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A conceptual review on polymer gel electrolytes and its conduction mechanism

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Abstract
The review critically describe advantage and characteristics of the gel polymer electrolytes in the solid state batteries. The performance of gel polymer electrolytes is individually compared with their constituents. The role of host polymer, salt and liquid plasticizer in gel polymer electrolyte is critically signified. The various properties of gel polymer electrolyte are highlighted with their critical concepts. The preparation of polymer gel Nan composites by dispersing the various semiconducting, ceramic and insulating particles in the nano range are overviewed. Various advances in the GPE with various types and electrochemical utility by the different research workers are highlighted. The different types of models like Semi-empirical model, Effective medium theory and percolation model are well subjected. Vogel–Tamman–Fulcher (VTF) equation fits and interprets transport data and quasi thermodynamic data. Effective medium theory model relates the conductivity enhancement to the existence of a space-charge layer at the electrolyte/filler interface. The percolation model explains the presence of two peaks in the conductivity vs weight percentage of dispersoid in the gel polymer electrolyte composites. Chandra's Breathing polymer chain model explains initial increase of conductivity with polymer concentration in gel polymer electrolyte.

Keywords: A conceptual review polymer gel electrolytes its conduction mechanism

Introduction

In the recent years, there has been growing demand of polymer gel electrolyte due to their immense potential application in solid state batteries, fuel cell, dye sensitised solar cell and supercapacitors etc. [1-3]. Among all the polymer electrolytes, the polymer gel electrolytes have the enhanced conductivity beside good mechanical and chemical stability. Polymer gel electrolyte consist of the three terms polymer, gel and electrolyte. The term polymer stands the substances having high molecular weight which are formed by the union of the small molecular groups called monomer units joined through the covalent bond. The term gel stands for the solid like network which is swelled by the continuous dispersion of liquid phase. The role of the liquid is swelling in the solid frame network while solid network helps in preventing the liquid from flowing away. Due to this property, gel is a compromise between solid state and liquid state. At the high temperature, it behave liquid like behaviour and at the low temperature, it show the rubbery properties of solid. The third term electrolyte stands for salt in dissociable form in ions in some solvent.

Liquid electrolyte

The electrolyte which is in liquid state is called liquid electrolyte. If solute dissociate to small extent, then it is called weak electrolyte. Liquid electrolyte is the solution- a homogeneous mixture of the solute and the solvent i. e. solution= solvent + solute e.g. when NaCl is dissolved in water it gives Na^+ and Cl [4]. The conductivity of the liquid electrolyte is found of the order of 10^{-2} S/cm and because of their high value of conductivity, these had been used in batteries. Still liquid electrolytes have several disadvantages over polymer electrolyte such as:

Limited temperature range of operation: the liquid electrolyte for a wide temperature range because normally below 0^0C and above 100^0C, liquid electrolytes cease to work [5].

Corrosion of electrolyte: When liquid electrolyte is used in battery after operation of so many cycles there is deposition of uneven chemicals at the electrodes-electrolyte interface, which damage the battery.

Internal short circuiting: In liquid electrolyte there may happen internal short circuiting due to pressing of electrolyte.

Leakage of electrolyte: Since electrolyte is in liquid state there is a chance of leakage of electrolyte.

Bulky in size and low energy density: Due to large size of the liquid electrolyte it takes more space with low power and energy density.

Liquid plasticizer

The liquid electrolyte is prepared by blending some organic solvent like propylene carbonate (PC), ethylene carbonate (EC), dimethyl formamide (DMF), diethyl carbonate (DEC), dimethyl carbonate (DMC) etc with the alkali metal salt. The above prepared liquid electrolyte is also called plasticizer. The plasticizer should have low molecular weight and these should have high conductivity or the order of 10^{-3} S/cm.

Polymer electrolyte: Polymer electrolyte is usually formed by complexing polar polymer like PEO, PPO, PEG etc with ionic salt of monovalent alkali metal or divalent transition metal ammonium salt [6]. Polymer electrolytes are mostly prepared either by solution cast method or electro-deposition method. The polymer electrolyte is generally in film form [7-11].

Polymer gel electrolytes

Figure I shows the different steps involved in the preparation of polymer gel electrolytes. As discussed earlier, the polymer gel electrolytes, the liquid electrolyte is mixed with a polymer matrix and due to which liquid like conductivity is observed. The salt should be metal salt [MX] and should have the low lattice energy. Polymer like polyethylene oxide (PEO), polypropylene oxide (PPO), polyacrylic acid (PAA), polyethylene imine (PEI), polyethylene glycol (PEG), Polymers like polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), polyvinylidene fluoride (PVDF-HFP) etc are used as polymer host. So far as the choice of the solvent is concerned the solvent should have high dielectric constant and low viscosity. The high dielectric constant helps in complete dissociation of the salt and low viscosity provide maximum mobility of the ions in the electrolyte resulting the high value of conductivity. As stated in the section 1, polymer act as gelling agent in the preparation of polymer gel electrolyte. But high molecular weight of the polymer leads to increase of the viscosity resulting decrease in the mobality of the ions from the following relation $\mu = q/6\pi r\eta$. As a result of which the conductivity decreases. It means

σ (gel) < σ(liquid)

However it has been found that the decrease in the ion conductivity is not very large. It means the polymer plays the role of the stiffner in the polymer gel electrolyte.

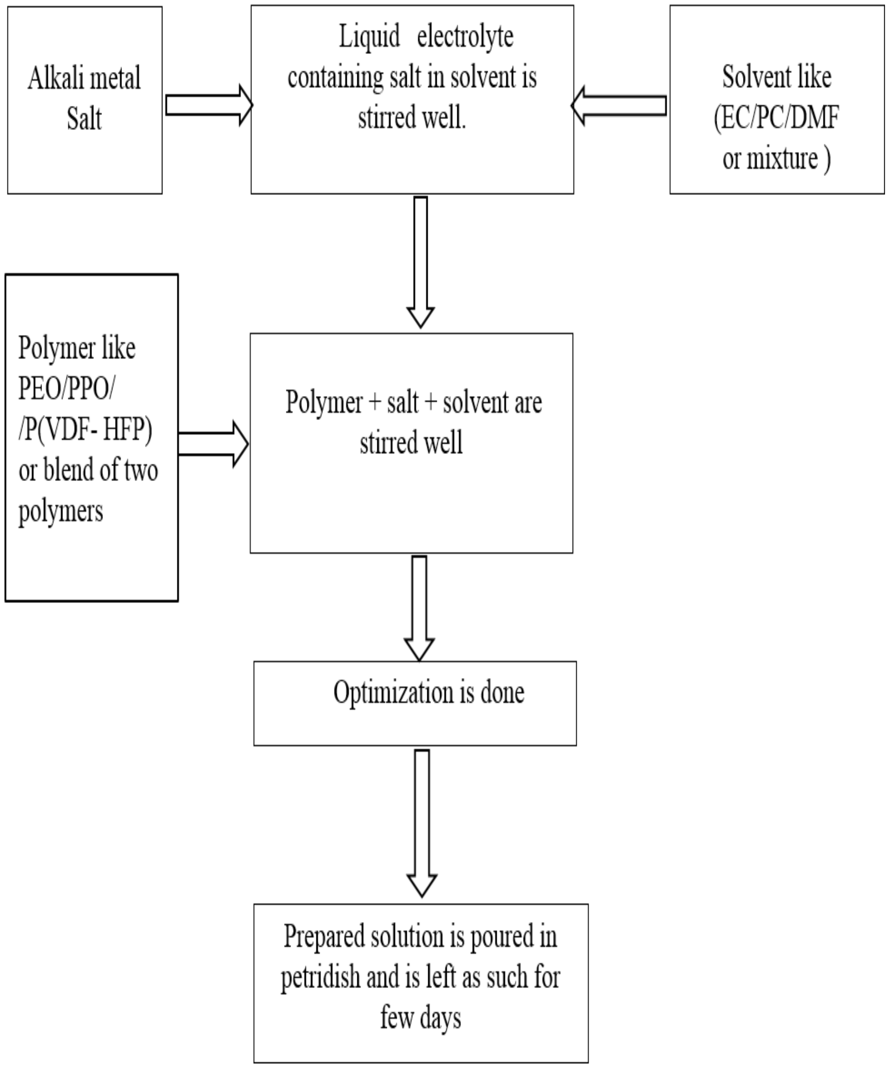

Fig 1: Different steps involved in the preparation of polymer gel electrolytes

The conductivity lineally increases with the increase of concentration of salt obtaining the maximum value. This could be explained as follows, initially with the salt concentration the no of free ion increases resulting increase in the conductivity toward the saturation value due to the ion association. Also the effect of concentration of polymer is studied. With the increase in the concentration of polymer in the polymer gel electrolyte, the conductivity decrease. This could be attributed to the following fact. With the increase of polymer concentration, the viscosity increases and the dielectric constant decrease. Both the above changes lead to the decrease of dissociated ions in the polymer gel electrolytes. As a result of which the conductivity is decreased [12-13].

Polymer gel nanocomposites

The polymer gel electrolyte has the conductivity range of the order of 10^{-3} S/cm. But with the longer time of use of it, conductivity falls due to some reasons like leakage of liquid electrolyte solvent from the polymer electrolyte which may cause the damage of electrode and other constituents. The problem could be solved by preparation of polymer gel nanocomposites, in which small sizes (in the nano range) fillers are dispersed in the gel polymer electrolytes. The examples of the nano fillers could be SiO_2, TiO_2, Al_2O_3 and CeO_2. It has been observed that by the dispersal of fillers, the porous structure of the polymer is maintained which helps in the absorption of liquid electrolyte in the polymer electrolyte resulting decrease of leakage problem and more safety for the device applications. Hence with synthesis of nanocomposites gel electrolytes, there have been improvement in the electrical and electrochemical properties of polymer gel electrolyte. The lot of work is done in the similar direction by various groups [14].

Early work of the polymer gel electrolyte was concentrated on the lithium ion polymer gel. For the lithium ion conducting PGE, the salt used are $LiCFSO_3$, $LiClO_4$, LiN $(SO_2CF_3)_2$ etc. With the choice of polyethylene oxide (PEO) and EC/PC as the plasticizer, the conducitivity has been found to be of order of 10^{-3}S/cm. As polyethylene oxide is not so much soluble to above solvent, hence the PGE show the poor mechanical strength. To the above PGE, if the PEO is replaced by the polyacrylonitrile (PAN), then PGE show the good transference number of lithium ion. PMMA based PGE in above case, the conductivity of 10^{-3}S/cm had been reached. In the case of PVDF with lithum and sodium salt and EC/PC as solvent, the electrochemical properties are much highlighted, but the polymer is much reactive to the salt. Working with the different PGE, the different groups has achieved different observations [15].

Thakur et al. worked in the system PMMA+ PC + x wt. % $NaClO_4$ and PMMA+ (EC+ PC) + x wt.% $NaClO_4$ and observed the conductivity of 10^{-3} S cm^{-1} at the room temperature [16].

Wachtler et al. worked on the system PVDF+EC+PC+SiO_2+ lithium salt and concluded that structure of the host polymer depends on the multifactor like preparation method, concentration of its constituents [17].

Akashi et al. worked the on the lithium ion polymer battery and concluded that PVDF PGE are better than lithium ion polymer battery in the voltage range 4.2 V [18].

Panero and Scrosati worked on PAN+ (EC+DMC) + $LiPF_6$ PGE system and concluded tha application of PGE in the advanced design and plastic based electrochemical devices [19].

Reale et al. worked on the ceramic filler dispersed PGE composites and concluded with the enhanced mechanical stability keeping other properties unchanged. PGE finds the application in the rechargeable batteries [20].

Appetecchi et al. worked on PAN and Li^+ based polymer gel electrolyte which is well dispersed with the ceramic filler like Al_2O_3. They concluded that composted PGE has enhanced conductivity, no leakage, enhanced electrochemical stability and good electrode electrolyte interface which find the application in the solid state batteries [21].

Fardis et al. studied the system (PEO+LiI - I_2 based PGE which is mixed with the filler TiO_2) with the different studies like NMR, diffusion and relaxometry measurement [22].

Sekhon et al. investigated that polymer is vital constituent of PGE. The different molecular weight of the polymer has different conductivity…. solvent helps in the dissociation of the salts into the ion and hence providing the conduction medium. They also found that conductivity lithium ion PGE decreases with concentration of polymer while the conductivity of proton conducting PGE increases to the optimum value with the concentration of polymer [23].

Zhang et al. prepared the lithium ion and [P (VDF- HFP)] based PGE by phase separation method and investigated the physical and electrochemical properties [24].

Balaji et al. studied the new host polymer Polyurethane (PU) based polymer gel electrolyte and found that new PGE is better than PAN or PAN-PEO based PGE in concern to application propertied in the electrochemical devices. The conductivity on new PGE has been found to be 10^{-3} S/cm [25].

Renganathan et al. stressed the application of PGE in carbon aerogel supercapacitor which has been found with conductivity 10^{-2} S/cm. the new capacitor is characterized with complex impedance spectroscopy, Galvano static cycling and cyclic voltammetry [26].

Peng et al. have reviewed the recent progress of gel polymer electrolyte with enhanced electrochemical properties and specified functionalities for the storage devices [27].

Kim et al. worked on the system PVDF-co-HFP+ NMP based GPE. PVDF-co-HFP works as separator just like existing separator polypropylene (PP) and have conductivity of 2.3×10^{-3} S/cm at room temperature. The prepared GPE finds the application in the light emitting diode (LED) [28].

Models for conductivity in gel polymer composites

The conduction mechanism phenomena in gel polymer composites is difficult to understand because of their complicated structures. Moreover, polymers are weak electrolytes and ion association leads to the formation of ion pairs, triplets and multiplets.

Macroscopic approaches

The conductivity in polymer gel electrolytes is generally fitted in terms of the Vogel–Tamman–Fulcher (VTF) equation which satisfies transport data. Quasi thermodynamic models like free volume and configurational entropy leads to fitting the data in term of following equation. However, their applications is limited to simple monophase system where the salts are almost fully dissociated.

$\sigma\ (T) = AT^{-0.5}\, e^{-(B/T-T_0)}$

Semi-empirical model

In the ion conductors, conductivity σ (T) may display Arrhenious or VTF behaviour or a mixture of the two or even more complex behaviours at all temperatures. For a wide range of fast ionic conductors (FIC), the conductivity is Arrhenious, the pre-exponential factor σ_o, and the activation energy E_a, are connected by the Meyer–Neldel (MN) rule (or Compensation Law):

$\ln \sigma_0 = \alpha E + \beta = E_a/kT_D + \ln K\omega_0$

The above equation was initially applied to atomic diffusion in metals [29]. Here, T_D is a characteristic temperature, K is the concentration term and ω_o is the ions attempt frequency. T is the temperature of an order/disorder transition. The general MN rule is valid for a number of blend-based and mixed-phase polymer electrolytes

Effective medium theory

This model relates the conductivity enhancement to the existence of a space-charge layer at the electrolyte/filler interface. According to the model, the composite electrolyte can be treated as a quasi-two-phase system consisting of a ionically conducting polymer matrix with dispersed composite units.

General Effective Medium (GEM) equation is

$$\frac{f({\sigma_1}^{1/t} - {\sigma_m}^{1/t})}{{\sigma_1}^{1/t} + A{\sigma_m}^{1/t}} + \frac{(1-f)({\sigma_2}^{1/t} - {\sigma_m}^{1/t})}{{\sigma_2}^{1/t} + A{\sigma_m}^{1/t}} = 0$$

Where, σ_1, σ_2 and σ_m are the conductivities of the two phases and of the composite material, respectively. Constant *A* depends on the particular composite medium and the approach to the problem, *t* is an exponent related to the filler volume, PEO fraction *f* and to the grain shape.

For the microscopic view, composite gel electrolytes were studied as addition of the fillers improves both, transport and mechanical properties of gel electrolyte films. The maximum enhancement in σ Vs filler concentration was found to be for 10-20 wt % of the ceramic additive.

Percolation model

In the case composite gel electrolytes, the plot between the conductivity as the function of dispersoid concentration (p) has shown initially increase, attaining the maxima and then rapid fall of conductivity. Also there have been found the two maxima, one at the low concentration and other at the high concentration. Bunde *et al.* [30] showed the critical properties of both, random resistor network and a random superconducting network near threshold concentration at p_c and (1- p_c), respectively.

The composites are considered to be three component systems consisting of matrix of bonds which can be normally conducting with conductivity σ_b, insulating or high conducting with conductivity $\sigma_a >> \sigma_b$. The dispersoids are randomly distributed in the conducting matrix with a high conducting interface between them. Bunde and coworkers assumed a two phase model for four different concentrations p of insulating material. The special feature of this model is the presence of two threshold concentrations p_c' and p_c''. For the smaller values of p, very few high conducting bonds occur and the total conductivity is due to normally conducting bonds. For the larger p values, a critical concentration p_c' ($0 < p_c' < 0.5$) exists corresponding to onset of interfacial percolation. For still higher values of p, conductivity is governed by high conducting bonds and hence, increases drastically. If p is increased further, then a second critical concentration p_c'' ($0.5 < p_c'' < 1$) is attained where all conduction paths become disrupted and conductor-insulator transition takes place. Above p_c'', the conductivity drops to zero.

Breathing polymer chain model

In the case of proton conducting polymer, in conductivity as a function of wt. % of polymer, the conductivity first increases and then decreases. Chandra *et al*. suggested the breathing polymer chain model. It is assumed that, polymer chain breathe while it opens and or folds occupying different volume in this phenomenon. This is the pressure controlled changes which either breaks the neutral paired ion or unblocking the mobility of the ions which is controlled by the viscosity. Both the above factor leads to increase of the conductivity of ions in the polymer chain. At the very high concentration of the polymer in GPE, the viscosity factor dominates and resulting decrease of the conductivity [31].

Conclusion

Concept of polymer gel electrolytes and its constituents are critically overviewed. The different characteristics and potential application of the gel polymer electrolytes are highlighted. The various advances and types with application of GPE in the electrochemical devices are discussed. The ion conduction mechanism in the gel polymer electrolytes are compared with different theories like Semi-empirical model, Effective medium theory and Percolation model and Chandra's breathing polymer chain model etc.

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