A Review: Polymer Blend Electrolyte Systems as a Promising Alternative for Improving Ionic Conductivity

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This review explores the principles, materials, highlights and challenges related to Polymer Blend Electrolytes (PBEs). The fundamentals of miscible and immiscible polymer blends (PBs) are discussed, along with how to foresee blend compatibility using thermodynamic models such as the Gibbs free energy theory. Measurement approaches for understanding ionic transport phenomena in PBEs are also considered, including the Arrhenius and Vogel Tamman Fulcher (VTF) models, to ascertain the effects of factors including morphology and intermolecular impacts on the ionic conductivity of blends. PBEs have good potential to fulfil various functional requirements in fuel cells, batteries, supercapacitors, and other applications. Further research and development efforts focused on enhancing blend composition and resolving technical difficulties would result in more efficient and sustainable energy storage innovations.

Keywords: Polymer blend electrolyte; energy storage; Gibb's free energy; Flory-Huggins theory; Ionic conductivity

Polymer blend electrolyte (PBE) systems have gained significant attention in recent years for their potential use in various applications such as fuel cells, batteries and supercapacitors [1]. Researchers have explored the use of polymer blends as an electrolyte material to achieve high conductivity, biocompatibility and stability in battery applications [2]. However, most battery systems still contain hazardous components that may result in undesired pollution [3]. To overcome this issue, various methods have been employed to address environmental issues associated with traditional battery technology such as blending different polymers, introducing nanofillers, and using binary salt systems [4]. Nevertheless, choosing biodegradable materials stands out as a favourable option because these can naturally decompose over time through biological processes, thus reducing the potential environmental impact associated with battery disposal and waste management [5].
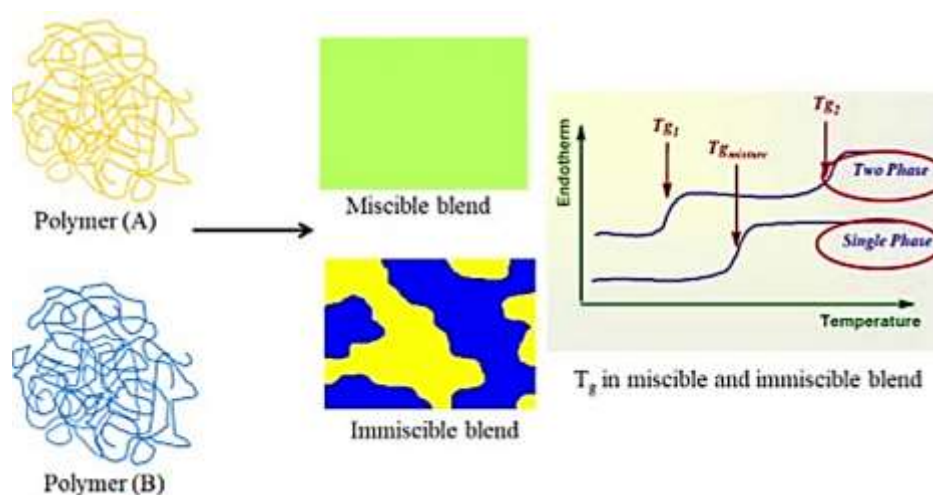

Figure 1. The glass transition temperature (T_g) of different polymer blends as shown in their DSC thermograms [10].

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A polymer blend is a combination of at least two different polymers that do not have strong chemical bonds between them. Polymer blends have emerged as a viable solution to achieve the desired properties of new polymeric materials [4]. The first systematic study on polymer blends was carried out by Parkes in 1846, in which natural rubber (NR) and gutta-percha (GP) were blended in the presence of carbon disulfide (CS_2). The resulting blend was partially crosslinked, or co-vulcanized, and its rigidity was controlled by varying the composition of the blend [6]. Valdes et al. (2013) stated that polymer blends have found extensive use in numerous industries such as food packaging, electrical and electronic materials, as well as drug delivery systems [7-8]. Figure 1 shows the classification of polymer blends based on Differential Scanning Calorimetry (DSC) results [9].

Polymer electrolytes come in various forms, each with unique properties derived from both synthetic and natural sources. They can be found in solid, gel, composite and plasticized forms, and the materials used greatly affect how they behave in electrochemical systems as shown in Figure 2 [7], [11]. Peter Wright was the first to use poly(ethylene oxide) (PEO) as the polymer host to create a dry solid polymer electrolyte in the 1970s. When inorganic salts are mixed into a polymer mixture, a network structure is formed and this allows movement of ions, thus improving the ionic conductivity of the system. Compared to single-polymer electrolytes, these offer superior thermal stability, mechanical strength and increased ionic conductivity, all of which are critical for optimising the performance of electrochemical

devices. Numerous researchers have contributed to the progress of battery technology through the use of PBEs, which offer distinct functional characteristics [4, 12-14].

1.0.   Overview of Polymer Blends and Polymer Blend Electrolyte Systems

Polymer blends are categorized as either immiscible or miscible and have a broad range of applications and properties, particularly for electrochemical devices such as batteries, supercapacitors and sensors. Careful studies on these blends enable a thorough understanding of how different polymers interact at the molecular level, thus identifying the overall blend that could optimize the overall performance of these devices. These blends can be explored using measuring approaches such as the Gibbs free energy theory and Flory-Huggins theory. The evolution from polymer blends to polymer-based electrolytes improves the system by creating miscible polymeric electrolytes containing additional elements such as salt, ionic liquids, etc., for improved ionic conductivity [4, 15]. When creating PBEs, a combination of polymers with strong ion mechanisms and great mechanical properties is chosen. PBEs are widely used in many different applications and energy storage systems. Arrhenius and VTF models are two examples of measurement models used to gain a better understanding of ion transport in PBEs. The VTF model describes the behaviour of materials around their glass transition temperatures, thus gaining further insights into the functionality of the PBE. Meanwhile, the Arrhenius model is mostly employed in chemical kinetics and ionic conductivity [16-19].
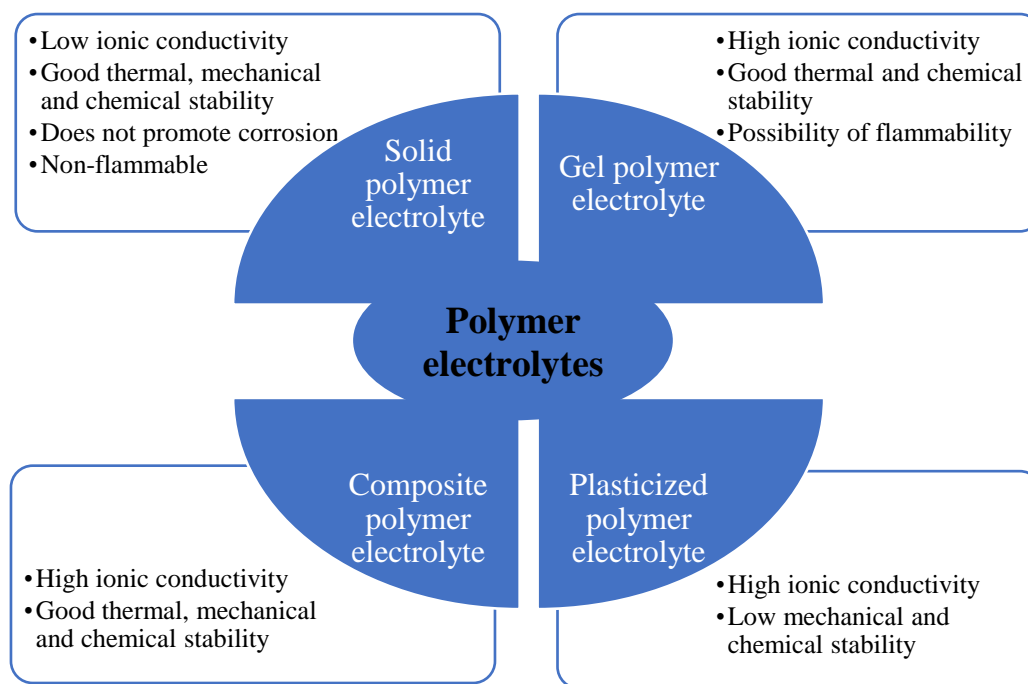

Figure 2. Classification of polymer electrolytes with their corresponding characteristics.

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Table 1. Division of polymer blends [8].

Division of polymer blends	Characteristics
Miscible	• A homogenous blend. • Forms a single-phase blend. • One T_g observed
Immiscible	• A heterogenous blend. • Forms a two-phase blend. • Two T_g observed

T_g = Glass transition temperature.

1.1. Principles of Polymer Blend Systems: Measurement Approaches

Polymer blending is simply a modification process involving at least two different polymers to create a new polymeric material with different physical properties. Through this method, the functionality of the material is improved, potentially making it usable for a variety of applications [20]. Polymer blends can be categorized as shown in Table 1.

The fundamental thermodynamics that determine whether two components are compatible are represented by the Gibbs free energy theory. This theory determines whether components have a tendency to mix evenly (homogeneous blends) or to separate into different phases (heterogeneous blends) [21, 22]. A miscible polymer blend is called a homogeneous blend when different polymers form a single-phase solution when mixed. These blends are said to be thermodynamically stable and have a negative free energy of mixing (ΔGm <0) [6, 23]. Miscible polymer blends have a negative enthalpy change (ΔHm <0) because the reaction system is exothermic and releases heat during the blending process to break down the intermolecular interactions between molecules [24, 25]. Usually, the excess energy in this system is used to arrange the polymer molecules in various ways, which raises the entropy (ΔSm >0) of the surroundings and forms a single-phase solution [26]. In the case of a disordered system, more molecules entangle themselves in chains, which causes the system to become more disordered and lowers the free mixing value [8]. According to the Gibb's free energy equation:

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

where:
ΔG_m is the free energy of mixing
ΔH_m is the enthalpy/heat of mixing
T is the temperature
ΔS_m is the entropy of mixing

Comparatively, immiscible polymer blends are referred to as heterogeneous blends, where different polymers create a two-phase solution when mixed. According to previous studies [8, 27], these mixtures are not thermodynamically stable and have a positive free energy of mixing (ΔG_m >0). As opposed to miscible polymer blends, immiscible polymer blends have a positive enthalpy change (ΔH_m >0) because the reaction system is endothermic and absorbs heat during the blending process to break down the intermolecular interactions between molecules [24-25]. However, the energy needed to separate the molecules in these blends is insufficient and this leads to a higher free mixing value and a decrease in system disorder; hence, a two-phase solution is formed [6, 16, 25].

Experimental methods such as differential scanning calorimetry (DSC) can be used to understand how composition affects the glass transition temperature (T_g), and predict blend compatibility in polymer blends. T_g can be used as a simple way to determine whether a polymer combination is miscible or immiscible. A single T_g is seen in miscible blends, indicating that the various polymers have been mixed uniformly. Conversely, immiscible blends show two different T_g values, indicating the existence of different phases. Blend compatibility can be quantitatively predicted using an empirical equation (2) to predict the correlation between T_g and different blend compositions [21].

$$\ln\left(\frac{T_{g12}}{T_{g1}}\right) = \beta\left(1 - \gamma spe\,\ln\left(\frac{z-1}{e}\right)\right)\left(\frac{\emptyset_1}{r_1}\ln\emptyset_1 + \frac{\emptyset_2}{r_2}\ln\emptyset_2\right) + \emptyset_2\ln\left(\frac{T_{g2}}{T_{g1}}\right) \qquad (2)$$

where;
T_{g1} is the T_g of the pure polymer 1
T_{g12} is the T_g of the blend of polymers 1 and 2
$\emptyset_1$ and $\emptyset_2$ are the volume fractions of component 1 and component 2
Z is the lattice coordination number
γ_{spe} is a proportionality constant representing the specific interaction
$\beta = zR / (M_{1u}\,\Delta C_{pp})$. RM_{1u} of polymer 1

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Table 2. Simplified explanation of miscible blends and immiscible blends as they relate to the Gibb's free energy equation [6, 16, 25].

Elements	Miscible	Immiscible
Free energy of mixing, ΔG_m	Negative: thermodynamically stable, indicating complete mixing	Positive: not thermodynamically stable, indicating incomplete mixing
Enthalpy, ΔH_m	Exothermic: energy is released during the blending process	Endothermic: energy is absorbed during the blending process
Entropy, ΔS_m	Higher entropy of mixing: there is <u>sufficient energy</u> to	Lower entropy of mixing: there is <u>insufficient energy</u> to
	▪ break down intermolecular forces between molecules ▪ arrange the molecules in various ways	
Temperature, T	Can occur at both low and high temperatures	

While both Gibbs energy and the Flory-Huggins theory are concepts used in the study of phase equilibria, they operate at different levels of complexity and are applied to different types of systems. Further insights into the entropy and enthalpy of mixing can be derived through the Flory-Huggins theory, which is based on the mean-field lattice model. In Figure 3, a representation of macromolecules (like polymers) is shown within this lattice framework. This model simplifies the examination of polymer behaviour by portraying the polymer chain as a series of interconnected beads on a lattice grid. Each lattice site is associated with a specific volume, resembling a grid layout. The bonds between neighbouring beads illustrate the lattice's connectivity. In the context of binary mixtures of polymer chains, A and B have distinct segment counts (N_A and N_B) [28]. A homogeneous mixture of binary polymers can be described by the Flory-Huggins equation (3):

$$v \frac{\Delta G_m}{k_B T} = \emptyset_{polymer} \left(\frac{\emptyset_A In \emptyset_A}{N_A} + \frac{\emptyset_B In \emptyset_B}{N_B} + \chi \emptyset_A \emptyset_B \right) \quad (3)$$

where:
v is the reference volume (nm^3)
ΔG_m is the free energy of mixing per unit volume
K_B is the Boltzmann constant
T is the absolute temperature (K)
N_i is the number of repeating units in chain A or chain B
$\emptyset_{polymer}$ is the total polymer volume fraction
$\emptyset_i$ is the salt-free polymer volume fraction of chain A or chain B
χ is the Flory-Huggins interaction parameter which is expressed by:

$$\chi = z \left[\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})/2 \right]/k_B T \quad (4)$$

where:
z is the coordination number of the species
ε_{ij} is the interaction energy between species A and B
(jj = AA or BB)
K_B is the Boltzmann constant
T is the absolute temperature (K)

The value of ΔF greatly depends on the value of the χ parameter. Equation (4) describes the phase behaviour of a polymer-polymer or polymer-solvent system. It represents the energetic contribution to the free energy of mixing in a polymer mixture. A positive value of χ indicates a favourable interaction, while a negative value denotes an unfavourable interaction resulting in phase separation or immiscibility [28].

The challenges associated with Gibbs free energy in polymer blends include the complexity of determining the Gibbs energy of mixing quantitatively and qualitatively, as it involves considering both the enthalpy of mixing and the entropy factor. Certain interactions between blend components, like hydrogen bonding, dipole-dipole interactions, and ionic interactions, can change the enthalpy of mixing, which is the amount of heat that is used up or created during mixing. Understanding and quantifying these interactions can be challenging and may impact the miscibility of polymer blends. An important factor in figuring out miscibility is entropy, which measures how chaotic or random the system is. This is especially true for polymer solutions with monomers that have high molecular weights. Balancing the enthalpy and entropy contributions to the Gibbs energy of mixing can be complex, and requires a thorough understanding of molecular interactions in polymer blends.
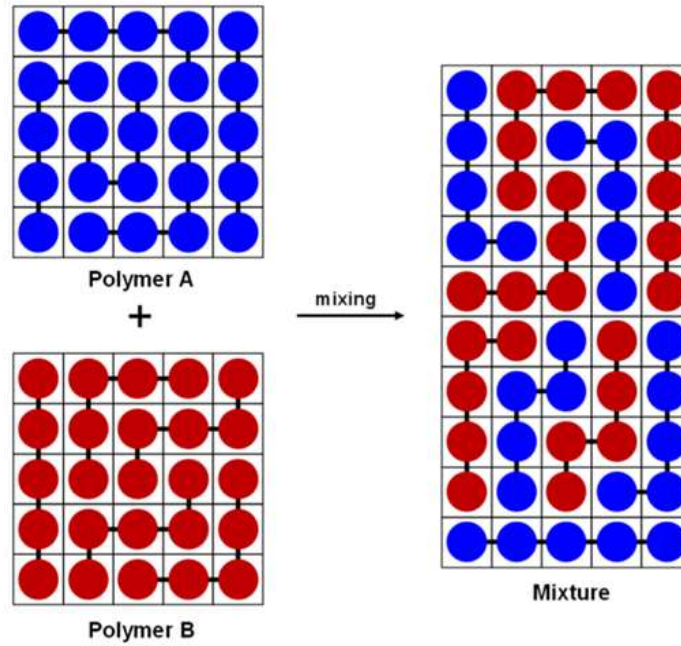
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Figure 3. A lattice chain model representing a mixture of polymers A and B.

Moreover, the Flory-Huggins theory, which is commonly used to describe the thermodynamics of polymer blending, has limitations in accurately predicting phase behaviour in complex polymer systems. The high viscosity of macromolecular species in polymer blends hinders the mobility of molecules, leading to slow diffusion towards equilibrium. This sluggish diffusion can impede the establishment of thermodynamic equilibrium, making it difficult to accurately determine phase behaviour. The theory is based on the idea that mixing should work perfectly, but it does not take into account how certain interactions between polymer chains can change the way real polymer blends behave. Incorporating more realistic molecular interactions and non-ideal mixing effects into the Flory-Huggins theory is difficult, which poses a challenge in accurately predicting phase separation and morphology in polymer blends. Overall, the challenges associated with using Gibbs free energy and the Flory-Huggins theory for polymer blends highlight the complexity of understanding and predicting the thermodynamics

and phase behaviour of these systems, particularly with specific interactions and non-ideal mixing effects [16, 25].

1.2. Principles of Polymer Blend Electrolyte Systems: Measurement Approaches

PBEs are a flexible family of materials having two or more polymers that produce synergistic capabilities for ion conduction. As the medium for ion movement between electrodes, these electrolytes are essential to many electrochemical devices such as fuel cells, lithium-ion batteries and electrochemical capacitors. Analysing the compatibility of blend components in PBEs can help predict and address prevalent challenges such as phase separation, chemical incompatibility, and deterioration. This ensures the long-term reliability and performance of these electrochemical devices [7, 11]. The extended equation 5 is used for a blended system containing salts:

$$v\frac{\Delta G_m}{k_B T} = \emptyset_{polymer}\left(\frac{\emptyset_A ln\emptyset_A}{N_A} + \frac{\emptyset_B ln\emptyset_B}{N_B} + \chi_{eff}\emptyset_A\emptyset_B\right) \tag{5}$$

where:

v is the reference volume (nm^3)

ΔG_m is the free energy of mixing per unit volume

K_B is the Boltzmann constant

T is the absolute temperature (K)

N_i is the number of repeating units in chain A or chain B

$\emptyset_{polymer}$ is the total polymer volume fraction

$\emptyset_i$ is the salt-free polymer volume fraction of chain A or chain B
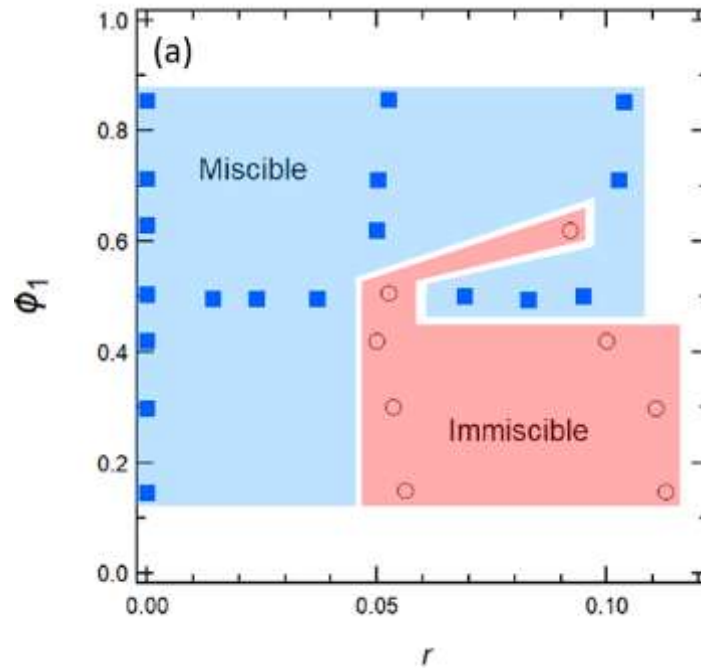
Figure 4. PEO/PMMA/LiTFSI blend electrolytes with a salt-free volume fraction of PEO (ϕ_1) as a function of salt concentration (r) [29].
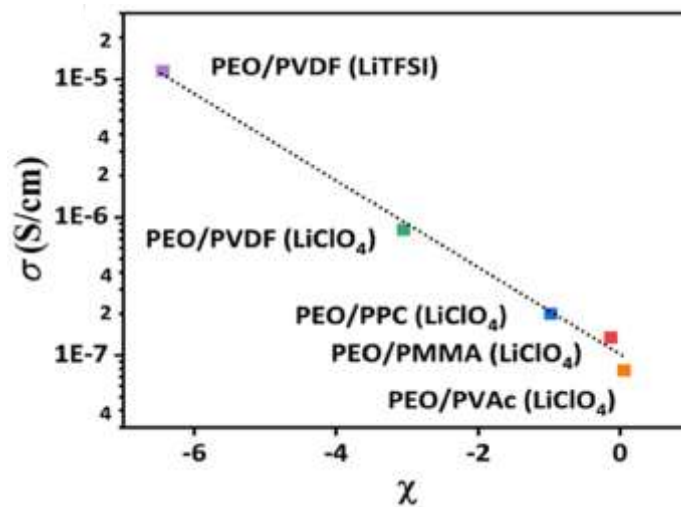

Figure 5. Ionic conductivities of polymer blends against the interaction parameter, χ [30].

In a recent study conducted in June 2023 [29], Shah et al. used the extended Flory-Huggins theory to observe the phase behaviour of poly (ethylene oxide), poly(methyl methacrylate) and lithium bis (trifluoromethane) sulfonimide (PEO/ PMMA/LiTFSI) blend electrolytes across varying salt concentrations (r) and PEO concentrations. The study revealed that in the absence of salt, χ consistently exhibited negative values, indicating homogeneous mixtures, regardless of PEO concentration. When salt was added, PEO/PMMA blends with lower PEO concentrations showed positive χ_{eff} values, which implies there were areas where the two materials could not mix. Meanwhile, blends with higher PEO concentrations displayed negative χ_{eff} values, suggesting a miscible region. The introduction of salt-induced modifications to the phase diagram resulted in a chimney-like pattern with a narrow immiscible region extending into the previously miscible area, as shown in Figure 4. The presence of filled blue squares denotes a blend that is miscible, whereas the circles represent a blend that is immiscible [29].

In July 2023, Mei et al. looked into how to improve the conductivity of ions in PBEs for solid lithium batteries by tuning the macrodynamics and interfaces. In this work, the researchers decided to only use the χ parameter due to the specific characteristics of the system under study and the simplicity of the model in capturing the blend behaviour. The χ parameter revealed the thermodynamic interaction between the components, which was directly linked to the ionic conductivity of the PBEs. The slope of the curves in Figure 5 show that χ-poly(ethylene oxide)/poly(vinylidene fluoride) (χPEO/PVDF) was lower than that of χ-poly(ethylene oxide)/poly(propylene carbonate) (χPEO/PPC), followed by χ-poly(ethylene oxide)/poly(methyl methacrylate) (χPEO/PMMA), and finally χ-poly(ethylene oxide)/poly(vinyl acetate) (χPEO/ PVAc) (note that a lower χ suggests a stronger interaction). Therefore, PEO/PVDF had the highest ionic conductivity of 1.4×10^{-4} S/cm compared to other blend electrolytes [30].

Gao et al. (2020) employed the extended Flory-Huggins theory to investigate the compatibility of poly(ethylene oxide)/poly(1,3,6-trioxocane)/lithium bis(trifluoromethane)sulfonimide (PEO/P(2EO-MO)/LiTFSI) blend electrolytes [31]. The study focused on understanding how varying salt concentrations, ranging from 0.02 to 0.014, influenced χ_{eff} within these polymer blend electrolytes. In the absence of salt, PEO/P(2EO-MO) blends exhibited homogeneous and negative values of χ. However, at lower salt concentrations $(0.02 < r < 0.06)$, the blends demonstrated immiscibility and had positive values of χ_{eff}. Interestingly, with an increase in salt concentration to 0.10, the blends transitioned

to a state of miscibility and compatibility, as evidenced by the negative χ_{eff} values. The study further highlighted a correlation between temperature and χ_{eff}, demonstrating an elevated χ_{eff} at higher temperatures, which was especially evident in blends incorporating salt (refer to Figure 6). This indicates a direct influence of salt concentration on the compatibility of the polymer blend electrolytes [31].

Ionic conductivity is another key property of PBEs as it serves as an ion conducting medium known as an electrolyte. The ion mechanism in PBEs was created by dissolving salts with low lattice energy in polar polymers. Ion transport often takes place in the amorphous area of polymer chains in macromolecules, where the movement of cations is thought to be the cause of the ionic conductivity values [32-33], which are calculated using equation (6):

$$\sigma = \frac{t}{RA} \qquad (6)$$

where:
σ is ionic conductivity (S/cm),
R represents bulk resistance (Ω) derived from the Nyquist plot (impedance spectra),
A denotes sample area (cm^2),
t is sample thickness (cm).

Rechargeable batteries and other electrochemical devices depend on the flow of ions, especially cations like lithium (Li$^+$), sodium (Na$^+$), and magnesium (Mg$^+$). These materials, used in electrochemical devices such as rechargeable batteries, are vital where cation transport allows the movement of ions during charge and discharge cycles [11, 34-35].
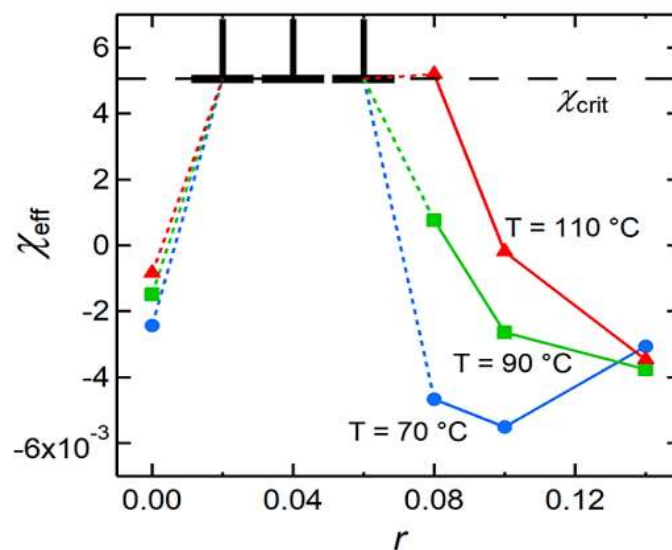

Figure 6. The χ_{eff} of PEO/P(2EO-MO)/LiTFSI blends at different temperatures as a function of salt concentration [31].

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There are two measurement models used to better understand ion transport in PBEs, the Arrhenius model and the VTF model. The temperature dependence of ion mobility in polymer chains is described by the Arrhenius model. It implies that ionic conductivity rises inversely with temperature. In general, higher temperatures supply more thermal energy, allowing ions to overcome energy barriers and travel more easily. The following represents the Arrhenius equation for ionic conductivity:

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \tag{7}$$

where:
σ is ionic conductivity,
σ_0 is the pre-exponential factor,
E_a is activation energy,
k_B is the Boltzmann constant,
T is temperature in Kelvin

Understanding the temperature dependency of ionic conductivity is vital in energy storage devices as it affects the performance of the material. The above equation explains that the cation motion is related to ion hooping in ionic crystals, and is not dependent on the molecular motion of the polymer host. The direct current (dc) ionic conductivity increases as a result of the ions jumping to the closest empty sites in the ion hopping mechanism. Additionally, the exponential dependence suggests a thermally activated process similar to the hopping of ions in ionic crystals [7, 34, 36].

Perk et al. (2021) presented a fascinating study on the ionic conductivity of polyethylene-based multiblock copolymers, with a particular focus on single-ion conducting polyethylene (PE).

Their research investigated the temperature dependence of ion transport when decoupled from polymer chain dynamics, revealing an Arrhenius-like behaviour that suggested a strong relationship between temperature and ion transport. The study also delved into the nanoscale morphologies of these polymers, uncovering layered, gyroid, and hexagonal ionic aggregates, as shown in Figure 7.

Of particular interest was the gyroid morphology, which stands out for its superior ionic conductivity compared to hexagonal morphology. The interconnected channels within the gyroid structure likely provide more effective pathways for ion movement, reducing the influence of defects or barriers within the material [36]. This indicates that the effectiveness of ion transport does not rely solely on the dynamics of the polymer chain but rather on its structural features. This finding highlights the importance of nanoscale morphology in determining the performance of polymer materials in applications such as ion conductors [36-38].

The VFT equation describes the temperature dependence of properties in systems that exhibit super-Arrhenius behaviour and a strong interrelation between conductivity and segmental relaxation in polymers. The VFT plot of temperature-dependent dc conductivity data in polymer electrolytes can be calculated by equation (7) as follows:

$$\sigma(T) = AT^{-1/2} \exp[-B/k_B(T-T_0)] \tag{7}$$

where:
A is the pre-exponential factor,
k_B is the Boltzmann constant,
B is the pseudo-activation energy,
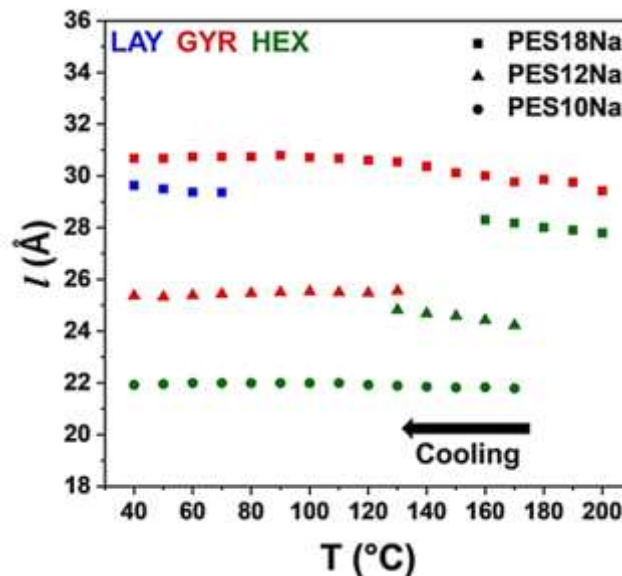T_0 is the reference temperature ($T_0 = T_g - 50\ K$).

Figure 7. The nanoscale morphologies of PES$_x$Na polymers [36].

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Most systems exhibit a more pronounced change in their properties with temperature compared to systems that follow Arrhenius behaviour. This gives a more accurate picture of how ions move around in polymer electrolytes, and takes into account the effects of segmental relaxation in the system [39-40].

Mohammad et al. (2010) investigated the VTF behavior of polymer electrolytes, specifically epoxidized natural rubber with a 50 % epoxidation level, polyethyl methacrylate, and ammonium triflate (ENR-50/PEMA-NH$_4$CF$_3$SO$_3$) [41]. They found that at up to a 40 % salt concentration, conductivity increased with temperature due to reduced viscosity and increased chain flexibility. This facilitated charge carrier mobility and dissociation rates, enhancing conductivity. However, beyond this concentration, conductivity decreased due to ion aggregation, contrary to predictions. The formation of ion clusters hindered ion mobility, despite a high concentration of charge carriers. [41-42].

2.0.   Advantages and Limitations of Polymer Blend Electrolyte Systems

PBEs offer numerous advantages over single-component polymer electrolytes, such as the capability to enhance material properties. By adjusting the proportions of different polymers in a blend, one can customise the electrolyte to attain specific characteristics, including mechanical strength, flexibility and thermal stability. This allows for the fulfilment of diverse application requirements [43]. Better ionic conductivity is usually due to the synergistic effects of mixing polymers with good properties that make it easier for ions to move around. Blending polymers with compatible characteristics may minimise phase separation, promoting a more uniform and stable material. Therefore, compatibility within the polymer matrix must be ensured to allow all materials to interact synergistically and deliver the required performance outcomes. Additionally, it implies that enhanced molecular interactions between different polymers may improve molecular adhesion and elevate the overall durability of the blended material [43].

However, PBEs also have certain limitations or challenges which include poor mechanical properties, such as low elasticity and tensile strength. Insufficient mechanical strength in PBEs may lead to structural issues such as fractures or cracking. These issues are noticeable during the cyclic expansion and contraction cycles that batteries undergo during charging and discharging [44]. In some cases, maintaining good ionic conductivity stands as a pivotal challenge in improving the efficiency of solid-state batteries without jeopardising other essential properties that are vital to the functionality and safety of the battery system. PBEs also face challenges induced by limited solubility among some polymers within a blend electrolyte. This limitation may affect both the homogeneity and stability of the blend. When polymers with low solubilities are mixed, the resulting material may not homogeneous, which can affect how well the electrolyte works and how uniform it is [45].
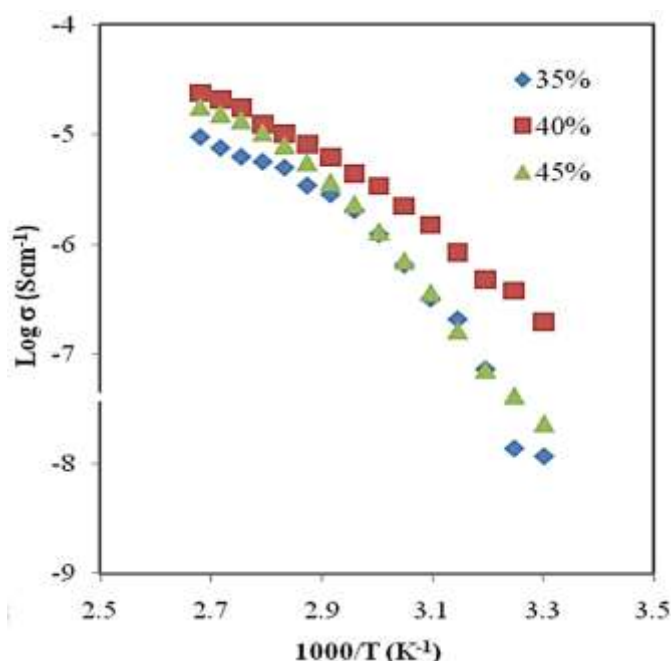

Figure 8. VTF plots of ENR-50/PEMA-NH$_4$CF$_3$SO$_3$ polymer electrolytes [41].

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Additionally, the blend becomes even more complex due to the existence of interfaces between several polymer phases. These interfaces can give rise to increased interfacial resistance, hindering the smooth transport of ions within the electrolyte. Moreover, these interfaces could be prone to degradation over time, which would affect the electrolyte's strength and possibly result in a drop in battery performance [44-45].

3.0.   Materials used in Polymer Blend Electrolyte Systems

This section explores the benefits and uses of natural and synthetic blends in PBE systems. Synthetic blends allow for precise control of material properties, making them useful in a variety of applications. Conversely, natural blends are valued for their sustainability, biocompatibility, and cost-effectiveness, often finding niches where their characteristics serve to provide unique advantages. By examining the features and applications of both types of blends, a comprehensive understanding of their roles in advancing electrochemical technology is achievable.

3.1.   Synthetic Blends

A synthetic blend electrolyte is an electrolyte system that is made by combining various synthetic (man-made) materials. This may involve mixing different synthetic polymers, salts, ionic liquids, or other substances to create specific properties. The types and amounts of polymers used may have a big effect on the synthetic blend electrolyte's properties, such as its ability to conduct electricity, be strong, and stay stable at high temperatures. Additionally, other desired properties of synthetic blend electrolytes can be optimised and improved by using plasticizers, additives and additional substances [11, 46].

The ion-conductive and thermal properties of a blend electrolyte composed of poly(ethylene carbonate)/poly(trimethylene carbonate)/lithium bis-trifluoromethanesulfonimide) (PEC/PTMC/LiTFSI) were studied [47]. It was observed that PEC-based electrolytes had low thermal stability, but the system improved significantly when PTMC was combined with the PEC-based electrolyte. PTMC not only addressed thermal stability concerns but also brought additional benefits in terms of superior electrochemical properties. This implied that the addition of PTMC contributed positively to the overall performance of the electrolyte system. Additionally, blend electrolytes of PEC and PTMC exhibited better conductivities than PEC or PTMC alone. The blending approach appears to have a synergistic impact, thus increasing the conductivity of the electrolyte beyond what may be achieved with its individual components [47, 48]. Infrared spectroscopy (FTIR) was used to figure out how the polymers and LiTFSI molecules interact in the mixed electrolyte system. The addition of LiTFSI caused a shift towards lower wavenumbers, notably around 1716-1722 cm^{-1} in the blend electrolyte, as shown in Figure 9. This shift was caused by an interaction between the C=O groups and Li$^+$ ions in both the 100 mol % PEC and 100 mol % PTMC phases.
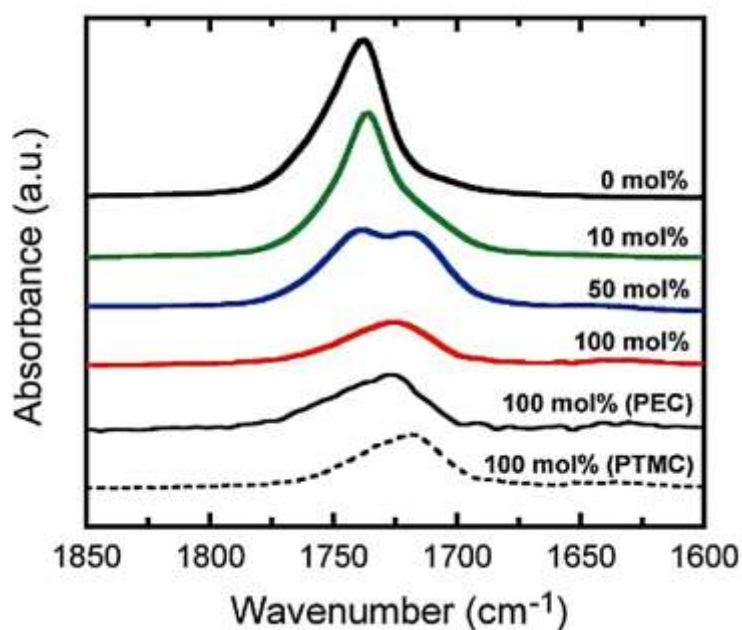

Figure 9. FTIR spectra of PEC (100 mol %), PTMC (100 mol %), and PEC/PTMC/LiTFSI blends from 0 to 100 mol % in the C=O stretching region [47].

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Additionally, the shift observed in the blend electrolyte system was more pronounced with increasing mol % of LiTFSI. This shift showed that adding LiTFSI to the system could actively promote the development of complexes. Thus, this phenomenon resulted in a better synergy within the blend electrolyte system by improving the compatibility of and interaction between PEC and PTMC. The improved interaction between the polymers also contributed to better conductivity in the blend electrolyte system [47].

A recent study [49] focused on developing a succinonitrile-based plastic crystal polymer electrolyte (SCPE) for lithium metal batteries. *In-situ* thermal polymerization was used to mix succinonitrile (SN), vinylene carbonate (VC), and acetylene black with a binder made of polyvinylidene difluoride (PVDF). The blend showed good ionic conductivity at room temperature, suggesting its potential use as an electrolyte in lithium-ion batteries. Moreover, EIS results revealed a low bulk resistance of 5.5 ohms at room temperature for the SCPE, indicating strong ionic conductivity. Following testing at various temperatures, it was found that SCPE (σ) had a far higher ionic conductivity at room temperature than standard polymer electrolytes, reaching 1.3×10^{-3} S/cm. The rise in conductivity was due to the high permeability of SN, which allows for the efficient transport of lithium ions within the polymer matrix of the blend electrolytes.

Chiu et al. (2004) [50] studied the effect of miscibility on the ionic conductivity of a ternary synthetic blend electrolyte, specifically PEO/PCL/LiClO$_4$. The work aimed to decrease crystallinity by introducing PCL in PEO-based SPEs in order to improve their ionic conductivity. FTIR spectroscopy and impedance measurements were used to study the interactions in the synthetic blend electrolyte. FTIR analysis showed that PEO was the primary factor responsible for the decrease in the crystallinity of the PEO/PCL binary blend. This can be observed by the decreasing intensity of the PCL peak as the PEO content increased. However, when LiClO$_4$ was added to the binary blend, PCL disrupted the crystalline structure of PEO in the ternary PEO/PCL/LiClO$_4$ blend.

The results of the impedance analysis showed that adding PCL or PEO to the binary blend made the ions move more easily at lower temperatures. The authors highlighted that adding PCL or PEO to the blend served to improve ionic conductivity by disrupting the crystalline structure and facilitating ion mobility in the ternary blend electrolyte systems [46]. The Arrhenius plots of the PEO/PCL/LiClO$_4$ electrolyte systems demonstrated a decrease in activation energy when PCL or PEO was introduced into the blend, as shown in Figure 11. The ternary blend of PEO, PCL and LiClO$_4$ achieved the highest ionic conductivity at a composition of 60/15/25 [50].
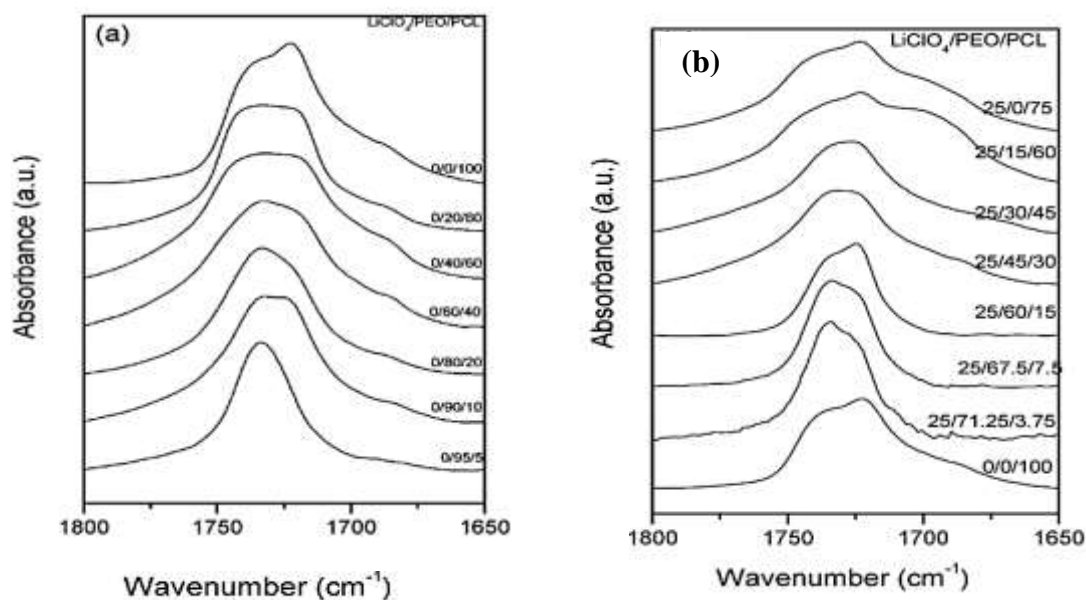

Figure 10. Infrared spectra displaying the carbonyl stretch of (a) binary blends of PEO/PCL at room temperature and (b) ternary blends of 25 wt.% LiClO$_4$/PEO/PCL at room temperature [50].
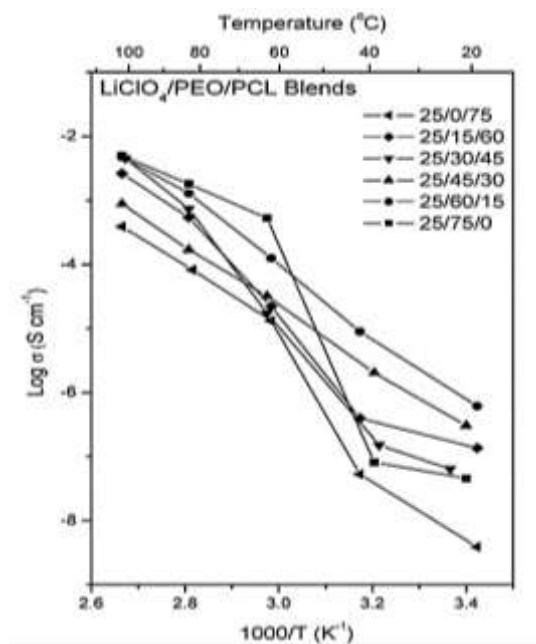
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Figure 11. Arrhenius plot as a function of temperature for LiClO$_4$/PEO/PCL ternary blend electrolyte systems [50].

3.2. Natural Blends

With growing environmental concerns related to synthetic materials, especially their non-biodegradability and potential ecological impact, there has been a notable shift towards adapting natural blend electrolytes as a sustainable solution. The use of natural polymers with specific functional groups that have been carefully designed to help ions move while keeping the electrolytes stable is becoming more popular in this field. Biopolymer components such as chitosan, starch, ENR and kappa-carrageenan are mixed with other polymers to optimise their properties. The demand for sustainable and environmentally friendly energy storage solutions is further driven by the natural blend electrolytes' improved biodegradability and compatibility with green energy projects. Natural blend electrolytes make energy storage solutions more biodegradable and compatible with green energy initiatives, which increases the need for long-lasting and eco-friendly energy storage solutions [51-52].

Polymers such as chitosan, cellulose or starch serve as biocompatible alternatives, making them valuable in bio electrochemical devices including rechargeable batteries, implantable medical devices, and biosensors. For example, plasticized solid PBEs based on chitosan and methylcellulose have been studied for their structural and electrochemical properties [53]. Biopolymer blend electrolytes with polyvinyl alcohol (PVA) and chitosan have also been created to allow decoupled ion mobility and improve the performance of EDLC devices. Despite potential limitations in mechanical and ionic conductivity, ongoing research

and development efforts are dedicated to improving their electrochemical efficacy [54].

Last year, Lu et al. (2023) developed CPZ-H, a biodegradable hydrogel electrolyte for zinc-ion batteries, using a mixture of chitosan and poly(aspartic acid). The researchers used these natural biomaterials due to their unique properties, specifically their ability to adsorb substances onto their surface, and their capacity to respond to external stimuli. Together, these characteristics set off a multifaceted network of interactions known as the double coupling network and a collaborative inhibition mechanism. In turn, this improved the overall performance of the battery by successfully inhibiting side reactions on the zinc anode. The CPZ-H blends had stable ionic conductivity (ion diffusion coefficient: 4.1 × 10^{-10} S/cm), high tensile strength (53.2 kPa), a high fracture strain (1298 %), and a maximum strain three times that of the C-H electrolyte, all of which indicated better mechanical properties. The study also explored the recyclability of CPZ-H blend electrolytes. The electrolyte underwent drying and grinding into powder, treatment with water to form a solution, transfer into moulds, and heating to obtain a recovered hydrogel electrolyte. The recovered rCPZ-H electrolyte displayed excellent scratch resistance and hardness, suggesting its recyclability and potential for use in large-scale recycling technologies [55].

Another study by Dannoun et al. (2020) also included chitosan in the production of electric double-layer capacitor (EDLC) devices. The electrochemical stability of the plasticized magnesium ion-conducting
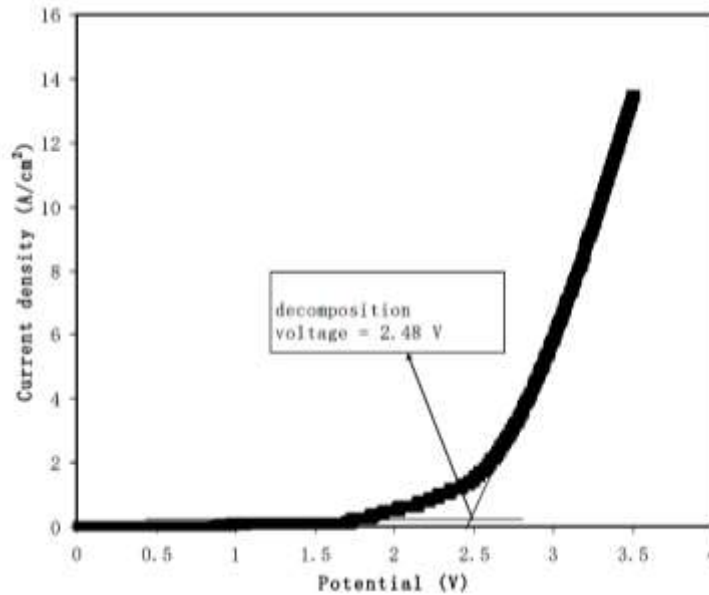
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Figure 12. Current density vs. potential curve for CS:MC blend electrolytes [56]

PBEs based on chitosan:methylcellulose (CS:MC) was demonstrated through linear sweep voltammetry (LSV) analysis, showing its potential stability up to 3.5 V, as shown in Figure 12. The decomposition voltage of the electrolyte was determined to be 2.48 V. It was concluded that the produced electrolyte could be used as an electrode separator in the fabrication of EDL [56].

In addition to chitosan, a combination of hexanoyl chitosan and ENR-25 was used in EDLCs due to its improved conductivity and adhesive properties. The study found that the addition of lithium bis(trifluoromethanesulfonyl) imide (LiCF$_3$SO$_3$) salt increased conductivity up to a certain point before it decreased. The controlled percolation of inorganic

salts in the multiphase blend made this improvement possible. This meant that both the distribution of ions and the percolation pathway were under control. The PBEs exhibited improved conductivity compared to neat hexanoyl chitosan, with the highest conductivity of about 6.4×10^{-9} S/cm achieved with a 90:10 blend of hexanoyl chitosan and ENR25, as shown in Figure 13. Temperature was found to significantly influence conductivity, with higher temperatures leading to increased conductivity. It was also shown that adding ENR-25 increased the elasticity of hexanoyl chitosan, indicating better mechanical properties. The immiscibility of ENR-25 and hexanoyl chitosan in this blend suggested that further study into the modification of material properties for specific applications was required [57].
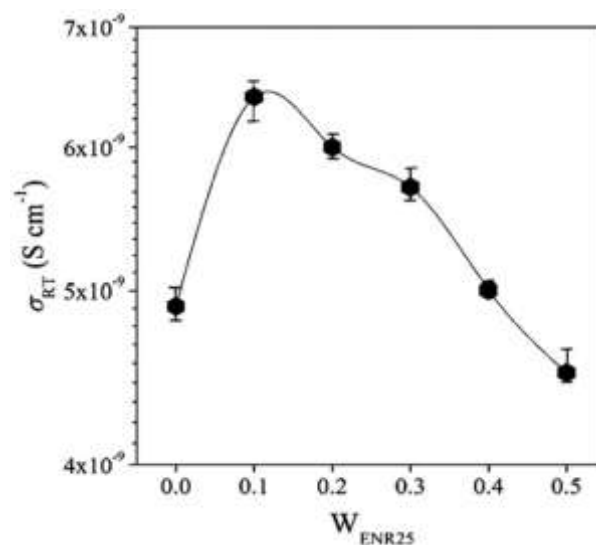

Figure 13. Variation of room temperature conductivity with mass fraction of ENR25 at a fixed concentration of LiCF$_3$SO$_3$ salt [57].

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A new trend in *in-situ* polymerization methods for PBEs is to use green solvents and renewable monomers to improve performance and address specific challenges. In a study conducted by Barbosa et al. (2022), sodium alginate, a natural polymer, was combined with poly(ethylene oxide) (PEO) to develop SPEs for lithium-ion batteries. The study aimed to create sustainable SPEs based on natural polymers, aiming to reduce the environmental impact associated with lithium-ion batteries. The outcomes of this work included the fabrication of a solid electrolyte with high ionic conductivity, thermal stability, and a stable electrochemical window up to 3.4 V [58].

A study by Rajeswari et al. (2013) focused on the development and characterization of a lithium-ion conducting solid polymer blend electrolyte (SPBE) using PVA blended with poly(vinyl pyrrolidone) (PVP). The study concluded that the PBE exhibited high conductivity and low activation energy, making it a promising material for lithium-ion battery applications. The biodegradable properties of PVA and PVP, containing hydroxyl and carbonyl groups in their structure, act as electron pair donors and enable complexation with lithium ions. This complexation facilitated ion transport and increased the number of mobile charge carriers, thus leading to enhanced ion conductivity in the PBE [14].

The complex formation between lithium nitrate ($LiNO_3$) and the biodegradable polymer blend (70% PVA:30% PVP) improved the conductivity of the electrolyte system, as shown in Figure 14. The interaction between the polymer blend and $LiNO_3$ facilitated ion transport by creating efficient pathways, reducing resistance, and allowing a more effective flow of charge carriers. The shifts in the FTIR peaks suggested interactions occurred that could lead to complexation or coordination bond formation, making the polymer matrix more structured and conductive.

The complex impedance plots showed a decrease in the semicircle arc with increasing salt concentration, indicating improved conductivity as shown in Figure 15. This suggests that the biodegradable polymer blend, when complexed with $LiNO_3$, exhibited enhanced ion transport properties, which are crucial for the sustainability of the electrolyte system. Numerous studies have shown interest in the application of PVA-based solid polymer electrolytes in lithium-ion batteries. Through the resolution of concerns regarding synthetic blend electrolyte electrolytes such as safety concerns and low ion selectivity, these studies demonstrate the potential of PVA-based polymer electrolytes to improve the performance and safety of lithium-ion batteries [59-60].

In comparison to synthetic polymers, biodegradable polymers offer the advantage of being environmentally friendly and sustainable. They also have good film-forming properties, are non-toxic, and soluble in common solvents, making them suitable for various applications. Additionally, the presence of functional groups in biodegradable polymers allows for interactions with lithium ions, contributing to improved conductivity in the PBEs. The choice between synthetic and natural blends hinges on the specific demands of the application, with some researchers exploring combinations of both to strike a balance between performance, sustainability and cost-effectiveness.
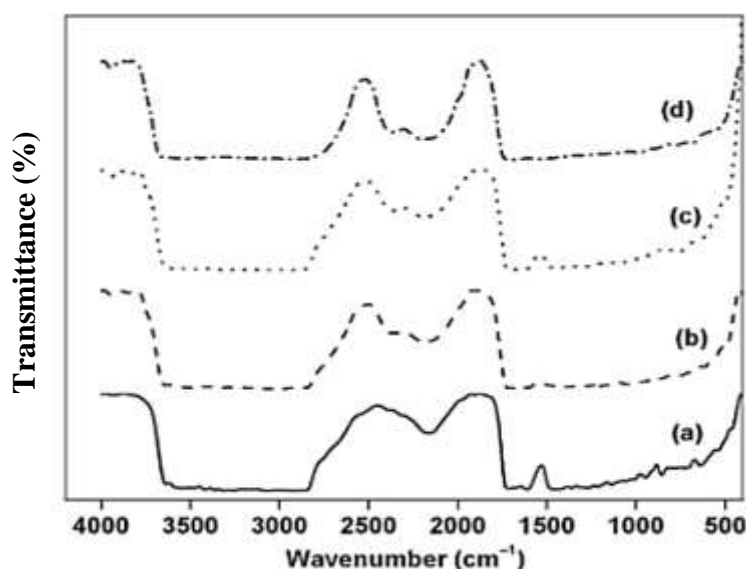

Figure 14. FTIR spectra of (a) 70 PVA:30 PVP, (b) 70 PVA:30PVP:20 Mwt.% $LiNO_3$, (c) 70 PVA:30PVP:25 Mwt.% $LiNO_3$, and (d) 70 PVA:30PVP:30 Mwt.% $LiNO_3$ [14].
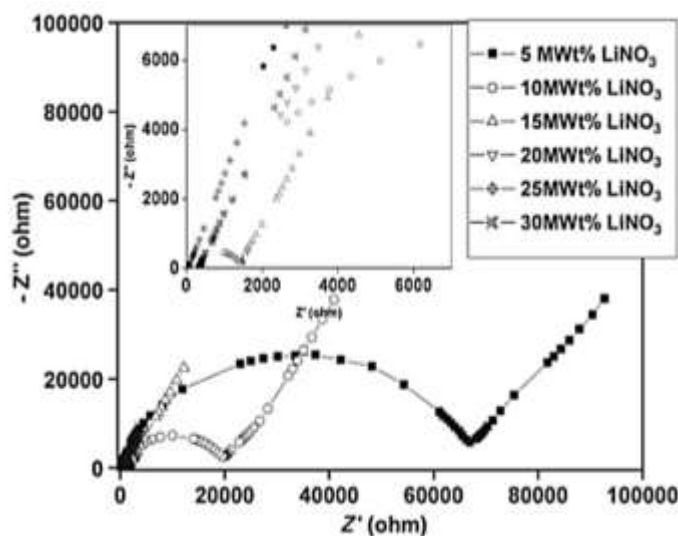
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Figure 15. Cole-Cole plots for PVA:PVP blends with different $LiNO_3$ concentrations at room temperature [14].

4.0. Highlights and Challenges in Polymer Blend Electrolyte Systems

Due to their unique properties and benefits, PBEs have shown great potential in improving the performance and safety of rechargeable batteries such as lithium-ion batteries [61-62]. The flexibility of polymer blends is a significant advantage as it helps to meet specific application requirements that cannot be achieved with individual polymers. The enhanced mechanical properties and highly amorphous characteristics of PBEs have made them highly suitable for diverse applications in energy storage and electrochemical devices [63]. One of the key advantages of PBEs lies in their ability to address the challenges of immiscible blends that may arise from the blending of incompatible polymers. This issue is often encountered in the development of electrolytes, where different polymers with distinct properties are combined. To improve the compatibility of such blends, various strategies can be employed. For instance, the addition of plasticizers or the incorporation of nanostructured fillers can enhance the miscibility of polymers within the blend, leading to a more homogeneous and effective electrolyte [7, 54].

The ion conductivity of PBEs represents a notable advantage over individual polymers in energy storage and electrochemical devices. While the ionic conductivity of individual polymers can be limited, especially in solid-state electrolytes, the synergistic combination of different polymers in PBEs often results in enhanced ionic conductivity [64-65]. A blend of polymers with different properties, such as one providing mechanical strength and another facilitating ion transport, can create a more favourable environment for ion conduction. The amorphous nature of PBEs further contributes to improved ion mobility, as amorphous regions generally allow for easier movement of ions compared to crystalline

structures [4, 66]. This enhanced ion conductivity in PBEs is crucial for the efficient operation of batteries, fuel cells, and other electrochemical devices. It leads to faster charge and discharge rates, reduced internal resistance, and overall improved electrochemical performance. The ability to tailor the composition of PBEs allows researchers to optimize ion conductivity based on the specific requirements of a given application. In contrast, individual polymers may exhibit lower ion conductivity, and their properties may not be as easily optimized for specific applications. Therefore, the synergistic combination of polymers in PBEs provides a valuable means to enhance ion conductivity, making it a highlight in the field of polymer electrolytes for advanced energy storage technologies [67].

Finding the ideal balance between ionic conductivity, mechanical strength and thermal stability is a major challenge for PBEs. Improving ionic conductivity is crucial for their performance, but it may compromise the mechanical integrity of the electrolyte, affecting the long-term stability and durability of the system. Higher operating temperatures may also accelerate the degradation of polymer electrolytes, stressing the need for heat-resistant materials without abandoning their key features [68], [69]. Biodegradable-based polymers like cellulose, lignin, and ENR are some of the heat resistant natural polymers that are commonly used in PBE systems. Cellulose is a complex carbohydrate found in the cell walls of plants, and it exhibits good thermal stability. It can be processed into various forms, such as films or fibres, and incorporated into PBEs to enhance their thermal resilience without compromising ionic conductivity [70-71]. Lignin is a complex organic polymer that provides rigidity to plant cell walls. It is renewably-sourced, biodegradable, and possesses natural UV resistance and antibacterial activity. The thermal stability of lignin and its potential contribution

to the thermal stability of PBE systems have been the subject of research. Lignin has been studied in the context of carbon-based materials and pyrolysis, and has shown potential in terms of thermal stability and conversion. The incorporation of lignin into industrial polymers has also been explored, indicating its potential for various applications, including heat resistance [70]. Another unique polymer is ENR, which exhibits good heat resistance due to its chemical structure that includes epoxide groups that enhance its thermal stability and mechanical properties. This makes ENR a valuable material for applications that require resilience to elevated temperatures, without compromising essential properties [72-73].

Yet another important factor to consider for the practical use of PBEs is their electrochemical stability and long-term durability [74-75]. The cost factor is important, as the development and production of PBEs may involve complex synthesis procedures and the use of specialized materials, potentially reducing the overall cost-effectiveness of the system [45]. Safety concerns regarding the flammability and volatility of certain PBEs must be carefully addressed to ensure the safe functioning of blend electrolyte systems [46]. Addressing these challenges will be crucial for advancing the practical implementation of PBE systems in the future.

CONCLUSION AND FUTURE DEVELOPMENT OF PBEs

Polymer blend electrolyte (PBE) systems have good potential for a variety of electrochemical applications due to their ability to combine the favourable features of multiple polymers. PBEs have been explored in a wide range of literature that includes studies on polymers such as ENR, PVA, PVS, chitosan, lignin, and cellulose, both in synthetic and natural blend electrolytes. This review highlights the potential of PBEs in improving ionic conductivity, enhancing mechanical properties, and addressing challenges in immiscible blends. Both synthetic and natural blend electrolytes have been explored for their unique properties and potential applications in various industries. Ionic conductivity is a critical feature of PBEs, which can be improved by increasing the amorphous percentage of the polymer host. Numerous studies have indicated that PBEs offer advantages over individual polymer electrolytes. The flexible nature and improved ion conductivity of PBE systems make them well-suited to diverse application requirements. The synergistic effects of the combination of different polymers in PBE systems allow for improvement of their properties. PBEs also gain a sustainable aspect from their exploration of blended electrolytes made from natural and synthetic materials. The use of natural blend electrolytes which contain chitosan, lignin and cellulose, contributes environmentally friendly elements to the development of PBE systems.

Future research will likely focus on developing advanced synthesis methods that allow precise control over film composition, tuneable pore structures, and the pore structure of polymer blend electrolytes, facilitating electrolyte uptake and ion transport. It is possible to improve and combine techniques like electrospinning, solvent casting, phase inversion, and templating to make the shape and microstructure of PBEs fit specific needs. Additionally, incorporating multifunctional additives into polymer blend electrolytes can significantly enhance their performance across various parameters. For instance, ionic liquids offer high ionic conductivity, while nanostructured materials, like silica nanoparticles, improve mechanical strength. Functionalized polymers, such as PEO, contribute to thermal stability, and tailored electrolyte salts, like LiTFSI, ensure compatibility with electrodes. For example, adding an ionic liquid like 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) can improve conductivity, and adding nanostructured silica particles can make the structure stronger.

Innovative approaches are needed to improve the compatibility between polymer blend electrolytes and diverse electrode materials. Strategies like surface modification, interfacial engineering, and polymer coatings will address interface-related challenges including resistance, dendrite formation, and degradation. For instance, surface modification of electrodes with conductive polymers like polypyrrole (PPy) enhances electron transfer and reduces interfacial resistance. Interlayers composed of materials like graphene oxide can prevent dendrite formation in lithium-ion batteries. These methods optimise device performance and stability by promoting efficient charge transfer and preventing detrimental reactions at the electrode-electrolyte interface. In conclusion, PBEs have a great deal of potential for integration into battery systems, despite some challenges. Continued research and development efforts focused on optimising PBE compositions and processing techniques are essential to unlocking their transformative potential within battery technology.

ACKNOWLEDGEMENTS

REFERENCES

1.   Jinisha, B., KM, A., Manoj, M., Pradeep, P. and Jayalekshmi, J. (2017) Development of a novel type of solid polymer electrolyte for solid state lithium battery applications based on lithium enriched poly (ethylene oxide) (PEO)/poly (vinyl

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pyrrolidone) (PVP) blend polymer. *Electrochim Acta*, **235**, 210–222. doi: 10.1016/j.electacta.2017.03.118.

2. Zhang, J., Cao, L. and Chen, Y. (2022) Mechanically robust, self-healing and conductive rubber with dual dynamic interactions of hydrogen bonds and borate ester bonds. *Eur. Polym. J.*, **168**, Apr. 2022. doi: 10.1016/j.eurpolymj.2022.111103.

3. Fonseca, C. P., Rosa, D. S., Gaboardi, F. and Neves, S. (2006) Development of a biodegradable polymer electrolyte for rechargeable batteries. *J. Power Sources*, **155**, 2, 381–384. doi: 10.1016/j.jpowsour.2005.05.004.

4. Yazie, N., Worku, D., Gabbiye, N., Alemayehu, A., Getahun, Z. and Dagnew, M. (2023) Development of polymer blend electrolytes for battery systems: recent progress, challenges, and future outlook. *Materials for Renewable and Sustainable Energy, Springer Science and Business Media Deutschland GmbH, 2023*. doi: 10.1007/s40243-023-00231-w.

5. Juqu, T., Willenberg, S. C., Pokpas, K. and Ross, N. (2022) Advances in paper-based battery research for biodegradable energy storage. *Advanced Sensor and Energy Materials*, **1**, 4, 100037. doi: 10.1016/j.asems.2022.100037.

6. Utracki, L. (2002) Polymer Blend Handbook. *Kluwer Academic Publishers*, **1**.

7. Yazie, N., Worku, D., Gabbiye, N., Alemayehu, A., Getahun, Z. and Dagnew, M. (2023) Development of polymer blend electrolytes for battery systems: recent progress, challenges, and future outlook. *Materials for Renewable and Sustainable Energy, Springer Science and Business Media Deutschland GmbH, Aug. 01, 2023*. doi: 10.1007/s40243-023-00231-w.

8. Valdes, S. S., Valle, L. F. R. and Manero, O. (2013) Polymer blends, 505–517.

9. Goettler, L. A. and Scobbo, J. J. (2014) Applications of Polymer Blends. doi: 10.1007/978-94-007-6064-6.

10. Mei, E. L. H. (2019) A Short Review on Latex Blends. [Online] Available: https://www. research gate.net/publication/342122439

11. Blatt, M. P. and Hallinan, D. T. (2021) Polymer Blend Electrolytes for Batteries and beyond. *Industrial and Engineering Chemistry Research, American Chemical Society*, **60**, 48, 17303–17327, Dec. 08, 2021. doi: 10.1021/acs.iecr.1c02938.

12. Parameswaran, V., Nallamuthu, N., Devendran, P., Nagarajan, E. R. and Manikandan, A. (2017) Electrical conductivity studies on Ammonium bromide incorporated with Zwitterionic polymer blend electrolyte for battery application. *Physica B Condens Matter*, **515**, 89–98, Jun. 2017. doi: 10.1016/j.physb.2017.03.043.

13. Nagaiah, N., Samartharama, B. N., Ambika, M. R. and Demappa, T. (2022) Studies on structural and electrical properties of NaI doped PEO/CMC blend solid polymer electrolyte. doi: 10.21203/rs.3.rs-1465678/v1.

14. Rajeswari, N., Selvasekarapandian, S., Prabu, M., Karthikeyan, S. and Sanjeeviraja, C. (2013) Lithium ion conducting solid polymer blend electrolyte based on bio-degradable polymers.

15. Blatt, M. P. and Hallinan, D. T. (2021) Polymer Blend Electrolytes for Batteries and beyond. *Industrial and Engineering Chemistry Research, American Chemical Society*, **60**, 48, 17303–17327, Dec. 08, 2021. doi: 10.1021/acs.iecr.1c02938.

16. Parameswaranpillai, J., Thomas, S. and Grohens, Y. (2015) Polymer Blends: State of the Art, New Challenges, and Opportunities. In *Characterization of Polymer Blends: Miscibility, Morphology and Interfaces, Wiley Blackwell*, 9783527331536, 1–6. doi: 10.1002/9783527645602.ch01.

17. LITERATURE REVIEW SPE_ARRHENIUS (2010) *Literature Review*, 7–33.

18. Kuray, P., *et al.* (2020) Ion Transport in Solvated Sodium-Ion Conducting Gel Polymer Electrolytes. *Front Earth Sci (Lausanne)*, **8**, 1–15, October, 2020. doi: 10.3389/fenrg.2020.569387.

19. Garca-Coln, L. S., Del Castillo, L. F. and Goldstein, P. (1989) Theoretical basis for the Vogel-Fulcher-Tammann equation. *Phys. Rev. B.*, **40**, 10, 7040–7044. doi: 10.1103/PhysRevB.40.7040.

20. Nyamweya, N. N. (2021) Applications of polymer blends in drug delivery. *Futur. J. Pharm. Sci.*, **7**, 1. doi: 10.1186/s43094-020-00167-2.

21. Chasib, K. F. and Kadhim, B. M. (2019) Prediction of The Behavior for Polymer Blends Using Thermodynamic Model Petrochemical Science Introduction and Theoretical Framework. doi: 10.19080/RAPSCI.2019.06.555699.

22. Gao, K. W., *et al.*, "(2020) Miscible Polyether/Poly(ether-acetal) Electrolyte Blends. *Macromolecules*, **53**, 14, 5728–5739, Jul. 2020. doi: 10.1021/acs.macromol.0c00747.

23. He, Y., Zhu, B. and Inoue, Y. (2004) Hydrogen bonds in polymer blends, **29**, 1021–1051. doi: 10.1016/j.progpolymsci.2004.07.002.

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24   İçöz, D. (2008) Understanding Molecular and Thermodynamic Miscibility of Carbohydrate Biopolymers.

25.   Manias, E. and Utracki, L. A. (2014) Thermodynamics of polymer blends. In *Polymer Blends Handbook*, *Springer Netherlands*, 171–289. doi: 10.1007/978-94-007-6064-6_4.

26.   Chasib, K. F. and Kadhim, B. M. (2019) Recent Adv Petrochem Sci Prediction of The Behavior for Polymer Blends Using Thermodynamic Model Petrochemical Science Introduction and Theoretical Framework. doi: 10.19080/RAPSCI.2019.06.555699.

27.   Ibrahim Khan, Muhammad Mansha, and Mohammad Abu Jafar Mazumder (2018) *Polymer Blends*, **1**, August, 2018. doi: 10.1007/978-3-319-95987-0.

28.   Seiffert, S. (2020) Polymer thermodynamics. In *Physical Chemistry of Polymers*, *De Gruyter*, 89–128. doi: 10.1515/9783110672817-004.

29.   Shah, N. J., *et al.* (2023) Chimney-Shaped Phase Diagram in a Polymer Blend Electrolyte. *ACS Macro Lett*, **12**, 7, 874–879, Jul. 2023. doi: 10.1021/acsmacrolett.3c00285.

30.   Mei, X., *et al.* (2023) Improving Ion Conductivity in Polymer Blend Electrolytes by Tuning Microdynamics and Interfaces. *ACS Appl. Polym. Mater.*, **5**, 11, 9225–9235, Nov. 2023. doi: 10.1021/acsapm.3c01658.

31.   Gao, K. W., *et al.* (2020) Miscible Polyether/Poly(ether-acetal) Electrolyte Blends. *Macromolecules*, **53**, 14, 5728–5739, Jul. 2020. doi: 10.1021/acs.macromol.0c00747.

32.   Aziz S. B., Woo T. J., Kadir, M. F. Z.and Ahmed, H. M. (2018) A conceptual review on polymer electrolytes and ion transport models. *Journal of Science: Advanced Materials and Devices*, *Elsevier B. V.*, **3**, 1, 1–17, Mar. 01, 2018. doi: 10.1016/j.jsamd.2018.01.002.

33.   Yang, H. and Wu, N. (2022) Ionic conductivity and ion transport mechanisms of solid-state lithium-ion battery electrolytes: A review. *Energy Science and Engineering*, *John Wiley and Sons Ltd*, **10**, 5, 1643–1671, May 01, 2022. doi: 10.1002/ese3.1163.

34.   Aziz, S. B., Woo, T. J., Kadir, M. F. Z. and Ahmed, H. M. (2018) A conceptual review on polymer electrolytes and ion transport models. *Journal of Science: Advanced Materials and Devices*, *Elsevier B.V.*, **3**, 1, 1–17, Mar. 01, 2018. doi: 10.1016/j.jsamd.2018.01.002.

35.   Ruiz-Martínez, D., Kovacs, A. and Gómez, R. (2017) Development of novel inorganic electrolytes for room temperature rechargeable sodium metal batteries. *Energy Environ. Sci.*, **10**, 9, 1936–1941. doi: 10.1039/c7ee01735a.

36.   Park, J., Staiger, A., Mecking, S. and Winey, K. I. (2021) Structure-Property Relationships in Single-Ion Conducting Multiblock Copolymers: A Phase Diagram and Ionic Conductivities. *Macromolecules*, **54**, 9, 4269–4279, May 2021. doi: 10.1021/acs.macromol.1c00493.

37.   Liew, C. W., Ramesh S., Ramesh, K. and Arof, A. K. (2021) Preparation and characterization of lithium ion conducting ionic liquid-based biodegradable corn starch polymer electrolytes. *Journal of Solid State Electrochemistry*, **16**, 5, 1869–1875, May 2012. doi: 10.1007/s10008-012-1651-5.

38.   Wheatle, B. K., Fuentes, E. F., Lynd, N. A. and Ganesan, V. (2019) Influence of host polarity on correlating salt concentration, molecular weight, and molar conductivity in polymer electrolytes. *ACS Macro Lett*, **8**, 8, 888–892, Aug. 2019. doi: 10.1021/acsmacrolett.9b00317.

39.   Nigro, V., Angelini, R., Bertoldo, M., Bruni, F., Ricci, M. A. and Ruzicka, B. (2017) Dynamical behavior of microgels of interpenetrated polymer networks. *Soft Matter*, **13**, 30, 5185–5193. doi: 10.1039/c7sm00739f.

40.   Saeed, M. A. M. and Abdullah, O. G. (2020) Effect of high ammonium salt concentration and temperature on the structure, morphology, and ionic conductivity of proton-conductor solid polymer electrolytes based pva. *Membranes (Basel)*, **10**, 10, 1–16, Oct. 2020. doi: 10.3390/membranes10100262.

41.   Mohammad, S. F., Idris, R. and Mohamed, N. S. (2010) Conductivity studies of ENR based proton conducting polymer electrolytes. in *Advanced Materials Research*, 561–565. doi: 10.4028/www.scientific.net/AMR.129-131.561.

42.   Aziz, S. B., Hamsan, M. H., Abdullah, R. M. and Kadir, M. F. Z. (2019) A promising polymer blend electrolytes based on chitosan: Methyl cellulose for EDLC application with high specific capacitance and energy density. *Molecules*, **24**, 13. doi: 10.3390/molecules24132503.

43.   Aziz, S. B., Hamsan, M. H., Brza, M. A., Kadir, M. F. Z., Muzakir, S. K. and Abdulwahid, R. T. (2020) Effect of glycerol on EDLC characteristics of chitosan:methylcellulose polymer blend electrolytes. *Journal of Materials Research and*

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Technology, **9**, 4, 8355–8366, Jul. 2020. doi: 10.1016/j.jmrt.2020.05.114.

44. Ahmad, Z., Al-Awadi, N. A. and Al-Sagheer, F. (2007) Morphology, thermal stability and visco-elastic properties of polystyrene-poly(vinyl chloride) blends. *Polym Degrad Stab*, **92**, 6, 1025–1033, Jun. 2007. doi: 10.1016/j.polymdegradstab.2007.02.016.

45. Sivakumar, M., Subadevi, R., Rajendran, S., Wu, N. L. and Lee, J. Y. (2006) Electrochemical studies on [(1 - x)PVA-xPMMA] solid polymer blend electrolytes complexed with LiBF4. *Mater. Chem. Phys.*, **97**, 2–3, 330–336, Jun. 2006. doi: 10.1016/j.matchemphys.2005.08.018.

46. Rhoo, H. -J., Kim, H. -T., Park, J. -K. and Hwangb, T. -S. (1997) Ionic conduction in plasticized PVC/PMMA blend polymer electrolytes. *Ekevier Science Ltd*.

47. Li, Z., Mogensen, R., Mindemark, J., Bowden, T., Brandell, D. and Tominaga, Y. (2018) Ion-Conductive and Thermal Properties of a Synergistic Poly(ethylene carbonate)/Poly(trimethylene carbonate) Blend Electrolyte. *Macromol. Rapid Commun.*, **39**, 14, Jul. 2018. doi: 10.1002/marc.201800146.

48. Whba, R., Sukor, M., Tiankhoon, L., Ibrahim, S., Sabirin, N. and Ahmad, A. (2021) In-situ UV cured acrylonitrile grafted epoxidized natural rubber (ACN-g-ENR) – LiTFSI solid polymer electrolytes for lithium-ion rechargeable batteries. *React Funct. Polym.*, **164**, 104938, December 2020. doi: 10.1016/j.reactfunctpolym.2021.104938.

49. Su, Y., Bai, Y. and Lu, Y. (2023) Succinonitrile Plastic Crystal Polymer Electrolyte for Lithium Metal Battery. In *Journal of Physics: Conference Series*, *Institute of Physics*. doi: 10.1088/1742-6596/2563/1/012001.

50. Chiu, C. Y., Chen, H. W., Kuo, S. W., Huang, C. F. and Chang, F. C. (2004) Investigating the effect of miscibility on the ionic conductivity of LiClO4/PEO/PCL ternary blends. *Macromolecules*, **37**, 22, 8424–8430, Nov. 2004. doi: 10.1021/ma0488156.

51. Varshney, P. K. and Gupta, S. (2011) Natural polymer-based electrolytes for electrochemical devices: A review. *Ionics (Kiel)*, **17**, 6, 479–483. doi: 10.1007/s11581-011-0563-1.

52. Rayung, M., *et al.* (2020) Bio-based polymer electrolytes for electrochemical devices: Insight into the ionic conductivity performance. *Materials*, **13**, 4. doi: 10.3390/ma13040838.

53. Dannoun, E. M. A., *et al.* (2020) The study of plasticized solid polymer blend electrolytes based on natural polymers and their application for energy storage EDLC devices. *Polymers (Basel)*, **12**, 11, 1–19, Nov. 2020. doi: 10.3390/polym12112531.

54. Aziz, S. B., *et al.* (2023) Design of biodegradable polymer blend electrolytes with decoupled ion motion for EDLC device Application: Electrical and electrochemical properties. *Results Phys.*, **51**, Aug. 2023. doi: 10.1016/j.rinp.2023.106692.

55. Lu, H., *et al.* (2023) A recyclable biomass electrolyte towards green zinc-ion batteries. *Nat. Commun.*, **14**, 1, Dec. 2023. doi: 10.1038/s41467-023-40178-0.

56. Dannoun, E. M. A., *et al.* (2020) The study of plasticized solid polymer blend electrolytes based on natural polymers and their application for energy storage EDLC devices. *Polymers (Basel)*, **12**, 11, 1–19, Nov. 2020. doi: 10.3390/polym12112531.

57. Winie, T., Jamal, A., Saaid, F. I. and Tseng, T. Y. (2019) Hexanoyl chitosan/ENR25 blend polymer electrolyte system for electrical double layer capacitor. *Polym. Adv. Technol.*, **30**, 3, 726–735, Mar. 2019. doi: 10.1002/pat.4510.

58. Barbosa, J. C., Gonçalves, R., Costa, C. M. and Lanceros-Méndez, S. (2022) Toward Sustainable Solid Polymer Electrolytes for Lithium-Ion Batteries. *ACS Omega*, *American Chemical Society*, **7**, 17, 14457–14464, May 03, 2022. doi: 10.1021/acsomega.2c01926.

59. Brza, M., *et al.* (2020) Energy storage behavior of lithium-ion conducting poly(Vinyl alcohol) (pva): Chitosan(cs)-based polymer blend electrolyte membranes: Preparation, equivalent circuit modeling, ion transport parameters, and dielectric properties. *Membranes (Basel)*, **10**, 12, 1–20, Dec. 2020. doi: 10.3390/membranes10120381.

60. Rochliadi, A., Bunbun Bundjali, I Made Arcana, and Hariyawati Dharmi (2015) Polymer Electrolyte Membranes Prepared by Blending of Poly(vinyl alcohol)-Poly(ethylene oxide) for lithium battery application.

61. Olmedo-Martínez, J. L., *et al.* (2020) High Lithium Conductivity of Miscible Poly(ethylene oxide)/Methacrylic Sulfonamide Anionic Polyelectrolyte Polymer Blends. *Macromolecules*, **53**, 11, 4442–4453. doi: 10.1021/acs.macromol.0c00703.

62. Hashim, H., *et al.* (2010) Natural rubber-grafted with 30% poly(methylmethacrylate) characterization

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for application in lithium polymer battery. *CSSR 2010 - 2010 International Conference on Science and Social Research*, no. Cssr, 485–488. doi: 10.1109/CSSR.2010.5773825.

63. Wheatle, B. K., Lynd, N. A. and Ganesan, V. (2020) Effect of Host Incompatibility and Polarity Contrast on Ion Transport in Ternary Polymer-Polymer-Salt Blend Electrolytes. *Macromolecules*, **53**, 3, 875–884, Feb. 2020. doi: 10.1021/acs.macromol.9b02510.

64. Mallaiah, Y., Jeedi, V. R., Swarnalatha, R., Raju, A., Narender Reddy, S. and Sadananda Chary, A. (2021) Impact of polymer blending on ionic conduction mechanism and dielectric properties of sodium based PEO-PVdF solid polymer electrolyte systems. *Journal of Physics and Chemistry of Solids*, **155**, Aug. 2021. doi: 10.1016/j.jpcs.2021.110096.

65. Singh, T. H. J. and Bhat, S. V. (2003) Morphology and conductivity studies of a new solid polymer, **26**, 7, 707–714,.

66. Mei, X., *et al.* (2023) Improving Ion Conductivity in Polymer Blend Electrolytes by Tuning Microdynamics and Interfaces. *ACS Appl. Polym. Mater.*, **5**, 11, 9225–9235, Nov. 2023. doi: 10.1021/acsapm.3c01658.

67. Ahmed, H. T. and Abdullah, O. G. (2020) Structural and ionic conductivity characterization of PEO:MC-NH4I proton-conducting polymer blend electrolytes based films. *Results Phys.*, **16**, Mar. 2020. doi: 10.1016/j.rinp.2019.102861.

68. Sunandar, M., Yulianti, E., Deswita, D. and Sudaryanto, S. (2019) Study of solid polymer electrolyte based on biodegradable polymer polycaprolactone. *Malaysian Journal of Fundamental and Applied Sciences*, **15**, 3, 467–471. doi: 10.11113/mjfas.v15n3.1185.

69. Yang, C. and Lin, S. (2002) Alkaline composite PEO – PVA – glass-fibre-mat polymer electrolyte for Zn – air battery, **112**, 497–503.

70. Kaplan, H. and Seireg, A. (2002) Lateral thermal expansion of cellulose Iβ and IIII polymorphs. *J. Polym. Sci. B. Polym. Phys.*, **40**, 11, 1095–1102, Jun. 2002. doi: 10.1002/polb.10166.

71. Saha, B., Patra, A. S., Mukherjee, A. K. and Paul, I. (2021) Interaction and thermal stability of carboxymethyl cellulose on α-Fe2O3(001) surface: ReaxFF molecular dynamics simulations study. *J. Mol. Graph Model*, **102**, Jan. 2021. doi: 10.1016/j.jmgm.2020.107787.

72. Rayung, M., *et al.* (2020) Bio-based polymer electrolytes for electrochemical devices: Insight into the ionic conductivity performance. *Materials*, **13**, 4. doi: 10.3390/ma13040838.

73. Vincent, C. A., *et al.* (2020) A Biodegradable Secondary Battery and its Biodegradation Mechanism for Eco-Friendly Energy-Storage Systems. *Polymer Bulletin*, **7**, 4, 1–10. doi: 10.1002/adma.202004902.

74. Wang, D. and Han, C. (2020) Energy density issues of flexible energy storage devices. *Energy Storage Mater*, **28**, 264–292, March, 2020. doi: 10.1016/j.ensm.2020.03.006.

75. Abraham, K. M. (2015) Prospects and Limits of Energy Storage in Batteries. doi: 10.1021/jz5026273.