

POLYMER-BASED IONIC CONDUCTORS

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Abstract: Polymer electrolytes consist of polymer matrices with ion transport capabilities and can exist in either a solid or gel state. In both states, the incorporation of plasticizers and fillers will enhance the ionic conductivity. Gel polymer electrolytes (GPEs) exhibit ionic conductivity levels remarkably akin to those of liquid electrolytes, owing to the direct solvation of salts within solid polymer electrolytes.

Keywords: Polymer electrolytes, gel polymer electrolytes, ionic conductivity, filler and plasticizers

1. Introduction

The term “solid state ionics” (SSI) was initially used by Takehiko Takahashi in 1967 (Yamamoto, 2017). SSI is a multi-disciplinary subject that includes various aspects of science and engineering. SSI also covers research related to charge transfer in electrolytes that are in the solid and gel states. Solid-state electrolytes comprise inorganic as well as polymer electrolytes. In this article, discussion is restricted to polymer electrolytes.

Polymer electrolytes are highly flexible films that conduct ions when acted on by an electric field. Electrode-electrolyte contact is excellent and the cost is low (Liu et al., 2020). Ion transport is achieved by means of ion hopping and segmental motion. Ionic conductivity (σ) depends on the availability of free ions (n) and ion mobility (μ) as in the equation $\sigma = n\mu e$ with e being 1.6×10^{-19} C. Solid polymer electrolytes ensures high safety (Zhang et al., 2021). However, the ionic conductivity of solid polymer electrolytes is low and they exhibit high interfacial resistance with the electrodes. Apart from these, the cycling performance is also poor (Chae & Lucht, 2023). Gel polymer electrolytes (GPEs) exhibit good flexibility, processability and ensures high safety features (Aruchamy et al., 2023). GPEs are used in devices. The possibility that the device will encounter leakage problems is slim. The device will also be thermally stable (Long et al., 2022). Poor safety and unstable electrochemical performance are some disadvantages of liquid electrolytes (Yao et al., 2019). These greatly limits its further development and wider applications.

2. Polymer Electrolytes

For application as an electrolyte, a polymer must have polar groups with electron donor atoms to coordinate with cation of the salt. Ion conduction in polymer electrolytes was initially demonstrated using dye-sensitized solar cells (DSSCs) (Hagfeldt, Boschloo, Sun, Kloo, & Pettersson, 2010). In a DSSC, the electrons that make up the current are returned to the dye material by way of the reduction-oxidation (redox) reactions that occur in the electrolyte. The electrolyte electrically connects the positive and negative terminals of the solar cell.

There are many polymers used in polymer electrolyte research. These include chitosan (Arof et al., 2001; Khair, Puteh, & Arof, 2006; Morni & Arof, 1999), poly (ethylene oxide) (Quartarone, Mustarelli, & Magistris, 1998; Yan et al., 2023), poly (vinylidene fluoride) (Zhou et al., 2023), poly (vinyl alcohol) (Moorthy, Sivasubramanian, Kannaiyan, & Deivanayagam, 2023), poly (methyl methacrylate) (S Ramesh & Arof, 2021; Uktamaliyev et al., 2023), poly (vinyl pyrrolidone) (Sangwan, Mathela, Dhapola, Singh, & Tomar, 2022), poly (caprolactone) (Li et al., 2022) and poly (vinyl chloride) (Subramaniam Ramesh & Arof, 2000). In all these polymers there are atoms with unused electrons. These electrons are not shared with other atoms from the same molecule. In chitosan and poly (vinyl pyrrolidone), the oxygen and nitrogen atoms have unused electrons. In poly (ethylene oxide) or PEO, poly (methyl methacrylate) or PMMA, poly (caprolactone) and poly (vinyl alcohol) or PVA, the oxygen atoms are the sites that contain the unused or what is also known as “lone pair” electrons. In poly (vinylidene fluoride), the unused electrons are at the fluorine atoms and in poly (vinyl chloride) at the chlorine atoms. Cations from the added salt can form “loose” bonds with atoms that contain these lone pair electrons. In the presence of an electric field, these ions will be transported to the appropriate terminal. Thus ion conduction occurs.

2.1 Types of Polymer Electrolyte

Polymer electrolytes can be divided into four groups: (i) solid, (ii) gel, (iii) plasticized and (iv) composite polymer electrolytes.

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2.1.1 Solid Polymer Electrolytes (SPEs) Or Polymer-Salt Complexes

A polymer-salt complex or SPE is a solvent-free salt solution in a polymer host. An example of a solid polymer electrolyte (SPE) is 65 wt.% chitosan–35 wt.% adipic acid. Room temperature conductivity of the SPE was only $1.4 \times 10^{-7} \text{ S m}^{-1}$ (Idris, Aziz, Zambri, Zakaria, & Isa, 2009). The conductivity was attributed to protons from the acid. The protons hop from one nitrogen to the next or via the oxygen atoms in the hydroxyl groups in the polymer. As another example, consider the solid electrolyte 69 mol% PEO-23 mol% PVC-8 mol% LiBF_4 (Rajendran, Babu, & Usha Rani, 2011) that contains two types of polymers. The room temperature ion conductivity was $7.9 \times 10^{-4} \text{ S m}^{-1}$. The Li^+ ion is transported between the electrodes via hopping along the oxygen atoms in PEO and along the chlorine atoms in PVC. The availability of more active sites for ion hopping is probably the reason conductivity is able to reach the order 10^{-4} S m^{-1} .

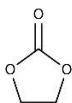
2.1.2 Gel polymer electrolyte

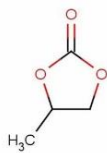
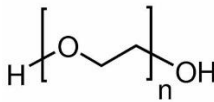
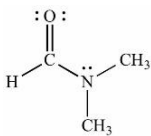
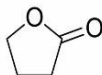
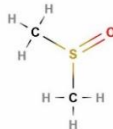
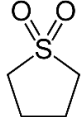
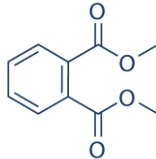
Gel polymer electrolyte (GPE) was first proposed by Feullade and Perche in 1975 (Feuillade & Perche, 1975). The physical phase of a GPE is between that of solid and liquid electrolytes. Thus, the ionic conductivity of GPEs is higher than that of solid electrolytes. As stated above, GPEs are safe as leakage is less likely to occur in devices employing GPEs. It has been demonstrated that a GPE containing LiPF_6 salt exhibited a conductivity of 0.888 S m^{-1} at 25°C (Wang, Qiu, Peng, Li, & Zhai, 2017).

2.1.3 Plasticized polymer electrolyte

Plasticized polymer electrolyte is a mixture containing at least a polymer, a salt and a material that when added in the suitable amount can increase ionic conductivity. The added material that helped to increase ionic conductivity of the polymer-salt electrolyte is known as plasticizer. The plasticizer enhances ion conduction in the polymer electrolyte by weakening the interactions within and among the polymer molecules that compete with ion-polymer interactions. Some examples of plasticizers are listed in Table 1.

Table 1. Listed of common plasticizers used as additive in polymer electrolyte

Plasticizer	Molecule Structure	Molecular Weight (g mol^{-1})
Ethylene carbonate	 $(\text{CH}_2\text{O})_2\text{CO}$	88.1

Propylene carbonate	 $\text{C}_4\text{H}_6\text{O}_3$	102.1
Polyethylene glycol	 $\text{C}_2\text{H}_6\text{O}_2$	62.07
Dimethyl formamide	 $(\text{CH}_3)_2\text{NC(O)H}$	73.09
γ -butyrolactone	 $\text{C}_4\text{H}_8\text{BrO}_2$	164.99
Dimethyl sulfoxide	 $(\text{CH}_3)_2\text{SO}$	78.13
Sulfolane	 $\text{C}_4\text{H}_8\text{O}_2\text{S}$	120.17
Dimethyl phthalate	 $\text{C}_{10}\text{H}_{10}\text{O}_4$	194.18

The oxygen atoms in ethylene carbonate (EC) contain unused electrons just as in the atoms with unused electrons in the polymers for preparing the electrolytes. It is to be noted that plasticizers do not bond covalently with the polymer chain. With the addition of plasticizer such as EC, the cation of the salt has more transit sites to move or hop along the electrolyte. The energy required by the cations, i.e. the activation energy to hop along the electrolyte in the absence of EC is more than the activation energy of the cations in electrolytes containing plasticizers (Banitaba, Semnani, Heydari-Soureshjani, Rezaei, & Ensafi, 2020). Activation energy is the minimum energy required by the cations to hop from one site to another in an electrolyte.

The activation energy can be obtained from the gradient of the $\ln(\sigma T)$ versus $1000/T$, which is known as the Arrhenius plot. Here T is absolute temperature. In the Arrhenius plot for the GPE with tetrabutyl ammonium iodide (TBAI) salt, the lowest activation energy is $\sim 13 \text{ kJ mol}^{-1}$ (Chowdhury et al., 2020). This was the highest conducting sample.

Since plasticizers can weaken the forces within and between the polymer chains, they make the polymer electrolyte films less rigid, more amorphous and more salt can be dissociated in the electrolytes. The glass transition temperature is also reduced (Storck, Dotter, Brockhagen, & Grothe, 2020). With increase in salt dissociation, more free ions will be available. The presence of more free ions will increase ion conductivity. Although plasticizer addition can increase ion conductivity, it also lowers the mechanical strength of the electrolyte.

Polymer electrolytes utilizing plasticized polyacrylonitrile (PAN) have demonstrated impressive ion conductivity levels exceeding $10^{-3} \text{ S cm}^{-1}$ at a temperature of $30 \text{ }^\circ\text{C}$ (Singh et al., 2020). In this study, the researchers employed propylene carbonate (PC) as the plasticizing agent, resulting in a notable ionic conductivity of 0.328 S cm^{-1} for PAN-Mg(ClO₄)₂-PC.

2.1.4 Composite polymer electrolytes (CPEs)

CPEs contain inorganic fillers, which are typically ceramic materials. Examples of these inorganic fillers are Al₂O₃ (Kotobuki, 2020), BaTiO₃ (Sadiq, Arya, Ali, Singh, & Sharma, 2020), CeO₂ (Augustine, Zahid, Hasan, Dalvi, & Jacob, 2020), ZrO₂ (Xiao, Song, Huang, Yang, & Qiao, 2020), TiO₂ (Ruiz Gómez, Mina Hernández, & Diosa Astaiza, 2020), SiO₂ (Lyu, He, & Liu, 2020), ZnO (Chan et al., 2018), carbon nanotubes (Alateyah, 2019) and boehmite (AlOOH) nanoparticles (Meera & Ramesan, 2022). They have high dielectric constants that can enhance ion conductivity by preventing the formation of ion-pairs and ion-triplets in the electrolyte. Boehmite is a crystalline mineral that contains Al₂O₃ and Al(OH)₃. Boehmite is found in bauxite. The addition of inorganic filler is effective in increasing the amorphousness and segmental motion of a polymer electrolyte and improves mobility of the Li⁺ cation (Lyu et al., 2020) and hence cationic conductivity. The increase in amorphousness creates the formation of more ionic conductivity pathways in the polymer matrix. T_g of the polymer phase also decreased (Fu, Li, Zhou, & Guo, 2022). The addition of fillers only lead to conductivity enhancement up to a maximum concentration. Beyond the maximum filler concentration, the conductivity shows a decrease.

In all the electrolytes described above, the conductivity is observed to decrease after a maximum value is attained at a particular salt, plasticizer or filler concentration. When the quantity of these materials is increased, there will be more charge carrying ions and the conductivity is observed to increase. If the number of ions has increased above a certain concentration, conductivity decreased. This is because, above a certain concentration of these materials, the ions will be closer together and begin to interact with each other leading to

recombination. Thus, although more salt, plasticizer or filler is added, there will be less free ion concentration, and this led to the decrease in ionic conductivity.

3. Conclusion

In this article we have shown how the conductivity of a polymer electrolyte can be maximized. Conductivity can be increased by adding the right amount of salt concentration, using more than one polymer, gelling the electrolyte and adding plasticizers and fillers.

4. References

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