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Gel polymer electrolyte based on PVDF-HFP:PMMA incorporated with propylene carbonate (PC) and diethyl carbonate (DEC) plasticizers: electrical, morphology, structural and electrochemical properties

Khusbhu Gohel1, D K Kanchan2,*, Hiren K Machhi1, Saurabh S Soni3 and C Maheshwaran1

1 Department of Physics, Faculty of Science, The M.S. University of Baroda, Vadodara 390002, Gujarat, India
2 Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India

E-mail: d_k_kanchan@yahoo.com

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Abstract

To overcome the drawbacks of organic solvent—based liquid electrolytes and a solid polymer electrolyte as a separator in lithium polymer battery, in the recent study gel polymer electrolyte (GPE) using poly(vinylidene fluoride—hexafluoropropylene) (PVDF—HFP) and poly (methyl methacrylate) (PMMA) as host polymers, lithium perchlorate (LiClO4) salt as conducting species and propylene carbonate (PC) and diethyl carbonate (DEC) plasticizers as an organic solvent has been prepared. The solution casting technique has been adopted to fabricate gel polymer electrolyte (GPE). The prepared GPE films were analyzed using different experimental techniques to discover the properties of GPE. The ionic conductivity of GPE films has been carried out using electrochemical impedance spectroscopic technique. The maximum ionic conductivity of 3.97E-4 S cm−1 has been obtained for GPE having 60 wt% PC:DEC. As an evidence of change in ionic conductivity, structural characterization has been analyzed using FTIR and SEM where, FTIR spectra reveal complex formation taking place between polymers, salt, and plasticizers and SEM micrograph shows a change in surface morphology with a change in plasticizers amount. Dielectric analysis has been also carried out in terms of dielectric constant (ε′) and dielectric loss (ε′′). Cyclic voltammetry (CV) has been applied to find electrochemical stability window.

1. Introduction

Nowadays, research has been focused on the development of energy storage and conversion field due to the demand for electrochemical devices in our day to day life. In any electrochemical devices, the electrolyte plays an important role [1]. It is used as a separator to avoid contact between the electrodes and conduction of ions takes place through this electrolyte as shown in figure 1 which depict the basic structure of a battery. As a separator, polymer electrolyte (PE) has been used as a potential candidate in energy storage devices which has taken place of liquid electrolyte (organic solvent + salt) due to certain drawbacks such as leakage of liquid electrolyte, internal shorting of electrodes and explosion etc [2]. These properties of liquid electrolyte make it unsafe during application as separator in electrochemical devices [3]. A number of researches have been attempted to deal with these problems by replacing the liquid electrolyte with polymer electrolyte. As a separator in lithium polymer battery, polymer electrolytes should possess following characteristics: (i) high values of ionic conductivity, (ii) better mechanical integrity, (iii) large electrochemical stability window \( > 4 \text{V} \), (iv) Li⁺ transport number \( t_Li^+ \approx 1 \), and (v) low electronic conductivity. Polymer electrolytes (PEs) are formed by doping ionic salt/inorganic acid in polymer doped with ionic salt or inorganic acid which results in the Lewis acid-base complex electrolytes. The ionic conduction in polyether (PEO)—salt complexes to electrochemical devices was first explained by Fenton in 1973 [4]. These polymer electrolytes have been the attraction of many researchers owing to unique properties such as free from leakage, high mechanical strength, more flexible, easy to form in any shape and size [5, 6]. Despite such interesting properties, these solid polymer electrolytes suffer from some
drawbacks such as low value of ionic conductivity, electrochemical stability window prevent its applications in electrochemical devices [7]. To face the above shortcomings, the research has been carried out on preparing gel polymer electrolyte(GPE) because of its high ionic conductivity very near to the value of liquid electrolyte [8].

In fact, the GPE has the cohesive properties of solid and diffusive properties of the liquid. The GPE can be prepared by trapping the liquid electrolyte (plasticizers/organic solvents + salt) in the host polymer such as as poly(ethylene oxide)(PEO) [9], poly(methyl methacrylate)(PMMA) [10], poly(vinyl pyrrolidone)(PVP) [11], poly(acrylonitrile)(PAN) [12], poly(vinyl acetate)(PVAc) [13], poly(vinylidene fluoride) (PVDF) [14], and poly (vinylidene fluoride – co – hexafluoropropylene) (PVDF – HFP) [15]. Among all of the above polymers, PVDF – HFP copolymer has been found as a promising polymer host on account of its many excellent properties such as semicrystalline nature, excellent thermal stability, good mechanical, and wider electrochemical stability. Another properties including high dielectric constant ($\varepsilon \approx 8.4$) as well as low glass transition temperature ($T_g \approx -62^\circ$C) assist for greater dissociation of lithium ion species which delivers more mobile ions in the system that take part in conduction process [16, 17]. The structure of PVDF – HFP is made up of a crystalline part (VDF unit) and amorphous part (HFP unit) [18]. The crystalline part provides mechanical integrity whereas higher free volume due to the amorphous part assist for a trapping liquid electrolyte which results in high ionic mobility hence ionic conductivity [19]. In addition to these, the existence of strong electron withdrawing functional groups (–C–F) in PVDF polymer chains provides better anodic stability [8]. The main component required to prepare GPE is plasticizers which are low molecular weight organic carbonates having slow evaporation. The GPE is comprised of single plasticizer or mixture of two or more includes ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), dimethyl formamide (DMF) [1]. Recently, various GPEs system have been reported by a group of researchers by using various plasticizers to boost the structural, electrical and electrochemical properties [20, 21]. Subbu et al [22] have designed the GPE system comprised of PEO/PVdC – co – AN /LiClO$_4$/X plasticizers. In their report, they studied the physical and electrochemical properties of GPE with various plasticizers i.e. EC, PC, gBL, DEC, DMP, DBP and reported maximum ionic conductivity of $3 \times 10^{-4}$ S cm$^{-1}$ at ambient temperature for the film with EC plasticizers by virtue of its high dielectric constant.

When these plasticizers are added to host polymer, it plays following roles (i) reduce ion pairing (dissociation of salt) results in increasing free charge carriers which take part in conduction process and (ii) soften the polymer backbone promotes the higher segmental motion of polymer chains [23]. Thus by introducing plasticizers into polymers, the physical structure can be modified that assist for the easier transportation of ions through polymer and leads to enhancement of ionic conductivity and overall performance of the lithium – ion battery. Hence, the fundamental key to promote greater ion-pair dissociation, high dielectric constant and low viscous properties of plasticizers are essential. In the present study, the combination of PC (dielectric constant, $\varepsilon \approx 64.4$ and viscosity, $\eta \approx 2.53$ mPa S) and DEC (dielectric constant, $\varepsilon \approx 2.82$ and viscosity, $\eta \approx 0.748$ mPa S) have been chosen. A serious drawback of using plasticizers is degrading mechanical strength of polymer electrolytes. To eliminate this issue, blending with poly(methyl methacrylate) (PMMA) has been considered as an effective approach to strengthening mechanical integrity in our present study. In the current study, the investigation on structural,
electrical and electrochemical properties of PVDF–HFP:PMMA–LiClO₄ based gel polymer electrolyte system with different amount of PC and DEC plasticizers is reported.

2. Materials and methods

2.1. Materials

As host polymers, Poly(vinylidene fluoride–co–hexafluoropropylene) (PVDF–HFP) (\(M_W = 400,000 \text{ g mol}^{-1}\)) and poly(methyl methacrylate) (PMMA) (\(M_W = 350,000 \text{ g mol}^{-1}\)) was purchased from Sigma Aldrich and Alfa Aesar respectively. Lithium perchlorate (LiClO₄, 99.99%) from Sigma Aldrich is used as conducting species. The organic solvents propylene carbonate (PC, anhydrous, 99.7%) and diethyl carbonate (DEC, anhydrous, 99.7%) were procured from Sigma Aldrich and it is used as plasticizers to prepare gel polymer electrolyte.

2.2. Methods

The solvent casting technique was used to prepare gel polymer electrolyte system PVDF–HFP:PMMA–LiClO₄ – PC:DEC with different concentrations of PC:DEC and the compositions of the system are shown in table 1. Fixed amount of polymers, i.e. PVDF–HFP and PMMA in the equal ratio (1:1) were dissolved in acetone. A weighed amount of LiClO₄ salt was then mixed into the polymer blend solution. This mixture was stirred for 8 to 10 hours using a magnetic stirrer to get a homogeneous solution. Upon continuous stirring, evaporation of acetone was done and viscous solution were obtained. After that, it was poured onto Petri dish and the solution was kept at about 60 °C to form the solution in the form of film. The films were peeled off having thickness of 0.22 mm approximately which was homogeneous and flexible in nature. All films were stored in vacuum desiccators for the further experimental studies. AC impedance spectroscopy method was used to analyze the ionic conductivity of different GPE films in the frequency range 1 Hz to 32 MHz by using a high precision Solartron 1260 Impedance analyzer. The GPE films were sandwiched between two stainless steel electrodes under constant spring pressure to carry out impedance studies. The surfacing morphology of the films was examined by a JEOL JSM-6010LA scanning electron microscope (SEM). Gel polymer electrolyte films were subjected to Fourier transform infrared (FTIR) study to investigate the complexation behavior. FTIR spectroscopic studies were carried out using FTIR 4100 JASCO model in the wave number range of 400–4000 cm⁻¹ with the spectral resolution of 4 cm⁻¹. Cyclic Voltammetry (CV) were performed using Solartron 1287 electrochemical interface and 1260 impedance gain phase analyzer by sandwiched polymeric gel electrolyte between two stainless steel electrode sweeping over a frequency range of 1.2 MHz to 0.1 Hz with 10 mV input of AC amplitude with 50 mV scan rate.

3. Results and discussion

3.1. Ionic Conductivity

Figure 2 represents the complex impedance plots of PVDF–HFP:PMMA–LiClO₄ – PC:DEC GPE system with various concentrations of PC:DEC plasticizers at 303 K. From the figure, it can be seen that low–frequency spikes is followed by high–frequency semicircle [24]. A high–frequency semicircle represents the parallel combination of a resistor and a capacitor whereas spikes at low–frequency region is indication of charge accumulation due to blocking electrodes [25]. Obviously, the diameter of the semicircle reduces as the amount of PC:DEC plasticizers increases and also the disappearance of semicircle have been observed for GPE with the highest amount of plasticizers i.e. 60 wt%.PC:DEC. The inset of the figure 2 shows an equivalent ac electrical circuit of the impedance information of GPE material consisting of a parallel combination of resistor (\(R_b\)) and constant phase element (CPE1) with a constant phase element (CPE2) in series and the importance of the same circuit was addressed previously [26].

The bulk resistance (\(R_b\)) of GPE system were extracted by fitting the semicircle using the Z-view software. Generally, \(R_b\) is the difference between the real values (\(Z'\)) of high-frequency and low-frequency values of semicircle.

The ionic conductivity (\(\sigma\)) of electrolyte is given by

\[
\sigma = \frac{t}{R_b A}
\]

(1)

where \(R_b\) is the bulk resistance, \(t\) represents the film thickness, and \(A\) represents the contact area between the film and electrodes. The variation in ionic conductivity with different concentration of PC:DEC plasticizers at 303 K for PVDF–HFP:PMMA–LiClO₄ – PC:DEC GPE system is shown in figure 3. The values of ionic conductivity
are also listed in Table 1. It can be seen that the value of ionic conductivity reaches from 1.24E-8 S cm\(^{-1}\) to 3.97E-4 S cm\(^{-1}\) with an increasing amount of PC:DEC plasticizers from 20 wt% to 60 wt%. Similar effect has also been observed by Johan et al\[^{[27]}\] in PEO–LiCF\(_3\)SO\(_4\)–EC complexations with different concentrations of EC plasticizer. According to authors, when plasticizer is added to the system, it can interrupt polymer–polymer interaction due to polymer plasticizer interaction and ion plasticizer coordination. This process will create more free volume and a new path for the conduction of ions. The change in ionic conductivity of the polymer electrolyte (\(\sigma\)) can also be explained by

\[
\sigma_{dc} = \sum n_i \mu_i q_i
\]  

(2)
where \( n_i \) is the density of mobile charge carriers, \( \mu_i \) is the mobility of charge carriers and \( q_i \) is the charge of mobile charge carriers [18]. From the above equation, it can be explained that ionic conductivity depends on two-factor \( n_i \) and \( \mu_i \), as \( q_i \) is same for all GPE. From equation (2), we can conclude that the addition of plasticizers results in a change in mobility and number of charge carriers. The mobility of charge carriers is associated with the structure. Addition of plasticizers softens the polymer backbone which increases the flexibility of polymer segments through which ion can move easily and interact with the polymer matrix ultimately affect the structure. The second conclusion can be drawn that high dielectric constant of plasticizer can dissociate the charge carriers cause an increase in the \( n_i \). Therefore, the information regarding the micro-structural features could provide some better explanation on the experimental phenomenon mentioned above.

3.2. SEM analysis

To investigate the change in the morphology of the gel polymer electrolyte film with a change in concentrations of PC:DEC plasticizers, films were subjected to SEM analysis. The SEM micrographs are shown in figure 4. Microspores with large size have been observed in GPE film with a lower amount of PC: DEC i.e. 20 wt% PC: DEC. It reveals that these microspores are not filled with the liquid electrolyte due to an insufficient amount of PC: DEC. Addition of more amount of PC: DEC plasticizers to polymer electrolyte leads to increment in more number of embedded small pores with swelled nature of GPE. These micropores filled with liquid electrolytes provide the conducting pathway for a lithium ion [28]. These type of observation have also been reported by Senthil Kumar et al [29] in their study on plasticized PVDF−HFP/PEMA blended polymer electrolyte. In our study, surface morphology shows the remarkably increase in swelled nature of the film by incorporating a higher amount of plasticizer.

3.3. FTIR analysis

In the present study, the FTIR assessment was used to define the functional groups in a sample and to evaluate changes in the molecules’ vibrational modes in the polymer electrolyte due to the interaction between polymer, plasticizer and ion [30].

The FTIR spectra of PVDF−HFP:PMMA−LiClO4−PC:DEC GPE with different concentrations of PC: DEC in the wave number range 400−2600 cm\(^{-1}\) and 2600−3500 cm\(^{-1}\) are presented in figures 5(a) and (b) respectively.

The wave numbers for PVDF−HFP:PMMA−LiClO4−PC: DEC complexation are tabulated in table 2. The FTIR spectra of pure polymers and salt have been already reported in our previous study [26].

The assigned bending and wagging vibrations of −CF\(_2\) of PVDF−HFP at 509 cm\(^{-1}\) and 435 cm\(^{-1}\) get shifted to higher wavenumbers 511 cm\(^{-1}\) and 440 cm\(^{-1}\), respectively, with increasing amount of PC:DEC. The vibration of amorphous phase at 879 cm\(^{-1}\) and 836 cm\(^{-1}\) exhibited by PVDF−HFP are observed to be shifted to a higher frequency at 880 cm\(^{-1}\) and 838 cm\(^{-1}\) respectively. The peak assigned at 1401 cm\(^{-1}\) of PVDF−HFP is corresponds to the crystalline phase are getting broadened with reduction in intensity and shifted to 1403 cm\(^{-1}\), specifying that interaction between polymers and plasticizers as well as salt has been taken place. and the intensity of other crystalline peaks at 1072 cm\(^{-1}\) and 1182 cm\(^{-1}\) of pure PVDF−HFP get reduced and becomes
flatten with addition of more amount of PC:DEC plasticizers. The characteristic peak at 2981 cm\(^{-1}\) is ascribed to symmetrical stretching of CH\(_2\) group of pure PVDF−HFP is shifted towards lower frequency side. The CH\(_3\) asymmetric stretching vibration of PMMA at 2842 cm\(^{-1}\) gets shifted to 2846 cm\(^{-1}\). The C = O group (carbonyl group) of PMMA at 1727 cm\(^{-1}\) shifts towards the lower frequency side at 1725 cm\(^{-1}\) and at the same time intensity is reduced significantly upon the addition of plasticizers. This suggest that the occurrence of strong interaction between Li\(^+\) and the carbonyl group of PMMA with the addition of plasticizers because when low molecular plasticizers are added to polymer results in dissociation of salt. Apart from these, intensity of many other peaks has been found to be reduced significantly. This indicates complex formation takes place between polymers, salt, and plasticizers [22].

In addition to this, remarkable changes in the ClO\(_4^-\) anion group has been noticed in the range of 600–650 cm\(^{-1}\) of FTIR spectra. The intensity and asymmetry of peak change with PC:DEC concentration in this range has been observed. The asymmetry in the perchlorate band arises due to the presence of ion pairs (Li\(^+\)ClO\(_4^-\)) along with free anion (ClO\(_4^-\)) in the polymer matrix as reported by Shukla \textit{et al.} [31] in their solid polymer electrolyte based on PMMA−LiClO\(_4\). In present study to confirm this, the deconvolution of the ClO\(_4^-\) mode of LiClO\(_4\) salt has been carried out in the wavenumber range 600–650 cm\(^{-1}\) for PVDF−HFP:PMMA−LiClO\(_4\)−PC:DEC complexation using peak fit software. The de−convoluted spectra for GPE with 40 wt% PC:DEC is shown in figure 6. Two degenerate modes have appeared at 624 cm\(^{-1}\) of free anions (ClO\(_4^-\)) and 633 cm\(^{-1}\) of ion pairs (Li\(^+\)ClO\(_4^-\)) in the de-convoluted spectra. The fractional amount of free anions and ion pairs has been calculated by using the following formulas and the variation in fractional amount as a function of PC:DEC is

**Table 2.** List of wave numbers for PVDF−HFP:PMMA−LiClO\(_4\)−PC:DEC complexation.

| Materials          | Assigned characteristics frequency (cm\(^{-1}\)) | Wavenumbers (cm\(^{-1}\)) |
|--------------------|--------------------------------------------------|---------------------------|
| PVDF−HFP           | 3021                                            | 3021 shifted to 2996      |
|                    | 2981                                            | 2981 shifted to 2952      |
|                    | 1401                                            | 1401 shifted to 1403      |
|                    | 879,836                                         | 879 shifted to 880 and 836 shifted to 838 |
|                    | 509                                             | 509 shifted to 511        |
|                    | 484,435                                         | 435 shifted to 440        |
| PMMA               | 752                                             | 752 shifted to 750        |
|                    | 985                                             | 985 shifted to 987        |
|                    | 1727                                            | 1727 shifted to 1725      |
|                    | 2842                                            | 2842 shifted to 2846      |
| LiClO\(_4\)        | 628                                             | 628 shifted to 624        |

**Figure 5.** FT−IR spectra of PVDF−HFP:PMMA−LiClO\(_4\)−PC:DEC (a) spectra range 400–2600 cm\(^{-1}\) (b) spectra range 2600–3500 cm\(^{-1}\), with PC:DEC content of (S1) 20 wt%, (S2) 30 wt%, (S3) 40 wt%, (S4) 50 wt% and (S5) 60 wt%.
depicted in graphical form in figure 7.

\[
\text{Fraction of free anions} = \frac{\text{Free anion peak area}}{\text{Total peak area}}
\]  

\[
\text{Fraction of ion pairs} = \frac{\text{Ion pair peak area}}{\text{Total peak area}}
\]  

The change in the fraction of free anions and ion pairs can be correlated with change in the ionic conductivity. From figure 7, it clearly shows an increase in the fraction of free anions with increasing PC:DEC plasticizers which in turn increases in ionic conductivity. Highest fraction of anions and the lowest fraction of ion pairs is observed for the highest conducting sample. This is due to dissociation of salt which in turns to enrich charge carriers when low molecular weight plasticizers are added to the polymer. According to Pal et al [32], the cations form a complex with the polar group of polymer while free anions have an affinity to form ion pairs. Hence in the polymer complexes, the fraction of free anions and ion pairs are responsible for the conduction process.

3.4. Dielectric analysis

For ionic transport and relaxation phenomena occurring in polymer electrolyte, dielectric analysis has been carried out [33].
been increased plasticizer content at 10 KHz, 1 KHz and 100 Hz at 303K. It can be seen that the value of dielectric constant has following the same trend as dielectric constant. This means that with an increasing amount of PC: DEC, polymer chain segments becomes frequency as well as with the increasing amount of plasticizers because of motion of free charge through gel. The first one may be due to an increase in the charge carriers as a result of dissociation when low frequency region is high which is due to accumulation of charges near blocking electrode surface as a result of short time period of AC reversal field. At higher frequency region, charge carriers and dipoles are not able to follow the direction of electric field due to short time period of AC reversal field. As a consequence, the dielectric constant (\(\varepsilon\)) is found to be decreased. Inset of figure 8 shows the variation in \(\varepsilon\) as a function of plasticizer content at 10 KHz, 1 KHz and 100 Hz at 303K. It can be seen that the value of dielectric constant has increased (i) with increasing the concentrations of PC:DEC plasticizers (ii) change in frequency of applied AC field. The first one may be due to an increase in the charge carriers as a result of dissociation when low molecular weight PC:DEC plasticizers are added to the polymer. The second one is due to the ability of orientation of present dipoles with the time of AC field direction resulting in the increase of the dielectric constant [17].

The dielectric loss represents the dissipation of energy by means of dipole orientation and movement of ion under the effect of the applied field. Figure 9 represent the dielectric loss (\(\varepsilon\)) as a function of frequency for PVDF–HFP :PMMA–LiClO \(_4\) – PC:DEC GPE system at 303 K. The dielectric loss (\(\varepsilon\)) is also following the same trend as dielectric constant (\(\varepsilon\)). The dielectric loss (\(\varepsilon\)) value also became larger at a lower frequency as well as with the increasing amount of plasticizers because of motion of free charge through gel polymer electrolyte. This means that with an increasing amount of PC: DEC, polymer chain segments becomes more flexible and promote mobility of ions, charge carriers and dipoles [35].

### 3.5. Electrochemical Stability Window

From the point of view of the application of polymer electrolyte in the battery, high conductivity is an essential property, but it is also necessary to measure the electrochemical stability window of an electrolyte [22]. The electrochemical stability window (ESW) is defined as the working voltage(potential) range of a substance [36]. From the cyclic voltammetry(CV) profile, the difference of reduction and oxidation potential gives the stability window of materials. The test of GPE film exhibiting maximum ionic conductivity was done by using Cyclic Voltammetry CV at a scan rate of 50 mV/s as shown in figure 10 and measurement configuration for the same is SSE/GPE/SSE, where SSE is a stainless steel electrode. The oxidation and reduction peak has not been recorded which might be due to the noninteracting nature of ion species of gel polymer electrolyte with stainless steel electrodes. Cyclability nature of gel polymer electrolyte has also revealed form this CV curve. Electrochemical stability window of \(\approx 4.2\) V for the PVDF–HFP–LiTFSI–EC:DMC GPE system has been reported by Bose et al [37]. Lie et al have shown the stability window of \(\approx 4.5\) V for the PVDF–HFP–EC:DEC–LiClO \(_4\) system [38]. In the inset of figure 10, electrochemical stability window is shown for the system havin 60 wt% PC:DEC. Obviously,
the observed value of ESW is about −2.55 to 2.34 V, i.e. 4.89 V (total) indicates the present gel polymer electrolyte is compatible for implementation in the lithium-ion battery.

4. Conclusions

- In the present study, the gel polymer electrolyte based on PVDF−HFP and PMMA incorporated with different concentrations of mixture of PC: DEC plasticizers have been prepared via solution casting technique.
- Ionic conductivity of present GPE system increases from 1.24E−8 S cm−1 to 3.97E−4 S cm−1 with addition of PC:DEC plasticizers. This might be due to increase in the free charge carriers as a result of dissociation and decrease in rigidity of polymer chain to avail migration of Li+ ions. Furthermore, the change in electrical property of GPE is well explained with SEM, FTIR and dielectric studies.
- FTIR study revels that the complex formation is taking place between polymers, salt and plasticizers. The fraction of free anions increases whereas ion−pair decreases with addition of PC:DEC leading to enrichment in the ionic conductivity.
- The cyclic voltammetry curve showed the electrochemical stability window of the electrolytes ≈4.89 V which implies that the present gel polymer electrolyte is applicable as separator in lithium ion batteries.
ORCID iDs

D K Kanchan  🍁 https://orcid.org/0000-0002-7083-6677

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