% between the years 2023 and 2030. Damage caused by LIBs is a serious risk issue at the moment, taking place along with great economic expansion. According to a report from Island Tel of Prince Edward Island, there were two instances in which the batteries of cellular phones that had been short-circuited constituted a risk of fire. There was yet another incident that took place on November 11, 2004, which involved an explosion with lithium-ion, and it resulted in two researchers being injured. Around the world, there are a great number of examples of this kind. As a consequence of this, the biggest disadvantage of using lithium-ion batteries is the safety problems that are linked with their use.

A microporous separator, a liquid electrolyte, a positive electrode (anode), and a negative electrode (cathode) are the typical components that make up a lithium-ion battery (LIB). A mixture of organic solvents, lithium salts, and functional additives is the fundamental component of modern lithium-ion battery liquid electrolytes. The organic solvents are primarily composed of typical linear and cyclic carbonates. Lithium salts are also a component of the mixture. Oxidation reactions take place at the anode of the battery. It is necessary for the anode to supply the cathode with a suitable amount of electrons in order to meet its requirements. When the cathode's potential is exceeded by the pace at which the anode provides electrons, a phenomenon known as an electron choke takes place. In most cases, the materials that are used as anode materials are graphite, acetylene black, PVDF, and NMP. At an electrode known as a cathode, a reduction reaction takes place between two electrons. The cathode is responsible for acquiring electrons from the anode. As part of the manufacturing process for cathodes, lithium metal oxides are utilized. Electrolytes are the medium via which electrons are transferred from the anode to the cathode in conventional lithium-ion batteries through the use of a conduit. Electrolytes that are liquid are often utilized in situations like this one. As a composition for the electrolyte, water or other solvents that contain dissolved salts, acids, or alkalis are utilized. Separators function to differentiate between the anode and the cathode in conventional lithium-ion batteries, making them an indispensable component. If the separator is not there, the anode and cathode will come into touch with one another, which will result in a short circuit. As a result of their lower flash point, which is 31 degrees Celsius, linear carbonates make the electrolytes completely flammable. Because of this, liquid electrolyte is one of the key factors that contribute to thermal runaway in lithium-ion batteries. In an effort to find a solution to this problem, numerous initiatives have been completed. Over the course of the past several years, a multitude of projects regarding the incorporation of novel solvents, salts, and additives, including organosulfur compounds, have been conducted. Propylene sulfite, fluorine-substituted compounds like fluoroalkyl carbonates, organophosphorus compounds, lithium bis(oxalate) borate (LiBOB) and lithium trifluoroethyl phosphate (LiFAP), organonitrates, sulfates, phosphates, reactive gases like sulfur dioxide and carbon dioxide organoboron complexes, olefins, vinylene carbonate, and aromatic compounds that are used as overcharge protection agents are some examples of such substances. A significant number of the solutions that were described earlier have not been able to demonstrate that they are feasible for mass production. This is because of the limitations that are associated with efficacy, performance evaluation, and large-scale manufacturing.

Due to the fact that electrolytes are responsible for the vast majority of mishaps and damages that are associated with lithium-ion batteries (LIB), great efforts are currently being made to produce LIBs that do not require liquid electrolytes during their operation. Researchers are actively focusing their attention on solid-state electrolytes, in particular solid polymer electrolytes (SPEs), which are capable of performing the functions of both electrolytes and separators. In addition, they are investigating a variety of alternative approaches to the identification of safer electrolytes. SPEs are ion-conducting solid materials that are mostly made of polymers. In this context, the term "SPE" represents these materials. Using solid polymer electrolytes (SPEs) rather than liquid electrolytes has a number of advantages, the most important of which is the elimination of short circuits, issues regarding leakage, fire dangers, and manufacturing problems. There are a number of different materials that are currently being utilized for the preparation of solid polymer electrolyte (SPE). These materials include the garnet structure $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), the perovskite structure $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ (LLTO), the LASICON structure $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$ (LZGO), the NASICON structure $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ge}_{1.5}(\text{PO}_4)_3$ (LAGP), and

$\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ (LATP) . Among these, LATP is the one that receives a lot of attention because of its higher Li-ion conductivity and stability. Despite this, the utilization of LATP in commercial lithium-ion batteries is met with challenges due to the fact that it is susceptible to air, has a high cost, and is thermally unstable .Through the utilization of a solid polymer electrolyte (SPE) membrane, this research proposes a novel method to the construction of lithium-ion batteries (LIBs) that are both cost-effective and thermally stable. The goal of this strategy is to enhance electrochemical performance while simultaneously addressing issues of thermal instability and high cost. Lithium chloride (LiCl) and polystyrene (PS) were utilized in the production of solid polymer electrolyte (SPE), which exhibited homogenous microporosity and proved thermal stability up to 400 degrees Celsius. The battery that was built exhibits excellent electrochemical efficiency during the charging and discharging evaluations, as well as robust air stability throughout the procedure. Therefore, this battery has the potential to be considered a viable alternative to conventional lithium-ion batteries when it comes to applications in the industrial sector..

EXPERIMENTAL

Battery fabrication

The process of fabricating a battery involves the preparation of the anode, the cathode, and the solid polymer electrolyte membrane. For the manufacture of the graphite anode, a viscous slurry is created by combining 80 weight percent graphite nanoparticles, 10 weight percent acetylene black (conductive carbon), and 10 weight percent polyvinylidene fluoride (PVDF) as a binder. This mixture is then mixed with N-methyl-2-pyrrolidone (NMP) solvent. A mixture of 85 weight percent LMO/Graphene nanocomposites, 5 weight percent acetylene black, and 10 weight percent polyvinylidene fluoride was used as the binder in N-methyl-2-pyrrolidone solvent. This mixture was used to make the LMO/Graphene cathode slurry. After that, the viscous slurries were applied on aluminum foils with a bar coater, and then they were placed in an oven at a temperature of 120 degrees Celsius for an entire night. A subsequent fabrication of the SPE membrane was carried out by means of the sol-gel apparatus. During the course of one hour, polystyrene and NMP were subjected to agitation at temperatures ranging from 95 to 100 degrees Celsius. This caused polystyrene to dissolve in NMP. It was possible to create a polymeric solution that was transparent. At the same time, LiCl and NMP were stirred in another magnetic stirrer at a temperature of 100 °C until a clear solution was obtained. These two solutions were then mixed and stirred for about 30 min to obtain a LiCl, PS, and NMP solution. Finally, the resultant homogeneous solution was cast onto a glass plate and was kept overnight to fabricate a microporous membrane. The ratio of LiCl and Polystyrene was maintained at 1:5. Then a Pouch cells prototype battery was manufactured with the anode, solid electrolyte membrane, and cathode shown in Fig. 1. Solid electrolyte membrane was placed in between the anode and cathode in such a way so that anode and cathode cannot be touched to each other, which causes short circuit of the battery. The resulting cell was sealed by a pouch and the positive and negative terminals were left outside the pouch, which allowed the performance test of the prepared solid electrolyte battery.

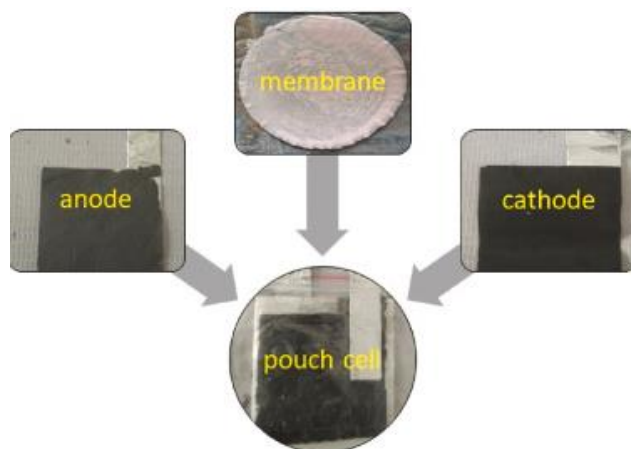


Fig1 SPE-integrated Li-ion battery

Characterization

Using the Fourier transform infrared spectroscopy (FTIR) model of the FT/IR-4700, the functional groups of the SPE membrane were examined. The spectrum wavelength range for this analysis was from 500 cm^{-1} to 4000 cm^{-1} . A scanning electron microscope (SEM) (Hitachi, SU1510) was used to investigate the surface morphology of the membrane that was manufactured, and a thermogravimetric analyzer (TGA) (SDT 650) was utilized to investigate the thermal properties of the membrane. This experiment made use of PS and PVDF that were readily available for commercial use and were purchased from the local market. Polystyrene (PS), which is extensively used as an industrial material, normally has a weight-average molecular weight (M_w) that falls somewhere between 150,000 and 400,000. This is the case for commercially available PS. According to the results of gel permeation chromatography (GPC), the molecular weight (M_w) of PVDF powder is approximately 275,000 on average. Polystyrene (PS) has a polydispersity index (PDI) that is lower than 1.1, whereas polyvinylidene fluoride (PVDF) has a PDI that is 2.57.

Charging and discharging test

An apparatus that performed manual charging and discharging was utilized in order to investigate the electrochemical performance of the battery that was created. For the purpose of determining the voltage and current parameters, a digital multimeter was utilized. The voltage was first measured at a lower value of 0.4 V when it was first taken. For the purpose of charging the pouch cell under conditions of constant voltage, a direct current (DC) power supply was utilized. Over the course of a predetermined charging period, there is a one-volt increase in voltage. During the time that the battery was being charged, the supply current was measured. In order to evaluate the air's stability, the pouch cell did not have an airtightness. We did not observe any response or instability. During the discharging test, a resistor with a resistance of 100 kilohms was utilized in order to determine the discharge rate.

RESULTS AND DISCUSSION

Physiochemical analysis

The SEM images of the solid polymer electrolyte (SPE) membrane are shown in Fig. 2. The textures exhibit a random overlapping pattern and are intricately arranged inside a three-dimensional network characterized by a porous structure. The membrane is appropriate for the fabrication of LIB because there is a clear porosity channel for the Li-ion to flow through

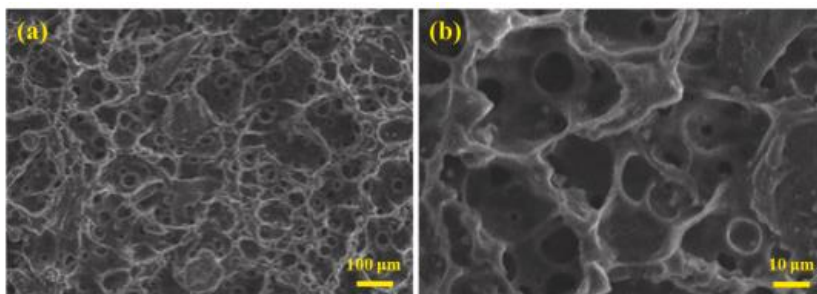


Fig 2 SEM images of SPE membrane at (a) 100 μm and (b) 10 μm magnification

In FTIR analysis, various types of functional groups are observed, such as OH stretching, N stretching, C stretching, CH bending, OH bending, and CO stretching, as shown in Fig. 3. Strong and broad alcohol stretching bond is observed at 3356.78 cm^{-1} . At 1442.37 cm^{-1} , a medium O–H bending is observed, which is mainly carboxylic acid. Strong azide and aromatic ester are present at 2128.09 cm^{-1} and 1285.97 cm^{-1} respectively. Conjugated alkene, alkane, and carboxylic acid are found at 1638.86 cm^{-1} , 1476.05 cm^{-1} , and 1442.37 cm^{-1} respectively in medium appearance.

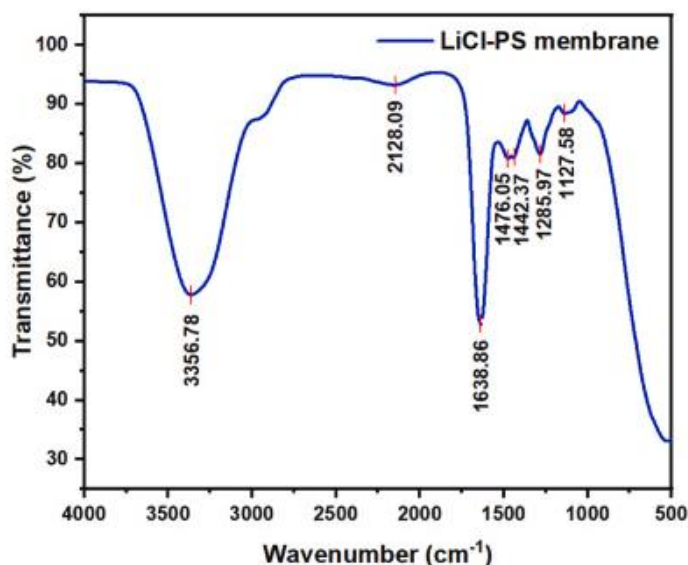


Fig 3 FTIR spectrum of SPE membrane

The thermogravimetric analysis (TGA) of the SPE membrane is observed up to $600\text{ }^{\circ}\text{C}$ as shown in Fig. 4. Two phases of mass loss are visible on the curve. The observed decrease in mass at temperatures below $200\text{ }^{\circ}\text{C}$ can be attributed to the progressive evaporation of moisture that was absorbed, as indicated by the presence of the

hydroxyl functional group in the FTIR test. The degradation of the polystyrene matrix was responsible for the second mass loss seen throughout the temperature range of 200 °C–400 °C.

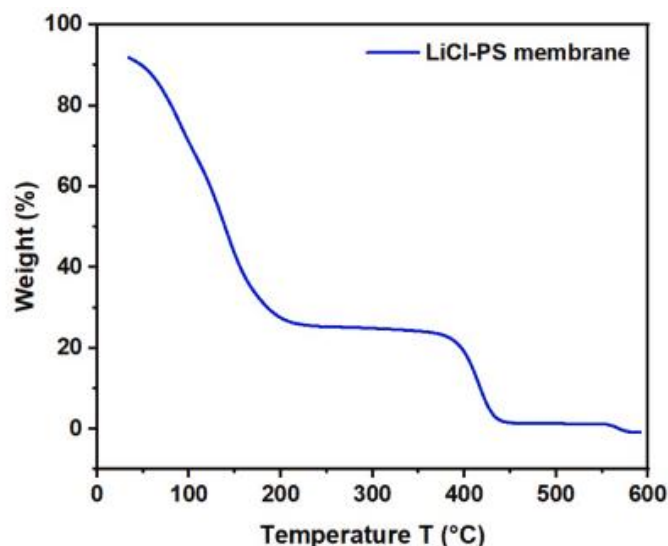


Fig 4 TGA curves of SPE membrane

CHARGING DISCHARGING PERFORMANCE ANALYSIS

The fabricated battery with a solid electrolyte membrane is tested repeatedly to analyze the battery performance. To analyze the battery performance, 5 cycles of charging and discharging were performed, as shown in Table 1 and Table 2. As the pouch cell is a small portion compared to the conventional Li-ion battery, 5 cycles are sufficient to understand the fabricated battery performance. In each cycle, the cell was charged for 30 min. The discharging data were collected for a constant time duration of 90 min.

Table 1 Charging conditions of the fabricated battery

Cycle	Charging		Voltage applied (V)	Average Current (mA)	Time (min)
	Initial Voltage (V)	Final Voltage (V)			
1	0.4	0.97	4.0	0.568	30
2	0.63	1.0	4.0	0.519	30
3	0.46	0.95	4.0	0.47	30
4	0.41	0.90	4.0	0.486	30
5	0.52	0.86	4.0	0.485	30

Cycle	Average Current (μA)	Standard Deviation of Average Current (μA)	Load ($\text{k}\Omega$)	Specific Capacity ($\mu\text{Ahr/gm}$)	Standard Deviation of Specific Capacity ($\mu\text{Ahr/gm}$)	Time (min)
1	5.32	0.762594256	100	7.89	1.121730805	90
2	5.37		100	7.99		90
3	4.23		100	6.23		90
4	3.97		100	5.93		90
5	3.76		100	5.63		90

the current versus time curve during charging conditions. In cycle 1, the initial current flow was observed at 0.2 mA, whereas the highest current flow recorded in this cycle was 0.64 mA. The average current flow was found 0.568 mA. In this way, the battery was charged for 30 min and then was discharged for 90 min periods.

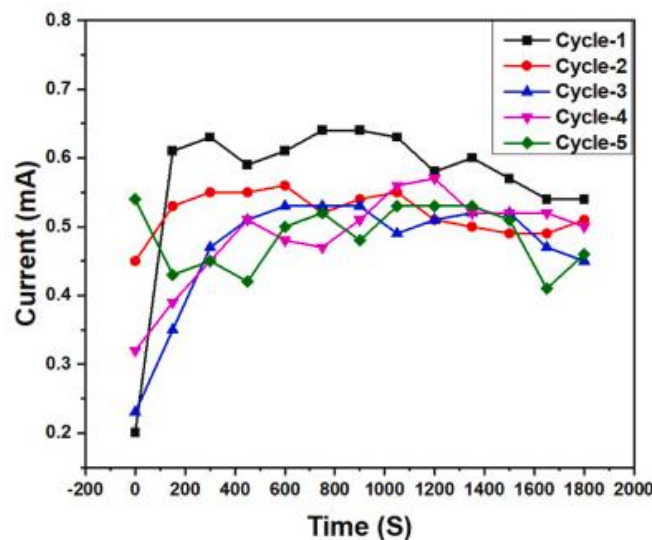


Fig 5 Current vs time curve during charging

Following a period of ten minutes consisting of discharge, the second charging cycle started. At the beginning of the second charging cycle, the current that was given was measured to be 0.45 milliamperes, which is a very significant amount. In the course of this cycle, the highest recorded current flow was 0.56 milliamperes, while the average current flow was 0.519 milliamperes. There is a fluctuation of 0.08 milliamperes in the maximum current flow when compared to the first charging cycle. Also, charging cycles 3, 4, and 5 were carried out, and the results showed that the average current flow gradually decreased throughout the course of the experiment.

This graph shows the relationship between voltage and time for five different charging cycles. Every cycle was broken up into 150-second chunks for the purpose of data collection. An starting voltage of 0.4 V was used to initiate the charging process during cycle 1. Following a period of thirty minutes, the voltage came to a stable state, reaching a maximum recorded value of 0.97 V. It is the process of discharging that the battery goes through. It was found that there was a 10-minute pause after a discharge cycle that lasted for ninety minutes. During cycle 2, the beginning voltage reading was 0.63 V, and after thirty minutes of charging, the maximum voltage that was recorded was 1 V. When compared to the performance of the previous cycle, the performance of cycle 2 was significantly better. When compared to cycle 2, the voltage experienced during cycles 3, 4, and 5 was shown to be lower.

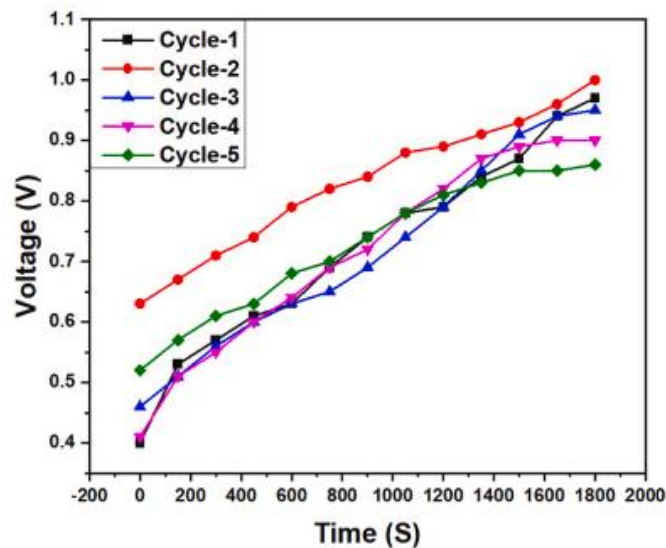


Fig 6 Cell voltage vs time curve during charging

In order to investigate the discharge characteristics of the battery that was created, a resistor with a value of 100 kilohms was utilized between the anode and the cathode. At regular intervals of three minutes and sixty seconds, a digital multimeter was used to record the voltage that was present across the resistor. Because of the magnitude of the resistance and the voltage that was measured, Ohm's law was utilized in order to calculate the existing current. Following that, the graph depicting the relationship between current and time was built for a total of five discharging cycles, as shown in Figure 7. In the first cycle, the average current flow was measured to be 5.32 microamperes (μA). During the second cycle, the value increases to 5.37 μA . In cycles 3, 4, and 5, there is a slight decrease in the value of the current flow. A determination was made regarding the particular capacity of the battery for each cycle. A period of ninety minutes was reserved for the purpose of monitoring the discharge cycle.

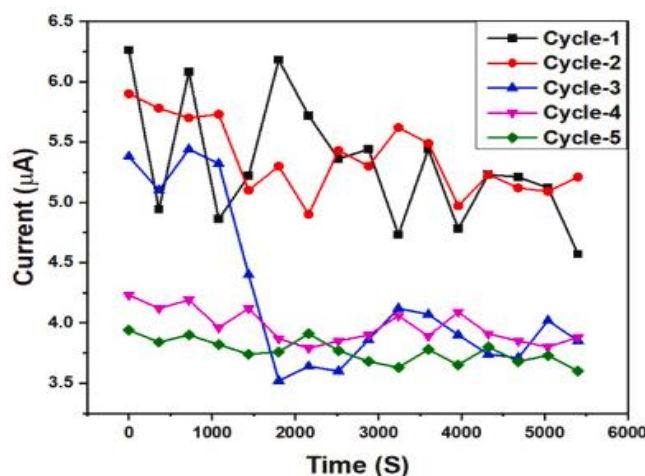


Fig 7 Current vs. time curve during discharging

The specific capacity of the battery that was manufactured was calculated by multiplying the instantaneous current by the time interval and then dividing the result by the total weight of the battery. Figure 8 and Figure 9 show the plotting of the voltage across the resistor as a function of time and the time versus particular capacity. Both of these plots may be seen in the figures. The specific capacity of the battery was observed to gradually decrease with each charging and discharging cycle that occurred during the five discharge cycles. This was observed to be the case. There is a strong correlation between a battery's longevity and a reduced variance in its specific capacity. Over the course of the second cycle of discharge, the specific capacity reached its highest point of 7.99 $\mu\text{Ahr/gm}$.

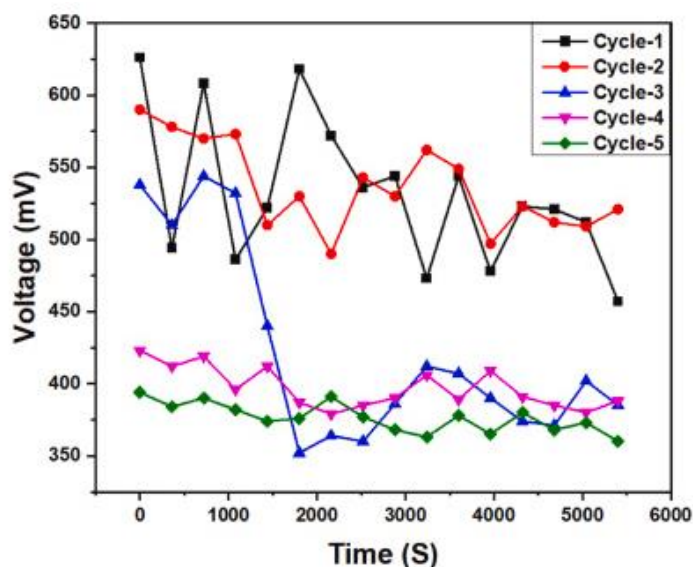


Fig 8 Voltage vs. time curve during discharging

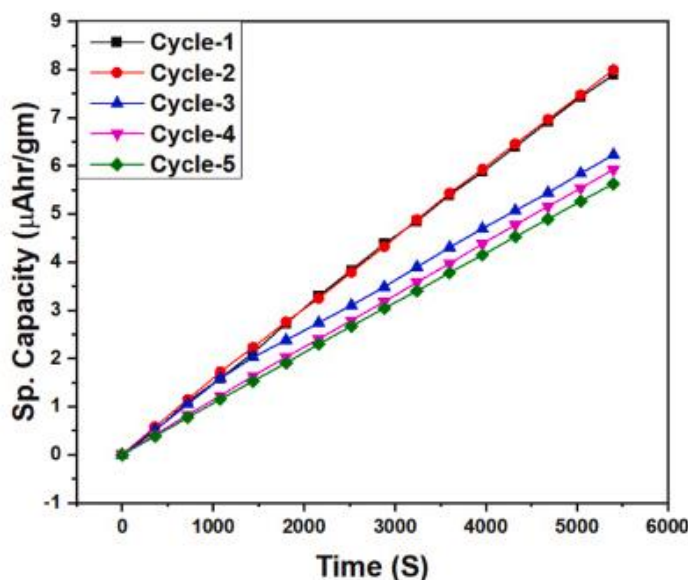


Fig 9 Specific capacity vs. time curve during discharging

In spite of the fact that the aforementioned findings shed light on the thermodynamic features of the produced membrane and the prototype battery, a more in-depth comparison with the Flory-Huggins interaction would be beneficial to the advancement of knowledge. There is a correlation between thermodynamic compatibility and mechanical stability, as indicated by the Flory-Huggins interaction value (χ) from .When the value of χ is decreased, it leads to an increase in miscibility, which in turn leads to an improvement in thermodynamic compatibility and mechanical properties, such as tensile strength and flexibility .On the other hand, an increase in χ might lead to a decrease in compatibility and mechanical characteristics, which can create difficulties for solid polymer electrolyte (SPE) membranes

For the purpose of its potential use in energy storage systems, polymer is a material that is widely investigated. One of the most important advantages of choosing polymer is that it is miscible. Over the course of several decades, it has been applied in a variety of research In polymer mixes, it is essential to have a solid understanding of the degree of miscibility. The information is provided by the Florry–Huggins interaction parameter, denoted by the symbol χ . There is a miscible polymer known as polystyrene. In the case of PS/PMMA polymer blends, the temperature dependence of χ is often described by the equation $\chi = 0.0284 + 3.902/T$ [47]. Additionally, polystyrene (PS) and lithium chloride (LiCl) are both dissolved in N-methylpyrrolidone (NMP), which acts as the solvent. The vapor pressure of NMP is 0.29 mm Hg when it is at 68 degrees Fahrenheit. NMP is a volatile organic molecule. Numerous studies have demonstrated that NMP is a good solvent for coatings and has been used in a variety of applications. There is a significant impact that the Li salt has on the ion conductivity of the PS membrane, which in turn has an effect on the Flory-Huggins interaction parameter.However, even minute amounts of salt can have a considerable impact on the phase behavior of these materials, which in turn can have an effect on their ionic conductivity and mechanical properties.

This subject has not been subjected to any empirical investigation in this work. The exploration of the mechanical stability of solid polymer electrolyte (SPE) membranes is one possible direction that could be pursued in the course of future research. In order to determine whether or not polystyrene (PS) and lithium chloride (LiCl) are compatible with one another thermodynamically, the Flory-Huggins interaction parameter

can be utilized. This work is anticipated to produce new insights that can be utilized in subsequent research pertaining to applications of energy storage.

CONCLUSIONS

The purpose of this study is to present a method that is efficient in the fabrication of solid polymer electrolyte membranes for lithium-ion batteries. This method offers a simple and straightforward approach. A solid electrolyte membrane composed of LiCl-PS was subsequently utilized in the construction of a battery. A developed chemical structure and good microporosity are both shown by the scanning electron microscopy (SEM) study of the membrane. Moreover, the TGA test demonstrates that the material possesses an excellent thermal stability of 400 degrees Celsius in contrast to linear carbonate electrolytes. During the performance examination, the pouch cell that was produced was not hermetically sealed, and there was no reaction that was found. There is a remarkable degree of stability that it possesses in the air. During the capacity test, the pouch cell displays a noteworthy level of physical stability after being subjected to five cycles of charging and discharging. In order to overcome the problems that are connected with conventional lithium-ion batteries, such as air sensitivity and thermal runaway, a viable solution has been developed. Because of these features, it is possible to begin a fresh scenario using this battery rather than the typical LIB. For the purpose of gaining a deeper understanding of the underlying mechanism, it will be possible in the future to investigate the thermodynamic compatibility between polystyrene (PS) and lithium chloride (LiCl) by employing the Flory-Huggins interaction parameter.

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