FABRICATING AND ANALYZING LIQUID AND POLYMER ELECTROLYTES FOR SODIUM-ION BATTERIES.

A Thesis submitted

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By

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ABSTRACT

Augustine, Kekule. M.S.M.S.E., Department of Mechanical and Materials Engineering, Wright State University,2024. Fabricating and Analyzing Liquid and Polymer Electrolytes for Sodium-Ion Batteries.

The abundance and the cost-effectiveness of sodium resources have made sodium-ion batteries (SIBs) viable alternatives to lithium-ion batteries. Developing low-cost and high-performance electrolytes is one of the key areas for the advancement of SIB technology. The highly conductive liquid or solid electrolytes have the potential for practical sodium-ion battery applications. Long-term stability, alternative polymers, and full-cell integrations are other avenues that need further research to improve scalability and performance for SIBs.

This research covers preparing and evaluating liquid and polymer electrolytes, with a focus on ionic conductivities. Liquid electrolytes were prepared by the dissolution of different sodium salts including NaCl, Na_2S, Na_2SO_3, and NaF in methanol, water, DMF (dimethyl formamide), n-propanol, and DMSO (dimethyl sulfoxide) solvents, in a concentration range from 0.01 M to 0.1 M. It is aimed to investigate the impacts of the solubility, polarity, and concentration on the ionic conductivities. Polymer electrolytes were prepared using the solvent casting technique. The films contained NaCl as the salt and PEO (polyethylene oxide) as the polymer host. The impacts of the two solvents, methanol and DMF, with and without plasticizer EC (ethylene carbonate) on the ionic conductivity of the polymer electrolytes were analyzed. The study validates that optimizing solvent and additive selection are paramount in developing high-performance electrolytes for SIBs.

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CHAPTER 1: INTRODUCTION

The world's energy configuration is dramatically changing, given increasing environmental preoccupation and pressing demand for sustainable energy storage. Energy storage systems have become paramount in the present era owing to the escalating global demand for renewable and sustainable energy sources (1). Lithium-ion batteries have been the go-to choice for portable energy storage for many years, and their use ranged from portable electronics to cars. While lithium-ion batteries are widespread, there is a need to explore better and more flexible battery technologies. Moreover, energy storage demand coupled with limited lithium availability and increasing cost have led to the development of new solution-seeking technologies. What grants them their importance is their capacity to furnish an economically workable or viable, and copious alternative to conventional lithium-ion batteries without relinquishing energy density or cycle life (2)(3).Efforts toward sustainability drive the demand for powerful battery technologies (4).

Most recently, sodium ion batteries (SIBS) have been advanced owing to the abundance of sodium in the Earth's crust and more uniform distribution than lithium. Sodium can be derived from seawater thus it is suitable for large-scale production (5). Sodium-ion batteries, among the various energy storage devices, are emerging as a promising alternative to the extensively utilized lithium-ion batteries primarily. A significant part of this growing interest in SIBs is related to their ability to be embedded into different battery market sectors, including the ones where the requirements for energy storage are very tough, like in EVs. They can also be a viable source of energy storage suitable in clean energy areas like wind, solar, and tidal power. The transition from lithium to sodium in battery technology will reduce the costs of EVs and improve energy storage systems. The central argument states that SIBs are an efficient replacement for traditional batteries as well as having the potential to provide cutting-edge breakthroughs on the issue of renewable energy storage.

Conceptually, the working of a SIB is quite similar to that of its lithium counterpart, wherein sodium ions shuttle between the electrodes through an electrolyte medium. Indeed, such similarity in operational mechanism has allowed the researchers to draw upon the already developed manufacturing infrastructure and experience, possibly accelerating their commercialization timeline. Recently, sodium-based batteries have shown remarkable progress in energy density, just like lithium. They compete with low-end lithium-ion batteries manufactured ten years ago, represented by early commercial EVs such as Tesla Roadster. This has resulted in the emergence of these batteries, driven by the increasing demand for reliable, affordable, and effective energy storage systems (6).

While sodium-ion batteries hold significant promise, realizing their full potential faces the hurdle of improving their electrochemical function. The larger ionic radius of sodium compared to lithium, 1.02 Å versus 0.76 Å, brings different complications in electrolyte design and electrode material selection. The heavy mass and a large radius of Na^+ ions pose challenges like low specific energy, unsatisfactory rate capability, and short cycling life. In addition, research has been carried out to make the whole battery highly performing, safe, and economical. So novel battery design and material optimization are needed (7). Resolving these problems requires preparing efficient host materials for swift, consistent, and effective sedation-sodiation and the best electrode and electrolyte.

It is important to note that electrolytes can also be used instead of solid-state traditional liquid electrolytes. That means that threats to safety, such as leakage and flammability, are impossible to experience. Manufacturers and developers have often preferred polymer composite electrolytes. This is because they have a good combination of electromechanical traits that are unique and flexible and are accompanied by ion transport properties that are improved significantly. When trying to evaluate these electrolytes so they can be used in sodium-ion batteries, the best combinations must be established and incorporated for them to be used with the ionic fillers that will act as conductors. When the composition is correctly done and with a lot of caution, a balance can be established for the functioning components of the cell.

1.1 Development and Evolution of Sodium-based Battery Technology

The origin and evolution of sodium ion battery (SIB) technology can be traced back to the late years of this century. Researchers explored high-temperature sodium-based batteries, including the Na-S battery that operated above 300°C during the 1980s. These early models were limited by safety and practical complications from the high temperature.

Scientists focused their attention on ambient temperature sodium-ion batteries. This occurred due to the need for simpler and safer energy storage systems. SIBs used a layered oxide based as cathode material and hard carbon as the anode. Hard carbon was identified as the most suitable anode material in SIBs and has been used since 2000. It has shown remarkable powers in many cycles. This finding proved that SIBs can work effectively at room temperature. Over the last decade, there have been tremendous improvements in cathode and anode materials, electrolyte formulations, and battery engineering (8). Incorporating mixed metal oxides and polyanionic compounds has raised energy density and cycling stability. The improvements of SIBS with enhanced safety and efficiency are also hinged on highly advanced electrolytes. Concurrently, a rising emphasis on sustainable and economically viable energy storage systems has fueled the desire to use SIBs (8). SIBs have been proved possible for medium scale uses such as grid storage and renewable energy systems. Sodium-based batteries are experiencing a faster evolution today, and their future is focused on improving operating efficiency, reducing commercialization costs, and achieving different applications. Based on materials science development and future improvements in battery technologies, further opportunities will likely bring about more hope for realizing SIB's dreams (9). Ultimately, the emergence of sodium-based battery technology has been a tale involving the discovery of uncharted waters and innovation inspired by nature's peculiarities about sodium. Being sustainable, economical, and efficient, SIBs will take over the energy-storage market as new technologies emerge.

1.2 Basic Operation Mechanism

SIBs exploiting favorable characteristics of the elemental ion sodium operate on the same principal basis as LIBs. Specifically, SIBs employ the intercalation of ions into electrodes as an operation mechanism (10). The ion intercalation/de-intercalation in/out of the electrode is key during energy storage or release utilizing SIBs. Sodium ions move through the electrolyte, while electrons travel through the external circuit. The electrolyte facilitates this ion transport and is a critical determinant of the battery's overall performance and safety profile (11)(12).

Seen in figure 1, anode and cathode store sodium, while electrolyte carries charged ions. In the charge-discharge cycle, the electrochemical process in SIBs involves sodium ion transport between the cathode and anode (13). This process involves the migration of sodium ions through electrolyte (14). During the discharge period, the anode releases sodium ions to the electrolyte for moving to the cathode. The movement of sodium ions creates free electrons at the anode. This generates the flow of electrons from anode to cathode. The current then flows from the current collector of electrode to the device being powered by the battery, such as a smartphone, to the negative current collector. While charging, the sodium ion moves from the cathode to the anode, whereas the electrons flow through the outer circuit on the opposite side.

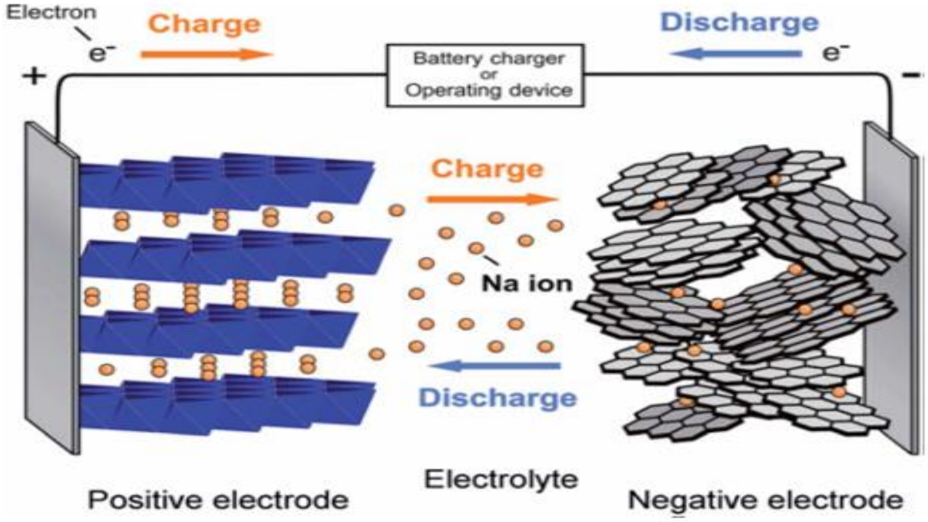


Figure 1: Schematics of working principle of a Sodium-Ion Battery (14)

Figure 2: A typical sodium-ion battery showing various impacting materials components (15).

1.3 Controlling Factors in Sodium-based Batteries

A battery is an electrochemical device containing one or more cells that uses redox reaction to convert chemical to electrical energy. The battery cell consists of three major components namely anode, cathode, and electrolytes providing appropriate voltage and current required through the series or parallel connection. Controlling factors of a battery encompass many variables, including the nature of component materials and the makeup of their structural design. SIBs carry distinct forms, chemistry, and physics characteristics that necessitate special considerations (see figure 2). Specifically, a SIB can comprise an alkaline-based active cathode, either alkali-based or non-alkali active anode like carbon or metal alloy, with an electrolyte like dissolved salted in polar solvent solution (16). Each electrode also contains binders and additives. These controlling parameters are fundamental for SIB technology development and advancement towards application (17).

1.4 Key Materials in SIBs

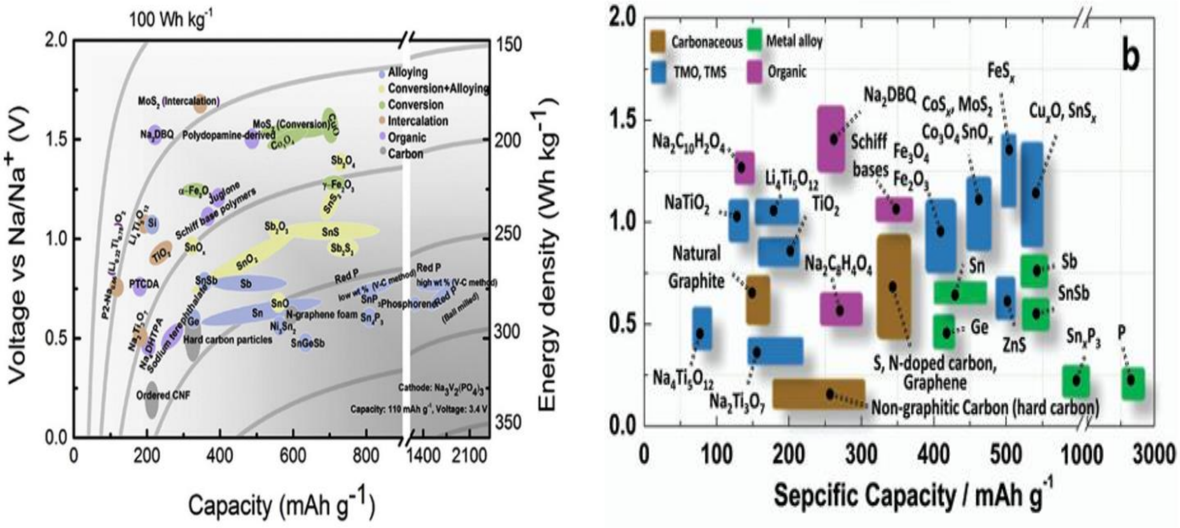
1.4.1 Anode

Anode is an essential component of the SIBs. The anode material composition must yield stable and high volumetric and gravimetric capacities by been able to accommodate large quantity of sodium ions per formula unit. It should also have low atomic weight. To have a working capacity equal that of cathode, the anode should possess the properties of a pure sodium metal the same for sodium content. It should also not have a side reaction tendency and have high electronic and ionic conductivity.

Due to sodium's special physical and electrochemical features, specially purposed materials should be used in SIB, not Li-battery ones. The large ionic radii of sodium ion (1.02 Å) compared to lithium ion (0.76 Å), low energy density and volume expansion make it difficult to find an appropriate anode material for SIBs. Na metal cannot be used as anode because it results in dendrite formation. As seen in figure 3(a), anode for SIBs can be classified as carbon-based materials, alloying compounds, conversion/conversion-alloying materials, and organic compounds (18).

Carbon-based materials are commonly utilized, among which hard carbon has proved reperformance in year 2000. Nitrogen-doped hard carbons demonstrate high specific capacities and promise improved performance (18). Investigations of other carbon-based materials as seen in figure 3(a) have also yielded good results. Significantly, these include carbon arsenide monolayers/bilayers with their high energy density and fast charging ability/discharging capability. These are notable steps toward improving the efficiency and speed of operating SIBS, see figure 3(b).

A second area of anode innovation lies in using metals like Sn and semi-metals like Ge and P that form stable alloys with sodium into SIBs. Conversion anodes for SIBs include oxides, sulfides, and phosphides etc. Depending on the metal present in the compounds, these materials can store sodium ion via inserting or alloying mechanism following by the conversion reaction. The theoretical capacity range is from 800 to 2569 mAh/g. Nonetheless, these materials undergo significant volume changes while forming, which may negatively impact the long-term stability of the material. Organic anodes for SIBs include small organic conjugated molecules or polymers where reactions sites can be conjugated or C=N, C=O. Studies have shown good reversible capacity and cycle life(19).

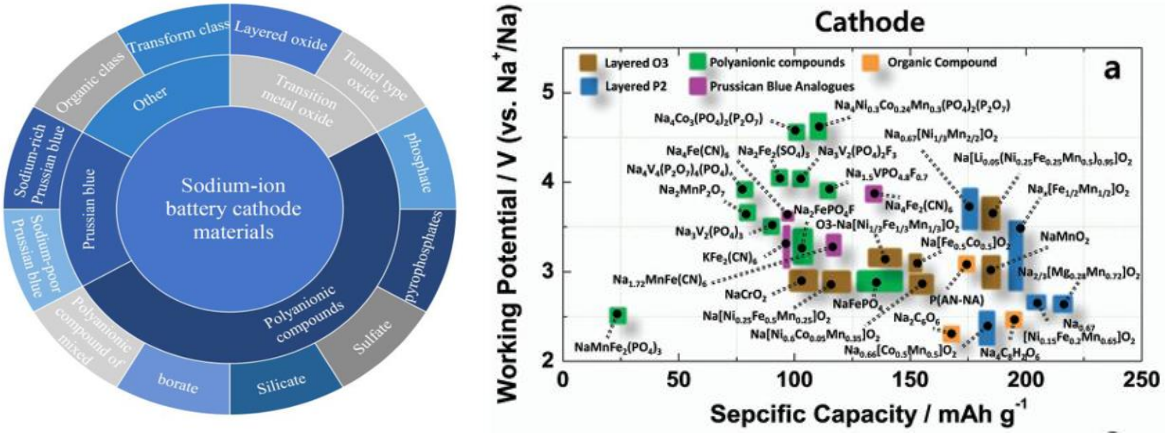


(a) (b)

Figure 3:Anode materials including carbonaceous, alloying, intercalation and conversion, and organic materials studied for SIBs show the voltage (a) and energy density as a function of (specific) capacity (19).

1.4.2 Cathode

Cathode is the most expensive component of the battery and accounts for twice the total cost of the anode. The theoretical capacity and thermodynamics of the cathode material are the limiting factors of the energy density, voltage, and rate capability of a full cell. The Na-containing compounds is the major containing factor for the cathode material that provides Na ions for operation of the battery assembled in discharged state. For a good cathode for SIBs it must have an oxidizable transition metal ion with a stable structure in which Na^+ ions undergo reversible intercalation/de-intercalation. It should have the capability to store a large number of sodium ions for high energy density, and be a good electronic conductor. The large ionic radius of the sodium ion is a major challenge in proper SIBs cathode selection. Preparation of sodiated cathode material requires careful handling because they are highly hygroscopic. When exposed to air NaOH can form that degrades the insulating properties (20).



(a) (b)

Figure 4:(a) Classification of sodium-ion battery cathode materials (b) and typical working potential and specific capacities of cathode materials for sodium ion batteries (21).

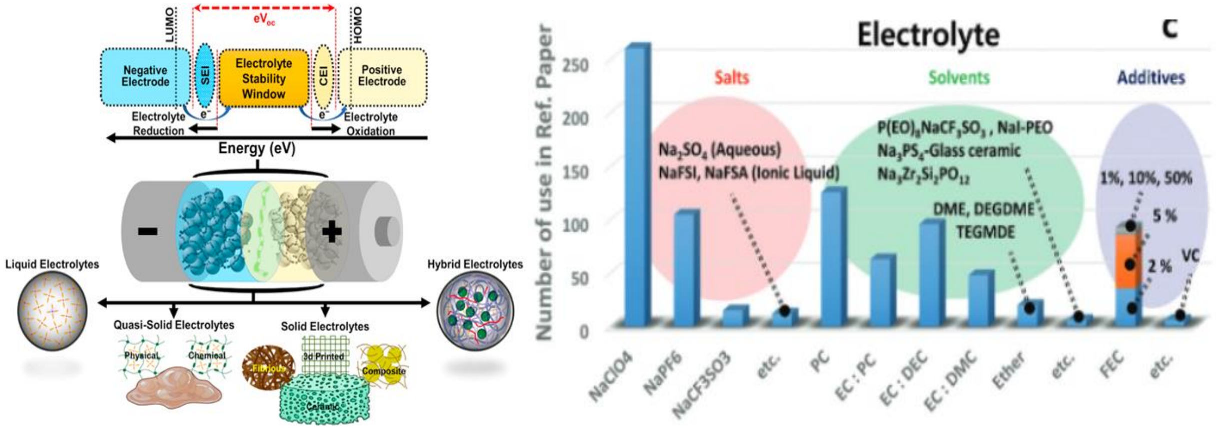
At present, the common cathode materials used as seen in figure 4(a) include: transition metal oxides, polyanionic compounds, Prussian blue compounds, and organic compounds. Their typical working potential and specific capacities can be seen in figure 4(b). Transition metal oxide has a layered structure and generally has a chemical formula of NaxMO2 where M is one or more of the 3D transition metal elements such as Ni, Mn, Fe, Co and Cu.

Polyanionic compounds are another common cathode material formed via the covalent bonding of polyanionic polyhedral and transition metal polyhedral distributing the Na+ in the network gap. Polyanionic compounds have NaxMy (XaOb)zZw as its chemical formula, where X is P, S, As, Si, B, Z is F, OH, and M is one or more of the valence metals including Ti, V, Cr, Mn, Fe. The strong 3D framework structure and strong X–O covalent bond of these cathode materials has a potential for strong application. Ion substitution and doping, as well as carbon coating, are needed to improve their electrochemical performance even though it has high specific capacity, high redox potential, high charge and discharge voltage, high safety.

Prussian blue compounds is the third group of the cathode material. Structure of this category involves sodium ions, transition metals, crystal water, and vacancies. Three-dimensional channel structure is formed through the Na+ location in the transition metal ion Mn+, which forms and its vacancies with C and N of ferrocyanide. Ion migration includes sodium-poor content or sodium-rich content. These cathode materials show high working potential and long cycle life (21).

1.4.3 Electrolytes of sodium Ion Batteries

Electrolyte plays a great role in ions transportation between cathode and anode. One significant factor for a high-performance electrolyte is to have high ionic conductivity. High electrochemical stability is also required for the high voltage difference between the anode and cathode materials essential for the performance without any side reactions. The electrolyte can significantly impact batteries’ overall performance, safety, and longevity (22). Historically, SIBs have employed liquid electrolytes. These have demonstrated efficacy. They also present several associated challenges, including the risk of leakage, flammability-induced safety concerns, and compatibility complications with electrode materials (23). Accordingly, numerous investigations have endeavored to address these limitations by exploring alternative electrolyte types, encompassing solid-state polymer electrolytes, gel polymer electrolytes, and ceramic electrolytes. Examples of SIBs electrolytes composition and recent research progress in sodium ion batteries electrolyte are seen in figure 5(a) and (b). Each potential solution has unique advantages and limitations. The characteristics and development of the electrolyte details will be discussed in chapter 2.



(a)

(b)

Figure 5:) Classification of electrolytes used in SIBs and corresponding energy diagram of the electrolyte interface with positive and negative electrodes. (b) Recent research progress in sodium ion batteries electrolyte (24).

1.5 Challenges of SIBs

SIBs are attractive in consideration of abundance of sodium resources and low cost of raw materials. At present, the typical performances of SIBs including charge/discharge characteristics, cycling stability, rate capability etc can be seen in figure 6 . Although significant progress has been achieved, low energy/power density (see figure 7), limited cycle life, and rate capability are still incomparable with the state-of-the-art LIBs, hindering its commercialization and broad applications. These are limited by the above-mentioned key materials. At the oxidation-reduction reaction stage in the process of battery functioning, the crystal structure of electrode gets disturbed and finally destroyed. The other crucial factors influencing total battery performance include solid-state diffusion of ions in the active materials and electrochemical reactions at the electrode/electrolyte interface.

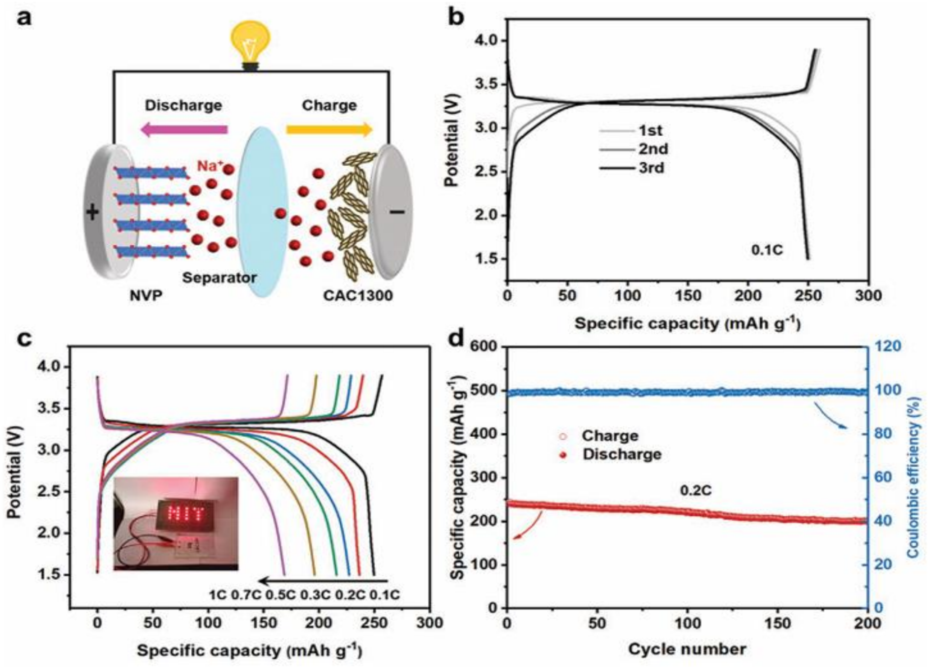


Figure 6:Electrochemical performances of sodium-ion battery based on CAC1300 (carbonized anthracite) anode and NVP (Na3V2(PO4)3) cathode. a) Schematic illustration of CAC1300// NVP SIB. b) Initial three charge–discharge curves of CAC1300//NVP SIB at the current density of 0.1 C. c) Charge–discharge curves of CAC1300//NVP SIB at various current densities. Inset shows the photograph of 19 LEDs lighted by a simple CAC1300//NVP pouch cell. d) Cycling performance of CAC1300//NVP SIB at the current density of 0.2 C (25).

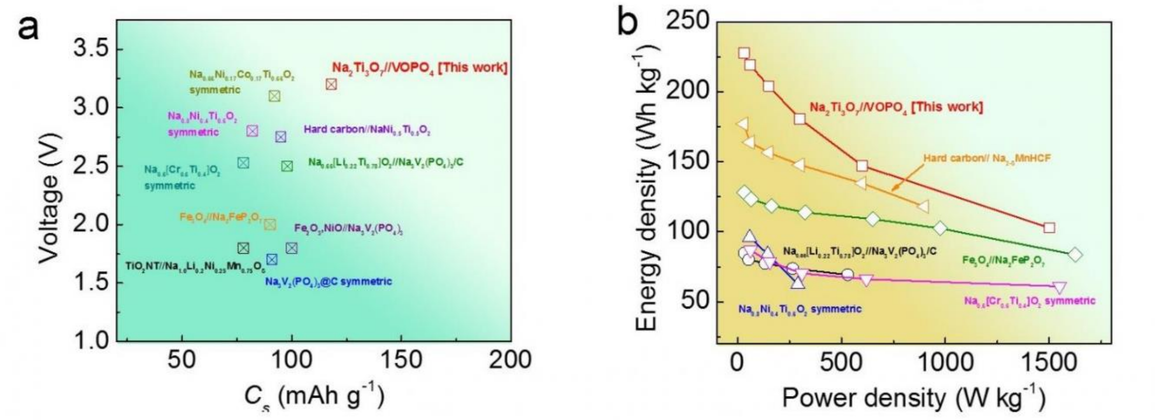


Figure 7:Typical sodium-ion battery performances in terms of (a) voltage and capacity (b) energy density and power density (26).

1.7 Outline of this Thesis Research

In the advancement of sodium-ion technology, one important aspect has been the development of electrolytes that are able to have high ionic conductivity while still maintaining the level of safety and stability. Carefully developing properly functioning electrolyte systems will be crucial to the evolution of SIB technology. To achieve the maximum performance of these batteries, it is important to analyze and understand fundamentally what kinds of electrolytes can be used. This research will fabricate a few liquid and polymer electrolytes in a formulation with different sodium salts in polar and non-polar solvents. It is aimed to investigate the impacts of solubility, polarity, and concentration on the ionic conductivities.

This thesis research firstly examines the principle underlying SIBs regarding their distinctive functionality, key materials utilized in SIBs and the status of SIBs, which is presented in this chapter.

Chapter II is focused on the electrolyte considerations from fundamental to recent progress. The role of various components in different types of electrolytes, such as sodium salts, solvents, polymers, plasticizers, fillers are discussed based on the literature review.

Chapter III describes the experimental aspects of this study, including materials, processing, and analytical techniques.

Chapter IV presents the results and discussion of this study obtained from liquid electrolytes prepared by dissolving the sodium salts: NaCl, Na_2S, NaF and Na_2SO_3 in both aqueous and non-aqueous solvents: Water, DMF, DMSO, Propanol and Methanol. Also, the solid polymer electrolyte films obtained from the casting of NaCl salt in PEO-Methanol, PEO-Methanol-EC, PEO-DMF, and PEO-DMF-EC medium respectively.

Chapter V concluded this research and offered suggestions on areas that need improvement.

CHAPTER 2: LITERATURE REVIEW ON ELECTROLYTE DEVELOPMENT

Electrolyte is one primary component in a battery for ion transport between cathode and anode. The energy density, safety, stability and cycling performance of the battery cell is determined by the electrolyte contribution. To achieve this, the electrolytes must have significant properties such as ionic conductivity, electrochemical stability, chemical stability of electrode material, transference number of ionic species. The electrolytes should maintain electrochemical stability and the formation of a high-quality passivation layer during cell operation. Its chemical stability with electrode can also affect the cycling stability and safety. Electrolytes are divided into liquid, polymer, and ceramic electrolytes three categories based on the kind of matrix material. Liquid electrolytes are commonly used in batteries for their high ionic conductivities. Sodium is more reactive with conventional electrolyte solvents than lithium; this may result in an accelerated degradation and safety risk. These challenges have driven intensive research in new electrolyte composition development, including developing sodium-specific organic solvents, and polymer-based systems. No leakage, less flammability, less corrosivity with the electrodes and the ability to function as the separator between the electrodes are some of the many reasons why solid electrolytes are highly preferred. This electrolyte category is gaining attention now due to overcoming battery safety issues. Polymer electrolytes have great adhesion and free-standing film properties compared with inorganic ceramic electrolytes, and less risk of flammability compared to the traditional liquid electrolytes. Additionally, been in the solid state there is no possible side reaction with the electrodes.

Research projects have been conducted on increasing the ionic conductivity of polymer electrolytes, conjunction with thermal and mechanical properties for various applications. Approaches comprise the addition of liquid plasticizer into polymer matrix and the combination of polymeric and inorganic components (27), which results in gel-like polymer composite electrolyte and solid polymer composite electrolyte, respectively.

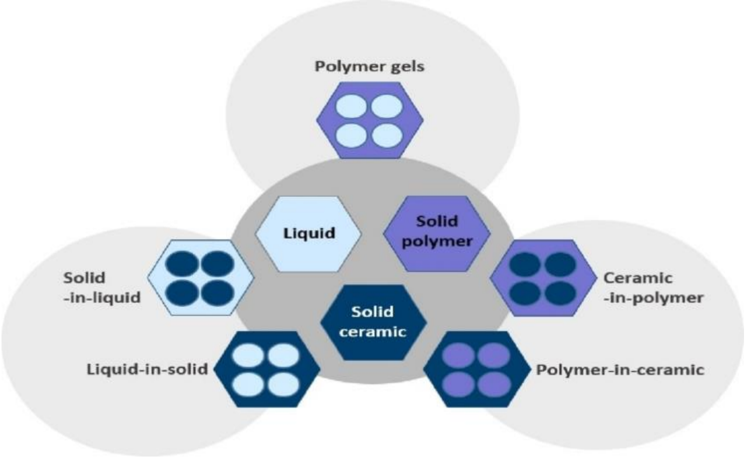


Figure 8:(a) Overview of different types of hybrid electrolytes and schematic representation of their constituents (28).

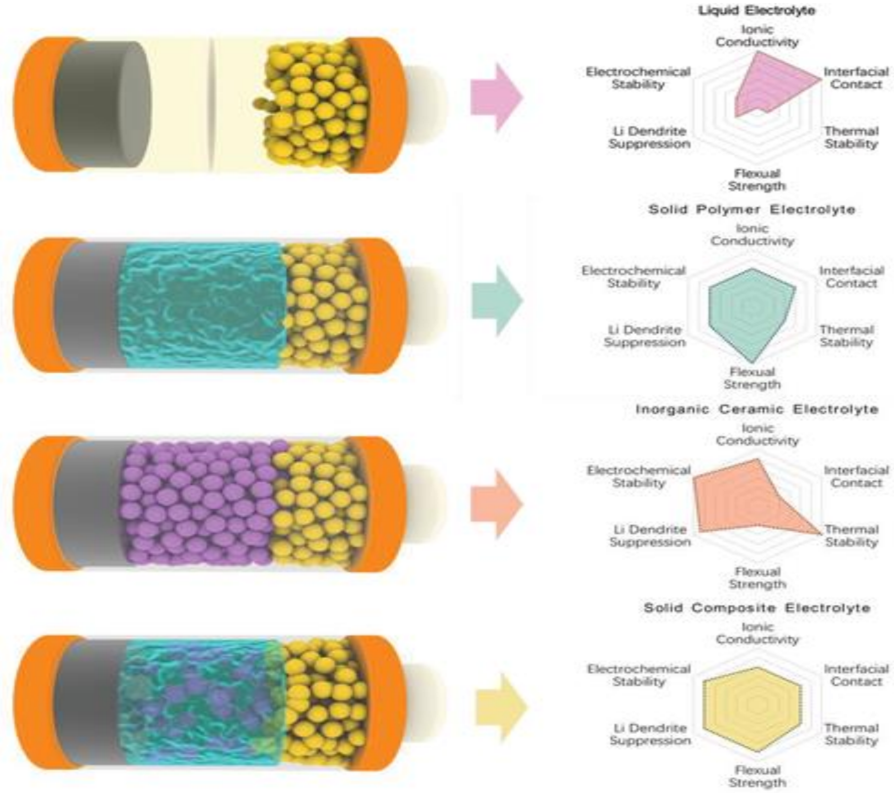


Figure 9:The performance comparisons of liquid electrolytes, Solid polymer electrolytes, Inorganic ceramic electrolytes, and Solid composite electrolytes (29).

The current research status of the five types of electrolytes (see figure 8), i.e. liquid electrolyte, ceramic electrolyte, dry polymer electrolyte, gel polymer electrolyte, and polymer-ceramic composite electrolyte, will be discussed in the following. Figure 9 compares the key characteristics of the four types of electrolytes in terms of ionic conductivity, interfacial contact, electrochemical stability, thermal stability, and flexual strength. This comparative study will contribute to a more profound comprehension of the potential merits of various electrolytes and their integral role in augmenting the electrochemical performance of sodium-ion batteries. In the forthcoming sections, literature review will be provided to delineate the ionic conductivities, the key properties of various electrolytes employed in SIBs.

2.1 Liquid Electrolytes

Liquid electrolyte is chosen for sodium-ion systems because of the high ionic mobility in the liquid state. This involves the dissolution of a sodium based ionic salt in a single mixture of organic solvents or in water. Accordingly, they are divided into two groups: aqueous and aqueous electrolytes. Both these electrolytes have their advantages and demerits. Aqueous electrolytes have safety and environmental gains, they generally produce low voltages and comparatively low energy density. Non-aqueous (organic) electrolytes are usually volatile, flammable, but have a wide voltage range (30).

2.1.1 Aqueous electrolyte

In electrochemical energy storage systems, aqueous electrolytes are an interesting aspect to be studied due to been highly safe and cost effective. Most aqueous electrolytes have a stable operating voltage of 1.23V, lower than the non-aqueous/organic system. This contributed to the electrolysis of water to H2 and O2 which may take place beyond this voltage and hence affecting the battery cycle life. The ability to widen this thermodynamic window (see figure 10) and discover new high-capacity electrodes is now the focus in the aqueous SIBs (ASIBs) research. (31). ASIBs are more attractive in large-scale energy storage systems and safety-oriented wearable devices.

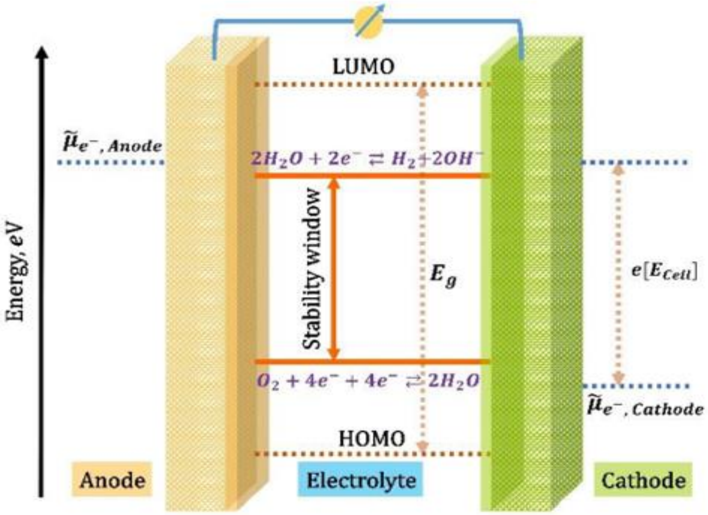


Figure 10:Schematic representation of an aqueous Na-ion battery (32).

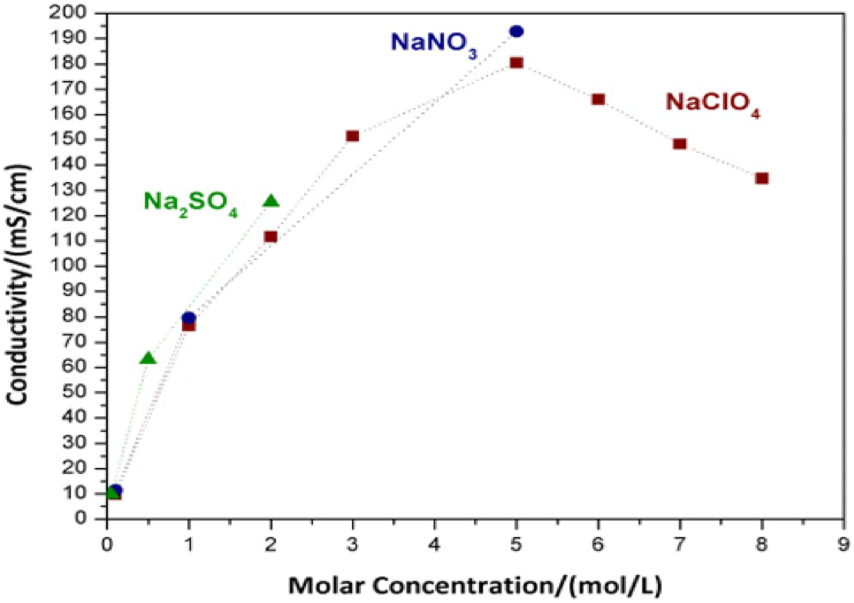


Figure 11: Ionic conductivities of aqueous Na2SO4, NaNO3 and NaClO4 electrolyte with different molarities at 25◦C (37).

Water has high solubilities, high dissociation constants and less viscosities resulting that aqueous electrolytes have high ionic conductivity. Water can dissolve most sodium salts to form the solvation structure. Na_2SO_4, $NaNO_3$, and $NaClO_4$ are some of the common sodium salts used in aqueous rechargeable batteries. Na-ion aqueous solution (salt-in water) can be grouped into diluted (less than 1M or 2M) and concentrated (up to 10 M) solution. The typical conductivity of some of the sodium salts used in aqueous electrolytes is shown in figure 11 In salt-in-water solutions, Na+ ions are encapsulated by water molecules forming a solvation shell. Most of the aqueous electrolyte's function in neutral pH conditions. Typical battery performances using the aqueous electrolytes are listed in Table 1.

Table 1:Electrochemical Properties of Various Aqueous Rechargeable Na-Ion Batteries

Salt in the Electrolyte	Concentration	Cathode	Anode	Working potential (V)	Capacity (mAhg−1)
Na_2SO_4	1M	$Na_4Mn_9O_{18}$	Activated carbon	1.2	45
Na2SO4 and MgSO4	1M, 2M	MnO2	$NaTi_2(PO_4)$3	1.1	83
NaCl	2M	$Na_{0.35}MnO_2.0_2\cdot 0.75H_2O$	-	-	130
NaNO3	5M	NaVPO4F	Polyamide	1.1	40
$NaClO_4$	10M	$Na_3V_2O_2x(PO_4)_2F_3$-x	Zn	1.65	54

Sodium sulfate (Na_2SO_4) can ionize completely in water, producing Na^+ and SO_4^{2-} ions, being a strong electrolyte with good ionic conductivity (33). 1M Na2SO4 is the most widely reported dilute electrolyte. Whitacre et al. in 2010(34) reported a working aqueous SIB using 1 M Na_2SO_4 aqueous electrolyte and $Na_4Mn_9O_{18}$ cathode. The results showed the specific capacity of 45 $mAhg^{-1}$ and a voltage range of 0.5 V. Another study in 2011 reported a SIB with $NaTi_2(PO_4)$3 as anode and 2 M Na_2SO_4 aqueous electrolyte with a reversible discharge capacity of 123 $mAhg^{-1}$ at a rate of 2.0 $mAcm^{-2}$, which is 93% of the theoretical capacity. Liu and colleagues developed aqueous Na-ion batteries using manganese oxides like $K_{0.27}MnO_2$ and λ-MnO_2 cathode and $NaTi_2(PO_4)$3 as anode with 1M Na_2SO_4 electrolyte solution. Deng et al. (35) reported an ASIB using a novel anode of one-dimensional nanostructured $Na_2V_6O_{16}\cdot nH_2O$ with 1M Na_2SO_4 aqueous electrolyte (35), which showed a reversible capacity of 62 $mAhg^{-1}$ at a rate of 40 mAg^{-1} with an average voltage of 0.7 V.

Sodium chloride (NaCl) is another salt that was used in aqueous electrolyte solution, which is more suitable for supercapacitor applications. To determine the capacitive behavior of "ambigel" MnO_2, Reddy et al. (36) compared various electrolytes with sodium chloride (NaCl), potassium chloride (KCl), and sodium sulfate (Na_2SO_4). The highest capacitance of 130 Fg^{-1} at a scan rate of 5 mVs^{-1} was found when a 2M NaCl was added, this is due to the redox transition from the intercalation of Na+ ions into the MnO_2.

2.1.2 Non-aqueous electrolytes

Organic electrolyte greatly improved the electrochemical window and the electrode/electrolyte interface. Scientists have stressed several strategies for enhancing compatibility, cycling efficiency, and interfacial film formation, aiming toward safer, low-cost organic liquid electrolytes for the future technology of a sodium-ion battery (38). The Lewis acidity/basicity idea impact the electrochemical stability. Low acidity (basicity) anions and cations solvents are easily solvated while those with higher acidity (basicity) doesn't. This hard/soft acids and bases idea is used to determine the ion-solvent interaction. (39).

2.1.2.1 Role of Sodium Salts

The selection of sodium salt has a considerable effect on the ionic conductivity of the sodium ion battery electrolytes. The effectiveness of sodium fluoride (NaF) salt has been examined in the optimization of the stability of the electrolyte because of the incorporation of fluoride ions (40). NaF is also reported to improve the ionic transport and interestingly is a candidate for the election in SIBs systems (43). Sodium sulfide Na_2S based electrolytes have demonstrated the possibility of having higher values of ionic conductivities in comparison with sodium sulfite salts. Sodium nitrate salt mixed with glycerol makes up a hybrid electrolyte that could also be used (44).

Sodium perchlorate ($NaClO_4$) and sodium hexafluorophosphate ($NaPF_6$) are two salts that can be dissolved in organic solvents to have them ready for use (45). Sodium tetrafluoroborate ($NaBF_4$) and sodium bis(fluorosulfonyl)imide (NaFSi) are equipped with ion transport properties that are improved as compared to those found in traditional batteries, especially when they are dissolved in organic solvents. They are said to provide stability for the electrolytes that are generated (46). Being a compound that has high electrochemical stability, electrolytes that are developed primarily on glyme with sodium trifluoromethane sulfonate (NaOTF), are preferred for use in sodium-based batteries (47). The ionic conductivities of non-aqueous electrolytes are a function of salts, solvent, concentration, and temperature etc (see figure 12 and Table 12).

2.1.2.2 Solvent

Stability, non-toxicity and cheapness are some of the basic criteria to be satisfied as an electrolyte solvent. The solvents also need to have a wide electrochemical stability window, sufficient sodium salt solubility, high dielectric constant, low viscosity, and low melting point and high boiling point. Because of the high dielectric characteristic and an extensive fluid range, Propylene carbonate (PC), is the most common solvent used in lithium and sodium cells. Multiple solvents are often used in combination because it is most of the time difficult to achieve these requirements with a single solvent (49). Organic solvents are the main solvents currently used in sodium ion batteries which provide excellent battery performance. (50)

The research by Vidal-Abarca et al. (51) investigated the optimization of Na_2FePO_4F material for utilization in sodium test cells using $NaPF_6$ in EC: DEC electrolytes, the results indicated a better capacity retention and higher value of the sodium cells capacity at the cell voltage window (4.2–1.5 V). In a research study conducted by Jang et al. (52), 1 M $NaClO_4$ was dissolved in DEC/EC (1/1, v/v) or PC/EC (1/1, v/v) to examine the $NaPO_4)_2(P_2O_7)$ cathode performance. The PC-based electrolyte had greater ionic conductivities fixations than DEC when galvanostatic cycling of SIB at C/20 for pre-cycling and C/10 between 1.7 and 4.2 V was tested.

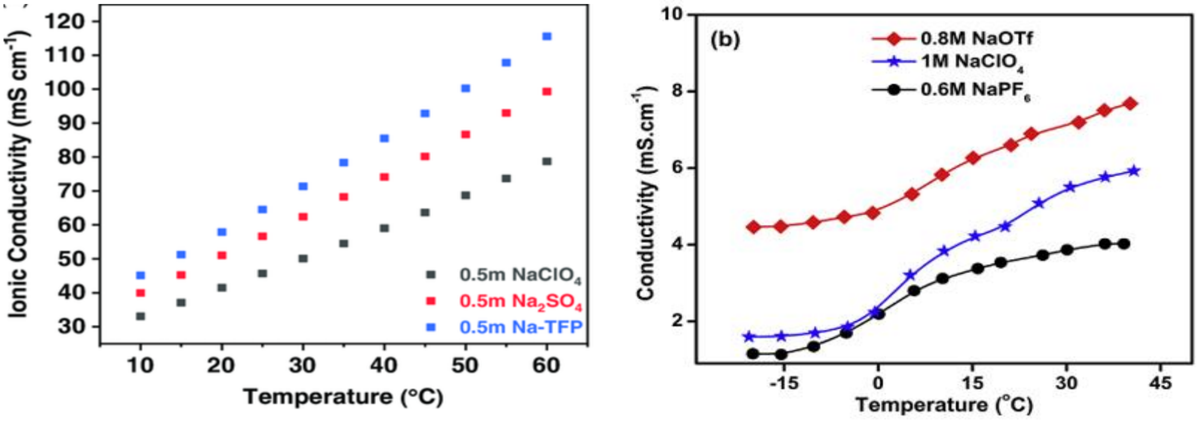


Figure 12:Ionic conductivity of non-aqueous electrolytes sodium salts in EC:DMC (30:70 wt%) at different temperatures (48).

Table 2:Electrochemical Properties of Various Non-Aqueous Rechargeable Na-Ion Batteries

Electrolytes	Average discharge voltage	Initial reversible capacity (mA h $g^{-1)}$	Cycle life (*n*)	Rate capability (mA h $g^{-1)}$	Ionic conductivity (S/cm)
1 M $NaClO_4$ in EC/DEC, 1 : 1	~0.2 V	312	1100	137	10.71×10^{-3}
0.8 M $NaClO_4$ in EC/DEC, 1:1	0.3 V	295	90	100	6.41×10^{-3}
1 M NaOTf diglyme	~0.3 V	245.2	N/A	88.2	12.55×10^{-3}
1 M NaFSI in EC/DEC 4:6	0.29 V	282	60	~150	6.2×10^{-3}
1 M $NaPF_6$ in EC/EMC, 3:7	~0.34 V	273	50	N/A	7.98×10^{-3}

2.1.3 Ionic liquid (protic and aprotic)

Ionic liquids are non-combustible, non-volatile and work over a wide range of thermally and chemically stable temperatures which is safe and high-performance electrolytes for Na- ion batteries. in the twentieth century, were called room temperature molten salts or ambient temperature melts, now becoming more popular. Ethyl ammonium nitrate, with melting temperature (T_m) = 14 ^oC was the first ionic liquid which its equivalent conductivity in relation to fluidity was documented 100 years ago. The mixture of an organic cation (ethyl pyridinium bromide) with an anion (aluminum chloride) at T_m =40^{o}C was the second low temperature ionic liquid discovered. Ionic liquids now have ionic conductivities comparable to that of molten salts with non-flammability and negligible vapor pressure characteristics (53).

The development and investigation of the application of ionic liquid-based electrolyte (NaTFSI-Pyr_{14}TFSI) in Na^+ battery was carried out by Hasa et al. [54]. According to their report the overall ionic conductivity of the ionic electrolyte is 10^{-2} S/cm and 10^{-3} S/cm 90◦C and at room temperature respectively. Ionic electrolyte is seen as a promising candidate for sodium ion batteries because of capacity ranging from 120 to 100 mAh g and a voltage of about 2.7 V proven by researchers. A higher conductivity of ionic liquid-based electrolyte compared to that of the organic electrolytes was reported by Usui et al. (55). (56) reported a high-rate capability and long-life Na-ion battery using anionic electrolyte at 60^{o}C. There is an excellent cyclability for Nb-doped TiO_2 electrodes at 60^{o}C using ionic liquid-based electrolyte.

2.1.4 Temperature Influences of Ionic conductivity of liquid electrolyte

Temperature significantly affects the Na^+ migration in the electrolyte. At low temperature, the viscosity increases decreasing the desolvation ability of large polarization. The effect of high temperature environments in liquid electrolyte leads to parasitic reactions and thermal instability unlike the capacity loss due to kinetic limitations at low temperature. In addition, accelerated temperature does not only decompose the electrolyte at the electrode surface but also dendrites from the decomposition deposits affect charge transfer and deactivate the sodium anode and erode the electrochemical. The decomposition at high temperature leads to release of gas and electrolyte volatility. Research focuses on modifying sodium salts by designing and optimization of functional electrolyte (56).

2.2. Inorganic Solid Electrolytes (ISE).

An inorganic solid electrolyte is a ceramic material with uniform skeletal structure in which sodium ions can move from one point of the skeleton to another causing ionic conduction. Ceramic electrolytes are characterized as having the ability to remain thermally stable, a factor viewed as a major part in the development of sodium-ion batteries that are expected to perform well. According to research done by (57), high sodium-ion conductivities ($>10^{-2}$ S/cm) in ISEs at room temperature would most probably result in a surge in all-solid-state sodium batteries (ASSSBs). On the contrary, their electrochemical stability is insufficient, as is their suitability with high capacity and voltage electrodes.

Sodium beta-alumina represents a prominent example of solid electrolytes known for their high ionic conductivity. Its crystalline structure is distinctive, encompassing a conduction plane that facilitates the unobstructed movement of sodium ions. The ionic conductivity of sodium beta-alumina usually lies between 1.3 ± 0.6 S/cm at escalated temperatures, specifically at 500^oC. Such conductivity attributes make sodium beta-alumina appropriate for applications necessitating high operational temperatures.

Sodium Super Ionic Conductor (NASICON) is a family of solid electrolytes with good sodium ion conductivity. NASICON electrolytes typically consist of a crystalline structure that provides pathways for sodium ion transport. A typical example is NASICON ($Na_3Zr_2Si_2PO_{12}$) which has been reported to have an ionic conductivity of approximately $1x10^{-3}$ to $3x10^{-3}$ S/cm at room temperature. Modifications of the NASICON-type materials are done to improve the ionic conductivity further. For instance, doping with elements like Ti can enhance conductivity. The reported conductivities for these materials can range up to $1x10^{-2}$ S/cm at room temperature, depending on the specific composition and synthesis method. Others include compositing sodium Beta-Alumina (Na-β-Al_2O_3) and sodium superionic conductors (NASICON)(58). Reportedly, it has a high conductivity of sodium-ion at high temperatures. The high-power density and long-term cycling performance of the battery is improved due to the ceramic electrolyte having a high Na^+ ion transfer rate and strong ionic conductivity.

The third type of ceramic electrolyte is sodium thiophosphate and glass ceramics, which are applied to the storage of ions (59). An example in this category includes a solid electrolyte, which is a chemical in the form of Na_3PS_4. It involves the use of sulfide in its development. It also has an ionic conductivity that has improved much further. Theoretically, at low voltage, it does not have safety concerns since its capacity is high (61). here are also sodium halides, such as cryolite, that are stable and are good conductors as well (61). Finally, sodium phosphates, such as sodium ion phosphate (62) are also considered due to their high ionic conductivity (62). As illustrated below in figure 13, these solid electrolytes are of much significance in the successful operation of sodium-ion batteries.

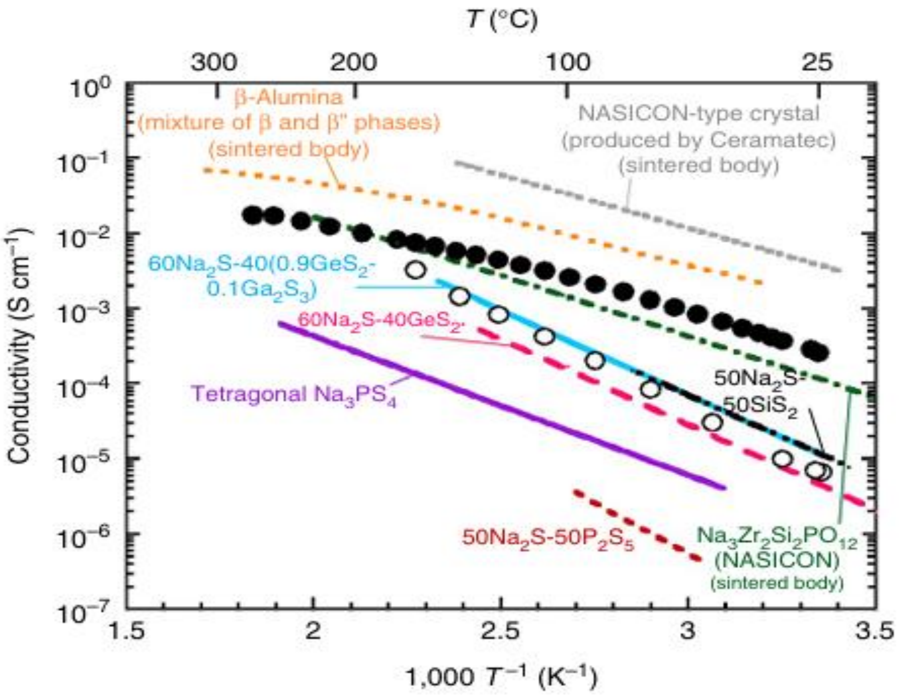


Figure 13:Conductivity of glass-ceramic electrolytes. (64).

2.3 Solid Polymer Electrolytes

Polymers with sodium solvating heteroatoms are used as polymer electrolytes. The electrolytes are flexible and secure and can be conducted at room temperature with high ionic conductivity. Polymer electrolytes are distinguishable from liquid electrolytes by their ion conduction mechanism and also the morphological difference between the two electrolytes. Sodium ions in polymer electrolytes move through the polymer network itself, while there is free movement of dissociated ions within the liquid as part of solvation in liquid electrolytes (63). SPEs are essential for developing safe and high–energy densities of Na–ion batteries.

Polymer matrix influences the ionic conductivity of SPEs have discussed some ion conduction mechanisms in the SPEs (64) . Mechanisms on a fundamental level include the dynamics of the polymer chains' segmental mobility and the ions' diffusion through the polymer matrix's free volume. Improvement techniques use plasticizers that enhance the mobility of the polymer segments and ceramic fillers that offer continuous paths for ion conduction (65). Typical ionic conductivities and electrochemical stability windows are listed in Table 3

Table 3: Solid polymer electrolyte ionic conductivity and Electrochemical Stability Windows

Polymer electrolyte	Ionic conductivity (S/cm)	Electrochemical Stability Window (V)
PEO-$NaClO_4$	$< 4.5 \times 10^{-5}$	-
PAM-PAN- $NaPF_6$	$10 - 3$ –10^{-2}	~2.8
PVDF/PEO- NaTFSI	$10^{-6} - 10^{-5}$	-
TEAOH–PVA- NaOTf	3×10^{-4}	2.69
PVA- NaFSI	1.23×10^{-5}	2.81
PEO- $NaClO_4$	1.86×10^{-3} (100 °C)	3

2.3.1 Polymer

Most polymers with nitrogen or oxygen in the monomer to solvate sodium ions. These can have both crystalline and amorphous domains making them semicrystalline.

PEO or polyethylene oxide has been used comprehensively in SPEs since this polymer can form stable complexes with alkali salts, a factor critical to forming promising pathways for ion transport. PEO-based electrolytes are capable of solvating a large variety of salts and are also known for their flexibility which is important to cling onto the electrodes during cycling (66). Nonetheless, the high crystallinity of PEO at room temperature leads to a low ionic conductivity; thus, the incorporation of plasticizers to increase the amorphous phase is required. According to (67), it is also essential to notice that ethylene carbonate is among the plasticizers that notably affect PEO-based electrolytes' performances (68).

Polyvinylidene fluoride (PVDF) is characterized as a semi-crystalline polymer with fine chemical inertness increased mechanical strength and electrochemical stability. PVDF has a high dielectric constant that is useful in encouraging the dissolution of sodium salts, and hence a good ionic conductivity. In addition to that, PVDF has the capability of dissolving with different plasticizers and solvents, which in turn, makes it a convenient ingredient in gel composite electrolytes. The dispersion of PVDF within a PEO matrix can enhance the electrolyte performance by equalizing the flexibility and mechanical stability of the given.

Other polymers such as Polycarbonates, PVA (polyvinyl alcohols) and PAN (polyacrylonitriles) have also been utilized in SPEs. According to research by D. Vanitha et al. (69), thin films made from sodium ion-conducting polymer blends have garnered much interest in technology due to their customizable physical and electrical characteristics. Such characteristics render them exceedingly appropriate for diverse applications encompassing sodium sulfur batteries, thermoelectric generators, and electrochemical sensors, to name a few. By employing polymers such as polyvinyl alcohol (PVA) and polyvinylpyrrolidone (PVP), complexed with sodium salt such as NaCl composite blend polymer electrolyte films capable of conducting sodium ions have been successfully fabricated.

Increasing the polymer's molecular weight or crystallinity level can also improve ion conductivities. This will enhance the membrane's mechanical qualities, but the ionic conductivity will require plasticizers to enhance the process (70). Nonetheless, the high crystallinity of PEO at room temperature leads to a low ionic conductivity; thus, the incorporation of plasticizers to increase the amorphous phase is required. Polyvinylidene fluoride or PVDF is another polymer that has wide applications because of its high Dielectric constant, and high chemical as well as mechanical strength (72). The incorporation of PVDF in the electrolyte increases the mechanical properties and durability of the synthesized composite electrolyte. This means that using PEO and PVDF in a composite electrolyte could utilize the characteristics of both polymers whereby high ionic conductivity and mechanical strength.

Two polymers with complementary properties can also be mixed co-dissolved in a common solvent refers to as polymer blending the one polymer has high solubility of salts while the other polymer exhibits excellent mechanical and thermal properties. High conductivity is achieved through the interaction between different polymer hosts that lowers the degree of crystallization. Wu et al. (82) prepared a new polymer matrix by blending PVDF-HFP with poly (3- {2- [2-(2- hydroxyethoxy) ethoxy] ethoxy} methyl-3′-methyloxetane (PHEMO), in which the ionic conductivity reached up to 1.64×10^{-4} S cm^{-1} at room temperature. Ye and co-workers (83) achieved an improved ionic conductivity by blending a polymer with silicone. Copolymer consists of two types of polymer monomers with one polymer as the ionic conductor block (such as PEO and PEG) the second polymer provides mechanical support. Co-linking of polymer chains with covalent bonds to contribute amorphous phase is known as the crosslinking method.

While the brittleness and elasticity become relatively low, cross- linked polymer electrolyte usually exhibits good ionic conductivity and fully amorphous features.

2.3.2 Salts

Several sodium salts such as sodium yttrium tetrafluoride ($NaYF_4$), sodium iodide (NaI), sodium per chlorate ($NaClO_4$) and sodium trifluoromethanesulfonate (NaTf) have been studied with the aim of having a completely dissociated salts in polymer matrices, obtaining high Na ion availability and ionic conductivity. presently, various sodium salts have been investigated for SPE-based sodium batteries (73).

2.3.3 Solvents

The selection of the solvent while preparing the solid polymer electrolytes plays a significant role in ion dissociation and, also significantly affects the solvation of sodium salts and the polymer–ion confrontation. Water is highly soluble and capable of dissolving most of the salt and hence widely used in the initial stage of sample preparation. Other common solvents used include *N*-Methyl-2-pyrrolidone (NMP), Acetonitrile, N, N-dimethylformamide (DMF). DMF is a polar aprotic solvent. The dissolving properties of both polymers and salts are enhanced hence enabling homogeneity of the mixture (74).

2.3.4 Ionic Conduction Mechanism

Ionic conductivity of polymer electrolyte is very complex because it features both microscopic and macroscopic levels multiphase structures. Polymers can have both crystalline and amorphous domains making them semicrystalline. There is the complexity of different phases provided by amorphous and crystalline phases coexistence due to the presence of polymer and salt (Na^+) providing different pathways for the ionic conductivity. The major contributing factor to the ionic conductivity is the amorphous region due to their mobile chains and more flexible less well-formed structures. Among the many research and theories formulated as regard to the transportation mechanism such as formation of weak coordination shell between Na^+ and monomer group, the key factors for the transport between the cation and anions is the sectional movement of the polymer backbone.

The movement of ions in the coordination sites involves the movement of polymer segments, leading to dynamic coordination sites creation along which ions as seen in PEO (figure 14). This is the major determining factor in solid polymer ion transportation. The coordination sites of some crystalline composition of PEO which are both the rigid and fixed and amorphous sites of PEO exhibit a similar ionic conductivity (10^{-6} S/cm) (75). Ion conduction also involves the ion-hopping along fixed coordination sites (75), in some polymers such as PVA and PAN. Polycarbonates show that the crystalline phases have no effect on the conductivity. The amorphous sites can be improved by copolymerization and /or the addition of a filler such as SiO_2, Al_2O_3 or $BaTiO_3$.

A low glass transition temperature is essential for dry polymer electrolytes to have good flexibility and adhesion. The limited ionic conductivities of 10^{-5} – 10^{-6} S/cm at room temperature is a drawback of using the salt-in polymer dry electrolytes and therefore have limited performance at ambient temperatures (77).

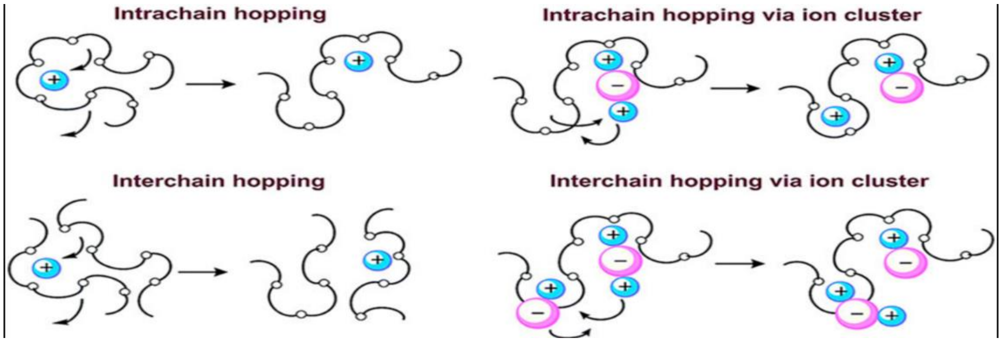


Figure 14:Sodium-ion occurring conduction occurring in the amorphous region of PEO-based polymer SSEs (76).

2.4. Gel Polymer electrolytes (GPEs)

Gel polymeric electrolytes (GPEs) contain a comparatively small number of polymers. They are usually polymer electrolytes with solvents or plasticizers like PEG, carbonate solvents, ionic liquids, or succinonitrile, in the matrix. GPEs blend the advantageous attributes of both polymer and liquid electrolytes, including flexibility, superior ionic conductivity, and safety enhancements (78). In GPEs ion conduction can exist both in liquid and solid mechanism depending on the polymer type and liquid amount in the gel, because GPEs contain both liquid and polymer phases. They present the potential to augment battery performance by mitigating several challenges intrinsic to traditional electrolytes. The interest in utilizing gel polymer electrolytes (GPEs) is significant for developing rechargeable sodium metal batteries due to their favorable electrochemical characteristics and enhanced safety. Nevertheless, it is essential to note that GPEs introduce their constraints, such as intricate fabrication processes and possible compatibility issues with electrode materials (78).

In gel polymer electrolytes in which both liquid and polymeric ionic conduction mechanisms exist. The addition of plasticizers to the solid polymers is a determining factor in ionic conduction by creating liquid phase within the polymer and improving the polymer chain mobility. A few of the most common plasticizers include ethylene carbonate (EC) and propylene carbonate (PC) (79). The addition of plasticizers such as EC or PC to a polymer matrix presents high ionic conductivity because there is reduced crystallinity and increased segmental motion of the polymers (80). The effect of EC is disrupting the crystallinity of the polymer matrices, enhancing the amorphous regions that offer the passage of ion transport (80). EC increases the polymer system's glass transition temperature, raises the chains' segmental freedom, and thus increases mobility through transient regions conducive to ionic flow. It is this kind of structural transformation that enhances the segmental motion of the polymer; hence, better ion dissociation acts to improve ionic conductivity (see Table 4). (81) reported a facile and scalable one-pot preparation method of a GPE based on highly safe poly(vinylidenefluoride-*co*hexafluoropropylene) (PVDF-HFP) polymer matrix.

Table 4:Gel polymer electrolyte ionic conductivity and Electrochemical Stability Window

Polymer electrolyte	Ionic conductivity (S/cm)	Electrochemical Stability Window (V)
PVdF-HFP- NaOTf -Nanowires	7.13×10^{-4}	-
PMMA-$NaClO_4$	6.2×10^{-3}	4.8
PEO-PMMA NaPF6	6.29×10^{-3}	4.9
PMMA- NaTFSI	4.3×10^{-3}	4.9

2.5 Polymer-Composite Electrolytes (PCEs)

Composite polymer electrolytes are classified according to the type of filler as active and passive conductors based. Challenges for the large- scale deployment of SSLSBs due to suboptimal contact at the electrode interfaces and the preparation process of the CPEs. Extensive research has been conducted to address these challenges, including the modifications of various structures based on inorganic ionic conductors in the CPEs and the integration with cathode materials, particle size optimization.

2.5.1 Passive conductors-based CPEs

Metal oxide fillers like like TiO_2, SiO_2, MgO Al2O_3,, and non- metal fillers like carbon materials, montmorillonite (MMT), and zeolites are some of the inert components used in CPEs.

Incorporating inert fillers can enhance the ionic conductivity of PCEs. These additives boost segmental movement, creating additional channels for ion migration and enhancing overall ion conductivity. Further, the mechanical strength, interface compatibility, and the electrical properties of CPEs are enhanced by incorporating passive nanoparticles into the polymer matrix with sodium salts, reducing internal resistance to mitigate the severe decay of battery capacity due to polysulfide during the cycling process and promoting uniform ion transport.

Dendrite-free SSLSBs with enhanced safety and practicality using nano-SiO2 as an inorganic filler in PEO-based CPEs was developed by Zhang et al. A stable performance over 360 h of galvanostatic cycling at a current density of 0.05 mA cm2 and a temperature of 70 ◦C of the symmetric cell 5 wt% SiO_2 within the PEO matrix was obtained compared to the cell without SiO2 particles in the PEO matrix. Incorporating large number of fillers in the polymer phase leads to the discontinuation of sodium-ion transport pathways. Studies have been conducted to improve Na+ migration by optimizing the concentration and modifying the surface properties of the nanofillers. An electrolyte using treated SiO_2 with double bonds as fillers for a mixture of poly(ethylene glycol) methyl ether methacrylate, poly (ethylene glycol) diacrylate, and acrylamide (P-P-A) was fabricated by (84).

A composite polymer electrolyte, PVDF-HFP/g-C_3N_4/$NaClO_4$, exhibiting outstanding properties, was developed. The introduction of g-C3N4 nanofiller into PVDF-HFP led to reduced crystallinity. This new structure facilitated better polymer interfaces and enhanced Na+ dissociation, boosting mechanical and ionic conductivity traits. The composite's use in solid-state sodium coin cell batteries resulted in superior cycle and safety performance compared to standard PVDF-HFP/$NaClO_4$ SPEs. This innovative approach heralds new research avenues for composite electrolytes, fostering the evolution of practical, large-scale energy storage and next-generation solid-state batteries.

2.5.2. Active conductors-based CPEs

Active conductors-based CPEs offer advantages over inert fillers and show great potential for enhancing the performance of CPEs. The active fillers are the ceramic ionic conductors mentioned in session 2.2. Multifunctional Inorganic nanoparticles have been shown to improve electrochemical performance, thus enhancing the ionic conductivity of CPEs.

Table 5:Gel polymer electrolyte ionic conductivity and Electrochemical Stability Window

Polymer	Filler	Sodium salt	Synthesis method	Ionic conductivity (S/cm)
PVDF	SiO_2	$NaCF_3SO_3$	Solution casting	6.0×10^{-3} at 25 °C
PVDF	Si_3N_4	$NaClO_4$	Electrospinning	4.1×10^{-3} at 25 °C
PVDF	HFP-glass fiber	$NaClO_4$	Coating and drying	46×10^{-3} at 80 °C
PVDF	HFP -TiO_2 (0.5 wt.%)	$NaPF_6$	Phase Inversion	1.3×10^{-3}
PEO	$Na_3Zr_2Si_2PO_{12}$ (40 wt.%)	NaFSI (EO/Na ≈ 20)	Solution casting	2.2×10^{-3} at 25 °C
PMMA-PVDF	HFP - $Na_3Zr_2Si_2PO_{12}$	$NaPF_6$	Electrospinning and in situ polymerization	2.78×10^{-3} at 30 °C

2.6 Assessment of Electrochemical Performances of Electrolyte

Evaluating the electrochemical performance of electrolytes is essential to ascertain their suitability in sodium-ion batteries (SIBs) (85). In pursuit of comprehensive analysis, various methodologies include Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV), and Charge/Discharge examinations.

EIS is usually used to quantify the electrolyte's ionic conductivity, a defining property that critically impacts the battery's performance. This process involves the application of a modest alternating current voltage across the electrolyte and subsequent measurement of the resultant current. The impedance (Z), indicative of the resistance to current flow, is then deployed to calculate the ionic conductivity (σ).

CV serves as another instrumental technique for investigating the electrochemical attributes of the electrolyte. This method provides pivotal information about the redox processes occurring within the electrolyte, the stability range of the electrolyte, and the electrochemical reversibility, all of which are essential for the performance and safety of the battery.

Charge/Discharge evaluations are conducted to scrutinize the battery's performance concerning its capacity, energy efficiency, and rate capability. The findings from these tests can offer valuable insights into the electrolyte's influence on the overall battery performance.

2.7. Fabrication of Polymer-based Electrolytes

Fabricating polymer-based electrolytes, dry, gel or composite for SIBs typically through two primary methods: solution casting and solvent-free procedures.

In solution casting, a polymer such as polyethylene oxide (PEO), a plasticizer like ethylene carbonate (EC), and a sodium salt (like $NaCF_3SO_3$) are dissolved in a suitable solvent, leading to a unified solution. The solution is poured into a mold. After casting and solvent evaporation, a thin film is obtained (87, 88). The selection of solvent can substantially influence the electrolyte's structure. A suitable solvent ensures a consistent and polished appearance. Drying conditions determine the film's mechanical and ionic characteristics.

For solvent-free procedure, the mixture is heated above the polymer's melting point to facilitate salt dissolution and promote ion mobility. Hot-pressing yields the formation of the polymer electrolyte without any harmful organic solvents. The mixture is positioned between heated plates before pressure is applied. The combined effect of heat and pressure fuses the mixture into a solid, flexible film. The parameters of temperature, pressure, and pressing duration can be varied to optimize the properties of the electrolyte (88).

Electrospinning is a relatively new technique for fabricating polymer electrolytes, which can produce fibers with diameters in the nanometer to micrometer range. The process involves dissolving the polymer, plasticizer, and salt in a solvent and using an electric field to draw fine fibers from the solution. These fibers are collected on a grounded substrate, and the solvent evaporates. Parameters like the electric field strength, solution concentration, and the distance between the needle and collector can impact the fiber diameter and porosity. Smaller fibers and higher porosities can provide more pathways for ion conduction, potentially enhancing the electrolyte's ionic conductivity.

2.8. Summary

Electrolytes in sodium-based batteries have experienced evolutions to become safer and functional, from liquid electrolytes to solid state electrolytes. However, most solid electrolytes have the drawback of relatively low ionic conductivity and non-compatibility with electrodes.

Recent advances in electrolyte engineering have shown impressive improvements in ionic conductivity, interfacial stability, and overall battery performance, showing that SIBs will soon reach near-practical energy densities suitable for grid-scale energy storage.

CHAPTER 3: MATERIALS AND EXPERIMENTAL ASPECTS

3.1 Materials

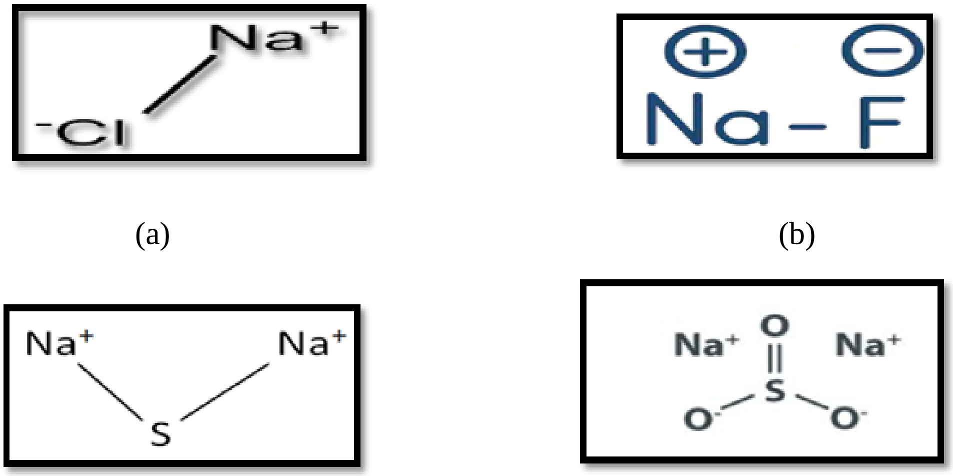
In this research liquid electrolytes obtained by dissolving four different salts dissolved in five different solvents were studied. The four salts are sodium chloride (NaCl), sodium sulfide (Na_2S), sodium sulfite (Na_2SO_3), and sodium fluoride (NaF). These salts are chosen because of their unique chemical properties. The five solvents are water, methanol, propanol, Dimethylformamide (DMF), and Dimethyl sulfoxide (DMSO). These solvents as classified as polar or non-polar according to the associated dielectric constant. All these solvents were selected due to their different polarities and ability to influence salt dissociation and ionic conductivity. Polymer electrolytes obtained by dissolving NaCl into polyethylene oxide (PEO) in different solvents with or without plasticizer EC. The structures of these components are illustrated in figures 15-17.

NaCl is a commonly used and relatively low-cost salt. NaCl is excluded because of the poor stability of electrolyte/electrode interface and co-intercalation. NaF is often used in polymer electrolytes to enhance electrochemical stability. The presence of fluoride ions helps to stabilize the electrolyte and prevent unwanted side reactions (89). NaF-based electrolytes have shown improved electrochemical stability and wider electrochemical windows compared to NaCl-based electrolytes. Na_2S is colorless and water-soluble. A recent study found that Na_2S-based electrolytes have higher ionic conductivity than other sodium salts for sodium-ion battery applications (90). Na_2SO_3 has been added to polymer electrolytes due to its efficiency in the enhancement of ionic conductivity. Depending on the concentration of Na_2SO_3 electrolytes, ionic conductivities are reported at reasonable levels and hence can be proposed for the use of composite electrolytes in SIBs (91).

High polarity solvents have better salt dissociation due to strong dipole interactions, hence higher ionic conductivity of solutions (92). Water is polar protic solvent with a high dielectric constant and can dissolve many inorganic salts. Sometimes water is used in the first steps of the polymer electrolyte sample preparation. However, in the final stage of preparation, the influence of water on the electrochemical stability of the electrolyte must be transduced (93). All other four solvents are polar protic solvents. Methanol is a good solvent for dissolving sodium salts and polymers. However, methanol's volatility and propensity to affect the electrochemical stability of the electrolyte must be controlled. By contrast, n-propanol has a relatively high boiling point, very low polarity making its interaction with sodium salts nearly impracticable. DMF has a generally high dielectric constant. This makes it a good solvent for dissolving either polymers or salts. DMF is employed more frequently in the synthesis of polymer electrolytes. It is especially useful in increasing the interaction of the polymer matrix with the sodium ions to enhance the ionic conductivity (94). In contrast, DMSO is more convenient to prepare and less toxic with a relatively high boiling point. DMSO gives moderate conductivities for its relatively low polarity. DMSO has some interesting electrochemical characterization of high discharge capacity, great battery performance and low charge potential.

PEO, also known as polyethylene glycol, is part of the ethylene oxide polymers that have been used preferably in polymer electrolyte systems because of its characteristic features (95). The repeating units of ethylene oxide in the formal structure of the polymer are rich in oxygen atoms which are effective in coordinating with sodium ions thus promoting their transport in the electrolyte. It finds wide application in preparing solid polymer electrolytes. PEO contributes to the flexibility and also the compatibility of the host matrix to form the above structures with other materials. The ionic conductivity of PEO-based electrolytes depends on the degree of crystallinity that in return could be managed with the help of the incorporation of plasticizers and other polymer components. PEO used in electrolytes has a molecular weight, which is usually between 100,000 and 5,000,000 g/mol to achieve the needed mechanical as well as electrochemical characteristics.

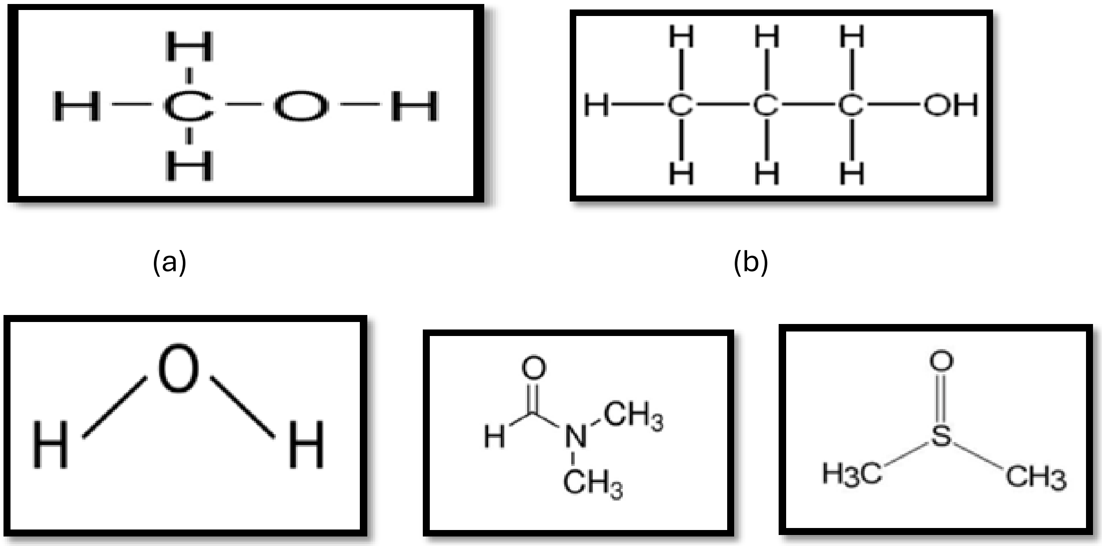
EC, an effective plasticizer was commonly added to selected electrolyte formulations. It tends to improve the mechanical and ionic conducting properties by reducing the crystallinity of the polymer matrix. EC is a cyclic carbonate with a higher dielectric constant; with the help of this, the dissolving of sodium salts takes place which in turn increases the amorphous phase of the polymer matrix (96). The incorporation of EC in PEO-based electrolytes affects PEO-crystalline structure in a way that the volume of amorphous phase that has a higher conductivity is enhanced (97). The usual loading of EC into the polymer matrix for polymer electrolytes is between 10-50 wt% in the proper context of the required conductivity and mechanical strength.



(a) (b)

(c) (d)

Figure 15:Chemical structure of (a) NaCl (b) NaF (c) Na2S and (d) Na2SO3



(a) (b)

(c) (d) (e)

Figure 16:Molecular structure of (a) methanol (b) n-propanol (c) water (d) DMF (e) DMSO

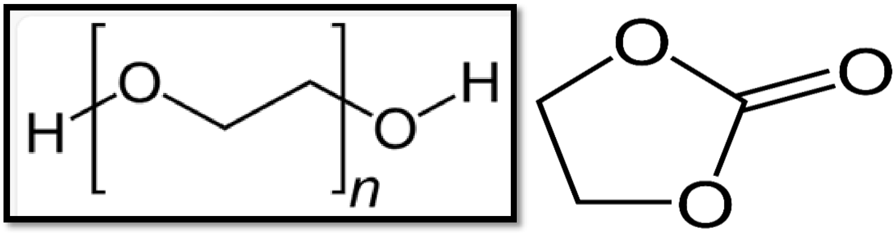


Figure 17:Structure of (a) PEO and (b) EC

PEO (molecular weight of 100,000), NaF, Na_2S, DMSO, and propanol were purchased from Sigma Aldrich. DMF was purchased from Millipore sigma. NaCl, Na_2SO_3, distilled water, and methanol (CH_3OH) were from fisher scientific. All chemicals are ACS grade and used without further purification. The structure of all these materials is shown in the figures.

3.2 Preparation of Liquid Electrolytes

Liquid electrolytes were prepared by dissolution of sodium salts in 50 ml solvents at different concentrations. The amounts of the salt used were calculated based on the molecular weights of the salts and the concentration selected. The mixture of the salt and solvent was stirred for 30 mins at selected temperature to ensure the complete solution. The concentrated solution with a larger amount of sodium salts took a longer time to dissolve and obtain a clear solution. The temperatures were set according to the boiling point of the five different solvents (Water, DMSO, DMF, Methanol and n-propanol). During the dissolving process the solution was covered to avoid evaporation and for laboratory safety. The final product was a liquid electrolyte exploring the effect of concentrations on the measured ionic conductivity.

3.3 Preparation of Polymer Electrolyte

The solid polymer electrolytes are prepared using the solvent casting technique, as illustrated in figure 18. In this study, sodium salt is NaCl. Solvent is either methanol or DMF. The sodium salt was first dissolved in the solvent for 30mins and then the PEO polymer was added and stirred to obtain a homogenous gel solution. The gel solution was casted on a glass plate and dried to obtain the free-standing membrane. The films were completely dried after 24 hours at a room temperature for methanol-based gel. The DMF based gel was dried at increased temperature, e.g. 80^{o}C, to eliminate the existence of any solvent in the solid polymer composite electrolyte membranes. For addition of EC, the process was repeated but was dried at 120^{o}c because the presence of EC makes the gel solution dries slowly. After that, these membranes were removed from the substrate and conveniently trimmed into smaller sizes before being used for conductivity measurements. In the absence of EC, the EO/Na ratio was varied. In the presence of EC, the molar ratios of EO/Na in all the samples were held at 8:1.

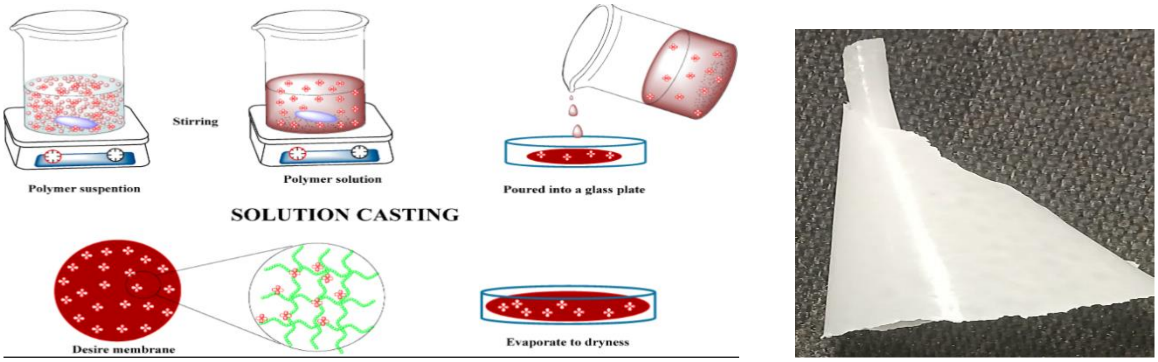


Figure 18:(left) Illustration of solid polymer electrolyte using the solution casting method (98). (right) Free-standing polymer electrolyte film obtained in this study.

3.4 Storage of Samples

After preparation, all solutions and membranes were transferred into tightly sealable moisture-proof vessels to avoid any bacterial contamination or changes in the solution's concentration due to the solvent's evaporation. They were marked accordingly with the type of salt used, concentration ratio and solvent used, date when the solution was prepared, and kept in a place away from light and heat.

3.5 Ionic Conductivity Equations

A paramount property typically calculated is the ionic conductivity (σ), given by the formula:

$$\sigma = \frac{1}{R} \times \frac{L}{A}$$

Herein, L represents the thickness of the electrolyte, R corresponds to the resistance derived from the impedance spectrum and A stands for the area of the electrolyte. The equation, an instrumental principle that delineates a relationship between ionic conductivity, the ion diffusion coefficient, and ion concentration within an electrolyte (99).

The ionic equation can describe the temperature dependence of ionic conductivity: The Arrhenius equation delineates the temperature dependence of ionic conductivity, defined as:

$$\sigma(T) = \sigma 0 \times \exp\left(\frac{Ea}{kT}\right).$$

In this formulation, σ(T) represents the ionic conductivity at a specific temperature T, σ0 refers to the pre-exponential factor, Ea is the ion conduction's activation energy, and k denotes the Boltzmann constant. Understanding and improving the ionic conductivity of Na-ion electrolytes is crucial for developing high-performance Na-ion batteries.

3.6 Ionic Conductivity Measurements

In this study, the ionic conductivity was determined at room temperature using electrochemical impedance spectroscopy (EIS) method on Gamry Ref 600. EIS parameters were at AC potential of 5 mV, and the applied frequency sweeps from 10,000 to 0.1 Hz. Each sample was tested more than once. The conductivity values presented are the average of the multiple measurements.

EIS experiments were conducted in a homemade conventional electrochemical cell consisting of reference and counter electrodes (shown in figure 20). For liquid electrolyte, the EIS was measured for each solution in 3ml, 6ml, 9ml, 12ml volumes in the container . The conductivity was calculated after each measurement. The conductivity values presented are the average of four measurements. The EIS of the polymer membranes was measured by using a stainless-steel cell with a measured diameter of 12mm film

Figure 19:(left) Illustration of solid polymer electrolyte using the solution casting method (98). (right) Free-standing polymer electrolyte film obtained in this study.

3.7. Ionic Conductivity of Electrolyte Using EIS technique

EIS determines impedance of an electrochemical system at different frequencies. It offers greater insight into the fundamental mechanism of electrochemical reactions and properties such as ionic resistances, charge transfer resistances, and double-layer capacitances (107). EIS is especially effective in separating the contribution of pure bulk ionic transport from the charge transfer processes involved at the electrodes–electrolyte interface (43).

Electrochemical processes can be expressed by equivalent circuit involving the resistors, capacitors, inductors. The circuit can be used to determine resistance of electrolyte solution (R_s), double layer capacitance at the surface of the electrode (C_{dI}), resistance of solution (R_s), double layer capacitance at the surface of the electrode (C_{dI}), charge transfer resistance (R_{ct}), etc. The diffusion process occurring at the electrode–electrolyte interface is the Warburg resistance. Nyquist diagrams are the most frequently employed graphical method to interpret EIS results and consist of the representation of imaginary part impedance ($Z''(\omega)$) versus real part impedance ($Z'(\omega)$), in which ω is the angular frequency. The simplifed Randles equivalent circuit and parameter changes in relation with Nyquist diagrams can be seen in figure 20.

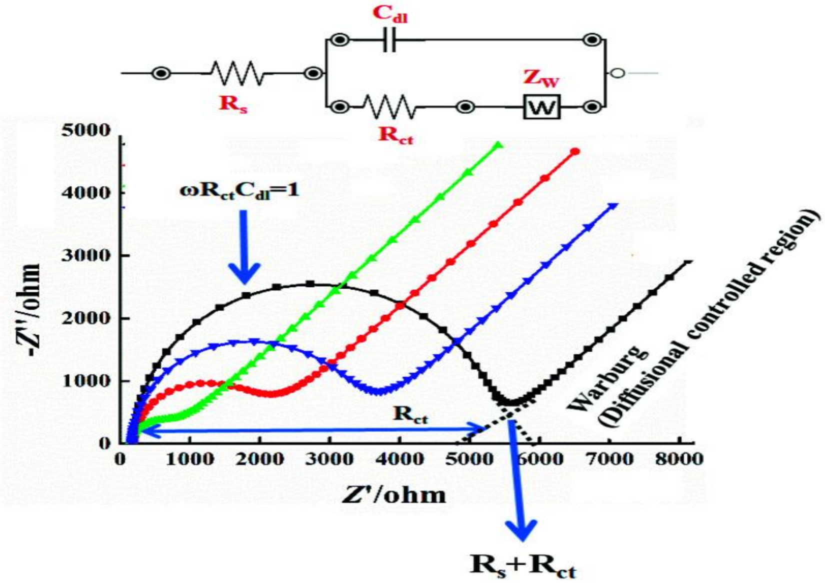


Figure 20:Experimental and simulated impedance spectra showing a simplified Randles equivalent circuit and Nyquist plot for an electrochemical system. (100).

CHAPTER 4: RESULTS AND DISCUSSION

4.1. Ionic Conductivity Characteristics of Liquid Electrolytes

Figures 21 – 25 present the ionic conductivities as a function of concentration obtained from the solutions of different sodium salts in different solvents. It can be seen generally that higher ion concentration in liquid electrolyte solution leads to greater conductivity.

In the aqueous solutions (see Figure 21) at the same concentration, sodium fluoride (NaF) solution shows the highest ionic conductivity. The solutions with conductivities from high to low in the sequence of NaF > NaCl > Na_2S > Na_2SO_3. At 0.1M concentration, the ionic conductivities in the four solutions are 3.34E-01, 3.94E-02, 3.36E-02, 5.41E-03 in (S/cm) respectively. Similar trend is also observed in DMF, methanol with conductivity from high to low in the sequence of NaF > NaCl > Na_2S > Na_2SO_3(see figures 22 and 23). However, the ionic conductivity values are one order magnitude lower than those of aqueous solution. At 0.1M concentration, the ionic conductivities in the NaF-DMF and NaF-methanol solutions are 8.00E-03 and 6.19E-04 in (S/cm). In propanol solutions, NaF still has the highest conductivity among the four salts. But the values are much lower than the other four solvents. In the NaF-propanol solution at 0.1M concentration, the ionic conductivity is 4.50E-04 (S/cm). Na_2SO_3 solution has the lowest values. But conductivity values in Na2S solution exceeds that in NaCl solution (see figure 24). In the DMSO solutions (see figure 25) the ionic conductivity of the sodium salts followed a different trend, i.e. Na_2S> NaCl > Na_2SO_3 > NaF, with Na_2S having the highest ionic conductivity but NaF salt having the lowest (see figure 25).

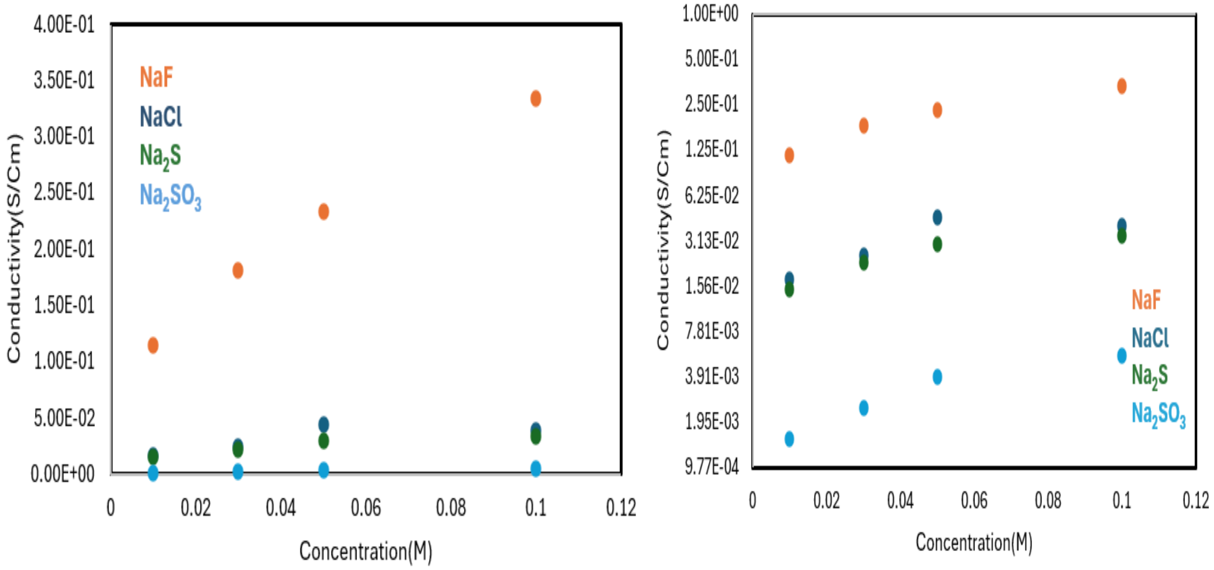


Figure 21:Liquid electrolyte conductivity of sodium salts in water (left) standard scale, (right) logarithm scale

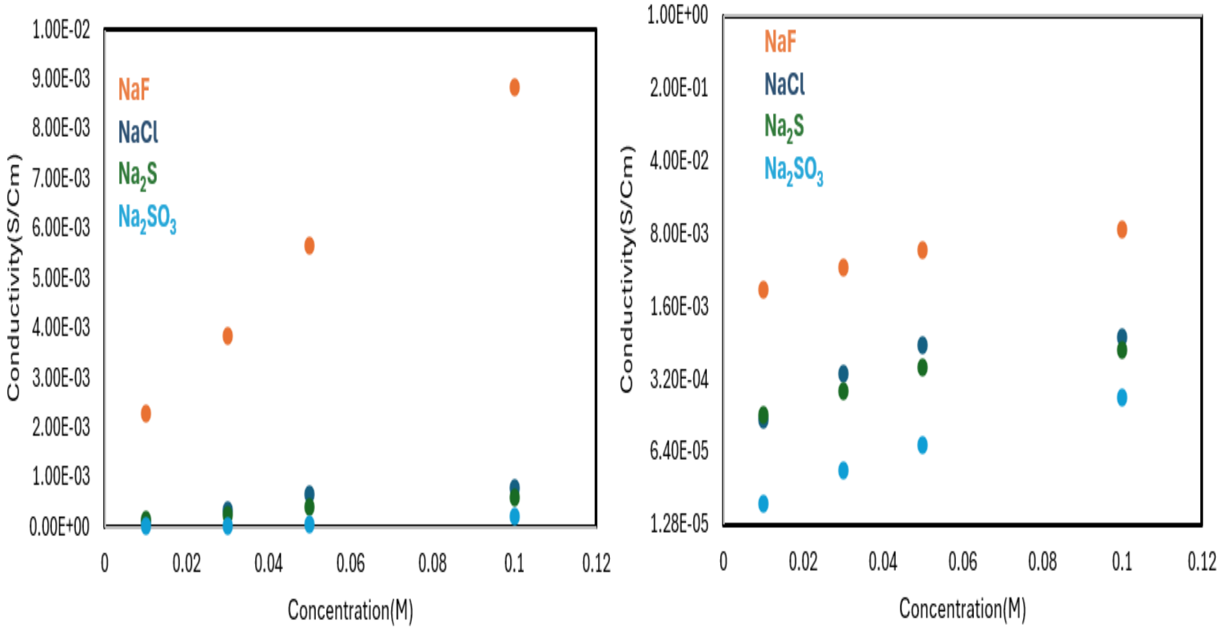


Figure 22:Liquid electrolyte conductivity of sodium salts in DMF solvent water (left) standard scale, (right) logarithm scale

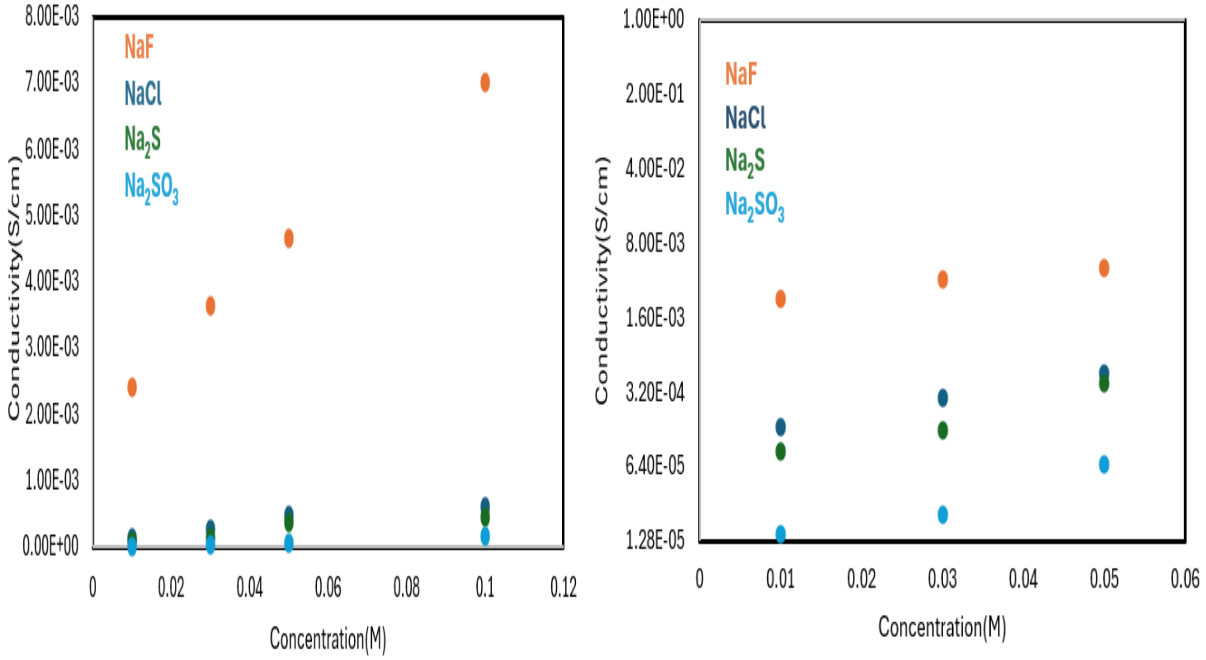


Figure 23:Liquid electrolyte conductivity of sodium salts in Methanol solvent (left) standard scale, (right) logarithm scale

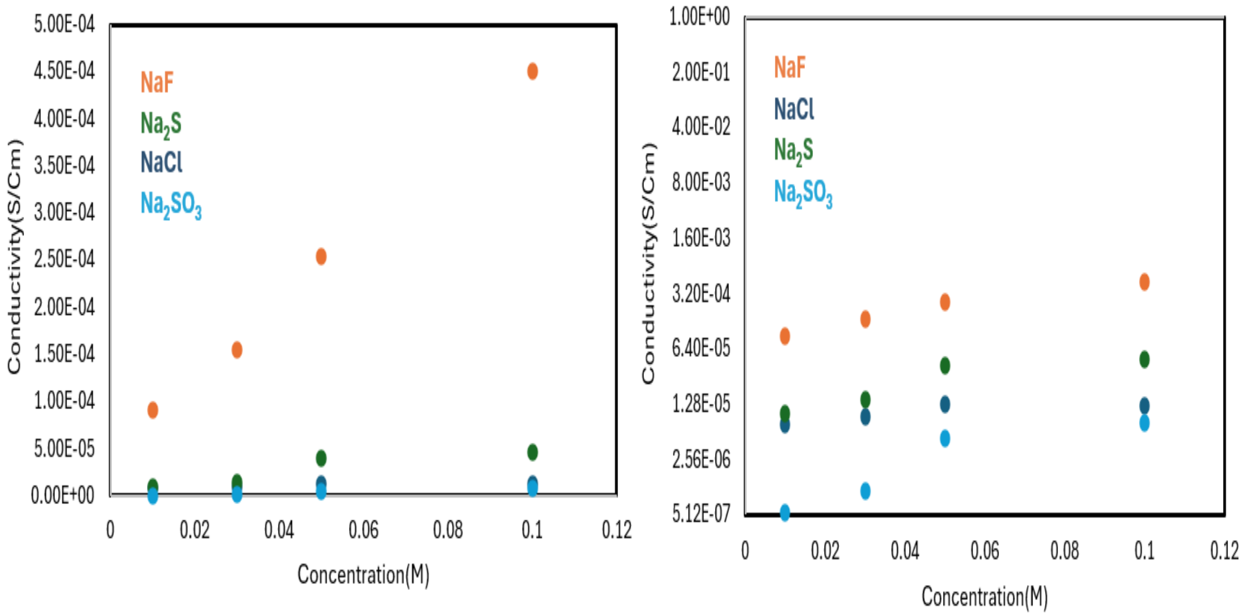


Figure 24:Liquid electrolyte conductivity of sodium salts in N-propanol solvent (left) standard scale, (right) logarithm scale

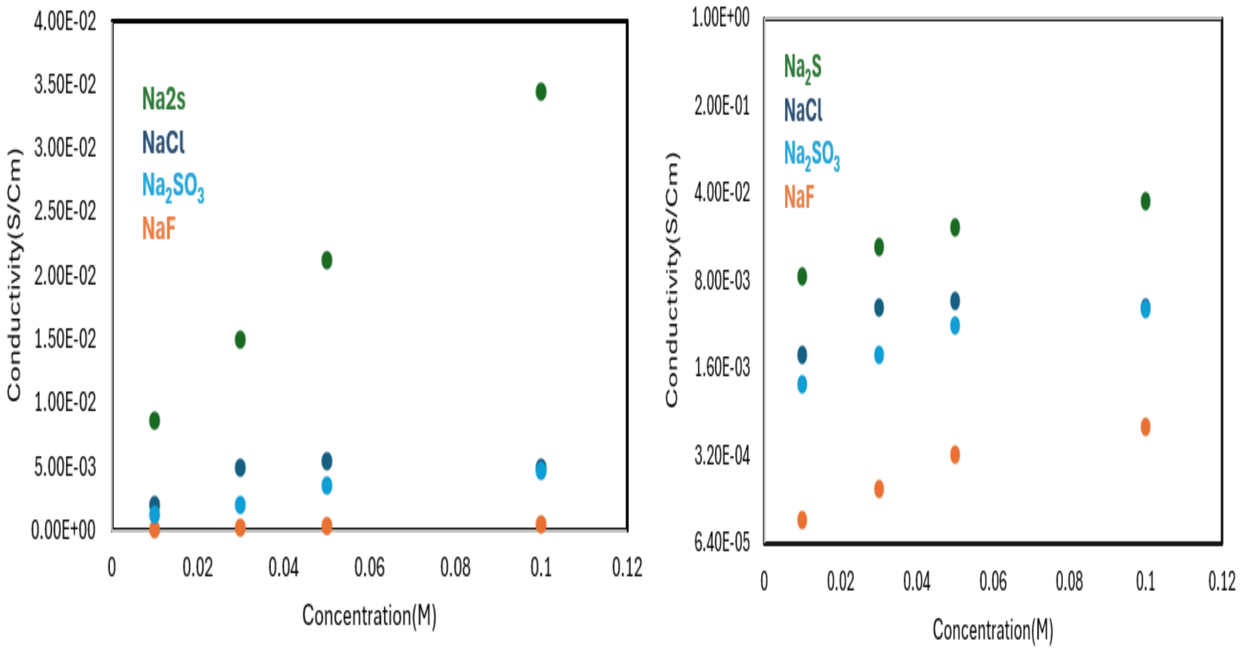


Figure 25:Liquid electrolyte conductivity of sodium salts in DMSO solvent (left standard and right logarithm scale)

4.2. Analyses of Conductivity Characteristics in Liquid Electrolytes

Ionic conductivity of a liquid electrolyte depends on the moving species in the solution, their amount, and their individual mobility. These variations are affected by a number of fundamental parameters including solubility, solvation, anion size, solvent dielectric constant, solvent viscosity etc. The information is collected and presented in Tables 7-9.

Table 6:Lattice energy of the salt, anion size, and the solubility of the sodium salts in each solvent. (101, 102, 103).

Salt	Lattice energy (kJ/mol)	Anion Size (pm)	Solubility (g/100mL)				
			DMF	DMSO	Methanol	N-propanol	Water
NaCl	769	1.81	0.455	0.4	1.375	-	26.45
Na_2SO_3	1827	1.33	-	<0.011	-	0.11	23.5
NaF	910	1.84	0.13	0.021	0.413	-	4.28
Na_2S	2199	2.18	0.0542	0.0499	5.13	1.79	17.1

Table 7:Typical properties of the solvents including dielectric constant, polarity, viscosity, boiling point

Solvent	Dielectric constant	Polarity index	Viscosity (cP)	Boiling point (°C)
Water	80.1	9.0	0.89	100
DMF	36.7	6.4	0.86 - 0.89	152.8
Methanol	32.7	5.1	0.55	64.7
N-propanol	20.3	4.0	1.95	96.0
DMSO	46.7	7.2	1.99	189

Table 8: Sodium salt anion-solvent solvation energy (104)

Anion	Solvation energy in water	Solvation energy in DMSO	Solvation energy in DMF	Solvation energy in Methanol	Solvation energy in n-propanol
Cl^-	3.83	0.69	0.49	0.46	0.67
F^-	5.22	0.69	0.45	0.46	0.66
S^{2-}	4.22	0.63	0.68	0.49	0.69
SO_3^{2-}	3.64	0.69	0.69	0.61	0.68

Table 9: Na- Ion-solvent solvation energy (105)

Solvent	Solvation energy ΔG_{solv}
Water	−693.34
DMSO	−693.32
Methanol	−1074
N-Propanol	−1122
DMF	−1109.1

4.2.1 Key parameters affecting salt solubility in solvent

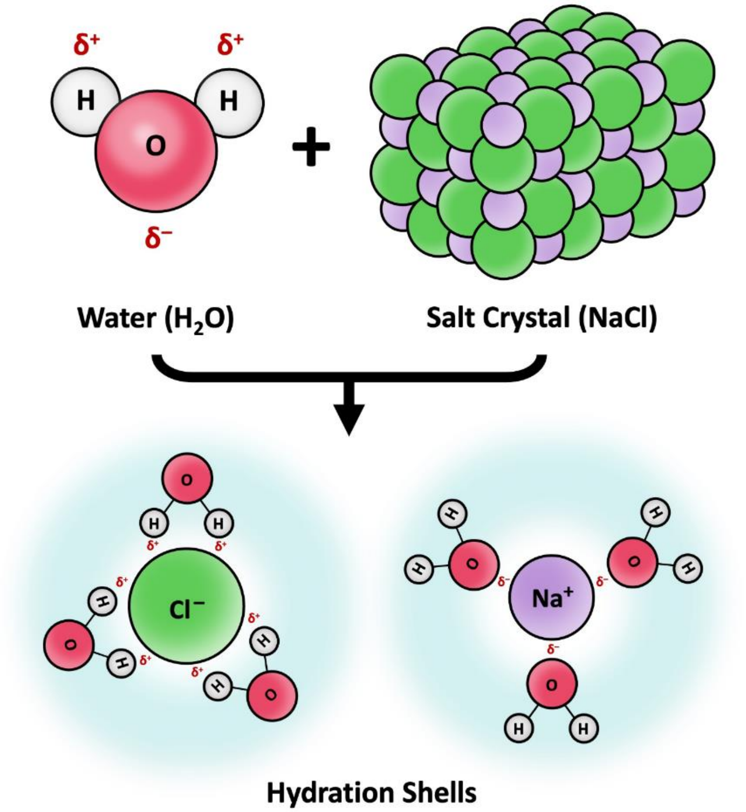


Figure 26: Schematic illustration of NaCl solvation

When salt is dissolved into a solvent, the lattice energy needs to be broken. The ions can be solvated by the solvent and exist in the solution. Seen in figure 26, when NaCl is dissolved in water, positively charged sodium ions and negatively charged chloride ions become surrounded by water molecules through oxygen and hydrogen ions. Bigger ions become easily solvated by being surrounded by solvent molecules during the dissolution.

Solubility is determined by the lattice energy of salt and the ion-solvent solvation energy. In general, solubility is high for the salt-solvent couple with low lattice energy and high solvation energy.

Solubility reduces dramatically with the solvent's growing non-polarity (and thus with reducing dielectric constant). It was observed that the sodium salt solutions in water yielded higher ionic conductivity, which agrees to the reported figures in table 6. Ionic conductivity is directly proportional to solubility. It can be concluded that sodium salts dissolved in water produced more stabilized ions, hence more probability of being highly conductive. Comparing the solubility of the different anions, it is seen that the larger anions have lower solubility than the smaller anions; for instance, the Na_2S and Na_2SO_3 have lesser solubility than Nacl and NaF.

Liquids with high dielectric constant solvents such as water and DMSO enable good ionic dissociation, conductivity, and solubility. On the other hand, low-polarity solvents such as methanol and n-propanol decrease these properties because of enhanced ion pairing or aggregation.

4.2.2 Key parameters affecting Ionic conductivity in liquid

In general, ionic conductivities in a liquid solution can be expressed as:

$$\sigma=(n_c u_c+n_a u_a)e$$

where σ is the ionic conductivity, subscript c refers to cations, subscript a refers to anions, n is the concentration of cations or anions, μ is the mobility of cations or anions. The extent of dissociation, solvation, and ion mobility will all influence the value of ionic conductivity.

Assuming no solvation occurs, the dissociation equations of the different sodium salts can be expressed as the following:

$$NaCl \leftrightharpoons Na^+ + Cl^-$$

$$NaF \leftrightharpoons Na^+ + F^-$$

$$Na_2S \leftrightharpoons 2Na^+ + S^{2-}$$

$$Na_2SO_3 \leftrightharpoons 2Na^+ + SO_3^{2-}$$

The more sodium salt dissociates in solution, the more concentrations of ions, the higher the ionic conductivity. Hence, in general conductivity is increased with the concentration in a dilute solution.

When salt dissolved in solvent, both cations and anions can be present in the solvated state. Large ions are readily solvated by the polar solvent. Free ions and solvated ions will have different mobility. Solvated ions will have low mobility. Further, ion mobility will be affected by the viscosity of solvent. Ion mobility is inversely related to solvent viscosity. A more viscous solvent hinders the movement of ions, making them less mobile.

4.2.4 Ionic conductivity in relation to viscosity

Among the five solvents, methanol has the lowest viscosity. Water and DMF have similar viscosity. Propanol and DMSO have the highest viscosity values. However, the results from this study show that the high conductivity values in in general in the sequence of Water > DMSO > DMF > methanol > propanol. From this point, the viscosity is not the primary factor contributing to the conductivities trend for the liquid electrolyte systems in this study.

4.2.5 Ionic conductivity in relation with anion size

At the same concentration and complete dissociated solution, the concentration of anions are the same but the concentration of cations in Na_2S and Na_2SO_3 solutions are doubled. Observed before, in water DMF, methanol propanol solvents except DMSO, ionic conductivities in the four solvents are in the trend of NaF > NaCl > Na_2S > Na_2SO_3. It is noticed that the anion radii in the four salts are in the sequence of F^- < Cl^- < S^{2-} < and SO_3^{2-} . Apparently ionic conductivities in these solutions are related to the size of anions, and hence, with the mobility of anions.

4.2.3 Ionic conductivity in relation with Dielectric constant

The extent of ion dissociation is related to the polarity of the solvent. Solvent with high dielectric constant has high polarity. Hence, the dielectric constant indicates the extent of ion stabilization and separation in the solvent; a higher dielectric constant represents a greater conductivity level. When the solvents have comparatively low dielectric constants like methanol ($\varepsilon = 32.7$) and n-propanol ($\varepsilon=20.3$) ionic dissociation is low; hence, the solution's conductivity is low due to ion pairing or aggregation (106).

Ionic conductivity for the aqueous liquid electrolyte was higher due to their higher polarity and dielectric constants of 80.1 see table 7 and 8 above, facilitating good salt dissociation and mobility of ions. The ionic conductivity of DMSO, DMF, methanol and n-propanol solvents are slightly lower conductivity because of their lower dielectric following the sequence

DMSO>DMF>Methanol>n-propanol. These results suggest solvent optimization is essential in improving the electrochemical performance of liquid electrolytes for sodium-ion batteries and that solvents with high polarity are preferable.

In figures 22 and 23, sodium salts dissolved in DMF solvent exhibited higher conductivity than in Methanol and n-propanol due to a higher dielectric constant and polarity index of ε=36.7 and 6.4 respectively. In figure 25, the ionic conductivity of the sodium salts showed variation. DMSO with a dielectric constant polarity of ε=46.7 and relatively high polarity index of 7.2 solvate S^{2-} due to less steric hinderance in ion mobility.

4.3 Limiting molar conductivity (λ)

To provide an in-depth analysis of the results of the liquid electrolyte conductivity above, the concept of limiting molar conductivity has been considered. molar conductivity is denoted by the symbol Λ_m and expressed in units of siemens per meter squared per mole ($S\ m^2\ mol^{-1}$). The molar conductivity of a very dilute solution at infinite dilution and/or the electrolyte’s molar conductivity as the concentration approaches zero is known as the limiting molar conductivity.

As the concentration decreases the molar conductivity increases, this is due to rise in the total volume containing one mole of electrolyte. This is better illustrated by Kohlrausch's law of Independent Migration of ions which states that when dissociation is completed at infinite dilution each ion makes a definite contribution towards the equivalent conductance of the electrolyte. A strong electrolyte has a high concentration of ions and gives a high ionic conductivity due to the complete ionization of the solute in the solvent. The concentration of the solute and ions present in the electrolyte system is directly proportional.

This concept is widely used to study very diluted liquid electrolyte solutions. The law can be expressed as:

$^{\Lambda}m={}^{\Lambda}0m - KCs_{½}$,

$^{\Lambda}m$= molar conductivity (expressed in siemens centimeter-squared per mole)

$^{\Lambda}0m$= molar conductivity at infinite dilution or limiting molar conductivity.

K = electrolytic conductivity (expressed in siemens per centimeter).

Cs= solute concentration (example: inorganic salt (Csalt)) (expressed in mole per centimeter cubic.

The Limiting ionic conductivity is inversely proportional to ionic size, because the smaller ions can move more easily through a solution with less resistance due to their size they have higher limiting ionic conductivity. Unlike the larger ions which, due to more hydrodynamic drag, hindering their movement have a lower limiting ionic conductivity.

For this research the lowest two conductivity values of each of the salts dissolved in different solvents were taken to fulfil Kohlrausch's law at infinite dilution. From the results at dilution, the degree of dissociation did not increase further as it is already at its maximum. However, cluster of ions decreases at dilution and more space for the ion mobility was provided, this increases the molar conductivity.

4.3.1 Limiting molar Conductivity to Dielectric Constant

Low molar conductance also exhibits the same trend as conductivity and molar conductivity by the increasing order recognized for the dielectric constant of the solvents. High dielectric constant solvents promote ionic dissociation even to infinite dilution, thereby higher is Λ^{o}.

Table 10: Limiting ionic conductivity (λ∞m) to dielectric constant

Solvent Dielectric constant	**Sodium salt**	**Anion Size (pm)**	**λ∞m of salt in Water solvent**	**λ∞m of salt in DMSO Solvent**	**λ∞m of salt DMF Solvent**	**λ∞m of salt in methanol Solvent**	**λ∞m of salt in n-propanol Solvent**
Water 80.1							
Dmso 46.7	NaCl	1.81	0.2922	0.0252	0.0015	0.0036	0.0001
DMF 36.7	NaF	1.33	0.9009	0.0015	0.0369	0.0407	0.0015
Methanol 32.7	Na2S	1.84	0.108	0.0063	0.0024	0.0015	0.0002
N-propanol 20.3	Na2SO3	2.18	0.0248	0.0194	0.0003	0.0002	0.00008

4.3.2 Molar Conductivity to Dielectric Constant

To investigate ionic mobility's dependence on the solvent dielectric constant. Molar conductivity measures up with conductivity similarly because the two are correlated. Water always indicated the highest molar conductivity when sorted at every concentration, owing to its ability to minimize ion pairing. For the same solution, molar conductivity reduces as the solvent's dielectric constant decreases due to ionic mobility or conductivity in low-polar solvents.

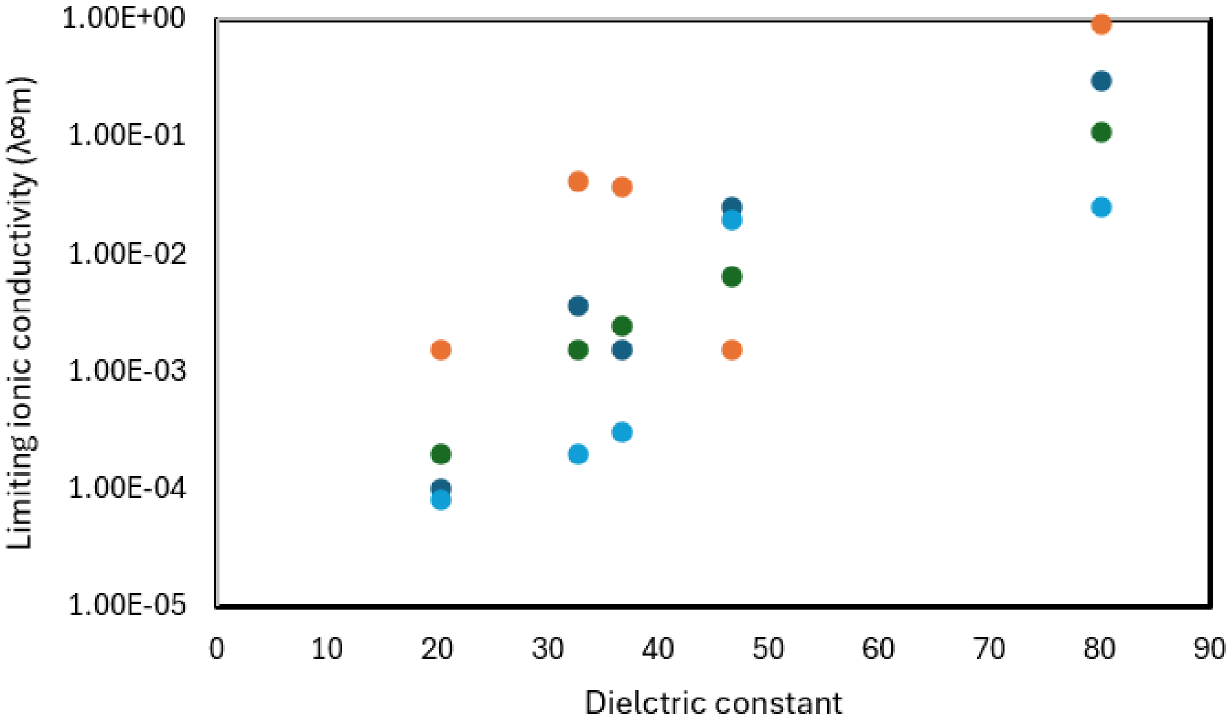


Figure 27:Limiting ionic conductivity (λ∞m) to dielectric constant

4.3.3 Limiting ionic conductivity (λ∞m) to ionic sizes (Å)

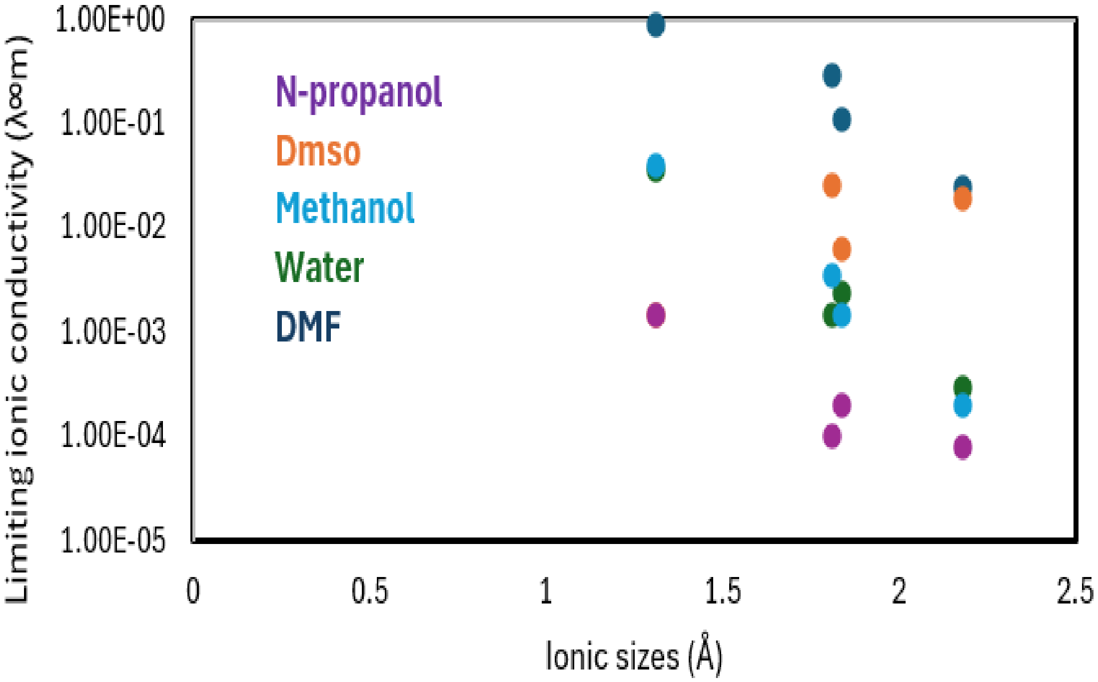


Figure 28: Limiting ionic conductivity (λ∞m) to ionic sizes (Å) of sodium salts in solvent

The larger anions of Na_2S and Na_2SO_3 make stronger ion pairs and aggregates disappear in less polar solvents and are less soluble and conductive. CONCISE The two differ in decreasing size and increasing ability to dissociate due to greater conductivity and solubility; thus, for ions in solution, will it mean that the anions are smaller? and F? the better.

4.2. Ionic Conductivity Characteristics of PEO-based Electrolytes

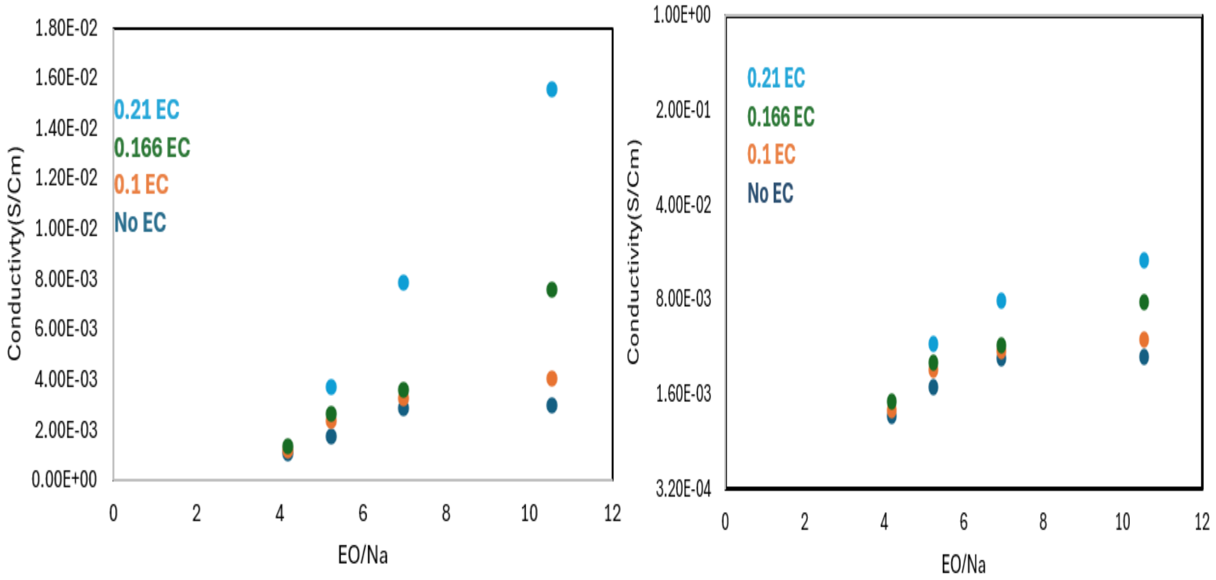


Figure 29:Solid polymer electrolyte in PEO-Methanol system

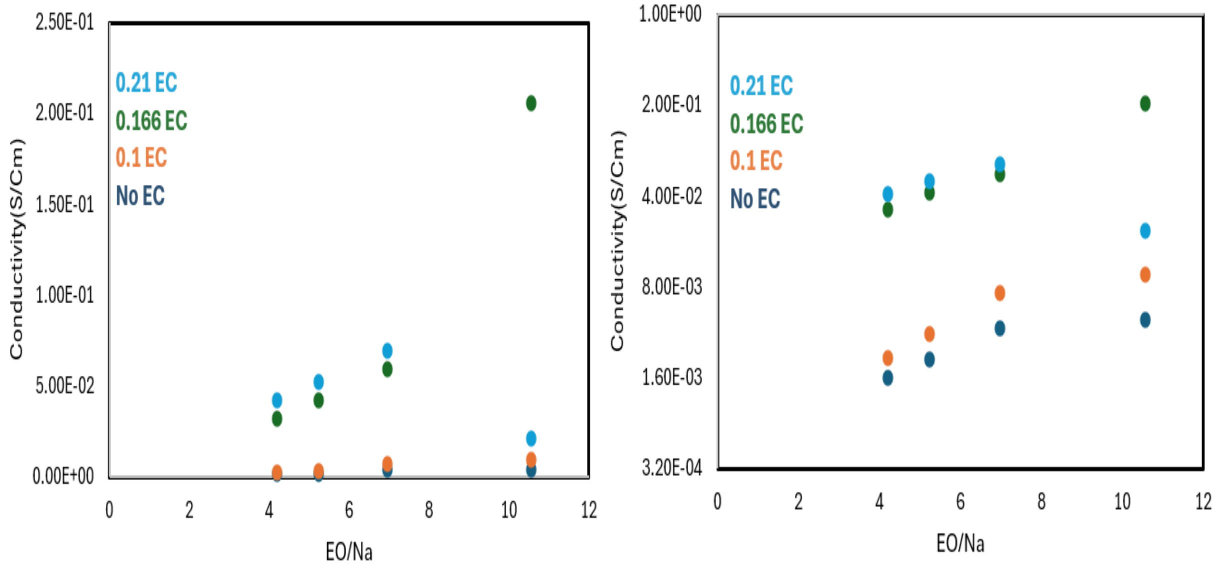


Figure 30:Solid polymer electrolytes of PEO-DMF system

Figure 29-30 presents the ionic conductivity of the solid polymer electrolytes in Methanol and DMF solvents respectively. Just as the liquid electrolytes results, higher ion concentration in solid electrolyte leads to greater conductivity. The conductivity of the obtained PEO-Methanol-NaCl electrolyte systems is 10^{-5} S/cm at room temperature this is because methanol can facilitate uniform chain alignment in solvent evaporation, producing a more orderly polymer-salt complexation. Decrease in the degree crystallinity leads to an increase in the polymeric backbone flexibility and ionic conductivity, the observed continuous increase in conductivity of the PEO-NaCl system with increasing salt concentration is due to a decrease in crystallinity.

Table 11:The amount of each component used to fabricate the PEO-NaCl-EC

Composition	EC(g)	PEO(g)	Na(g)	Moles PEO	Moles Na	EO:Na Ratio
PEO	-	0.5	0.166	0.0119	0.00284	4.195
PEO-0.1 EC	0.1	0.5	0.133	0.0119	0.00227	5.236
PEO-0.166 EC	0.166	0.5	0.100	0.0119	0.00171	6.964
PEO-0.21 EC	0.21	0.5	0.066	0.0119	0.00113	10.552

Ethylene carbonate (EC) acts as a plasticizer in this research to help reduce the crystallinity and increase the flexibility of the polymer’s local chain in the amorphous region hence enhancing the conductivity of the SPEs. This explanation agrees with Figure 38, as the concentration of EC increases from 0.1, 0.166 to 0.21 respectively the ionic conductivity increases. In figure 29, the conductivity of the PEO-DMF systems increases as compared to the PEO-Methanol. This is due to the high dielectric constant of DMF which is the determining factor in the dissociation degree of the electrolyte salt used. Furthermore, the volume of the solvent used was 5ml as compared to the 10ml in methanol.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The research work contributes significantly to developing appropriate methodologies for the fabrication and characterization of liquid and solid electrolytes in sodium-ion batteries, relating to sustainable energy storage technologies. The conducted research into NaCl, Na_2S, $NaSO_3$, and NaF sodium salt systems on various solvents showed a clear relationship between salt concentration and ionic conductivity, with the highest conductivity recorded at a 0.1 M concentration. In most cases, the Water, DMSO and DMF combinations gave the highest conductivity, mainly because of their highest dielectric constant and solvation capability, indicating how important the selection of the proper solvent is in optimizing the performance of the electrolyte. Hypothetically, stable and homogeneous films were produced in solid polymer electrolytes by a casting method using a solvent. Polyethylene oxide acted as an excellent host polymer for sodium ion conduction while adding ethylene carbonate as a plasticizer, which enhanced conductivity by suppressing crystallinity and increasing the mobility of polymer chains. Methanol-based films were more homogeneous than DMF-based systems, however the DMF systems exhibited higher conductivity. This can be argued to the fact that DMF have a high dielectric constant and polarity. In the final analysis, this work contributes to establishing sodium-ion batteries as one of the most promising alternatives to lithium-ion systems, making more green and large-scale energy storage possible. This study demonstrates that the solvent dielectric constant plays a vital role in sodium salts' conductivity, molar conductivity, and solubility. Typically, high dielectric constant solvents like water and DMSO increase solute ionization, leading to high conductivity and solubility. The findings are relevant for enhancing the attributes of electrolytes in purely electrochemical applications.

5.2. Recommendations

Further development concerning sodium-ion batteries should be focused on the search for other polymer hosts and additives, which can further improve the conductivity and stability of the electrolytes. PEO-based electrolytes' application looks promising; some other polymers still show higher ionic conductivity and mechanical strength. Other variants could be PVDF, PAN, and copolymer blends, which may show better ion transport properties and compatibility with sodium salts. The influence exerted by different plasticizers should also be investigated, with the assurance of better electrolyte performance within a wide operating range.

Another important direction of further investigation concerns the developed electrolytes' long-term stability and cycling performance. While promising, these results must be complemented with practical applications ensuring high performance for extended charge-discharge cycles. Accelerated aging tests and long-term cycling tests are mandatory in order to determine how such processes as degradation, ion migration, or interface stability influence the performance of electrolytes. The finally developed liquid and solid electrolytes must be assembled in a full-cell configuration for thorough testing. Full-cell testing will show these electrolytes' overall electrochemical behavior, energy efficiency, and practicality in real-world sodium-ion battery applications. This step will connect laboratory-scale findings with scalable, commercially viable energy storage solutions.

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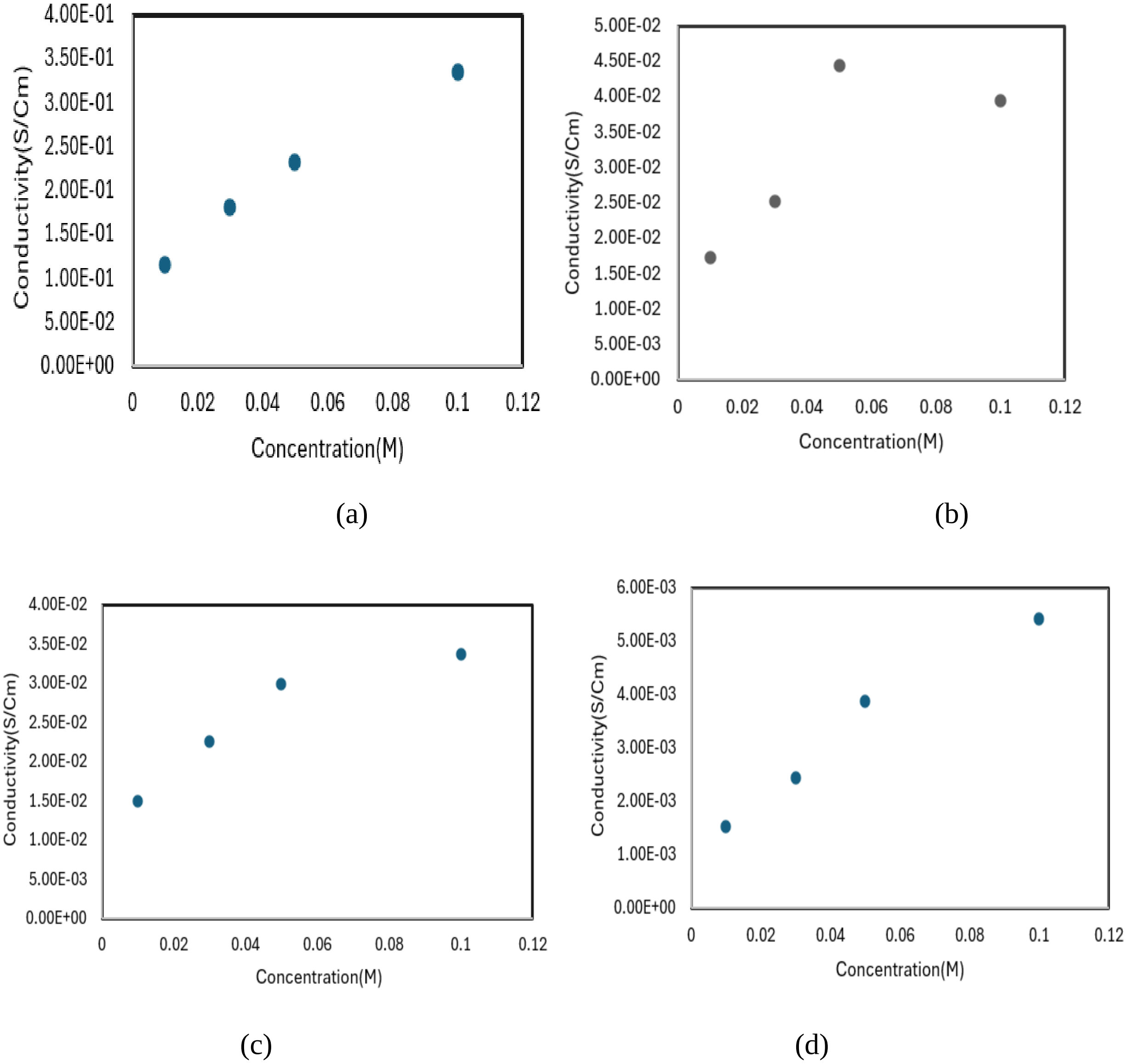
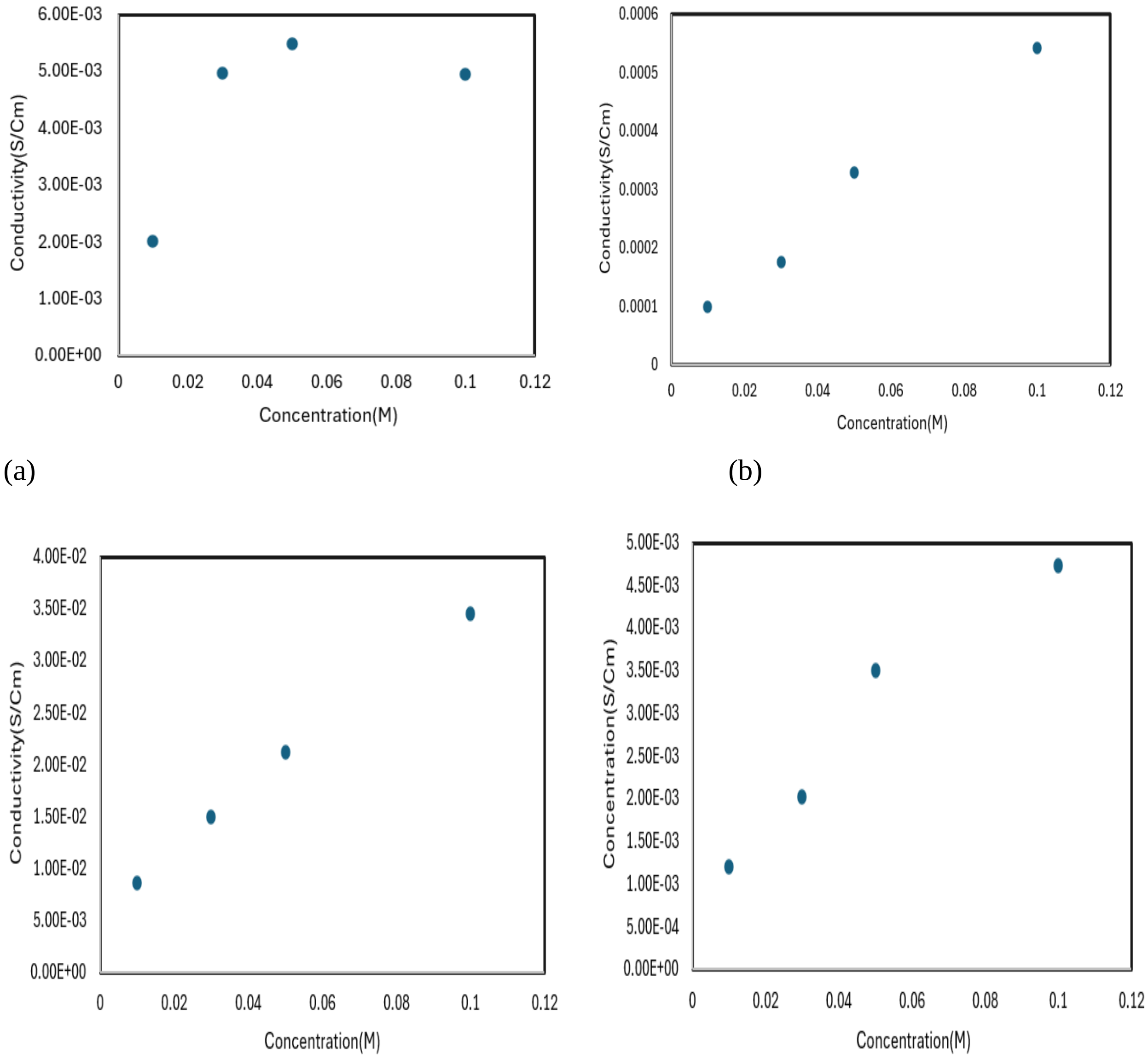
Supplementary Figures



(a) (b)

(c) (d)

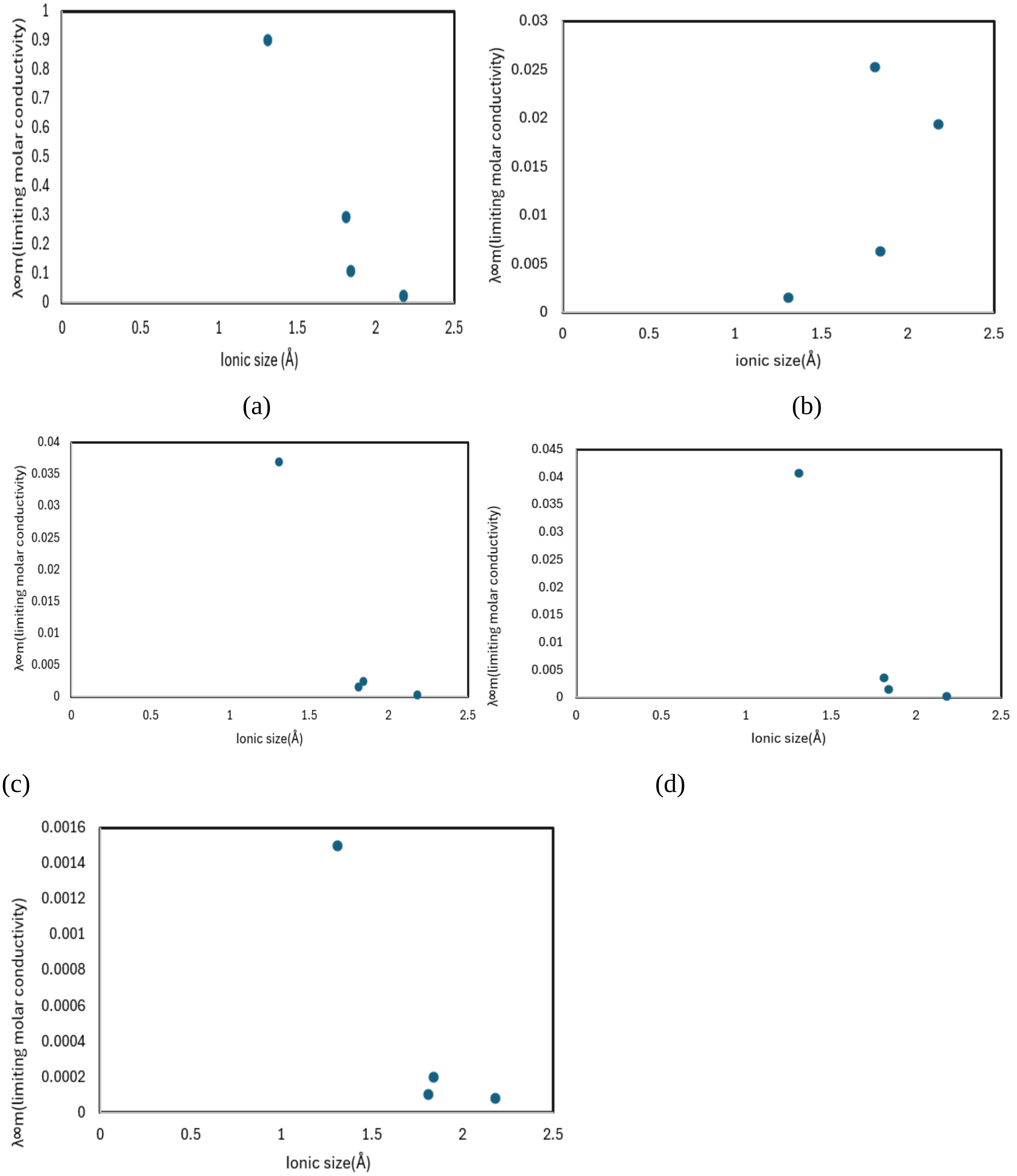
Liquid conductivity as a function of concentration of sodium salts (a) NaF (b) NaCl (c) Na_2S and (d) Na_2SO_3 in water solvent



(a) (b)

(c) (d)

Liquid conductivity of sodium salts (a) NaCl (b) NaF (c) Na_2S and (d) Na_2SO_3 in DMSO solvent



(a) (b)

(c) (d)

(e) Figure 27: Limiting ionic conductivity (λ∞m) to ionic sizes (Å) of sodium salts in: (a) water (b) DMSO (c) DMF (d) Methanol (e) n-propanol

The conductivity values for PEO-Methanol system

EO/Na(M)	Conductivity (S/cm) PEO	Conductivity (S/cm) PEO-0.1 EC	Conductivity (S/cm) PEO-0.166 EC	Conductivity (S/cm) PEO-2.1 EC
10.55194805	3.05924E-05	4.10739E-05	7.66497E-05	0.000156252
6.964285714	2.94807E-05	3.35673E-05	3.65959E-05	7.91424E-05
5.236305048	1.81614E-05	2.43363E-05	2.71914E-05	3.77307E-05
4.19535284	1.11673E-05	1.23849E-05	1.42735E-05	2.5483E-05

The conductivity values for PEO-DMF system

EO/Na(M)	Conductivity (S/cm) PEO	Conductivity (S/cm) PEO-0.1 EC	Conductivity (S/cm) PEO-0.166 EC	Conductivity (S/cm) PEO-2.1 EC
10.55194805	4.42478E-05	9.89984E-05	0.000179604	0.00021489
6.964285714	3.89381E-05	7.15773E-05	8.76983E-05	9.1835E-05
5.236305048	2.21239E-05	3.48907E-05	3.67202E-05	4.26952E-05
4.19535284	1.59582E-05	2.29588E-05	2.86309E-05	3.4013E-05