Review

Sodium Polymer Electrolytes: A Review

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Abstract: Lithium-based electrolytes are, at least from a thermodynamic standpoint, the most suitable ion-transport materials for energy storage systems. However, lithium-based ionic conductors suffer from safety concerns, and the limited availability of lithium in the Earth’s crust is at the root of the need to consider alternative metal ions. Notably, sodium stands out as the sixth most-prevalent element; therefore, when considering mineral reserves, it as a very attractive candidate as an alternative to the status quo. Even if the specific energy and energy density of sodium are indeed inferior with respect to those of lithium, there is substantial economic appeal in promoting the use of the former metal in stationary energy storage applications. For these reasons, the promise of sodium is likely to extend to other commercial applications, including portable electronics, as well as hybrid and electric vehicles. Widely used organic liquid electrolytes, regardless of their chosen metal cation, are disadvantageous due to leakage, evaporation, and high flammability. Polymer electrolytes are acknowledged as the most effective candidates to overcome these obstacles and facilitate the advancement of next-generation energy storage applications. In this contribution, an in-depth and comprehensive review of sodium polymer electrolytes for primary and secondary batteries is proposed. The overarching goal was to gain insight into successful synthetic strategies and their implications for conduction parameters and conductivity mechanisms. The focus lies on solid, gel, and composite polymer electrolytes. Our hope is that the proposed discussion will be helpful to all operators in the field, whether in tackling fundamental research problems or resolving issues of practical significance.

Keywords: sodium polymer electrolytes; sodium solid polymer electrolytes; sodium gel polymer electrolytes; sodium composite polymer electrolytes; sodium ion batteries

1. Introduction

In recent years, there has been an escalating worldwide effort to transition from a global energy system reliant on hydrocarbons to one based on carbon-neutral alternatives. A consequent epochal shift is underway, which has been gaining significant momentum and is often characterized as the grand challenge of our times. Given the limited availability of conventional fossil fuels, renewable energy sources such as wind, solar, and nuclear energy solutions have grown in importance [1]. However, the cyclical nature and uneven spatial distribution of the first two types of renewable energy resources prevent them from constituting a constant power supply. In contrast, nuclear energy is still considered too dangerous to be fully reliable. Regardless of the preferred energy solution mixture, stable and dependable energy storage will be a crucial part of the expected economic shift. Batteries are anticipated to claim a sizable share of the energy market, even though it is yet unclear which combination of energy storage technologies will prevail. As a
result, significant emphasis has been placed on research and development in this field. Rechargeable batteries are endowed with sufficient versatility to store energy and efficiently turn it into usable power [2]. Lithium-ion batteries (LIBs) have historically held a dominant position in the markets of portable electronics, electric vehicles, and hybrid vehicles due to their impressive performance parameters, such as high output voltages, substantial energy densities, and extended cycle lives. Nonetheless, the elevated costs of extraction and finite availability of lithium reserves impose constraints on the widespread adoption of LIBs for large-scale energy storage applications [3–5].

Due to the scarcity of earth deposits and unequal distribution of lithium resources (with 70% of known mineral reserves being located in South America), future commercial applications of LIBs are hampered by high costs and environmental concerns [6,7]. The availability of lithium resources has nearly doubled since 1991 [8,9], which is beneficial for commercial applications. Given the redox potential of sodium (−2.71 V vs. SHE, a mere 0.3 V higher than that of lithium), abundant sodium resources, and cost-effective sodium salts, sodium-ion batteries (SIBs) have garnered significant interest. Research in SIBs has continued to increase exponentially, other than some appreciable slow-down during the COVID-19 pandemic, as shown in Figure 1 [10].

![Figure 1. Number of publications on sodium batteries over time.](image)

SIBs are expected to emerge as strong contenders in stationary energy storage applications, even though LIBs are predicted to maintain dominance in conditions where energy density takes precedence [11]. Since Na atoms are larger and heavier than Li atoms, it is inevitable that the energy density of SIBs will never be higher than that of Li power sources [12]. However, in the context of large-scale electrical grid support, battery distribution and durability are the most crucial factors, not energy density [13]. Since lithium and sodium are both alkali metals, they exhibit similar chemistries, and their electrochemical processes in SIBs and LIBs are almost an exact match. These characteristics have sped up the development of SIBs to the point that they now have a high enough energy density to replace LIBs in many applications. SIBs generally consist of two electrodes, which are comprised of thin metallic current collectors coated with active materials for both the anodes and cathodes. These electrodes are interfaced with a non-aqueous liquid electrolyte, and a thin separator sheet, typically constructed from polyolefin or fiberglass, is used to keep them apart. Despite their competitive characteristics, SIBs have not yet gained significant commercial acceptance [14].

However, an important milestone in practical SIBs was recently achieved by Yang et al. [15]. SIBs were used to power 120 Wh/kg low-speed electric vehicles, suggesting
the impending widespread commercialization of SIBs. There have been substantial efforts addressed at developing cathode and anode active materials for SIBs with a variety of operating voltage ranges and reversible capabilities [16–18].

Presently available carbonate-based lithium-ion electrolytes, known for their high ionic conductivity and elevated dielectric constants, unfortunately suffer from flammability, inadequate thermal stability, and the propensity for leakage. There are valuable lessons to be learned from incidents involving burning consumer electronics powered by LIBs (as exemplified by the Samsung Galaxy Note 7 smartphones), primarily attributable to the use of liquid electrolytes. Conventional liquid electrolyte-based SIBs continue to be plagued by weighty disadvantages, including unfavorable interactions between electrodes and electrolytes, the inevitable formation of sodium dendrites, and associated safety concerns.

In response to the challenges affecting liquid electrolytes, researchers have explored alternative electrolyte options for high-performance SIBs. Among these, inorganic solid electrolytes stand out for their high ionic conductivities (>10^{-4} \text{ S}\cdot\text{cm}^{-1}) and enhanced thermal stability. However, these materials do present difficulties related to processability and compatibility with electrode interfaces [19,20]. Among the possible solutions, polymer electrolytes (PEs) exhibit exceptional properties that make them ideal for use in SIBs, including the absence of liquid leakage, minimal flammability, high processability in a variety of formats, and outstanding flexibility [21,22].

PEs are categorized primarily into three distinct groups: solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and composite polymer electrolytes (CPEs), as illustrated in Figure 2.

Figure 2. Classifications of polymer electrolytes.

The main benefits of PEs are related to their low processing costs. These electrolytic materials can be synthesized at relatively low temperatures, are considerably more likely to exhibit air stability, and can effectively undergo roll-to-roll production processes. Moreover, the interface between the electrode and electrolyte is typically stabilized by PEs, increasing their effective conductivity. The most practical route to all-solid-state batteries may be provided by PEs due to their combined benefits in terms of processability and performance. However, a number of issues still need to be resolved before their practical use is economically viable. Especially at or below room temperature, the conductivity of SPEs tends to be insufficient for practical real-world applications. Reports on sodium-based batteries date back to the same time as lithium-based batteries [23,24]. During the 1990s, these technologies were largely overlooked due to the emergence of commercially available lithium-based batteries, including Li–MoS_{2} and Li–Li_{x}MnO_{2} systems [25]. In the SIB system, sodium ions (Na⁺) shuttle back and forth between the two electrodes as the
battery charges and discharges, giving rise to a “rocking-chair” mechanism. During the charging phase, Na\(^+\) ions deintercalate from the cathode, diffuse through the electrolyte, and subsequently intercalate within the anode material. The process of discharge is the opposite phenomenon. In principle, the electrochemical window of a cell can be inferred by considering the LUMO and HOMO energies that are intrinsic to the electrolyte. In this contribution, we evaluated the main electrolyte categories, with special attention to current research progress relevant to SIBs.

Recent developments in battery-based electrochemical energy storage (EES) technologies are showing substantial progress. These technologies offer attractive features such as a high round-trip efficiency, adaptable power, energy characteristics suitable for various grid applications, a long cycle life, and cost-effective maintenance. The electrolyte must be endowed with chemical and electrochemical stability when in contact with both the cathode and anode surfaces. During operation, the electrolyte should remain chemically unaltered, and all Faradaic reactions should occur within the electrodes [26,27].

Due to their high energy and power density, rechargeable LIBs have been the subject of significant research. Nevertheless, the shortcomings of this technology, such as cost, limited lithium resources, dependability, and safety, are readily apparent. Figure 3 illustrates the relative quantity of different elements in the Earth’s crust. The relative abundance of lithium is restricted to 20 parts per million. In fact, the cost of key ingredients (the price of LiCoO\(_2\)) climbed dramatically throughout the first decade of this century and continues to rise to this day. In an effort to address the challenges mentioned above, extensive research has been conducted in the field of rechargeable batteries. These studies have focused on identifying host materials capable of efficiently mobilizing guest ions beyond lithium. These include monovalent ions such as Na\(^+\) and K\(^+\), as well as multivalent cations such as Mg\(^{2+}\), Ca\(^{2+}\), Zn\(^{2+}\), and Al\(^{3+}\). The abundance of sodium in the Earth’s crust is significantly higher compared to lithium, with sodium at 2.36% and lithium at 0.01%.

![Figure 3. Elemental abundance in the Earth’s crust (see also ref. [28]).](image)

Due to the aforementioned potential disadvantages associated with LIBs, it is imperative to consider SIBs as an alternative [29]. Thus far, significant research has been conducted in an effort to optimize the electrodes, the electrolyte, and the binder (Figure 4).
This review aims to present a comprehensive overview of recent research advancements in PEs for SIBs. The focus is on relevant physical chemical properties, ionic conductivity, conduction mechanisms, and potential applications. We have critically examined challenges in PE research, proposing potential solutions. The discussion is articulated in three main sections: SPEs, GPEs, and CPEs. The primary objective is not only to provide a balanced assessment of the current state of the art of Na ion-conducting PEs but also to offer guidance for designing superior PEs as a critical component of SIBs. Additionally, future perspectives in the field are provided, anticipating the expected developments of PEs for next-generation SIBs.

2. Polymer Electrolytes

In order to overcome safety concerns negatively affecting Li-based batteries and enable high-energy-density electrical devices, the use of PEs in place of conventional liquid electrolytes has been recognized as the best way forward [30]. Research and development efforts have extensively delved into the synthesis, analysis, and utilization of PEs. Alkali metal salts dissolved in PEO were the first examples of conductive electrolytic complexes known as PEs, as Wright et al. demonstrated in 1973 [31]. In 1978, Armand et al. introduced an SPE consisting of PEO-Li salt for lithium-based batteries with an ionic conductivity of $10^{-4}$ S·cm$^{-1}$ at 40–60 °C [32]. Another significant advancement took place in 1988 when Skaarup et al. demonstrated a conductivity of $10^{-3}$ S·cm$^{-1}$ at ambient temperature [33]. PEs have drawn significant attention as potential substitutes to liquid electrolytes (Figure 5) because of their low flammability, processability, flexibility, and increased resilience to vibrational forces, stress, and mechanical deformation [34].

PEs surpass inorganic solid electrolytes in the context of electrode/electrolyte interfacial contact, and they outperform liquid electrolytes in terms of electrode/electrolyte compatibility. When compared to ceramics and glasses, polymers are typically more flexible and less expensive. Numerous polymers have been explored for their potential use in PEs, with examples including PEO, poly(methyl methacrylate) (PMMA), poly(vinylidene fluoride) (PVDF), poly(vinylidene fluoride hexafluoro propylene) (PVDF-HFP), and various others. Among these polymers, PEO-based materials have received the most intense research attention. This interest is due to the ability of the CH$_2$CH$_2$O units within the PEO chain to effectively solvate cations such as Li$^+$ and Na$^+$, as well as the high mobility of the polymer chain segments within PEO [35]. Similar benefits are provided by poly(ethylene glycol) or PEG, an $\alpha,\omega$-terminated PEO (Figure 6) [15]. Despite the superior electrochemical properties of PEs, their battery performance parameters such as long-term cycle stability can scarcely satisfy the demands in the practical application of LIBs and SIBs.
Three main categories are considered when classifying PEs used in SIBs. The first type includes SPEs, in which only sodium salts (NaPF₆, NaBF₄, NaClO₄, etc.) are dissolved in polymer matrices [36,37]. The second type is represented by gel PEs (GPEs), which more stably combine solid and liquid phases. A liquid phase is trapped and swells into a polymeric network, thereby increasing the ionic conductivity of the polymeric phase and providing new conduction pathways [38,39]. The third type of PE is comprised of composite PEs (CPEs) [40]. We prefer to reserve the label of CPE for SPEs mixed with inorganic fillers [41,42]. Broadly speaking, a composite material is comprised of two or
more constituent materials, regardless of their nature. The introduction of additives in SPEs, whether organic or inorganic, technically still falls under the same definition. Unlike some authors, and in agreement with historical practice in the field, we prefer to refer to SPEs mixed with organic liquids as plasticized PEs (PPEs). Herein, this category is not discussed separately, but is considered only in conjunction with the main PEs. The principal reason for this choice is that few studies have been conducted in the direction of Na PPEs per se. Another category of PEs that will not be discussed in isolation is that of polymer ionic liquid electrolytes (PILEs), consisting of PEs mixed in with ionic liquids (ILs). The presence of inorganic fillers in CPEs imparts enhanced mechanical, thermal, and chemical stability while dramatically improving conductivity [43].

The ideal Na PE would be a solvent-free ion-conducting material with a conductivity above $10^{-3}$ S·cm$^{-1}$ at room temperature, a cation transport number close to unity, and fire-retardant characteristics. The anion would bear a delocalized charge and would interact tightly with the polymer host without adversely affecting the electrodes. The compatibility of the PE with the electrode materials would also be important to assure the formation of a stable SEI on the anodic surface and a stable cathode–electrolyte interphase (CEI) on the cathodic surface. Incidentally, the fact that the CEI is much less studied than the SEI has been the likely source of undetected failure mechanisms in PEs and should be a more vigorous area of study for future improvements. The redox stability window of the ideal PE would be above 4 V, as enabled by the choice of non-labile terminal groups of the polymer host. It would also exhibit a solid consistency which renders the need for a separator superfluous and prevents or suppresses the formation of anodic dendrites. The ideal PE would be flexible and mechanically stable. It would also be thermally stable, with a low and fairly constant activation energy in a wide temperature range. It would exhibit a low glass transition temperature that would enable the assembly of reliable SIBs in cold climates. The addition of inorganic fillers would result in a higher conductivity but would also introduce disadvantages such as more difficult processing. It should be stated that even when envisioning the ideal Na PE, one needs to consider that, unfortunately, some of the desirable properties have proven thus far to be mutually exclusive.

Hereafter, we separately cover Na ion-conducting SPEs, GPEs, and CPEs. As shown below, some degree of overlap exists amongst these categories.

2.1. Solid Polymers Electrolytes (SPEs)

SPEs have garnered significant attention owing to their appealing properties, including their ease of transformation into thin films, good mechanical behavior, electrochemical stability, well-defined electrode/electrolyte interface, safety, and no leakage [44]. These characteristics are in stark contrast with those of liquid electrolytes. Notably, the concern towards the safety of lithium-based rechargeable batteries is related to the use of flammable liquid electrolytes. Although the lithium ion transference number is low for liquid electrolytes, they are endowed with a higher ionic conductivity and assure an appreciable interfacial contact with the electrode materials. However, there are disadvantages in addition to potential leakage, such as electrode/electrolyte reactions, which leads to an increase in battery temperature with consequent generation of flammable and hazardous gases [45–47]. Enhanced mechanical stability is imparted by the polymer backbone, and this characteristic is especially required for batteries in wearable devices [48]. SPEs are widely used in the fields of sensors and electrochemical energy storage devices such as batteries and supercapacitors, fuel cells, and electrochromic displays [12,49–51].

SPEs have garnered extensive research attention due to their combination of a relatively high ionic conductivity, cost-effectiveness, and mechanical stability [52]. In 1995, Hashmi et al. [53] investigated PEs based on PEO and NaPF$_6$ sandwiched between Pt electrodes. This PE system exhibited the best conductivity of $5 \times 10^{-6}$ S·cm$^{-1}$ at room temperature. In 1999, Sreekanth et al. [54] reported a PEO and NaNO$_3$ PEs measured between Na electrodes. Alternatively, the cathode was chosen to be a mixture of molecular iodine, carbon, and PE. The discharge characteristics were recorded at a constant load of 100 kΩ, and the
conductivity of the PEs was as high as $2.83 \times 10^{-6}$ S·cm$^{-1}$. In 2001, Chandrasekaran et al. [55] reported a PE based on PEO and NaClO$_3$ with PEG, Na, and MnO$_2$ as the plasticizer, anode, and cathode, respectively. The authors concluded that the plasticizer activated the polymer chain relaxations, favoring an ion hopping mechanism within the polymer matrix. A higher conductivity value was observed with a lower salt concentration, measured at $9.47 \times 10^{-4}$ S·cm$^{-1}$.

In 2005, Anantha et al. [52] reported studies of PEO-NaNO$_3$ PEs with different compositions of the ether oxygen to sodium ratio (O/Na). These PEs were formed into thin films using the solution casting method. Based on characterization studies, it was found that a decrement in crystallinity occurs with increasing salt concentrations. The highest conductivity of $3.5 \times 10^{-6}$ S·cm$^{-1}$ was observed at room temperature. In 2006, Kumar et al. [56] prepared a PE based on PEO and NaClO$_3$ using a solution casting technique and studied its properties in a cell with a Na anode, PE, and a mixture of I$_2$, with carbon and PE as the cathode. The PE was found to exhibit a conductivity value of approximately $10^{-7}$ S·cm$^{-1}$.

In the years 2006 and 2007, Mohan et al. [57,58] examined ion transport and battery discharge behavior in PEs derived from PEO and either NaFeF$_4$ or NaLaF$_4$. The optical and electrical properties were studied for pure PEO and PEO doped with the salts. Both the sodium compounds were prepared using a solid-state diffusion method by mixing NaF with La(NO$_3$)$_3$ and Fe(NO$_3$)$_3$, respectively. The conductivity of the PEs was shown to increase with rising temperatures using cells comprised of Na as the anode and a mixture of I$_2$ and C soaked with the electrolyte as the cathode. The maximum conductivity was found to be $1.37 \times 10^{-7}$ S·cm$^{-1}$ using NaFeF$_4$ and $3.9 \times 10^{-7}$ S·cm$^{-1}$ using NaLaF$_4$.

Consecutively, in the years 2006 and 2007, Bhide et al. [59,60] reported a new PE system using PEO, NaPO$_3$, and different ratios of ethylene oxide and NaPO$_3$ with and without PEG as a plasticizer. NaPO$_3$ was synthesized by gradually cooling the molten mixture of Na$_2$CO$_3$ and (NH$_4$)$_2$HPO$_4$ within the temperature range of 900 °C down to room temperature. This PE exhibited a peak conductivity of $2.8 \times 10^{-8}$ S·cm$^{-1}$. Upon plasticization with PEG, the conductivity substantially increased to $8.9 \times 10^{-7}$ S·cm$^{-1}$. In 2012, Sasikala et al. [61] reported their investigation of PEs composed of PEO and NaF. The conductivity demonstrated an upward trend with increasing NaF concentration, reaching a maximum value of $4.73 \times 10^{-7}$ S·cm$^{-1}$ at a PEO:NaF ratio of 70:30.

In 2017, Ma et al. [62] introduced a new PE incorporating sodium (fluorosulfonyl)(n-nonafluorobutanesulfonylimide (Na[(FSO$_2$)(n-C$_4$F$_7$SO$_2$)]N), NaFNSI) and PEO. This PE exhibited a conductivity of $3.36 \times 10^{-4}$ S·cm$^{-1}$ at 80 °C. Another contribution was reported in the same year by Heratha et al. [63], who investigated the electrical and thermal characteristics of a PE system based on PEO and NaI, examining various PEO:NaI ratios. The highest conductivity recorded was $7.1 \times 10^{-5}$ S·cm$^{-1}$ at room temperature.

In 2019, Arya et al. [64] reported PEs based on PEO and NaPF$_6$ and studied their structural, morphological, electrochemical, and dielectric properties. These PEs, plasticized by succinonitrile, were found to exhibit a maximum conductivity of $2 \times 10^{-5}$ S·cm$^{-1}$. The same authors reported on PEs comprised of a blended mixture of PEO, PVP, and NaNO$_3$ [65]. Their study centered on the dielectric relaxations and transport characteristics of this innovative polymer blend. A peak conductivity of $2.90 \times 10^{-4}$ S·cm$^{-1}$ at a temperature of 100 °C was observed. Again, in 2020, they reported a Na ion-conducting PE system based on a PEO and polyethyleneimine (PEI), which exhibited a conductivity of $5.2 \times 10^{-4}$ S·cm$^{-1}$ at 100 °C [66]. In 2020, Zhang et al. [67] reported on a PEO-NaPF$_6$ PE which exhibited a conductivity of $6.3 \times 10^{-4}$ S·cm$^{-1}$ at 80 °C. In that same year, Youcef et al. [68] reported on PEs based on PEO and a Na(FSI-ethyl cellulose) system which exhibited good electrochemical and mechanical properties, with a conductivity value of approximately $10^{-4}$ S·cm$^{-1}$ at 80 °C.

In 2022, Kim et al. [69] published their findings regarding an anode-less seawater battery. This innovative battery utilizes an SPE based on a PEO polymer, facilitating energy storage from power to metal and metal to power. The precursors NaFSI, PEO, and Pyr$_14$FSI
were dried at 70 °C, 50 °C, and 90 °C, respectively, in a dry room for 24 h, followed by dissolution of benzophenone (a cross-linking agent) in Pyr14FSI to form a homogeneous solution. This mixture was added to PEO/NaFSI powder, mixed, sealed, and aged at 100 °C overnight. This material was then pressed into a thin polymeric film at 100 °C and treated with UV light. A peak conductivity of $1 \times 10^{-3}$ S·cm$^{-1}$ was recorded at room temperature. The SPE was integrated with a Na superionic conductor (NASICON) to achieve effective physical separation.

Chandra et al. [70] reported on their study of a PE based on PEO and NaCl with a ratio of 70:30. A peak conductivity of $4.5 \times 10^{-6}$ S·cm$^{-1}$ was recorded at room temperature. In 2006, Reddy et al. [71] studied the conductivity and discharge characteristics of a PE system based on PVC and NaClO$_4$. A viable solid-state electrochemical cell with a Na anode, the highest-conductivity PE, and a mixture of I$_2$, carbon, and PE as the cathode was fabricated. In 2017, Muhammad et al. [72] reported the properties of a PE based on PVC and NaI. The conductivity was $2.9 \times 10^{-8}$ S·cm$^{-1}$ at room temperature.

In 2006 and 2007, Bhargav et al. [73,74] reported on PE films based on PVA doped with NaBr and NaI salts. They studied the characteristics of PVA films with or without NaI or NaBr. It was found that as the concentration of the salts was increased, the films became more amorphous and, therefore, more conductive. Electrochemical cells were assembled using these electrolytes and characterized. The maximum conductivities obtained were $1.02 \times 10^{-5}$ S·cm$^{-1}$ and $1.12 \times 10^{-4}$ S·cm$^{-1}$ for NaI and NaBr, respectively. In 2018, Duraikkan et al. [75] studied the structural, thermal, and electrical properties of PEs comprised of PVA/PVP and NaNO$_3$. Similar to previous works, the amorphicity was found to increase, which in turn resulted in an increase of the conductivity to $1.25 \times 10^{-5}$ S·cm$^{-1}$ at room temperature. In 2021, Aziz et al. [76] reported on their study of a PE blend based on PVA and NaI using glycerol as a plasticizer, which was found to exhibit a maximum conductivity of $1.17 \times 10^{-3}$ S·cm$^{-1}$ at room temperature.

In 2013, Tiwari et al. [44] reported on starch-based sodium PEs. Potato starch was mixed with NaI, NaSCN, and NaClO$_4$ salts, and the effects of different anions were studied. The highest conductivity was measured for NaSCN at $1.12 \times 10^{-4}$ S·cm$^{-1}$. In 2015, Khan-mizraei et al. [77] reported a PE based on the ionic liquid 1-methyl-3-propylimidazolium iodide (MPII) and rice starch (RS) for use in dye-sensitized solar cells. TiO$_2$ was coated on a fluoride/tin oxide (FTO) sheet and used as the anode, whereas platinum-coated FTO was used as the cathode, with RS:NaI:MPII as the electrolyte. This system was found to exhibit a peak conductivity at $1.20 \times 10^{-3}$ S·cm$^{-1}$. In 2017, Ahmad et al. [78] carried out an electrical analysis of PEs based on cornstarch (CS) and NaCl. This simple PE exhibited the highest conductivity at $1.72 \times 10^{-5}$ S·cm$^{-1}$ for a weight ratio of 70:30 for CS:NaCl. In 2021, Awang et al. [79] studied the impact of adding sodium bisulfite, NaHSO$_3$, to cornstarch. The maximum observed conductivity was $2.22 \times 10^{-4}$ S·cm$^{-1}$ at room temperature. Similarly, in the same year, Asnawi et al. [80] reported the effects of adding NaCF$_3$SO$_3$ to a chitosan/dextran polymer blend. The resulting PE was found to exhibit a maximum conductivity of $6.10 \times 10^{-5}$ S·cm$^{-1}$ at room temperature.

In 2014, Rani et al. [81] conducted a comprehensive examination of the structural, thermal, and electrical attributes of PEs derived from hydroxypropyl methylcellulose (HPMC) doped with NaI. The best conductivity was recorded for the ratio of 5:4 for HPMC:NaI at 40 °C as $1.126 \times 10^{-6}$ S·cm$^{-1}$. An enhanced amorphicity was accompanied by a high conductivity. In 2015, Abiddin et al. [82] reported on the conductivity and electrical properties of methylcellulose (MC) salted with NaI. The maximum conductivity that was observed was $2.7 \times 10^{-5}$ S·cm$^{-1}$ at 60 °C. Again, in 2015, Bella et al. [13] reported on the fabrication of a photo-PE based on a sodium ion methacrylate for secondary battery applications. This was the first report for a photopolymerized sodium ion PE. This material was found to exhibit a thermal stability greater than 100 °C, a high specific capacity, excellent chemical stability, and a high conductivity of $5.1 \times 10^{-3}$ S·cm$^{-1}$ at 20 °C. In 2020, Sayed et al. [83] studied the influence of different metal acetates on carboxy methylcellulose (CMC) in CMC-Na/PVP PEs by comparing their spectroscopic, optical, and dielectric
In 2016, Cisneros et al. [84] proposed solvent-free sodium polymer batteries based on cross-linked CMC-Na to form the PEs. The maximum conductivity was measured at $1.81 \times 10^{-4}$ S cm$^{-1}$. In 2020, Shetty et al. [85] conducted a study investigating the electrical and optical properties of CMC mixed with NaBr at various mass ratios. The highest conductivity, reaching $5.15 \times 10^{-4}$ S cm$^{-1}$, was achieved for the PE containing 20 wt% NaBr at room temperature. Similarly, Aziz et al. [46] reported a similar PE based on methyl cellulose (MC) doped with NaI, which demonstrated a maximum conductivity of $3.01 \times 10^{-3}$ S cm$^{-1}$ with 50 wt% NaI.

In 2016, Singh et al. [85] reported PILEs based on an ionic liquid, 1-butyl-3-methyl imidazolium methylsulfate (BMIM-MS), PEO, and sodium methylsulfate salt. Various weight percentages of BMIM-MS were employed to formulate these electrolytes, which exhibited a maximum conductivity of $4.1 \times 10^{-4}$ S cm$^{-1}$ at 75 °C. In 2017, Zhang et al. [86] described the in situ formation of a PEG–divinyl ether PE. This ionic conductor was examined as a film on a polysulfonamide support alongside an Na$_3$V$_2$(PO$_4$)$_3$ cathode and a layered MoS$_2$ anode. The polymer, tri(ethylene glycol) divinyl ether, was polymerized in situ using LiBF$_4$ as an initiator, achieving a maximum conductivity of $1.2 \times 10^{-3}$ S cm$^{-1}$ at ambient temperature. In 2017, Pan et al. [87] reported an SIB utilizing a single ion-conducting sodium ion PE composed of poly(bis(4-carboxyl benzene sulfonyl)limide-co-2,5-diamino benzesulfonic acid) (NaPA). The highest conductivity recorded for this system was $4.1 \times 10^{-4}$ S cm$^{-1}$ at 80 °C. The cathodic material, Na$_3$V$_2$(PO$_4$)$_3$/AC was synthesized from the precursors H$_3$PO$_4$, NH$_4$VO$_3$, Na$_2$CO$_3$, and acetylene black. In 2018, Chen et al. [88] introduced a PE based on hyperbranched β-cyclodextrin (H-β-CD). The β-CD was modified using multiple oligo(methyl methacrylate)-block-oligo(ethylene glycol) glycol methyl ether methacrylate short chains and complexed with NaTFSI, resulting in a self-standing, transparent, and flexible SPE film. This electrolyte exhibited its highest conductivity of $1.3 \times 10^{-4}$ S cm$^{-1}$ at 60 °C. In the same year, Hassan et al. [50] investigated the structural and electrical spectroscopy of a PE composed of sodium 4-styrenesulfonate combined with ammonium nitrate. This PE displayed its highest conductivity at room temperature, reaching $3.16 \times 10^{-4}$ S cm$^{-1}$ with a 30 wt% ammonium nitrate content.

In 2019, Janakiraman et al. [89] reported an electrospun fibrous PE based on PVDF$_6$ for battery applications. In this technique, different concentrations of PVDF dissolved in DMSO and acetone were loaded into hypodermic syringes and were then subjected to electrospinning under an applied DC voltage. The resulting electrospun fibers were then soaked in an NaPF$_6$ solution and stretched for further analysis. This fibrous electrospun PE provided a maximum conductivity of $1.08 \times 10^{-3}$ S cm$^{-1}$ at ambient temperature. In 2019, Yang et al. [90] reported a flame-retardant quasi-solid PE for battery applications. Poly(methyl vinyl ether-alt-maleic anhydride) (P(MVE-alt-MA), bacterial cellulose, and triethyl phosphate/vinylene carbonate (TEP/VC)/sodium perchlorate (NaClO$_4$) were used as the host, reinforcement, plasticizer, and salt, respectively. This PE was found to exhibit a flame-retardant nature and longer cycle stability. This system had a maximum conductivity of $2.2 \times 10^{-4}$ S cm$^{-1}$ at room temperature. In 2021, Liu et al. [91] reported the synthesis of a single ion-conducting PE based on sodium bis(2-fluorocarboxy)malonato borate salt NaBFMB photocrosslinked to a tri-thiol(trimethylolpropane tris(3-mercaptopropionate) (TMPT) using a click thiol-ene reaction. This electrolyte exhibited a maximum conductivity value of $2 \times 10^{-3}$ S cm$^{-1}$ at 30 °C. It is unclear to what extent the ILs were purely part of the 3D structure and whether there was some plasticizing effect due to the non-crosslinked IL.

In 2022, Law et al. [92] reported a hybrid dual-salt sodium PE for SIB applications. NaTFSI and NaDFOB salts were mixed together, followed by the addition of PVDF powder to form a blended SPE. This electrolyte was found to exhibit a maximum conductivity of $3.1 \times 10^{-4}$ S cm$^{-1}$ at 23 °C. Cisneros et al. proposed solvent-free sodium polymer batteries based on cross-linked PEs [93]. These electrolytes are formed through the polycondensation of α,ω-di hydroxy-oligo(oxyethylene) with an unsaturated dihalide, resulting in the formation of amorphous
networked electrolyte films upon further curing. Utilizing NaClO$_4$ and NaCF$_3$SO$_3$ at varying O/Na ratios, the optimal PE exhibits cationic conductivity ($\sigma_+$) surpassing 1 mS·cm$^{-1}$ at 90 °C while maintaining mechanical integrity up to at least 120 °C.

Martínez et al. explored blends of PEO and poly(sodium 1-[3-(methacryloyloxy) propylsulfonyl]-1-(trifluoromethanesulfonyl) imide) (PNaMTFSI) in various proportions [94]. The blend composition significantly influenced the ionic conductivity, with the most notable results observed for blends containing 15 and 30 wt% PNaMTFSI. At elevated temperatures, specifically 85 °C, the highest ionic conductivity values were recorded, reaching $5.84 \times 10^{-5}$ and $7.74 \times 10^{-5}$ S·cm$^{-1}$, respectively. Furthermore, these compositions exhibited sodium ion transference numbers exceeding 0.83 and demonstrated electrochemical stability within the range of 3.5 to 4.5 V versus Na/Na$^+$. These findings suggest the potential use of these blends in sodium batteries.

The Na PEs explored thus far have been mostly based on PEO. Therefore, ethereal oxygens in a helical conformation appear to be the most reliable way to loosely coordinate and mobilize cations, including Na$^+$. Unfortunately, PEO, while enabling a relatively high conductivity ($\sim 10^{-4}$ S·cm$^{-1}$), is typically associated with a low transport number (below 0.5). An interesting alternative choice in polymer host has been that of cellulose derivatives, which provide the opportunity for using materials of biological origin. It remains unclear to what extent OH-rich phases can be fully dried of water traces and become thermally stable upon prolonged cycling. At the same time, the knowledge transfer of Li to Na as it pertains to salts (e.g., NaPF$_6$, NaTFSI, and NaFSI) did not present any particular surprises or improvements. Based on general cation solubility principles, it is doubtful that further fine tuning may come from structural modifications of already available anions.

2.2. Gel Polymers Electrolytes (GPEs)

GPEs have gained significant importance due to their ability to combine the advantageous characteristics of both solid and liquid electrolytes [95]. Feuillade et al. [96] conducted pioneering research on GPEs for Li batteries in 1975, the first of such studies on record. In their work, they explored cross-linked gel membranes composed of materials like polyvinyl butyral (PVB), epichlorohydrin with titanium/silicon alkoxy compounds, PVDF and dicinnamylidene hexanediamine dissolved in methyl ethyl ketone. Additionally, they investigated thermoplastic gels consisting of PAN, PC, and NH$_4$ClO$_4$. GPEs are produced by over-plasticizing the polymeric phase with low-molecular-weight molecules, usually organic solvents. As a result of its interaction with the plasticizer, the polymer expands and mostly becomes amorphous while maintaining adequate mechanical strength. The plasticizer’s presence enables new avenues for ionic movement. These reasons explain why SPEs without plasticizers often have lower conductivities than GPEs [97,98]. The precise ion-conduction mechanism and the nature of the interactions between the polymer, plasticizer (solvent), and salt have yet to be fully elucidated [99,100]. GPEs have recently attracted attention due to their superior characteristics over liquid electrolytes [101]. Their most attractive quality is their free-standing consistency, which facilitates handling, cell design, modularity, and dependability in many electrochemical devices [102].

In order to enable the functionality of GPEs, it is necessary to incorporate plasticizers or solvents possessing elevated dielectric constants. These are blended with different salts and fixed within the structure of polymer matrices, including materials such as PMMA, PAN, PVDF, and PVDF-HFP, among others [103–106]. GPEs can develop when appropriate ionic salts and small-sized organic solvents like EC, PC, and DEC are enclosed within the polymer hosts [107]. The co-polymer PVDF-HFP is widely used in high-performance GPE systems among the many host polymers because of its advantageous properties such as its low glass transition temperature (~35 °C), high dielectric constant (8.4), and structural uniqueness. GPEs have a strong ionic conductivity, exhibit increased safety, are inexpensive, and are simple to fabricate into the desired shapes and sizes. The thermal, mechanical, chemical, and electrochemical stability of GPEs are adequate. Further improvements in
GPEs would require electrolyte salts with a superior solubility and high liquid holding capacity.

Room-temperature ionic liquids (RTILs) have been employed as substitutes for organic additives in GPEs to enhance their thermal, mechanical, and electrochemical durability. ILs are molten salts composed primarily of organic cations and inorganic anions. They are appreciated for their versatility and their effective roles as plasticizers and suitable solvents. Their distinctive attributes include their robust ionic conductivity (0.01 S cm$^{-1}$), elevated thermal stability up to 400–500 °C, non-flammability, non-volatility, and impressive electrochemical window spanning the range of 4.0–6.0 V \cite{108}.

Wang et al. \cite{109} assembled Na-conducting GPE membranes using Na$_2$Zn$_2$TeO$_6$ as a filler, and their use in SIBs was shown to be effective. The incorporation of Na$_2$Zn$_2$TeO$_6$ filler led to a composite GPE (CGPE), with a substantial enhancement in ionic conductivity. This improvement can be attributed to the filler, which also functions as an ionic conductor, causing a reduction in the crystalline structure and an increase in the porosity within the polymer membranes. Consequently, the modified GPE membranes exhibit an impressive ionic conductivity of 2.52 × 10$^{-3}$ S cm$^{-1}$ at room temperature, along with an extremely low activation energy of approximately 0.040 eV. The assembled Na$_3$V$_2$(PO$_4$)$_3$/C | GPE | Na battery showcases excellent performance metrics, including a notable initial discharge capacity of 93.3 mAh g$^{-1}$ at 0.5 C, a promising capacity retention rate of 98.4% after 100 cycles, and outstanding high-rate performance, achieving 83.5 mAh g$^{-1}$ at 5 C.

This research establishes that ionic conductors such as Na$_2$Zn$_2$TeO$_6$ can be used to improve GPE performance. Using a conventional solid-state reaction approach carried out using high-energy ball milling, Na$_2$Zn$_2$TeO$_6$ filler was produced. PVDF-HFP/PMMA-based GPEs membranes with Na$_2$Zn$_2$TeO$_6$ were prepared using the solution casting process. X-ray diffraction was employed to examine the phase structure of the as-prepared Na$_2$Zn$_2$TeO$_6$ filler and the filler within the GPE membranes. Field emission scanning electron microscopy was used to analyze the microstructure and elemental distribution of the GPE membranes. Thermogravimetric analyses were performed from room temperature to 700 °C.

Wang et al. \cite{110} synthesized a new polymeric material termed polymeric sodium tartaric acid borate (PSTB), which was combined with poly(vinylene carbonate) to produce a single-ion-conducting GPE referred to as PSP-GPE. This PSP-GPE exhibited several notable characteristics, including a high sodium ion transference number of 0.88, an oxidation threshold of 4.5 V, and excellent compatibility with the sodium anode. Furthermore, it showed remarkable ionic conductivity, registering at 1 × 10$^{-4}$ S cm$^{-1}$, surpassing the performance of a room-temperature liquid electrolyte based on NaClO$_4$. A Na/PSP-10$^\text{th}$ GPE/Na$_3$V$_2$(PO$_4$)$_3$ battery was found to exhibit a 98.6% capacity retention and >99% coulombic efficiency for 200 cycles at 0.5 C, 25 °C. The same assembly at 60 °C exhibited an approximately 100% capacity retention and >99.3% coulombic efficiency for 50 cycles at 0.5 C.

Wang et al. \cite{111} prepared a novel CGPE membrane by blending PVDF-HFP/PMMA with Ti$_3$C$_2$Tx MXene. They then investigated the electrochemical performance of this membrane in SIBs. The presence of the Ti$_3$C$_2$Tx MXene filler, which is multilayered, significantly enhanced the electrochemical performance of the battery. This improvement was attributed to the filler’s ability to increase the contact sites for Na ions and enhance the porosity of the polymer membranes. Furthermore, the distinctive parallelly arranged layered structure of the MXene promoted uniform sodium nucleation and growth on the surface of the sodium electrode while inhibiting the formation of sodium dendrites during the sodium deposition process. The CGPE membrane containing 8 wt% Ti$_3$C$_2$Tx MXene exhibited impressive properties, including a maximum ionic conductivity of 3.28 × 10$^{-3}$ S cm$^{-1}$, excellent thermal stability, a relatively high sodium ion transfer number of 0.558, and a wide electrochemical window of 5.25 V. A Na$_3$V$_2$(PO$_4$)$_3$/GPE/Na battery after 300 room temperature cycles at 0.5 C showed a remarkable 95% capacity retention. The Na$_3$V$_2$(PO$_4$)$_3$ cathode was prepared using a sol-gel process \cite{45}.
To achieve good sodium ion conductivity at room temperature, Vo et al. [112] prepared GPE films employing a PVDF-HFP matrix. Microporous PVDF-HFP membranes were swelled and filled with various liquid electrolytes comprised of NaClO₄, NaPF₆, and NaTFSI salts dissolved in mixtures of carbonate solvents such as PC and fluoroethylene carbonate (FEC) or ionic liquids such as 1-ethyl-3-methylimidazolium bis(trifluoromethane). The influences of the different electrolytes on the structure, morphology, electrolyte absorption, and sodium ion conductivity of the resulting membranes were examined by the authors. The “sponge-like” structure of the GPEs was endowed with a high porosity (80–85%) and large pore sizes. At ambient temperature, the ionic conductivity of the GPEs was 1–2 mS·cm⁻¹. DSC, TGA, XRD, and FE-SEM were used for characterization. By employing GPEs as the ion-conduction layer, sodium intercalation into an Na₀.₄₄MnO₂ cathode was carried out in a coin-cell configuration. At room temperature, the cycling data of a sodium cell using PVDF-HFP/NaClO₄ 1 M-PC:2%FEC showed a consistent specific capacity of 100 mAh·g⁻¹. The best ionic conductivity was 1.91 mS·cm⁻¹ for NaClO₄ 1 M PC:2%FEC/PVDF-HFP. The temperature-dependent ionic conductivity exhibited VTF behavior, indicating the assistance of the backbone and polymer segmental mobility in the gel medium. The higher temperature of liquid electrolyte degradation when compared to the unsolvated microfiber membrane imparted a higher thermal stability to the final GPEs. Due to the high oxidation limit of 4 V ca. vs. the Na⁺/Na potential, the electrochemical stability window of the GPEs was compatible with 4 V sodium cathode materials. The assembly of a Na/GPE/Na₀.₄₄MnO₂ cell allowed the authors to demonstrate a reversible intercalation/deintercalation of Na⁺, as well as a steady discharge capacity in a cyclic voltammogram and charge-discharge test. After 20 cycles, the specific capacity of NaClO₄ 1 M—PC:2%FEC/PVDF-HFP remained constant at 100 mAh·g⁻¹, with no sign of capacity fading.

Harshlata et al. [113] demonstrated that a liquid electrolyte composed of sodium trifluoromethanesulfonate (NaCF₃SO₃) dispersed within an IL named 1-butyl-3-methylimidazolium trifluoromethanesulfonate (BMImCF₃SO₃) can be effectively immobilized using a porous membrane crafted from PVDF-HFP. The manufacturing process for these porous GPE membranes involved a phase-inversion technique. Various physical and electrochemical methods were utilized to characterize these electrolyte membranes. Notably, in the CGPE systems, the incorporation of TiO₂ nanoparticles led to interactions with the anion of the liquid electrolyte (CF₃SO₃⁻) and resulted in an increased amorphicity of the polymer network. As a result, the improved membrane exhibited enhanced electrochemical stability, with a window of approximately 4.3 V, a maximum room temperature ionic conductivity of 0.4 mS·cm⁻¹, and a Na⁺ ion transport number of roughly 0.27. This upgraded membrane was employed in the construction of a prototype sodium battery, which displayed a consistent open-circuit potential of 2.2 V and delivered a discharge capacity of 200 mAh·g⁻¹ at a drain current of 25 mAh·g⁻¹. To investigate the structural properties of the membrane, various characterization techniques were employed, including scanning electron microscopy (SEM), X-ray diffraction (XRD), and Fourier transform–infrared spectroscopy (FTIR).

Utilizing the highest-performing composite PILE membrane denoted as PEM0.5, a prototype sodium battery was assembled featuring a sodium–mercury (Na-Hg) anode and a phosphorus–carbon (P-C) cathode. When compared to pure sodium metal, Na-Hg serves as a superior reducing agent and is easier to handle. Phosphorus red, with a theoretical capacity of 2596 mAh·g⁻¹, emerges as an excellent candidate for the electrode material in a sodium battery, while carbon contributes the electronic conductivity [10].

Chen et al. [114] synthesized a flexible GPE (PGT32-5%) based on poly(poly(ethylene glycol) methacrylate) (PPEGMA) that was plasticized with nonflammable triethyl phosphate (TEP). The GPE was then stabilized by glass fibers using an in situ thermal curing process. A high ionic conductivity (9.1 × 10⁻⁴ S·cm⁻¹ at 27 °C) and wide electrochemical window are two characteristics of the improved flame-retardant electrolyte, PGT32-5% (4.8 V). To ensure excellent cycling stability of the quasi-solid-state Na₃V₂(PO₄)₃|PGT32-5%|Na battery (capacity retention of 91% after 400 cycles), an artificial interface between the GPE and Na
metal anode was formed. It was found that trace FEC on a hard-carbon anode can generate a stable SEI [115]. Furthermore, the interfacial modification and its impact on the discharge behavior were thoroughly examined, paving the way for the development of future PEs that exhibit superior performance parameters. The sol-gel process was followed to produce the Na$_3$V$_2$(PO$_4$)$_3$/C cathode [116].

Lonchakova et al. [117] prepared a highly effective polyacrylonitrile-based GPE for SIBs by using commercially available copolymer poly(acrylonitrile-co-methyl acrylate), propylene carbonate as a plasticizer, and either NaClO$_4$ or NaPF$_6$ as salts. These authors conducted AC impedance measurements, focusing on reversible rather than blocking electrodes, to determine the specific and molar conductivities at varying salt concentrations. The cation transference numbers were measured using the potentiostatic polarization method. The resulting electrolytes exhibited impressive ionic conductivities of up to $1.8 \times 10^{-3}$ S·cm$^{-1}$ at room temperature and high cation transference numbers of up to 0.89. The conductivity displayed Arrhenius behavior, with an activation energy ranging from 12 to 15 kJ·mol$^{-1}$. In sodium ion cells operating at both room temperature and 20 °C, the GPE demonstrated an excellent stability, enduring over 700 charge–discharge cycles. These findings indicate that polyacrylonitrile-based GPEs hold promise as alternatives to liquid electrolytes in SIBs.

Tian et al. [118] synthesized a new fluorine-containing ionomer using PVDF and propylene glycol carbonate (PGC). The result was the discovery of remarkable single-ion-conducting GPEs. The cation–carbonyl interactions, morphology, and ion-conduction characteristics of the GPEs were investigated using NMR, DSC, SEM, and complex impedance analyses. The GPEs were found to consist of three phases: a liquid electrolyte phase, an amorphous swelling phase, and a polymer crystalline phase according to the DSC and SEM examinations. Both the FT-IR study and the NMR data revealed that sodium ions form bonds with carbonyl groups of vinyl acetate and perfluoro(5-methyl-3,6-dioxo-8-fluoride sulfonyl-1-octene). Both the amount of PGC and the amount of fluorine-containing ionomer had a significant impact on the morphology and ionic conductivity of the samples. This new GPE system showed an ionic conductivity above $10^{-4}$ S·cm$^{-1}$ at ambient temperature, with a sodium ion transport number of more than 0.99 ($t_+ > 0.99$).

Parveen et al. [119] conducted a study focusing on the development of novel GPEs for battery applications. Their work centered on solvate ionic liquids (SILs), which featured complex cations [Na-(glyme)]$^+$ and ClO$_4^-$ anions. To produce these SIL-GPEs, they adjusted the NaClO$_4$ content in triglyme (G3) and immobilized the resulting electrolyte within a PVDF-HFP matrix. The result was the formation of flexible, self-supporting films. A comprehensive range of analytical techniques, including SEM, XRD, FTIR, Raman spectroscopy, and thermal gravimetric (TG) analyses, were employed to investigate the morphology, structure, and interactions between the salt, glyme, and polymer in these materials. In their ideal composition, which consisted of a 0.3:1 molar ratio of NaClO$_4$ to G3, electrochemical assessments demonstrated outstanding characteristics, including a high ionic conductivity of approximately $2.54 \times 10^{-3}$ S·cm$^{-1}$, a substantial Na ion transport number of approximately 0.73, and an extensive electrochemical stability window of 4.7 V.

The effectiveness of these SIL-GPEs was evaluated in a quasi-solid-state sodium ion battery by constructing a half-cell with a positive electrode composed of ball-milled V$_2$O$_5$. This battery exhibited a sustained capacity of approximately 55 mAh·g$^{-1}$ after 65 charge-discharge cycles at 0.1 C, achieving a maximum capacity of 111 mAh·g$^{-1}$ for the initial cycle at a current rate of 0.05 C. The active material for the electrodes was produced through a straightforward ball-milling procedure [120].

Kumar et al. [121] reported an innovative thermally and electrochemically stable sodium ion-conducting GPE including an ionic liquid at room temperature called 1-ethyl-3-methyl imidazolium trifluoro-methane sulfonate (EMI-triflate or EMITf) with sodium triflate (NaCF$_3$SO$_3$) as a salt, immobilized in PVDF-HFP. FTIR, SEM, and XRD were used to study the conformational and structural changes in PVDF-HFP caused by the entrapment of an EMImTf or EMImTf/NaTf solution. A total of 0.5 M of the electrolyte with the
formula EMImTf$_2$PVdF-HFP (4:1 w/w) in the form of a free-standing thick film exhibited an ionic conductivity of $5.74 \times 10^{-3}$ S·cm$^{-1}$ at room temperature ($\sim$27 °C), and NaTf showed exceptional dimensional stability. The ionic conductivity of the GPEs as a function of temperature was compatible with VTF behavior. The Na$^+$ ion transport number was found to be $\sim$0.23, indicating a large contribution from anionic transport as well as potential conduction of the component ions of the IL.

Kumar et al. [122] prepared flame-retardant GPEs based on trimethyl phosphate (TMP) for safer electrochemical applications utilizing the solution casting approach. XRD, DSC, EIS, and LSV were used to characterize these sodium ion-conducting materials. Physical investigations showed that the electrolyte using TMP solvent had a greater amorphicity and thermal stability compared to the binary mixture of ethylene carbonate (EC) and propylene carbonate (PC) that is commonly utilized. When compared to a membrane with an EC:PC solvent mixture, the TMP-based electrolyte membrane exhibited improved ionic conductivity ($\sim$1.40 mS·cm$^{-1}$), a wider electrochemical stability window of $\sim$4.5 V, and superior Na$^+$ transport properties. The electrolyte based on TMP has been used in an electric double-layer capacitor (EDLC) and in prototype sodium batteries. The best Na battery has a specific discharge capacity of 225 mA·h$^{-1}$ and an open circuit voltage of $\sim$2.3 V. The TMP-based electrolyte and activated carbon electrodes were used to produce an EDLC with a specific capacitance of $\sim$100 F·g$^{-1}$ that was stable for up to 4000 charge–discharge cycles.

Mishra et al. [123] introduced an ionic liquid (IL) into a PVDF-HFP matrix at a high loading level. To create GPE films with polar characteristics, various amounts of PVDF-HFP were blended with a 1 M solution of sodium bis(trifluoromethylsulfonylimide salt (S) in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide) IL to form what the authors called a salt–IL (SIL) solution. They employed a scaling technique and dielectric relaxation analysis to ascertain the temperature- and frequency-dependent ionic conductivities of these GPEs. The GPE containing 70 weight percent SIL (referred to as PSIL70) demonstrated outstanding thermal stability up to 368 °C, a high ionic conductivity of $1.9 \times 10^{-3}$ S·cm$^{-1}$, and a sodium ion transference number of 0.27. Additionally, it exhibited a broad electrochemical stability window of 4.2 V versus Na/Na$^+$ at 30 °C. To construct a coin cell (Na/PSIL70/Na-NMC), they paired a Na–NMC cathode with a Na–metal anode using the optimized electrolyte PSIL70. The charge–discharge results showed that the cell had a specific discharge capacity of 108 mAh·g$^{-1}$ at a rate of 0.1 C (equivalent to 21 mAh·g$^{-1}$). The sodium battery had a large capacity and a capacity retention of 94% after 200 cycles at 0.2 C.

The effects of mixing PMMA with PVDF-HFP and a non-aqueous liquid electrolyte of NaCF$_3$SO$_3$ in a binary mixture of EC and PC were reported by Mishra et al. [124]. Utilizing XRD, SEM, complex impedance spectroscopy, LSV, and determination of the ion transport number, it was shown how compositional changes in PMMA affect the GPE system. The improved electrolyte composition provided a sufficiently wide electrochemical stability window of 3.6 V. It was determined that the PVDF-HFP-based GPE had an ionic conductivity of $\sim$6.1 $\times$ 10$^{-4}$ S·cm$^{-1}$ at room temperature. When PVDF-HFP and PMMA were combined, the ionic conductivity of the GPE was raised to $\sim$7.5 $\times$ 10$^{-4}$ S·cm$^{-1}$ (9:1). The porous and predominately amorphous character of the GPEs upon polymer mixing was supported by SEM and XRD tests.

According to Chauhan et al. [125], sodium aluminate (NaAlO$_2$) active fillers that were dispersed in porous GPEs improved the electrochemical performance parameters. Phase inversion was used to synthesize microporous sodium ion-conducting GPE sheets. The filler particles in the resulting CGPE system improved the retention of the sodium salt solution, increasing the ionic conductivity from 0.22 mS·cm$^{-1}$ to a maximum of 0.68 mS·cm$^{-1}$ for an optimum composition of 0.50 wt% NaAlO$_2$. The improved compositions exhibited better electrochemical stabilities and Na$^+$ transference numbers than the unfilled GPE. Ion dynamics studies of the CGPE system, investigated via dielectric analysis, showed that the NaAlO$_2$ fillers introduced amorphicity into the polymer network. Ionic motion is
supported by the segmental motion of the polymer host and by the Na\(^{+}\)-AlO\(_2\)^{−} dipoles. The prototype Na-S battery based on the sample PGPE0.50 at RT exhibited a steady open circuit voltage of ~2.2 V. At drain currents of 0.10, 0.25, and 0.50 mA cm\(^{-2}\), the cell showed discharge capacities of ~210, 139, and 51 mAh g\(^{-1}\), respectively.

Janakiraman et al. [126] proposed a separator made from electrospun amorphous PVDF-HFP as a superior GPE material that is appropriate for sodium ion cells. To achieve an amorphous electroactive \(\beta\)-phase structure, a 16% polymer solution was electrospun at an 18 kV voltage. This electrospun material served as a separator membrane in a liquid electrolyte solution containing 0.6 M sodium hexafluorophosphate (NaPF\(_6\)) dissolved in a mixture of ethylene carbonate and propylene carbonate (EC:PC, 1:1, vol.%). The researchers conducted investigations into the ionic conductivity, electrolyte uptake, and linear sweep voltammetry (LSV) of this amorphous GPE. The GPE exhibited a wide electrochemical stability range, extending up to 4.6 V versus Na/Na\(^{+}\) at room temperature, and displayed a high ionic conductivity of \(1.28 \times 10^{-3}\) S cm\(^{-1}\). Furthermore, when applied to cells with the configuration Na/GPE/Na\(_{0.66}\)Fe\(_{0.5}\)Mn\(_{0.5}\)O\(_2\), these cells demonstrated exceptional cycling performance with minimal capacity loss.

Janakiraman et al. [127] explored the use of an electrospun fibrous membrane made from amorphous P(VDF-co-HFP) for sodium ion battery applications. They employed techniques like X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and atomic force microscopy (AFM) to examine the physical and chemical properties of the freshly produced fibrous polymer membranes. These fibrous membranes, produced in an argon-filled glove box, were combined with a liquid electrolyte solution containing 1 M NaClO\(_4\) in a mixture of ethylene carbonate and diethyl carbonate (EC:DEC, 1:1 by volume). In contrast to the commercial Celgard membrane, the electrospun PVDF-HFP-based polymer membrane exhibited an extremely porous structure and boasted a high ionic conductivity of \(1.13 \times 10^{-3}\) S cm\(^{-1}\). Furthermore, the electrochemical stability window of this separator-cum gel polymer electrolyte (SGPE) against Na\(^{+}\)/Na exceeded 4.8 V. The researchers also conducted electrochemical studies on a sodium half-cell where they used the SGPE as the separator, NaNi\(_{0.5}\)Mn\(_{0.5}\)O\(_2\) as the cathode, and pure sodium as the anode. After 50 cycles at a 0.1 C rate, the cell displayed a columbic efficiency of 97%, albeit with some capacity loss over time.

The development of sodium metal batteries (SMBs) is hampered by the drawbacks of typical organic liquid electrolytes, such as sodium dendrite formation, harmful side effects, and liquid leakage. A novel sodium poly(tartaric acid)borate (NaPTAB) salt was successfully synthesized by Yang et al. [128] through an environmentally friendly and cost-effective method known as aqueous-phase synthesis. To synthesize a single sodium ion conductor GPE called NaPTAB-SGPE, NaPTAB was combined with PVDF-HFP to form NaPTAB-SM. NaPTAB-SGPE demonstrated an exceptional thermal stability, with an initial decomposition temperature of 345 °C. It exhibited a noteworthy ionic conductivity of up to \(9.4 \times 10^{-5}\) S cm\(^{-1}\) at room temperature, a wide electrochemical stability window extending up to 5.2 V (vs. Na\(^{+}\)/Na) at 30 °C, and a high sodium ion transference number of 0.91 at 60 °C. Additionally, when incorporated into Na\(_3\)V\(_2\)(PO\(_4\))\(_3\)/Na cells, NaPTAB-SGPE displayed an outstanding charge–discharge performance and consistent cycling capabilities, even at elevated temperatures (60 °C). Notably, it exhibited improved cycle stability compared to liquid electrolyte cells containing 1 M NaClO\(_4\) (EC:PC, 1:1, \(v/v\), and 5% fluoroethylene carbonate (FEC)). The GPE membrane began to produce NaF after 50 cycles at a 0.1 C rate, the cell showed cycle voltages of ~2.2 V, with drain currents of 0.10, 0.25, and 0.50 mA cm\(^{-2}\), the cell showed discharge capacities of ~210, 139, and 51 mAh g\(^{-1}\), respectively. The use of a nonflammable electrolyte is important to overcome the safety concerns of SIBs. Due to their outstanding fire-extinguishing qualities, organic phosphorus compounds like phosphates and phosphonates have been actively investigated as flame-retardant additives [129,130]. Park et al. [131] report on ion-conductive polycaprolactone triacrylate-
containing gel precursors that were cross-linked in situ to produce nonflammable GPEs. Despite having a three-dimensional network structure, the GPEs have a high ionic conductivity of up to 6.3 mS cm$^{-1}$ due to the Na$^+$–carbonyl coordination and strong segmental mobility of polycaprolactone chains. By causing uniform Na deposition on the Na electrode, the ion-conductive polymer networks effectively inhibit the growth of Na dendrites, which improves the interfacial properties of the anode. The Na/GPE/Na$_3$V$_2$(PO$_4$)$_3$ cell shows remarkable cycle stability and offers high discharge capacities at high C rates. Additionally, these cells can operate safely because of the greater thermal stability of the GPE, which prevents short circuiting of the cell at high temperatures.

By using a self-catalyzed method, Niu et al. [132] prepared a novel GPE with a cross-linked polyether network (GPE-CPN). In situ copolymerization of two monomers, 1,3-dioxolane and trimethylolpropane triglycidyl ether, was successfully achieved with the use of sodium hexafluorophosphate (NaPF$_6$) as an initiator. The authors showed that the resulting GPE-CPN had an improved electrochemical stability window against Na$^+$/Na up to 4 V and a significant ionic conductivity of $8.2 \times 10^{-4}$ S cm$^{-1}$ at room temperature. The electrolytes inhibited the growth of sodium dendrites and stabilized the electrolyte/sodium anode interface. The as-prepared GPE-CPN showed promise for future use in rechargeable SBs when taking into account the advantages of its simple manufacturing and exceptional properties. Na$_3$V$_2$(PO$_4$)$_3$, Na(Li$_{0.05}$Ni$_{0.3}$Mn$_{0.5}$Cu$_{0.1}$Mg$_{0.05}$)$_2$O$_2$, and NaTi$_2$(PO$_4$)$_3$ electrode materials were utilized in this study. The GPE system presented superior interfacial stability toward both the cathode and the anode in electrochemical tests.

Farhana et al. [133] prepared GPEs using a poly(propylene) carbonate (PPC) polymer and various weight percentages of sodium iodide (NaI) salt. The plasticizers included ethyl carbonate (EC) and propyl carbonate (PC). At room temperature, a maximum ionic conductivity of 2.01 mS cm$^{-1}$ was attained. The structural characteristics of the GPEs were investigated using FTIR. A complexation between PPC and NaI occurred based on the FTIR study. Dye-sensitized solar cells (DSSC) were produced utilizing GPEs under one sunlight intensity and subjected to photovoltaic investigations. The greatest energy conversion efficiency of 6.38% was attained with the incorporation of 60 wt% of NaI. The ionic conductivity was indeed improved by adding NaI salt to PPC:EC:PC. The highest ionic conductivity was 2.01 mS cm$^{-1}$ with an activation energy of 0.150 eV, as predicted by the Arrhenius model.

Jyothi et al. [134] synthesized polyacrylonitrile (PAN)-based sodium ion-conducting GPEs using EC and DMF as plasticizing solvents using a solution casting technique. These GPEs were translucent, dimensionally stable, free-standing films. NaI was the source of Na$^+$ ions. The conductivity changes were studied as a function of salt concentration from 10 to 40 weight percent. The sample with 30 weight percent of NaI had the maximum conductivity, measuring $2.35 \times 10^{-4}$ S cm$^{-1}$ at 303 K and $19 \times 10^{-3}$ S cm$^{-1}$ at 373 K. With an activation energy in the region of 0.25 to 0.46 eV, the conductivity–temperature dependence of the PE sheets obeyed the Arrhenius equation. Using Wagner’s polarization approach, the transport numbers, both electronic ($t_e$) and ionic ($t_i$), were measured. It was revealed that the conducting species were predominantly due to ions. The highest cationic transport number was determined to be 0.991. The best conducting GPE system was used in the development of a solid-state battery with the configuration Na/(PAN/NaI)/(I$_2$/C/GPE), and the discharge characteristics of the cell were assessed against a load of 100 kOhm. The Na$^+$ ions were more mobile and contributed to cation conductivity because, according to the FT-IR spectra, they were situated adjacent to the C=O groups of the plasticizers and the C:N groups of PAN with only minor electrostatic contacts. According to the DSC thermograms, the addition of the plasticizing solvents EC and DMF made the PE more amorphous, whereas the addition of NaI salt made it stronger. As the NaI concentration rose, the conductivity rose as well, which was ascribed to an increase in amorphicity. The increase in conductivity with rising temperatures was attributed to ion hopping. It was recognized that as the ionic conductivity and dopant concentration increased, the activation energy decreased.
Zhang et al. [135] prepared a GPE by enclosing an improved Na⁺/Zn²⁺ mixed-ion aqueous electrolyte in a polycrylonitrile nanofiber polymer matrix. An innovative aqueous sodium ion battery (ASIB) system was constructed by employing this electrolyte, a zinc anode, and a Na₄Mn₉O₁₈ cathode. Na₄Mn₉O₁₈, which resembles nanorods, was synthesized via a hydrothermal soft chemical reaction. The distribution of the crystalline Na₄Mn₉O₁₈ nanorods on the cathode was validated via structural and morphological measurements. The Zn/GPE/Na₄Mn₉O₁₈ battery exhibited excellent cycle stability at a good performance rate, as established by electrochemical experiments. The battery was characterized by an initial discharge capacity of 96 mAh g⁻¹ and a 64 mAh g⁻¹ capacity after 200 cycles at a 1 C cycling rate. The Zn/GPE/Na₄Mn₉O₁₈ battery is a promising and safe high-performance battery. Using a hydrothermal soft chemical reaction (HSCR), Na₄Mn₉O₁₈ nanorods were successfully produced.

A sodium superionic conductor (NASICON) with the formula Na₃Sc₂P₃O₁₂ (NSP) exists in three crystalline phases, namely α-, β-, and γ. Its ion transport characteristics and other electrochemical properties depend on the crystal phase. Mei et al. [136] conducted a thorough investigation of the impacts of crystalline NASICON fillers with different stoichiometries, such as Na₃Sc₂P₃O₁₂, Na₃.₅Sc₂P₂.₅Si₂O₁₂, and Na₄Sc₂P₂SiO₁₂, on GPEs based on PVDF-HFP/PMMA. The three fillers had different adsorption capacities, and this resulted in a range of performances for the resulting CGPEs. At 64 °C and 166 °C, Na₃Sc₂P₃O₁₂ changes phase from α to β and from β to γ, respectively [137]. The results clearly indicated that the addition of fillers led to a reduction in the crystallinity and an improvement in the porosity of the pristine GPEs, subsequently enhancing their conductivity. Among the CGPEs tested, the one incorporating γ-Na₃Sc₂P₂SiO₁₂ fillers exhibited the highest conductivity at 2.783 × 10⁻³ S·cm⁻¹, a sodium ion transference number (t_{Na⁺}) of 0.57, an impressive electrochemical window of 5.27 V, and an exceptionally low activation energy of just 0.0320 eV. This specific CGPE performed exceptionally well in Na/CGPE/Na batteries, boasting an initial discharge specific capacity of 92.3 mAh g⁻¹ and retaining 98.18% of its capacity after 100 cycles. The CGPE-containing β-Na₃.₅Sc₂P₂.₅Si₂O₁₂ fillers exhibited a very good conductivity as high as 2.072 × 10⁻³ S·cm⁻¹, a t_{Na⁺} of 0.47, an electrochemical window of 5.17 V, and a modest activation energy of 0.0328 eV. It also demonstrated a promising electrochemical performance, with an initial discharge specific capacity of 93.8 mAh g⁻¹ and a capacity retention rate of 97.87% after 100 cycles.

In contrast, the CGPE-incorporating α-Na₃Sc₂P₂O₁₂ filler performed less favorably when compared to the β- and γ-crystal forms. It exhibited a narrower electrochemical window of 5.07 V, a lower t_{Na⁺} of 0.35, a conductivity of 1.92 × 10⁻³ S·cm⁻¹, and a slightly higher activation energy of 0.0370 eV. Its capacity retention rate after 100 cycles was 97.20%, and it displayed an initial discharge specific capacity of 93 mAh g⁻¹. This study underscores the significance of modifying the crystal structure (α-, β-, and γ-) of Na₃Sc₂P₂O₁₂ for improving the performance of GPEs.

Kim et al. [138] introduced a method to engineer the inner porous nanostructure of a PVDF-HFP polymer in GPEs for SIBs supported by glass fibers (GFs) using non-solvent-induced phase separation (NIPS). In terms of both the pore nanostructure and vertical position of the PVDF-HFP film, various types of porous GPEs inside the GF matrix exhibited different SIB performances. The improved GPEs in the GFs allowed for a higher ionic conductivity and exhibited superior cell properties with an excellent stability. The authors found various advantages depending on the morphology and placement of the porous PVDF-HFP film in the GF. During the phase inversion of PVDF-HFP, DI water and methanol served as pore inducers and positioners, respectively, in a binary non-solvent system. This resulted in a GPE with a uniform ion transport pathway for more uniform utilization of the electrode materials and a minimized interfacial resistance for effective ionic migration from electrolyte to electrode and vice versa. The electrochemical performance of the SIBs, in terms of their long cycling and high current density, was enhanced due to the synergic effects of two non-solvents, resolving the issue of parasitic capacity decay. This drawback
has been a persistent one for SIBs in previous studies due to the use of hollow GF structures. The proposed approach enables the production of cost-effective GPEs for SIB.

Kim et al. [139] used a cathode made of poly(2,2,6,6-tetramethylpiperidine-4-yl-1-oxyl vinyl ether) (PTVE) along with a microporous GPE based on an electrospun polyimide membrane to demonstrate an advanced organic radical battery (ORB). PTVE was used to functionalize carbon nanotubes (CNTs) via a dissolution–diffusion procedure to increase the low electrical conductivity of these nanostructures (65 weight % PTVE and 35 weight % CNT). The PTVE-functionalized CNTs could be shaped into a dense electrode with acceptable porosity due to π − π* interactions between the two components. PTVE (3 wt%) was added as a binder in place of traditional non-conducting materials. The GPE was highly compatible with the desired microporosity.

An ORB based on the PTVE-CNT composite electrode, the above-mentioned GPE, and a hard carbon anode exhibited a good rate capability and stable cycling. The battery was endowed with 100% coulombic efficiency, zero self-discharge, and discharging capacities of 128.6 and 68.2 mAh g\(^{-1}\) at 0.5 C and 10 C, respectively. Therefore, the resulting SIB is suitable for various high-power applications and is safe, light, and environmentally friendly.

Shin et al. [140] demonstrated that a cross-linked fibrous CGPE based on polyacrylonitrile (PAN) and mesoporous methacrylate-functionalized SiO\(_2\) nanoparticles effectively encases a liquid electrolyte without experiencing any solvent leakage. This same CGPE exhibited advantageous interfacial characteristics and showed excellent cycling performance. A study by Aravindan et al. [141] revealed substantial enhancements in both the mechanical stability and ionic conductivity of a PVDF-HFP polymer membrane with the incorporation of 10% AlO(OH)\(_n\). Nevertheless, it was observed that when the filler content surpassed a specific threshold, the nano-sized fillers exhibited a pronounced surface effect and a propensity to cluster together. Aggregated fillers can damage the ion conducting pathways, resulting in a drop in the ionic conductivity of the PE [142].

With the addition of 1-(4-cyanophenyl)-guanidine, Zhao et al. [143] improved the ion conductive properties of a GPE and gave rise to an adjustable porous 3D network structure (a CGPE). PVDF-HFP provides a pathway for the transport of sodium ions within the system, and the imino nitrogen atom of 1-(4-cyanophenyl)guanidine is a ligand for sodium ions which facilitates the conduction of Na\(^+\). The resulting CGPE (called PSGGSE) is characterized by a stable interface layer with the anode and an ionic conductivity of 0.232 mS cm\(^{-1}\) at 70 °C. After 400 h of cycling of a symmetric Na/PSGGSE/Na cell at various current densities, no short circuit was observed, indicating that PSGGSE can successfully stop the formation of Na dendrites. Additionally, the Na/PSGGSE/NiMoO\(_4\) battery exhibited superior cycling stability at a 100 mAh g\(^{-1}\) current density and continued to have a high capacity of 150 mAh g\(^{-1}\) after 200 cycles. The authors were able to produce a tunable porous structure and improved interface stability with the addition of SnO\(_2\) fillers. The PSGGSE exhibited a high t\(_{\text{Na}^+}\) (0.58), high conductivity (0.232 mS cm\(^{-1}\)), and high cycling performance in a symmetric cell configuration (Na/PSGGSE/Na). Additionally, the PSGGSE/anode interface was studied using SEM imaging, confirming that the electrode material was prevented from pulverizing due to volume expansion associated with the charging and discharging processes.

A porous composite polymer membrane was prepared from a GPE based on a blend of PEO, PMMA, and PVDF-HFP and nano-sized oxide fillers (Al\(_2\)O\(_3\), TiO\(_2\), and SiO\(_2\)) by Shi et al. [144]. The CGPE containing SiO\(_2\) fillers exhibited several advantageous characteristics. It possessed increased amorphous regions and a porous structure that could effectively accommodate more liquid electrolyte without leakage. Moreover, it showed higher cationic transport numbers for both Li\(^+\) and Na\(^+\), resulting in an improved ionic conductivity. The CGPE, prepared using a solvent casting technique, also offered a substantial electrochemical stability window, strong interfacial stability, and enhanced thermal resilience. The ion transport numbers of the CGPEs were determined through a combination of chronoamperometry and electrochemical impedance spectroscopy (EIS).
The pores and amorphous structure of the CGPEs increased as a result of the oxide fillers and the segmental motion of the polymer chain. The unique structure of these CGPEs was closely associated with their remarkable interfacial and electrochemical stability, impressive ionic conductivity, and a substantial capacity to hold liquid electrolytes. The presence of nano-sized particles played a crucial role in preserving the mechanical strength of the solid electrolyte interphase (SEI) coating and stabilizing the interface between the CGPE and alkali metal anode. These findings suggest that CGPEs incorporating nanoscale SiO$_2$ fillers represent a promising choice for rechargeable Li or Na metal batteries, offering improved safety and an extended cycle life.

A study by Zhu et al. [146] reports the successful production of a porous composite membrane in which a nonwoven P(VDF-HFP) membrane supported by polypropylene serves as the reinforcing material while P(VDF-HFP) acts as the polymer host. Notably, the tensile strength of this membrane closely resembles that of the Celgard 2730 separator in both wet and dry conditions. At ambient temperature, it was measured that the ionic conductivity ($0.82 \text{ mS} \cdot \text{cm}^{-1}$) was four times greater than that of the commercial separator ($0.16 \text{ mS} \cdot \text{cm}^{-1}$) saturated with the same electrolyte. Additionally, it was shown that the Na$^+$ ion transference number was quite high, and the liquid electrolyte was retained even at 110 °C. The aforementioned CGPE was used to study the electrochemical reversibility of a Na$_4$Mn$_9$O$_8$ cathode, as confirmed using cyclic voltammetry. The porous CGPE has excellent application potential for high-energy-density SIBs.

High energy densities in SMBs are theoretically possible, but severe sodium dendrite growth and side reactions make them impractical for use, especially at high temperatures. Lei et al. [149] designed an inorganic ionic conductor/GPE composite in which evenly cross-linked beta alumina nanowires are compactly coated by a GPE based on P(VDF-HFP) due to their reciprocal strong molecular interactions. Together with the gel polymer layer, these beta alumina nanowires generate dense and uniform solid–liquid hybrid sodium ion transportation channels that facilitate uniform sodium deposition and the development of a flat, stable, solid electrolyte interface on the sodium metal anode. SiO$_2$ additives were added to the above-mentioned GPEs to further enhance their characteristics [150], commercial glass fiber (GF) membranes [151], and polydopamine (PDA) [152].

In their study, Gao et al. [152] demonstrated that SIBs can be significantly improved through the integration of an economical composite gel polymer/glass fiber electrolyte. This CGPE consists of PVDF-HFP reinforced with a glass fiber paper which underwent modification with a polydopamine coating to fine-tune the mechanical and surface properties of the perfluorinated polymer. The resulting composite polymer matrix displayed exceptional mechanical strength and thermal stability, remaining stable even at temperatures as high as 200 °C.

After being saturated with a liquid electrolyte, the CGPEs exhibited a wide electrochemical window and strong ionic conductivity. When tested using a sodium ion battery with Na$_2$MnFe(CN)$_6$ as the cathode material, significant enhancements were observed in the rate capability, cycle performance, and coulombic efficiency. These findings suggest that this CPE could be highly beneficial in large-scale battery systems where safety and cost-efficiency are primary concerns, particularly when employed with a dual function as a separator. The precipitation process previously described was used to prepare the cathode material for Na$_2$MnFe(CN)$_6$ [153,154]. The glass fiber paper was used to impart the composite GPEs with a high thermal stability and good mechanical strength. The polydopamine coating was useful for expanding the electrochemical window, which enabled the use of the CPEs with different electrode designs and enhanced the ionic conductivity. Sodium ion half-cells with Na$_2$MnFe(CN)$_6$ as the cathode performed much better electrochemically when the CGPEs were used. The authors anticipated that the integrated strategy used for
CGPEs can easily be applied to other polymer and battery systems, ultimately enhancing the performance of other energy storage technologies.

In Na-S and Na-nickel chloride batteries that operate at 300–350 °C, polycrystalline Na beta alumina (Na-β-Al2O3) with a strong ionic conductivity and good thermal characteristics is employed as the solid electrolyte material. A straightforward procedure was used to prepare the NVP cathode material in accordance with earlier research [155]. Cross-linked β/β′-Al2O3 nanowire membranes were produced using an electrospinning technique and then heated through an annealing process. Thanks to the effective immobilization of the electrolyte facilitated by ANs-GPE and the establishment of a stable and flat solid electrolyte interphase (SEI) on the sodium (Na) metal anode, undesired side reactions between the Na metal anode and the liquid electrolyte, as well as the formation of Na dendrites, were successfully mitigated. Remarkably, even after 1000 cycles at 1 C and 60 °C, the Na/ANs-GPE/NVP cell exhibited impressive capacity retention, maintaining a rate of 78.8%. This study introduced the concept of solid–liquid hybrid sodium ion transport channels within hybrid electrolytes composed of ceramic electrolytes and GPEs. This innovative approach could also be adapted for use in batteries containing lithium (Li), potassium (K), or other metal ions.

A CGPE was formulated by Luo et al. [156] primarily using graphene oxide (GO) and PVDF-HFP. Notably, the compressive Young’s modulus of the sample, specifically the one containing 2 w% GO within the PVDF-HFP matrix, referred to as the 2-GPH composite GPE, exhibited a remarkable tenfold increase, reaching 2.5 GPa. This significant boost in modulus plays a crucial role in preventing the formation of sodium dendrites. Consequently, under high current density conditions (5 mA cm−2), the 2-GPH CGPE enabled uniform sodium deposition and achieved exceptionally long-lasting reversible sodium plating and stripping, extending beyond 400 h. Full SMBs were assembled from the metal sodium anode, NVP [157] cathode, and a number of electrolytes, such as 2-GPH GPE, PH GPE, and a LE. Additionally, the GO content enhanced the movement of sodium ions, as shown using a molecular dynamics simulation, leading to a high ionic conductivity of 2.3 × 10−3 S cm−1. An impressive initial capacity of 107 mAh g−1 was obtained when the composite GPE was combined with a Na3V2(PO4)3 cathode in a complete sodium metal battery. After 1100 cycles, the capacity retention rate was high at 93.5%, and the coulombic efficiency was high at 99.8%.

Mishra et al. [158] studied the impact of Al2O3 nanoparticle dispersion on the ionic conductivity of a non-aqueous PVDF-HFP/PMMA blend-based nanocomposite GPE (NGPE) containing a sodium trifluoromethanesulfonate liquid electrolyte. The ionic conductivity of the pristine GPE was measured to be 7.5 × 10−4 S cm−1. Different Al2O3 concentrations in the PVDF-HFP/PMMA were introduced, and the NGPE considerably altered the ionic conductivity of the system. The composition, including 6 weight percent Al2O3 nanoparticles, caused the ionic conductivity of the electrolyte to increase to a maximum of 1.5 × 10−3 S cm−1. A VTF behavior was observed for the optimum composition in the temperature range of 50 to 95 °C. Al2O3 nanoparticles were uniformly distributed throughout the porous structure of the NGPE, and the amorphylicity of the polymer matrix increased, as shown by SEM and XRD studies. The faster conduction of the dissociated ions of the liquid electrolyte trapped in the PVDF-HFP/PMMA matrix, as well as the amorphous gel phase, both contributed to the increased conductivity. The composition with the highest conductivity had a Na+ transport number of 0.30 and a significant electrochemical stability window of 3.6 V. These characteristics imply the viable application of the improved NGPE for SBs and supercapacitors. Using a Na-Hg/P-C cell (P-C is phosphorus-activated carbon) and the highest conducting NGPE composition, a prototype sodium battery was assembled. The battery exhibited a capacity reduction with cycling, an open circuit voltage of 2.5 V, and a first discharge capacity of 400 mAh g−1. Measurements made utilizing EIS, LSV, CV, and chronoamperometry were used in the electrochemical investigations of the NGPEs. Due to significant thickening in the passivation layer, which raised the cell’s internal resistance, a serious capacity fading was observed during cycling.
In general terms, the major focus on the synthesis of Na GPEs represents a tacit admission that Na SPEs have not met expectations. The awareness of the fact that organic liquid electrolytes such as EC and PC maintain their mainstream practical significance has led researchers towards the development of Na GPEs similar to Li GPEs. The trapping of EC, PC, or similar organic liquids in three-dimensional structures is a proven, clever strategy for preventing liquid leakage and preserving liquid-like conductivity. Thus far, the polymer host of choice seems to be PVDF-HFP. This perfluorinated copolymer seems to provide the most reliable confinement for liquid electrolytes. An aspect that we find interesting is that PVDF is a well-known piezoelectric material. Therefore, we wonder if the presence of PVDF is also associated with voltage-dependent electrostatic assistance to the conductivity process. The employment of fluorine-containing anions is expected to cause their preferential interaction with the perfluorinated polymer host. The use of PMMA in the assembly of electrolytes seems to be related mostly to the ease with which it can be polymerized in a variety of conditions. The use of inorganic fillers in the context of GPEs has proceeded in parallel to the development of CPEs, as discussed in the next section.

2.3. Composite Polymer Electrolytes (CPEs)

SPEs consist of a polymer matrix containing sodium salt and no liquid solvent. Unfortunately, SPEs suffer from a low ionic conductivity. The advancement of this field relies on the following approaches: (1) reducing the percentage of liquid plasticizers [159] and (2) adding inorganic fillers [32]. As explained above, we consider plasticized polymer electrolytes (PPEs) to be separate from CPEs, which include inorganic fillers. The physical properties of the components used in these types of CPEs are displayed in Figure 7. The use of these strategies in some cases comes at the price of sacrificing part of the mechanical, thermal, and chemical stability of SPEs. The addition of inorganic ceramic fillers seems to be the most promising route, as it usually increases ionic conductivity.

An ideal CPE should have a high ionic conductivity (up to the order of $10^{-3}$ S·cm$^{-1}$) in a wide temperature range to enable SIBs with a high cycle and rate performance (Figure 8). The following list of targeted requirements are desirable characteristics in CPEs. (1) In order to prevent sluggish reactions with the electrodes during the processes of sodium insertion

![Figure 7. Composite polymers electrolytes.](image-url)
and extraction, it is crucial for CPEs to possess a wide electrochemical stability range of up to 5 V. (2) To prevent deformation while operating at high temperatures, CPEs should have a strong dimensional stability and superior thermal stability of up to at least 150 °C. The deformation of PEs in SIBs generally results in significant risks including short circuits and thermal runaway due to the poor thermal stability of conventional PEs. (3) In order to achieve optimal power performance and mitigate issues related to ionic concentration polarization, CPEs should exhibit a high sodium ion (Na\(^{+}\)) transference number, ideally close to 1. Additionally, these CPEs need to possess substantial mechanical strength to effectively deter the penetration of sodium dendrites. (4) Mechanical robustness is a crucial attribute for CPEs, especially when considering their applications in wearable and flexible energy storage devices. (5) CPEs in SIBs ought to be cost-effective for a wide range of energy storage applications. (6) To ensure the safe and long-term supply of SIBs, CPEs should exhibit a low toxicity and should be comprised of materials that are abundant on Earth. It is important to bridge the gap between the actual performance of a practical electrolyte and the structural, chemical, and functional qualities of an ideal CPE [160].

Figure 8. Characteristic properties of composite polymers electrolytes.

It was discovered that GPEs filled with various inorganic oxides, including SiO\(_2\), Al\(_2\)O\(_3\), TiO\(_2\), ZrO\(_2\), BaTiO\(_3\), etc. [161–163] showed enhanced mechanical strength, higher ionic conductivity, and improved electrochemical stability of the Li/electrolyte interface compared to those without filling. These systems were labelled CGPE in the previous section. Similarly, the direct dispersion of active or inert inorganic oxide fillers within PEs without plasticizers leads to the formation of CPEs. Given that active fillers directly participate in the ion conduction process, their incorporation generally leads to increased conductivity and a greater mobile ion transference number compared to inert fillers.

In 2015, Ni’mah et al. [164] reported PEs based on PEO using a transition metal oxide filler for SIBs. Initially the PEO/TiO\(_2\) nanocomposite was prepared followed by the synthesis of the cathodic material Na\(_{2/3}\)Co\(_{2/3}\)Mn\(_{1/3}\)O\(_2\) using the carbonate co-precipitation method. The maximal ionic conductivity of a SPE with an equilibrium ratio of EO:Na = 20 is 1.35 \(\times\) 10\(^{-4}\) S cm\(^{-1}\), which increases to 2.62 \(\times\) 10\(^{-4}\) S cm\(^{-1}\) when TiO\(_2\) (3.4 nm, 5 wt\%) is added at a temperature of 60 °C.

A study by Verma et al. [165] investigated the dispersion of TiO\(_2\) nanofillers in Na-conducting nanocomposite polymer electrolyte membranes. The base material for the membranes was PVDF-HFP. Initially, TiO\(_2\) was immersed in a liquid electrolyte comprising NaPF\(_6\) and EC. The membranes containing TiO\(_2\) were then prepared using the phase inversion technique. It was discovered that the membranes were quite porous, with a maximum porosity of ~72% and a liquid electrolyte uptake of ~270%. It was determined
using complex impedance spectroscopy that the highest ionic conductivity at room temperature was \( \sim 1.3 \times 10^{-2} \) S·cm\(^{-1}\). It was found that the ionic conductivity, measured as a function of temperature, exhibited a VT behavior. DC polarization, complex impedance, and cyclic voltammetry were used to probe the electrochemical properties of the CPEs. It was determined that the membranes contained a \( \text{Na}^+ \) transport number of approximately 0.31. The electrochemical stability window of the membranes was 3.5 V. The pore density reached its maximum at 0.50 weight percent TiO\(_2\), and the pore size grew with TiO\(_2\) content.

Zhang et al. [166] described the preparation of a CPE for SIBs that are entirely solid-state. The sol-gel process was used to synthesize \( \text{Na}_3\text{V}_2\text{(PO}_4\text{)}_3 \) (NVP) using carbon nanotubes as the cathode material (NVP@CNTs). A novel electrolyte comprised of a PMMA/PEG hybrid polymer with 5% nano-Al\(2\text{O}_3\) was produced and first used in SIBs. The CPE performed quite well, and the following three characteristics stood out: (i) at 70 °C, a comparatively high ionic conductivity of \( 1.46 \times 10^{-4} \) S·cm\(^{-1}\) was attained; (ii) there was minimal anodic breakdown, even at 4.5 V vs. \( \text{Na}^+/\text{Na} \); and (iii) the mechanical flexibility of the CPEs assured intimate contact with the electrodes. The all-solid-state SIBs showed a high reversible capacity of 85 mAh·g\(^{-1}\) at 0.5 C and a 94.1% capacity retention after 350 cycles.

In 2018, Jinisha et al. [51] reported a PEO:NaNO\(_3\) PE with an Al\(2\text{O}_3\) filler, which exhibited its highest conductivity of \( 1.86 \times 10^{-4} \) S·cm\(^{-1}\) at room temperature. The first solid CPEs based on PEO and NaTFSI with an active ceramic filler (NASICON) were described by Zhang et al. [167]. The incorporation of NASICON fillers significantly improved both the thermal and electrochemical stability of the electrolytic complexes. A CPE with NASICON filler content of 50% by weight showed the highest conductivity of 2.8 mS·cm\(^{-1}\) (at 80 °C). Furthermore, solid-state batteries constructed using a sodium (Na) anode, CPE as the electrolyte, and \( \text{Na}_3\text{V}_2\text{(PO}_4\text{)}_3 \) as the cathode exhibited an excellent rate performance and impressive cycling stability. The NASICON electrolyte was synthesized using the sol-gel process, and \( \text{Na}_3\text{V}_2\text{(PO}_4\text{)}_3 \) was produced via a solid-state reaction [168]. NASICON (\( \text{Na}_{1-x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}, 0 \leq x \leq 3 \)) ceramic electrolytes have been previously researched for their excellent ionic conductivity, thermal stability, and broad electrochemical window [169].

Zhao et al. [170] studied PVDF-HFP, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF\(_4\)), and NaSCN that were electrospun as composite nanofibrous electrolyte membranes (CFEM). The interconnected multifibrous layers and ultrathin porous architectures of the electrospun CFEM and CFEM-NaSCN fibers were investigated using SEM. The fibers had an average diameter of 50–200 nm and showed substantial electrolyte solution absorption (370–880%). The decrease in crystallinity of the PEs was accompanied by a rise in their ionic conductivity. The composite material CFEM, incorporating 15% BMIMBF\(_4\), demonstrated a peak ionic conductivity of \( 5.6 \times 10^{-5} \) S·cm\(^{-1}\) at room temperature. The CPEs exhibited Arrhenius behavior. In comparison to electrospun pure PVDF-HFP without BMIMBF\(_4\) or BMIMBF\(_4\)-NaSCN, the CFEM-NaSCN electrolyte exhibited an increased electrochemical window, surpassing 4.5 V. It is expected that the CFEM electrolyte and the CFEM-NaSCN electrolyte are suitable for high-performance rechargeable batteries and super capacitors due to their outstanding performance characteristics. The BMIMBF\(_4\), an RTIL, was synthesized using a previously described method [171]. The preparation of CFEM and CFEM-NaSCN involved electrospinning, and the porous materials were immersed in an ionic electrolyte solution to produce the CPEs [172].

Song et al. [173] presented a CPE made by sandwiching poly(ethylene oxide) (PEO)-based PE between nanoporous ceramic layers. A superior ionic conductivity of \( 1.6 \times 10^{-4} \) S·cm\(^{-1}\) at ambient temperature, stable Na plating and stripping, as well as a wide electrochemical stability window of 4.2 V versus Na/Na\(^+\) were made possible using this laminated arrangement.

In 2017, Lee et al. [174] reported on the thermal and electrical conductivity properties of a PE composed of PEO, NaClO\(_4\), and barium titanate (BaTiO\(_3\)) as a filler. They noted that the addition of BaTiO\(_3\) further enhanced the conductivity, reaching a maximum value of \( 1.0 \times 10^{-5} \) S·cm\(^{-1}\) at room temperature.
 Moreno et al. [175] prepared membranes of NaTFSI complexed with PEO with various EO:Na molar ratios. Above 70 °C, all the membranes exhibited excellent ionic conductivities of approximately 10^{-3} S·cm^{-1}. Due to the anion’s plasticizing properties, the samples with higher concentrations of NaTFSI exhibited a sticky gum-like behavior. A compromise in the conductivity, thermal, and mechanical properties could be seen in the PEO_{20}:NaTFSI sample. The mechanical properties of the PEO_{20}:NaTFSI membranes were further improved by the addition of nanometric SiO_{2}. Additionally, the PEO_{20}:NaTFSI membranes with 5 weight percent SiO_{2} demonstrated a similar anodic electrochemical stability and ionic conductivity to the ceramic-free PEO_{20}:NaTFSI sample. When compared to a ceramic-free membrane, the addition of the ceramic filler significantly increased the interfacial resistance in a Na/PE/Na symmetrical cell that was monitored for 30 days. The anion and cation diffusion coefficients determined using NMR indicated that the presence of a filler may have had a favorable impact on the cation transfer number (t_{Na^{+}}), which was consistent with the electrochemical measurements. The neutralization reaction between HTFSI and Na_{2}CO_{3} in aqueous solution was used to synthesize the sodium salt [176]. PEO_{n}:NaTFSI PEs were prepared via a hot pressing (solvent-free) method [177]. These membranes exhibited conductivity and stability values that made them very promising materials for use as electrolytes in cutting-edge SIBs with innovative designs, particularly for grid applications requiring rapid production. Additional work is being carried out to confirm this expectation, particularly with the PEO_{n}:NaFSI system.

Kunteppa et al. [178] synthesized other PEO-based composites by stirring PEO and polyaniline in anhydrous acetonitrile for 5 to 6 h to create homogenous solutions or gels with various weight percentages. FTIR and SEM were used to characterize the composites. The formation of PEO:PANI:NaClO_{4} composites was confirmed based on the main peaks in the FTIR spectra. Based on the SEM measurements, the morphology of the CPEs with different weight percentages of NaClO_{4} significantly changed, going from ellipsoidal to square features. The hopping of polarons from one localized state to another, which is supported by Mott theory, contributed to the ionic DC conductivity that was observed. These composites can be excellent candidates for solid-state electrolytes, as seen in investigations of the DC conductivity and SEM.

Chen et al. [179] proposed a novel solid electrolyte named B-CPE (boron-modified CPE) which was designed for SIBs. B-CPE was prepared through in situ polymerization within a mechanically supportive matrix. This electrolyte exhibited an exceptional ionic conductivity at 40 °C, measuring 2.57 × 10^{-4} S·cm^{-1}, along with a high sodium-ion (Na^{+}) transference number of 0.66. It also demonstrated excellent compatibility with the sodium (Na) metal anode. This improvement was attributed to the formation of a continuous ion-conducting polymer phase, facilitated by a one-step in situ solidification process that fostered a suitable contact between the electrode and electrolyte interface.

Solid-state SIBs based on B-CPE displayed an outstanding electrochemical performance by leveraging the synergy of a high-performance electrolyte and an optimized cell design. The best-performing SIB exhibited an initial discharge capacity of 113.8 mAh·g^{-1} and retained 80.1% of its capacity after 320 cycles at 40 °C at 0.2 C and 80.4% after 700 cycles at 3 C. Notably, the addition of boron moieties significantly improved the battery’s rate capability. This research paves the way for the development of high-performance rechargeable solid-state batteries. The cathode material, NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_{2} (NFM), was prepared using a traditional solution casting technique, consisting of NFM active material/PVDF binder/Super-P in a ratio of 80/10/10 w/w/w. The NFM active material synthesis followed prior methods [180].

A novel CPE known as PVC-CPE based on poly(vinylene carbonate) was developed by Chen et al. [181] for the assembly of high-performance solid-state SIBs that operate at room temperature. The PVC-CPE was solidified in situ and exhibited several favorable characteristics including enhanced stability at the electrode/electrolyte interface, a high sodium ion (Na^{+}) transference number (t_{Na^{+}} = 0.60), and superior ionic conductivity (0.12 mS·cm^{-1} at 25 °C). Significantly, a composite cathode, NaNi_{1/3}Fe_{1/3}Mn_{1/3}O_{2} (c-
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NFM), was designed to minimize interfacial resistance and facilitate efficient ion transport across the electrode/electrolyte interfaces. This achievement was realized by forming the PE in situ within the electrode. In comparison to a reference sodium/PEO-CPE/c-NFM battery produced using a conventional ex situ approach, the solid-state sodium/PEO-CPE/c-NFM battery demonstrated markedly improved cell performance at room temperature. The device exhibited a high initial specific capacity of 104.2 mAh g⁻¹ at 0.2 C, retained 86.8% of its capacity over 250 cycles, and maintained a capacity of 80.2 mAh g⁻¹ at 1 C. PVC-CPE emerges as a highly promising electrolyte for solid-state SIBs.

A study was conducted by Ahad et al. [182] on the structural, thermal, and electrical characteristics of solid CPEs comprised of poly(vinyl alcohol) complexed with sodium salicylate. These CPEs were fabricated through a solution casting method, utilizing various weight-to-percentage ratios. Analysis using XRD revealed that the concentration of sodium salicylate resulted in an expansion of the amorphous regions within the polymer. It was observed that the breakdown of these CPEs decreased as the amount of sodium salicylate increased.

The electrical properties, including the conductivity and dielectric characteristics, were investigated. This analysis was carried out over a temperature range spanning from 303 K to 343 K and in the frequency range 20 Hz to 1 MHz. The results indicated that as both the temperature and sodium salicylate concentration increased, the conductivity of the CPEs also increased. Additionally, the dielectric constant increased with rising temperatures, while the dielectric loss decreased with higher sodium salicylate contents. The PVA-50 wt% sodium salicylate sample showed the best conductivity, lowest activation energy, highest amorphous nature, and highest thermal stability, making it perfect for application in electrochemical devices.

Yu et al. [183] investigated a CPE that integrates the flexibility characteristics of a PE with the high ionic conductivity found in ceramic electrolytes. A simple slurry-casting technique was used to create a composite electrolyte containing PEO, NaClO₄ salt, and a ceramic Na ion conductor (Na₃Zr₂Si₂PO₁₂) scattered in it. The resulting CPE showed increased dendrite suppression, improved electrode/electrolyte interface, and an elastic consistency. All-solid-state batteries with a sodium metal anode, PEO/NaClO₄/Na₃Zr₂Si₂PO₁₂ as an electrolyte, and a Na₂MnFe(CN)₆ cathode exhibited a stable long-term cycling performance. The polymer/ceramic composite was prepared using a straightforward slurry-casting technique to disperse a nanoparticle electrolyte material, Na₃Zr₂Si₂PO₁₂, into the PEO and sodium perchlorate. At a high temperature of 60 °C, the PEO/NaClO₄/Na₃Zr₂Si₂PO₁₂ CPE exhibited a Na ion conductivity of 5.6 × 10⁻⁴ S cm⁻¹. Long-term electrochemical stability and compatibility with the Na metal anode and the Na₂MnFe(CN)₆ cathode were demonstrated by the PEO/NaClO₄/Na₃Zr₂Si₂PO₁₂ electrolyte membranes. Due to their capacity to suppress the sodium dendrites during sodium plating, the Na₃Zr₂Si₂PO₁₂ nanoparticles considerably increased the stability of the Na/PEO-NaClO₄-Na₃Zr₂Si₂PO₁₂/Na symmetric cells. The Na/PEO-NaClO₄-Na₃Zr₂Si₂PO₁₂/Na₂MnFe(CN)₆ cells, which were entirely solid-state, presented a respectable rate capability and long-term cycle stability. The findings of this study show that the polymer/ceramic composite is a promising approach for the assembly of all-solid-state SBS.

Wang et al. [184] employed thin layers of ferroelectrics as a distinctive approach to customize the interfaces between electrodes and an all-solid-state CPE. An ionic conductivity of 7.9 × 10⁻⁵ S cm⁻¹ was recorded at ambient temperature. The incorporation of ferroelectric engineering also improved ion transport across the electrolyte–ferroelectric cathode/anode interfaces, effectively suppressing the formation of the SEI between the CPEs and the Na metal electrodes. Notably, after 165 cycles at room temperature, an exceptionally high discharge capacity of 160.3 mAh g⁻¹ with 97.4% retention was attained in the ferroelectric-engineered all-solid-state Na metal cell. Furthermore, despite the cell having been aged for two months, a remarkable stability was shown based on the high discharge capacity retention of 86.0% after 180 complete charge/discharge cycles. This research offers fresh perspectives on how to improve the stability and long-cyclability of
solid-state rechargeable batteries. NZSP ceramic frameworks with pores [185] and a KNN precursor solution [186] were prepared as described earlier. The interfacial ion transport at the electrolyte–ferroelectric–cathode/anode interfaces was improved, and the SEI growth was successfully inhibited.

In 2021, Dimri et al. [187] reported the study of a PE based on PEO and sodium triflate (NaCF$_2$SO$_3$) in conjunction with zinc ferrite (ZnFe$_2$O$_4$) nanoparticles. ZnFe$_2$O$_4$ was prepared via the citrate combustion method using the precursors zinc nitrate, ferric nitrate, and citric acid. The PE was prepared by adding ferrite nanoparticles to PEO and NaCF$_2$SO$_3$ in the presence of PC as plasticizer. This CPE was characterized as a film, and the ferrite nanoparticles were found to increase the amorphicity of the system. The conductivity of the electrolyte was 6 \times 10^{-5} \text{ S cm}^{-1} at room temperature. In the same year, Chauhan et al. [188] reported the enhancement of ion transport in PE based on PEO and NaClO$_4$ using sodium aluminate (NaAlO$_2$) as fillers. The addition of 5 wt% of NaAlO$_2$ filler increased the electrolyte conductivity from 1.6 \times 10^{-5} \text{ S cm}^{-1} at 25 \degree C to 7.4 \times 10^{-5} \text{ S cm}^{-1} at 30 \degree C. Similarly, in the same year, Yao et al. [189] reported the effects of the addition of 10 wt% of \(\beta\)-alumina as fillers to PEO/NaClO$_4$, which was found to increase the conductivity from 2.5 \times 10^{-4} to 3.95 \times 10^{-4} \text{ S cm}^{-1} at 60 \degree C. Again, in 2021, Mallaiah et al. [190] reported the impact of PVDF blending with PEO/NaClO$_4$ and found that PVDF addition increased the conductivity to 9.334 \times 10^{-5} \text{ S cm}^{-1} at room temperature for PEO:PVDF:NaClO$_4$ in a ratio of 80:20:5.

A solution casting process was used by Pradhan et al. [191] to produce a plasticized CPE (PCPE) based on PEO, NaI, and Na$_2$SiO$_3$ as the ceramic filler and PEG as the plasticizer. Investigations were performed to understand how plasticization affects the electrical and microscopic structure of the material. Utilizing XRD and SEM studies, it was determined how the addition of plasticizer alters the surface morphology and increases the concentration of amorphous materials. DSC showed that the presence of plasticizers reduces the internal viscosity of the polymers and increases their flexibility. With an increase in the plasticizer content, it was discovered that the grain boundary resistance decreased. At room temperature, adding the plasticizer caused the conductivity value to increase by a factor of three. The conductivity as a function of the reciprocal temperature demonstrates a thermally activated process of the Arrhenius type above and below the melting temperature $T_m$ of PEO.

Na CPEs represent a compromise between the properties of SPEs and those of inorganic fillers. Both PVDF and PEO have been used in this context. It is interesting that PEO becomes immediately relevant, though not exclusively, the moment that the use of liquid solvent additives is not allowed. PVDF and PEO can interact with nanosized oxides of different kinds through their respective polar moieties. It appears that the nanoparticles are quite effective in disrupting the long-range crystallinity of the polymer host. At the same time, they mediate local interactions of regions of the polymer host, which provide partially charged nanodomains that assist the motion of Na$^+$ cations. One issue of concern in Na CPEs is whether a true integration of the components occurs rather than a more or less stable formation of multiphasic materials with different ion conduction pathways.

3. Conclusions and Future Perspectives

Since 2010, the field of SIBs has shown widespread interest, and the related number of publications has been growing tremendously. The discovery of new electrolytes and the improvement of existing ones play a crucial role in the advancement of this area of research and development. The specific choice of electrolyte has a significant impact not only on the energy density and cycle life of batteries, but also their manufacturing processes, cost, and safety. Given the thermodynamic differences between sodium and lithium, the development of electrolytes for SIBs cannot solely rely on the experience gained from LIBs. PE-based SBs provide unique opportunities not only to reduce raw material costs but also to enhance the inherent safety of the batteries. Over the past 35 years, there has been a significant increase in the variety of Na ion-conducting polymer
matrices, sodium salts, and plasticizers or fillers, leading to notable advancements in the physicochemical and electrochemical properties. PEs offer the potential to merge the advantages of solid electrolytes, such as rigidity and durability, with the high ionic conductivity of soft-matter electrolytes. Furthermore, PEs are associated with additional benefits such as flame resistance, absence of leakage or volatility, flexibility, thermal stability, and electrochemical stability, all of which have the potential to enable robust battery technologies. The need to establish PE-based SIBs is quite pressing due to safety concerns and the limitation of lithium resources. Herein, we present an extensive examination of Na PEs designed for use in both primary and secondary SBs. The emphasis is placed on solid, gel, and composite polymer electrolytes, which are characterized by specific compromises of advantages and disadvantages (see Figure 9). The comparison of the conductivity versus temperature of the SPE, GPE, and CPE systems reviewed in this paper are presented in Figure 10. Similar information with additional details is given in Tables 1–3.

Figure 9. Advantages and disadvantages of SPEs, GPEs, and CPEs.

Figure 10. Comparison of conductivity of the PEs reviewed in this article. The formulas of the top-performing PEs are indicated. Lists of these materials are given in Tables 1–3.
### Table 1. Comparison of SPEs in terms of conductivity.

<table>
<thead>
<tr>
<th>Year</th>
<th>SPE</th>
<th>Temp</th>
<th>Conductivity</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>PEO + NaPF₆</td>
<td>25 °C</td>
<td>$5 \times 10^{-5}$ S·cm⁻¹</td>
<td>[53]</td>
</tr>
<tr>
<td>1999</td>
<td>PEO + NaNO₃</td>
<td>29 °C</td>
<td>$2.83 \times 10^{-6}$ S·cm⁻¹</td>
<td>[54]</td>
</tr>
<tr>
<td>2001</td>
<td>PEO + NaClO₃ + PEG</td>
<td>105 °C</td>
<td>$9.47 \times 10^{-4}$ S·cm⁻¹</td>
<td>[55]</td>
</tr>
<tr>
<td>2005</td>
<td>PEO + NaNO₃</td>
<td>25 °C</td>
<td>$3.5 \times 10^{-6}$ S·cm⁻¹</td>
<td>[52]</td>
</tr>
<tr>
<td>2006</td>
<td>PEO + NaClO₃</td>
<td>-30 °C</td>
<td>$10^{-7}$ S·cm⁻¹</td>
<td>[56]</td>
</tr>
<tr>
<td>2006</td>
<td>PEO + NaFeF₆</td>
<td>25 °C</td>
<td>$1.37 \times 10^{-7}$ S·cm⁻¹</td>
<td>[57]</td>
</tr>
<tr>
<td>2006</td>
<td>PVC + NaClO₃</td>
<td>-</td>
<td>-</td>
<td>[71]</td>
</tr>
<tr>
<td>2006</td>
<td>PVA + NaBr</td>
<td>-</td>
<td>$1.12 \times 10^{-6}$ S·cm⁻¹</td>
<td>[74]</td>
</tr>
<tr>
<td>2007</td>
<td>PEO + NaLaF₃</td>
<td>25 °C</td>
<td>$3.9 \times 10^{-7}$ S·cm⁻¹</td>
<td>[58]</td>
</tr>
<tr>
<td>2007</td>
<td>(PEO)ₓNaPF₆ + PEG400</td>
<td>36 °C</td>
<td>$8.9 \times 10^{-7}$ S·cm⁻¹</td>
<td></td>
</tr>
<tr>
<td>2007</td>
<td>PVA + NaI</td>
<td>-</td>
<td>$1.02 \times 10^{-5}$ S·cm⁻¹</td>
<td>[73]</td>
</tr>
<tr>
<td>2012</td>
<td>PEO + NaF</td>
<td>-</td>
<td>$4.73 \times 10^{-7}$ S·cm⁻¹</td>
<td>[61]</td>
</tr>
<tr>
<td>2013</td>
<td>Potato starch + NaSCN</td>
<td>-</td>
<td>$1.12 \times 10^{-4}$ S·cm⁻¹</td>
<td>[44]</td>
</tr>
<tr>
<td>2014</td>
<td>HPMC + NaI</td>
<td>40 °C</td>
<td>$1.126 \times 10^{-4}$ S·cm⁻¹</td>
<td>[61]</td>
</tr>
<tr>
<td>2015</td>
<td>MC + NaI</td>
<td>60 °C</td>
<td>$2.7 \times 10^{-3}$ S·cm⁻¹</td>
<td>[82]</td>
</tr>
<tr>
<td>2015</td>
<td>BEMA/PEGMA + NaClO₄</td>
<td>20 °C</td>
<td>$5.1 \times 10^{-3}$ S·cm⁻¹</td>
<td>[13]</td>
</tr>
<tr>
<td>2015</td>
<td>MIP + RS + NaI</td>
<td>-</td>
<td>$1.20 \times 10^{-3}$ S·cm⁻¹</td>
<td>[77]</td>
</tr>
<tr>
<td>2016</td>
<td>PEO + sodium methylsulfate salt + BMIM-MS</td>
<td>75 °C</td>
<td>$4 \times 10^{-5}$ S·cm⁻¹</td>
<td>[85]</td>
</tr>
<tr>
<td>2017</td>
<td>PEO + NaPF₆</td>
<td>80 °C</td>
<td>$3.36 \times 10^{-4}$ S·cm⁻¹</td>
<td>[62]</td>
</tr>
<tr>
<td>2017</td>
<td>PEO + NaI</td>
<td>25 °C</td>
<td>$7.1 \times 10^{-5}$ S·cm⁻¹</td>
<td>[63]</td>
</tr>
<tr>
<td>2017</td>
<td>PVC + NaI</td>
<td>25 °C</td>
<td>$2.9 \times 10^{-8}$ S·cm⁻¹</td>
<td>[72]</td>
</tr>
<tr>
<td>2017</td>
<td>Tri(ethylene glycol) divinyl ether + LiBF₄</td>
<td>Ambient temperature</td>
<td>$1.2 \times 10^{-3}$ S·cm⁻¹</td>
<td>[86]</td>
</tr>
<tr>
<td>2017</td>
<td>Poly(bis(4-carboxyl benzene sulfonimidide-co-2,5-diamino benzenesulfonic acid) + NaPA</td>
<td>80 °C</td>
<td>$4.1 \times 10^{-4}$ S·cm⁻¹</td>
<td>[87]</td>
</tr>
<tr>
<td>2017</td>
<td>CS + NaCl</td>
<td>-</td>
<td>$1.72 \times 10^{-5}$ S·cm⁻¹</td>
<td>[78]</td>
</tr>
<tr>
<td>2018</td>
<td>PVA + NaNO₃ + PVP</td>
<td>25 °C</td>
<td>$1.25 \times 10^{-3}$ S·cm⁻¹</td>
<td>[75]</td>
</tr>
<tr>
<td>2018</td>
<td>Oligo(methyl methacrylate)-block-oligo(ethylene glycol) methyl ether methacrylate + H-β-CD + NaTFSI</td>
<td>60 °C</td>
<td>$1.3 \times 10^{-4}$ S·cm⁻¹</td>
<td>[88]</td>
</tr>
<tr>
<td>2019</td>
<td>PEO + NaPF₆</td>
<td>25 °C</td>
<td>$2 \times 10^{-5}$ S·cm⁻¹</td>
<td>[64]</td>
</tr>
<tr>
<td>2019</td>
<td>PEO + NaClO₄ + PVP</td>
<td>100 °C</td>
<td>$2.90 \times 10^{-4}$ S·cm⁻¹</td>
<td>[65]</td>
</tr>
<tr>
<td>2019</td>
<td>PVDF + NaPF₆</td>
<td>Ambient temperature</td>
<td>$1.08 \times 10^{-3}$ S·cm⁻¹</td>
<td>[89]</td>
</tr>
<tr>
<td>2019</td>
<td>(P(MVE-alt-MA)) + TEP/VC + NaClO₄</td>
<td>25 °C</td>
<td>$2.2 \times 10^{-5}$ S·cm⁻¹</td>
<td>[90]</td>
</tr>
<tr>
<td>2020</td>
<td>PEO + PEI + NaPF₆</td>
<td>100 °C</td>
<td>$5.2 \times 10^{-4}$ S·cm⁻¹</td>
<td>[66]</td>
</tr>
<tr>
<td>2020</td>
<td>PEO + NaPF₆ + succinonitrile</td>
<td>80 °C</td>
<td>$6.3 \times 10^{-4}$ S·cm⁻¹</td>
<td>[67]</td>
</tr>
<tr>
<td>2020</td>
<td>PEO + Na(TFSI-ethyl cellulose)</td>
<td>80 °C</td>
<td>$10^{-4}$ S·cm⁻¹</td>
<td>[68]</td>
</tr>
<tr>
<td>2020</td>
<td>CMC-Na + PVP</td>
<td>-</td>
<td>$1.81 \times 10^{-4}$ S·cm⁻¹</td>
<td>[83]</td>
</tr>
<tr>
<td>2020</td>
<td>CMC + NaBr</td>
<td>25 °C</td>
<td>$5.15 \times 10^{-4}$ S·cm⁻¹</td>
<td>[84]</td>
</tr>
<tr>
<td>2020</td>
<td>MC + NaI</td>
<td>-</td>
<td>$3.01 \times 10^{-3}$ S·cm⁻¹</td>
<td>[46]</td>
</tr>
<tr>
<td>2021</td>
<td>PVA + NaI + Glycerol</td>
<td>25 °C</td>
<td>$1.17 \times 10^{-3}$ S·cm⁻¹</td>
<td>[76]</td>
</tr>
<tr>
<td>2021</td>
<td>CS-NaHSO₄</td>
<td>25 °C</td>
<td>$2.22 \times 10^{-4}$ S·cm⁻¹</td>
<td>[79]</td>
</tr>
<tr>
<td>2021</td>
<td>Chitosan/Dextran + NaCF₃SO₃</td>
<td>25 °C</td>
<td>$6.10 \times 10^{-5}$ S·cm⁻¹</td>
<td>[80]</td>
</tr>
<tr>
<td>2021</td>
<td>TMT crosslinked with NaBFMB</td>
<td>30 °C</td>
<td>$2 \times 10^{-3}$ S·cm⁻¹</td>
<td>[91]</td>
</tr>
<tr>
<td>2022</td>
<td>PEO + NaFSI + Pyrr₃FSI</td>
<td>25 °C</td>
<td>$1 \times 10^{-3}$ S·cm⁻¹</td>
<td>[69]</td>
</tr>
<tr>
<td>2022</td>
<td>PEO + NaCl</td>
<td>25 °C</td>
<td>$4.5 \times 10^{-4}$ S·cm⁻¹</td>
<td>[70]</td>
</tr>
<tr>
<td>2022</td>
<td>PVDF + NaTFSI + NaDFOB</td>
<td>23 °C</td>
<td>$3.1 \times 10^{-4}$ S·cm⁻¹</td>
<td>[92]</td>
</tr>
<tr>
<td>2023</td>
<td>PEO + NaClO₄ + NaCF₃SO₃</td>
<td>90 °C</td>
<td>$10^{-3}$ S·cm⁻¹</td>
<td>[93]</td>
</tr>
<tr>
<td>2023</td>
<td>PEO + PNaMTFSI</td>
<td>85 °C</td>
<td>$7.74 \times 10^{-5}$ S·cm⁻¹</td>
<td>[94]</td>
</tr>
</tbody>
</table>
Table 2. Comparison of GPEs in terms of conductivity.

<table>
<thead>
<tr>
<th>Year</th>
<th>GPE</th>
<th>Temp Conductivity</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1981, 2021</td>
<td>PVDF-HFP/PMMA-</td>
<td>-</td>
<td>[136,137]</td>
</tr>
<tr>
<td>2013</td>
<td>β-Na135Sc2P2Si6O12</td>
<td>Ambient temperature</td>
<td>Above 10⁻⁴ S cm⁻¹</td>
</tr>
<tr>
<td>2018</td>
<td>PVDF-HFP + NaClO₄ + PC</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2019</td>
<td>PVDF-HFP + NaCF</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2020</td>
<td>PVDF-HFP + NaCF</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2021</td>
<td>PVDF-HFP + NaClO₄ + PC</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2022</td>
<td>PVDF-HFP + NaClO₄ + PC</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2023</td>
<td>PVDF-HFP + NaClO₄ + PC</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2024</td>
<td>PVDF-HFP + NaClO₄ + PC</td>
<td>25 °C</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. Comparison of CPEs in terms of conductivity.

<table>
<thead>
<tr>
<th>Year</th>
<th>CPE</th>
<th>Temp Conductivity</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>P(VDF-HFP) + NaSCN + BMIMBF₄</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2014</td>
<td>PEO + NaTFSI + SiO₂</td>
<td>&gt;75 °C</td>
<td></td>
</tr>
<tr>
<td>2015</td>
<td>PEO + NaClO₄ + TiO₂</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2016</td>
<td>PEO + NaClO₄ + BaTiO₃</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2017</td>
<td>PEO + NaTFSI + NASICON</td>
<td>80 °C</td>
<td></td>
</tr>
<tr>
<td>2018</td>
<td>PMMA/PEG + NaClO₄ + Al₂O₃</td>
<td>70 °C</td>
<td></td>
</tr>
<tr>
<td>2019</td>
<td>PEO + NaClO₄ + Na₂Zr₅Si₄PO₁₂</td>
<td>60 °C</td>
<td></td>
</tr>
<tr>
<td>2020</td>
<td>PVDF-HFP + NaPF₆ + TiO₂</td>
<td>25 °C</td>
<td></td>
</tr>
<tr>
<td>2021</td>
<td>PEGMA + NaTFSI + TEGOME</td>
<td>40 °C</td>
<td></td>
</tr>
<tr>
<td>2022</td>
<td>PEO + NaClO₄ + NaAlO₂</td>
<td>25 °C</td>
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<tr>
<td>2023</td>
<td>PEO + NaClO₄ + β-Al₂O₃</td>
<td>60 °C</td>
<td></td>
</tr>
<tr>
<td>2024</td>
<td>PEO + NaTFSI + KNN-Na₂Zr₅Si₄PO₁₂</td>
<td>Ambient temperature</td>
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SPEs are based on the solvent-aided or solvent-free dissolution of salts into polymer hosts. Na ion-conducting SPEs have been proposed since the beginning of this area of research. The preferred polymers have been PEO, PEG, PEI, PMMA, PVP, PVC, PVA, RS, MC, HPMC, CMC, PVDF, PVDF-HFP, and P(MVE-alt-MA). Salts have included sodium halides, NaF, NaCl, NaBr, NaI, NaNO₃, NaSCN, NaPF₆, NaBF₄, NaClO₃, NaClO₄, NaPO₃, NaTf, NaFSI, NaTFSI, NaFNFSI, NaFeF₄, NaLaF₄, NaBF₄, and NaDFOB. These systems do not present very high conductivities in comparison to organic liquid electrolytes, but they do exhibit a wide electrochemical window, higher chemical and thermal stabilities, and reduced flammability. Additionally, they are conducive to a simplified battery design. Modifications of SPEs with ILs yielding PILE systems and photocrosslinking of the anions with the polymer host have been explored. The improvement of the ionic conductivity of SPEs has been relying on the control of salts and polymer matrices. However, understanding the characteristics of electrode/electrolyte interfaces, especially the SPE/sodium electrode interface that critically influences overall cell performance, cannot be straightforwardly predicted solely based on the molecular structure and interactions of the electrolyte components. Comprehensive investigations involving both experimental and computational approaches are essential to unravel these aspects.

GPEs provide higher ionic conductivities, approaching those of organic liquid electrolytes. However, challenges persist related to the leakage and volatilization of the incorporated liquid solvent, which can negatively impact the durability of these materials. Polymer networks have been synthesized using PVB, PAN, PMMA, PVC, PVDF, PVDF-HFP, P(AN-co-MA), PPEGMA, vinyl acetate, perfluoro(3-methyl-3,6-dioxy-8-fluoride sulfonyl-1-octene), polyacrolactone triacrylate, cross-linked polyethers, and PTVE. The organic liquids used have included EC, PC, PPC, PG, DEC, FEC, DMF, 1-(4-cyanophenyl)-guanidine, and dicinnamylidene hexanediamine. ILs such as EMMImTf, BMImTFSI, and solvate ionic liquids such as [Na-(glyme)]ClO₄ have been considered as additives. The salts that have been employed have included NaI, NaClO₄, NaPF₆, NaTf, NaTFSI, and NaPTAB. The addition of Na-containing or non-Na-containing inorganic fillers such as SiO₂, TiO₂, SnO₂, Al₂O₃, AlO(OH)ₙ, Na-β-Al₂O₃, NASICON (i.e., Na₃ₓ₋ₓSc₂P₃₋ₓSiₓO₁₂ with x = 0, 0.5, and 1.0), Na₂Zn₂TeO₆, NaAlO₂, and Ti₅C₃T₈ MXenes have resulted in viable CGPE materials. The use of a small percentage of GO proved to be beneficial to the preparation of a CGPE. Stabilization using a glass fiber was also an interesting strategy that was employed. The use of the flame retardants TMP and TEP imparted improved thermal stability. Epichlorohydrin with titanium/silicon alkoxyl compounds was used to synthesize hybrid inorganic organic CGPEs early on in this field. Despite significant advancements in gel polymer SIBs, practical applications still face challenges. The long-term cycle life of assembled half-cells is a crucial criterion for evaluating commercial battery performance. Currently, only a limited number of GPE-based SIBs exhibit a lifespan exceeding 1000 cycles, particularly with hard carbon and other anode materials. Additionally, achieving synergy between electrolytes and electrode materials is crucial for commercialization. This involves optimizing storage capacity and working voltage, matching suitable GPEs, and enhancing the stability and consistent application of the entire battery system. The integration of GPEs with environmentally friendly electrodes holds promise for advanced applications in various fields.

CPEs consist of PEs stabilized by inorganic fillers. The polymers that have been investigated include PEO, PEG, PVDF-HFP, PMMA, and PVA. The fillers were chosen among SiO₂, TiO₂, Al₂O₃, NaAlO₂, Na₃SiO₃, NASICON (i.e., Na₃₋ₓZr₂Si₃₋ₓO₁₂, 0 ≤ x ≤ 3), BaTiO₃, Na₃Zr₂Si₂PO₁₂, and ZnFe₂O₄. Boron-based CPEs were also studied. The salts included NaI, NaNO₃, NaPF₆, NaFSI, NaTf, NaTFSI, NaClO₄, and NaSCN. Engineering approaches have focused on the use of glass fibers for the mechanical stabilization of CPEs, the introduction of ferroelectrics to modulate the electrolyte–electrode interface, and the use of the IL BMIMBF₄ for electrospinning. Despite achieving desired Na ion conductivity, electrochemical properties, mechanical strength, and a well-established electrode–electrolyte contact in composite electrolytes, challenges persist in transitioning from the lab to industry.
Scientists grapple with the practical application of CPEs in SIBs, asking for new paradigms and efforts to bridge the experimental–commercial gap. Key challenges include addressing low ionic conductivity to meet the performance of highly conductive liquid electrolytes. Exploration of novel polymer materials and fillers with high ionic conductivities is essential. Tuning host polymers for CPEs using rational engineering techniques to enhance ionic conductivity and employing functionalization recipes like copolymerization, cross-linking, and grafting are crucial. Cost minimization is vital for large-scale SIB manufacturing, urging accelerated use of low-cost materials, bio-inspired polymers, and sustainable precursors. Additionally, designing innovative electrolyte systems is essential for constructing flexible, transparent, and electrochromic SIBs.

The best performance of Na batteries was measured using GPEs and CPEs as electrolytes. The best capacity was based on NGPEs in a Na-Hg/P-C cell. The open circuit voltage was 2.5 V, and the first discharge capacity was 400 mAh·g⁻¹. The best capacity based on CPEs was measured for a sodium/PVC-CPE/c-NFM battery at 104.2 mAh·g⁻¹. Therefore, GPE-based batteries appear to be the most significant in terms of practical applications.

It is expected that future research will extend to the study of tensile strength, shear strength, and elongation in the entire operational temperature range and not just under ambient conditions. More research is needed on PE to avoid or reduce dendrite formation. A clearer understanding is required concerning the underlying dynamics of dendrite formation. Studies focused on improving the interfacial layer between PEs and electrodes and methods for enhancing interfacial contact are highly desirable. Furthermore, additional exploration of hybrid inorganic–organic PEs may reveal new pathways for higher performance Na ion-conducting systems.

Taken together, increasing the ionic conductivity in Na ion-conducting SPEs, GPEs, and CPEs seems to have become an asymptotic process with an obvious ceiling. Optimization of these materials in isolation is not sufficient. The synthesis and characterization of PEs need to be understood and carried out in relation to the other specific components of fully assembled SIB systems. Applying high-throughput screening analysis techniques to extensive sets of electrolyte formulations, coupled with a combination of theoretical, electrochemical, and spectroscopic methods, can significantly accelerate the exploration and optimization process. There is a pressing need for a systematic approach to design electrolytes for future SIBs.

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Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AC</td>
<td>Activated charcoal</td>
</tr>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AGPE</td>
<td>Amorphous gel polymer electrolyte</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminum oxide</td>
</tr>
<tr>
<td>ASIB</td>
<td>Aqueous sodium ion battery</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>Barium titanate</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer–Emmett–Teller</td>
</tr>
<tr>
<td>BMIMBF$_4$</td>
<td>1-<em>butyl</em>-3-methylimidazolium tetrafluoroborate</td>
</tr>
<tr>
<td>BMIM-MS</td>
<td>1-<em>butyl</em>-3-methylimidazolium methylsulfate</td>
</tr>
<tr>
<td>CFEM</td>
<td>Composite nanofibrous electrolyte membranes</td>
</tr>
<tr>
<td>CMC</td>
<td>Carboxy methylcellulose</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CPE</td>
<td>Composite polymer electrolyte</td>
</tr>
<tr>
<td>CPN</td>
<td>Crosslinked polyether network</td>
</tr>
<tr>
<td>CS</td>
<td>Cornstarch</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>DEC</td>
<td>Diethyl carbonate</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMF</td>
<td>Dimethyl formamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethylsulfoxide</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye-sensitized solar cells</td>
</tr>
<tr>
<td>EC</td>
<td>Ethylene carbonate</td>
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<tr>
<td>EDLC</td>
<td>Electric double-layer capacitor</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive spectroscopy</td>
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<tr>
<td>EES</td>
<td>Electrochemical energy storage</td>
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<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ESW</td>
<td>Electrochemical stability window</td>
</tr>
<tr>
<td>Fe(NO$_3$)$_3$</td>
<td>Ferric nitrate</td>
</tr>
<tr>
<td>FEC</td>
<td>Fluoroethylenecarbonate</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform–infrared spectroscopy</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluoride/tin oxide</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>GPC</td>
<td>Gel permeation chromatography</td>
</tr>
<tr>
<td>GPE</td>
<td>Gel polymer electrolyte</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HPMC</td>
<td>Hydroxypropyl methylcellulose</td>
</tr>
<tr>
<td>HSCR</td>
<td>Hydrothermal soft chemical reaction</td>
</tr>
<tr>
<td>H-$\beta$-CD</td>
<td>Hyperbranched $\beta$-cyclodextrin</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>kΩ</td>
<td>Kiloohms</td>
</tr>
<tr>
<td>La(NO$_3$)$_3$</td>
<td>Lathanum nitrate</td>
</tr>
<tr>
<td>LE</td>
<td>Liquid electrolyte</td>
</tr>
<tr>
<td>LIB</td>
<td>Lithium ion battery</td>
</tr>
<tr>
<td>LSV</td>
<td>Linear sweep voltammetry</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MC</td>
<td>Methylcellulose</td>
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<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>MPII</td>
<td>1-methyl-3-propylimidazolium iodide</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NaAlO$_2$</td>
<td>Sodium aluminate</td>
</tr>
<tr>
<td>NaBFMB</td>
<td>Bis(fluoroallyl)malonato borate salt</td>
</tr>
<tr>
<td>NaBr</td>
<td>Sodium bromide</td>
</tr>
<tr>
<td>NaCF$_3$SO$_3$</td>
<td>Sodium trifluoromethanesulfonate</td>
</tr>
<tr>
<td>NaClO$_3$</td>
<td>Sodium chlorate</td>
</tr>
<tr>
<td>Code</td>
<td>Description</td>
</tr>
<tr>
<td>----------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>NaDFOB</td>
<td>Sodium-difluoro(oxalato)borate</td>
</tr>
<tr>
<td>NaF</td>
<td>Sodium fluoride</td>
</tr>
<tr>
<td>NaHSO₃</td>
<td>Sodium hydrogen sulfite</td>
</tr>
<tr>
<td>NaI</td>
<td>Sodium iodide</td>
</tr>
<tr>
<td>NaNO₃</td>
<td>Sodium nitrate</td>
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<tr>
<td>NaPA</td>
<td>Poly(bis(4-carbonyl benzene sulfonyl)imide-co-2,5-diamino benzesulfonic acid)</td>
</tr>
<tr>
<td>NaPF₂</td>
<td>Sodium difluorophosphate</td>
</tr>
<tr>
<td>NaPF₆</td>
<td>Sodium hexafluorophosphate</td>
</tr>
<tr>
<td>NaPTAB</td>
<td>Sodium-poly(tartaric acid)borate</td>
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<tr>
<td>NaSCN</td>
<td>Sodium thiocyanate</td>
</tr>
<tr>
<td>NaTFSI</td>
<td>Sodium trifluoromethanesulfonimide</td>
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<tr>
<td>NGPE</td>
<td>Nanocomposite gel polymer electrolytes</td>
</tr>
<tr>
<td>NIPS</td>
<td>Non-solvent-induced phase separation</td>
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<td>NMR</td>
<td>Nuclear magnetic resonance</td>
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<tr>
<td>ORB</td>
<td>Organic radical battery</td>
</tr>
<tr>
<td>P(MVE-alt-MA)</td>
<td>Poly(methyl vinyl ether-alt-maleic anhydride)</td>
</tr>
<tr>
<td>PAN</td>
<td>Poly(acrylonitrile)</td>
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<tr>
<td>PANI</td>
<td>Polyaniline</td>
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<tr>
<td>PC</td>
<td>Propylene carbonate</td>
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<tr>
<td>PCPE</td>
<td>Plasticizer composite polymer electrolyte</td>
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<tr>
<td>PDA</td>
<td>Polydopamine-plasticized polynye</td>
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<td>PE</td>
<td>Polymer electrolyte</td>
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<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
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<tr>
<td>PEGMA</td>
<td>Poly(ethylene glycol) methyl ether methacrylate</td>
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<tr>
<td>PEM</td>
<td>Proton exchange membrane</td>
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<tr>
<td>PEO</td>
<td>Poly(ethylene) oxide</td>
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<td>PFSAs</td>
<td>Perfluorosulfonic acid</td>
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<td>PILEs</td>
<td>Polymer ionic liquid electrolytes</td>
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<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<td>PPEGMA</td>
<td>Poly(poly(ethylineglycol)methacrylate)</td>
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<tr>
<td>PTVE</td>
<td>2,2,6,6-tetramethyypiperidine-4-y1-1-oxyl vinyl ether</td>
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<tr>
<td>PVA</td>
<td>Poly(vinyl alcohol)</td>
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<td>PVB</td>
<td>Poly(vinyl butyral)</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl chloride)</td>
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<tr>
<td>PVDf</td>
<td>Poly(vinylidene fluoride)</td>
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<tr>
<td>PVDf-HFP</td>
<td>Poly(vinylidene fluoride hexafluoro propylene)</td>
</tr>
<tr>
<td>PVP</td>
<td>Poly(vinyl pyrolidone)</td>
</tr>
<tr>
<td>RT</td>
<td>Room temperature</td>
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<tr>
<td>RTIL</td>
<td>Room-temperature ionic liquid</td>
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<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
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<td>SIB</td>
<td>Sodium ion battery</td>
</tr>
<tr>
<td>SEI</td>
<td>Solid electrolyte interphase</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SGPE</td>
<td>Separator-cum gel polymer electrolyte</td>
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<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
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<td>SIC</td>
<td>Single ion-conducting</td>
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<tr>
<td>SIL</td>
<td>Solvate ionic liquid</td>
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<td>SMB</td>
<td>Sodium metal battery</td>
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<td>SPE</td>
<td>Solid polymer electrolyte</td>
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<td>TEP</td>
<td>Triethyl phosphate</td>
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<tr>
<td>TGA</td>
<td>Thermogravimetric analyzer</td>
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<tr>
<td>TG-DTA</td>
<td>Thermogravimetric differential thermal analysis</td>
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<tr>
<td>TiO₂</td>
<td>Titanium dioxide</td>
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