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CLASSIFICATION AND CHARACTERIZATION OF POLYMER GEL ELECTROLYTE: A REVIEW

Santu Khatua[1], Dr. Ratnesh Tiwari[2] , Dr. Samit Tiwari[3]

[1]Research Scholar, Dr. C.V. Raman University, Kota, Bilaspur, (C.G.), 495113, India
[2]Professor Dept. of Physics, Dr. C.V. Raman University, Kota, Bilaspur, (C.G.), 495113, India
[3]Professor Dept. of Physics, Bhilai Institute of Technology, Durg, 490001, India

Abstract:

Polymer electrolytes are considered an alternative to liquid electrolytes for lithium-ion batteries due to their high thermal stability, flexibility, and wide applications. However, polymer electrolytes have low ionic conductivity at room temperature due to interfacial contact issues and growth of lithium dendrites in electrolytes/electrodes. Polymer gel electrolytes were prepared by a gelation method with different O/Na ratios using PVdF as the polymer host, sodium iodide as the salt, and DMF as the solvent. After synthesis it is characterized by different experimental techniques.

Keywords: Polymer Gel, Electrolyte, Lithium

Introduction:

Electrolyte:

An electrolyte is any substance that contains free ions that make the substance electrically conductive. An electrolyte is usually formed when a solute dissolves in a suitable solvent. E.g., $ZnCl_2 + HCl \rightarrow Zn^{+} + 2Cl^{-1}$, When $ZnCl_2$ dissolves in HCl it gives Zn^{+} and $2Cl^{-}$. Electrolytes are of two types depending on their condition: (i) liquid electrolyte and (ii) solid electrolyte. An electrolyte which is in a liquid state is called a liquid electrolyte. e.g. when *NaCl* dissolves in water it gives Na^{+} and Cl^{-}. The conductivity of liquid electrolyte is very high in the order of 10-1S/cm. An electrolyte in a solid state is called a solid electrolyte. They are also called super ionic or fast ionic conductors, which exhibit exceptionally high ionic conductivity at room temperature. The ionic conductivity of the electrolyte varies from 10^{-2} to 10^{-6} Scm^{-1}.

Need of Solid Electrolyte:

Still, the majority of electrochemical and electrochromic devices are liquid-aqueous electrolyte-based devices. These devices have several disadvantages which are given below:

- **Limited temperature range of operation:** We cannot use liquid electrolyte for a wide temperature range because generally below $0^{0}C$ and above $100^{0}C$, liquid electrolytes stop working. Electrolyte Corrosion: When liquid electrolyte is used in a battery after several cycles, dissimilar chemicals accumulate at the electrode-electrolyte interface, causing battery damage.
- Internal short-circuiting: Internal short-circuiting can occur due to electrolytic compression in a liquid electrolyte.
- Electrolyte Leakage: Since the electrolyte is in a liquid state, there is a possibility of electrolyte leakage.
- Large in size and low energy density: Due to the large size of liquid electrolyte it takes up more space with less power and energy density.

Classification of Solid Electrolyte:

Depending on various microstructures and physical properties; Solid electrolytes are divided into the following categories. These are

- framework crystalline materials,
- amorphous-glass electrolytes,
- composite electrolyte
- polymer electrolytes.

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Among these four types of solid electrolyte, the first one is ordered while the rest are disordered. Amorphous glassy and polymer electrolytes are microscopically disordered, while composite electrolytes are macroscopically disordered.

Polymer Electrolyte:

Polymer electrolytes typically consist of complex polar polymers such as PEO, PPO, PEG, etc., with ionic salts of monovalent alkali metal or divalent transition metal ammonium salts. Polymer electrolytes are mostly prepared by solution cast method or electro-deposition method. Polymer electrolytes have many advantages over liquid electrolytes such as freedom from leakage, good processability, design flexibility, space coverage, light weight, and the possibility of high energy and power density.

Classification of Polymer Electrolyte:

Depending on the method of preparation for the desired level of conductivity of polymer electrolytes, polymer electrolytes can be classified into the following categories:

- **Conventional Polymer Salt Complexes or Dry SPE:** Dry SPEs are prepared by dissolving ionic salts in polar polymer hosts, namely polyethylene oxide (PEO) and polypropylene oxide (PPO). Film casting is done either by solution cast method, electrodeposition method or sol gel method.
- **Plasticized polymer salt complex:** They are prepared by adding liquid plasticizers to dry SPE. Plasticized polymer salt complexes exhibit both liquid and solid behavior. The ambient conductivity is significantly increased by this process, but the mechanical stability deteriorates and the corrosive reaction of the polymer electrolyte also increases.
- **Polymer Gel Electrolyte (PGE):** A polymer gel electrolyte is usually obtained by adding a polymer to a liquid plasticizer and salt solution. Polymer electrolytes also have disadvantages as noted for plasticized polymer electrolytes. Later we will discuss more about PGE.
- **Composite Polymer Electrolyte (CPE):** CPEs are basically analogues of phase composite solid electrolyte systems. They are also prepared by dispersing a small fraction of micro/nano sized inorganic or organic filler particles in a conventional SPE host. SPEs act as phase-I, while fillers act as phase-II dispersions. As a result, ionic conductivity, mechanical stability and interfacial activity are usually greatly increased

Gel and Polymer Gel Electrolyte:

Gels are three-dimensional network structures of polymers and their swollen mats. They have both the cohesive properties of solids and the diffusive transport properties of liquids. Their properties vary from viscous liquids to hard solids depending on their chemical composition. The properties of polymer gel electrolytes have been found to depend on the structure of the polymer network forming the gel as well as the interaction between the network and the solvent. Gels generally have high mobility as the polymer networks are solvated by a large amount of entrapped solvent. A polymer gel electrolyte is usually prepared by adding a polymer to a solvent-salt solution.

Role of Polymer, Salt and Solvent in PGE:

In polymer gel electrolytes the salt generally provides free/mobile ions which participate in the conduction process and helps to dissolve the solvent salt and also acts as a conductive medium while the polymer provides mechanical stability by increasing the viscosity of the electrolyte. The salt used should generally have large ions and low dissociation energy so that it dissociates easily. Salts should also contain large amounts of ions. The solvent used should also have high dielectric constant, low viscosity and high boiling point, low melting point and low molecular weight. Polymers should have the following properties: high molecular weight, low glass transition temperature.

Table 1.1 Some of Organic Salt Generally Used for Plasticizer

Sr. No	Organic Salt	Melting Point	Boiling Point	Density G cm-3	Dielectric Constant
1.	Ethylene Carbonate	36.9	252	1.35	90.04

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2.	Polyene Carbonate	-47.9	243	1.207	66.43
3.	Dimethyl Carbonate	2.6	92	1.09	3.17
4.	Diethyl Carbonate	-42.7	127	0.981	2.91

Mechanism of Transport in Ionic and Super Ionic Solids:

Defects play an important role in ionic conduction in polymer electrolyte or gel polymer electrolyte. Ionic conduction can be explained by two mechanisms either the VTF equation or the Arrhenius equation.

Equation of VTF:

A group of polymer electrolytes follow the VTF type relationship expressed by the following equation.

$$\sigma = AT^2 exp[-E_a/(T - T_0)]$$

where A is the pre-exponential factor and T0 is the equilibrium glass transition temperature. In the VTF relation, conductivity is correlated with temperature which is typically non-linear indicating the conductivity mechanisms involved in relaxation/respiration or hope motion with segmental motion.

Equation of Arrhenius:

On the other hand, some polymer electrolytes obey the Arrhenius equation for the ion conduction mechanism, which is given by…

$$\sigma = \sigma_0 exp(-E_A/KT)$$

where $-E_A$ is the activation energy can be calculated from a linear-least-squares fit of the data in a log versus 1/T curve. Materials exhibiting a linear Arrhenius equation represent ion transport by a simple hopping mechanism decoupled from the respiration of the polymer chain.

Conclusion:

A series of polymer gel electrolytes are synthesized by gelation method using PVDF polymer DMF as solvent and sodium iodide as salt. After synthesis it is characterized by different experimental techniques. XRD was useful for structural properties, SEM for surface morphology and dielectric spectroscopy for electrical properties.

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