



Optical, Thermal and Electrochemical Impedance Studies of Mg²⁺ ion conducting PVDF-HFP Solid Polymer Electrolyte

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ABSTRACT

Solid polymer electrolytes (SPEs) made up of PVDF-HFP poly (vinylidene fluoride hexafluoropropylene) with different concentrations of Mg (ClO₄)₂ (Magnesium perchlorate) are produced using a solution cast technique. UV, DSC, and electrical impedance spectra are used to investigate optical, thermal, and electrical characteristics. Optical absorbance, direct and indirect band gaps of SPEs are revealed by studies of UV-visible spectra and found to decrease both band gap values with Mg salt concentration to PVDF-HFP polymer. The structural changes in the sample due to endothermic and exothermic heat flow are studied by DSC. Electrical impedance spectra disclosed the bulk resistance and ionic conductivity. Among all the samples of PVDF-HFP: Mg (ClO₄)₂ SPEs of 400mg of Mg (ClO₄)₂ included PVDF-HFP polymer electrolyte exhibits lower direct and indirect band gap, low bulk resistance, and good electrical conductivity ($\sigma = 5.70 \times 10^{-4} \text{ Scm}^{-1}$).

Keywords: PVDF-HFP, Magnesium perchlorate, DSC and Electrical impedance.

1.0 Introduction

In view of huge demand of Solid polymer electrolyte (SPE) for cutting edge of advanced technical application like fuel cell, energy storage devices like batteries, solar cell, sensors etc., the good conducting polymer electrolytes are required with thermal and mechanical stability for any application [1]. The advantages of SPEs are like no leakage problems, non-explosive, having good thermal stability, wide range of optical absorption capacity, and electrical sensitivity and flexible nature for the compatibility of advancement of present and future technology [2, 3]. Since lithium salt-based polymer electrolytes are currently in high demand despite some drawbacks like explosiveness, increased corrosivity, and rarity of the in the earth's crust, alternate materials like Na and Mg-based polymer electrolytes are needed to replace lithium [4]. A prior study found that PEO enriched with magnesium salt has the 10⁻⁴ order of ionic conductivity [5-7]. Among the disadvantages of PEO-based polymer electrolyte is the immobility of Mg ions because of the large interaction of oxygen with Mg salt; thus, PVDF-HFP with Mg-based polymer electrolyte is being investigated in this study. Semicrystalline PVDF-HFP [8] has the potential to exhibit strong ionic conductivity, and polymorphic state [9, 10] transitions induced by salt addition and temperature variations may further enhance ionic mobility. In the present study, the focus on optical, thermal, and ionic mobility of PVDF-HFP by the addition of Mg (ClO₄)₂ are investigated and reported in this paper.

2.0 EXPERIMENTATION

2.1 MATERIALS & METHODOLOGY

Polymer PVDF-HFP and salt Mg (ClO₄)₂ was bought from Sigma-Aldrich, and the solvent from Merck Millipore. In the solution cast method, 1000 mg of PVDF-HFP and various weight concentration of Mg (ClO₄)₂ salts are dissolved in THF (tetrahydrofuran) solvent, and are stirred to dissolve the total polymer

and magnesium salts into the solvent to produce a homogenous solution. In order to create polymer electrolyte films, the petri dishes were used to collect the samples and dried at room temperature. Polymer electrolyte complexation samples of varying weights are provided in Table 1. The SPEs are characterized by UV-visible spectroscopy (SHIMADZU-UV-1800 spectrometer), DSC (SHIMADZU-DSC-60 instrument), and electrochemical impedance spectra (PSM1700 LCR meter).

Table 1: The following is a list of various weight Mg (ClO₄)₂ complexation PVDF-HFP polymer electrolytes.

S.No.	Sample Code	Weight of PVDF-HFP (mg)	Weight of Mg (ClO ₄) ₂ (mg)
1	PS0	1000	000
2	PS1	1000	100
3	PS2	1000	200
4	PS3	1000	300
5	PS4	1000	400
6	PS5	1000	500

2.2 UV-visible spectroscopy

UV-visible spectroscopy was used to investigate the Mg (ClO₄)₂-based PVDF-HFP systems. The UV-vis spectral region displays a distinctive UV-vis absorption band in the ultraviolet-visible (UV-vis) region of the electromagnetic spectrum as shown in fig.1. The relation between the absorption coefficient (α) and the incident photon energy ($h\nu$) is given by the following relation [11, 12].

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \text{-----(1)}$$

Where,

A= constant.

E_g = band gap of material.

n=1/2, and for indirect allowed transition.

n=2, for direct band gap of the sample.

Graph plotted $(\alpha h\nu)^2$ vs $h\nu$ and the extending the straight curve on $h\nu$ axis at $\alpha = 0$. Indirect band gap of the sample is calculated by plotting $(\alpha h\nu)^{1/2}$ vs $h\nu$ the extending the straight curve on $h\nu$ axis at $\alpha = 0$.

For various weights of Mg (ClO₄)₂ incorporation in PVDF-HFP leads to optical behaviour changes in the PVDF-HFP along with structural changes. It is also fully used for measuring optical indirect and direct band gaps of polymer electrolyte as shown in Fig. 2 and 3. The absorption peak can be seen for the sample at 275 nm wavelength for the Pure PVDF-HFP. By incorporation of Mg (ClO₄)₂ to PVDF-HFP, the sharp absorption peak becomes broad which indicates the wide range of wavelength of optical activity in the polymer electrolyte. Hence, it can easily reveal the great changes in optical direct and indirect band gaps of polymer electrolyte. The broad absorption band may represent the higher wavelength and leads to lower optical energy band gap can be expected. The broad band of the Mg (ClO₄)₂ in PVDF-HFP i.e., at PS4 concentration sample result shows the lower band gap that the high Mg²⁺ ion dispersion due to interaction of PVDF-HFP and more over band gap also reaches to optimum to transfer electron from conduction band to valance band and it will support for easy ion movement in the polymer network. Fig. 4 and 5 represent the variation of indirect and direct band gap with the variation of Mg (ClO₄)₂ salt in PVDF-HFP polymer

electrolyte samples. The important modification of the indirect band gap can be noticed when the band gap decreases to a significant value of 3.946 eV. And more over less variation of direction band gap can be seen. It is finally noticed that PS4 samples represent low optical direct and indirect bandgap are recorded with good UV-visible spectrum absorption among all the samples.

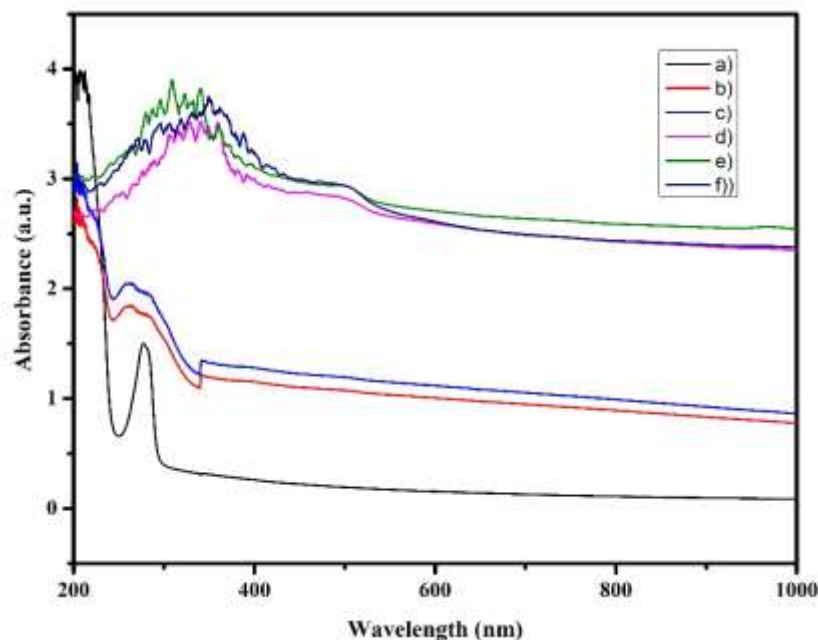


Fig.1 Absorption spectra with UV-visible wavelength for a) PS0, b) PS1, c) PS2, d) PS3, e) PS4, and f) PS5.

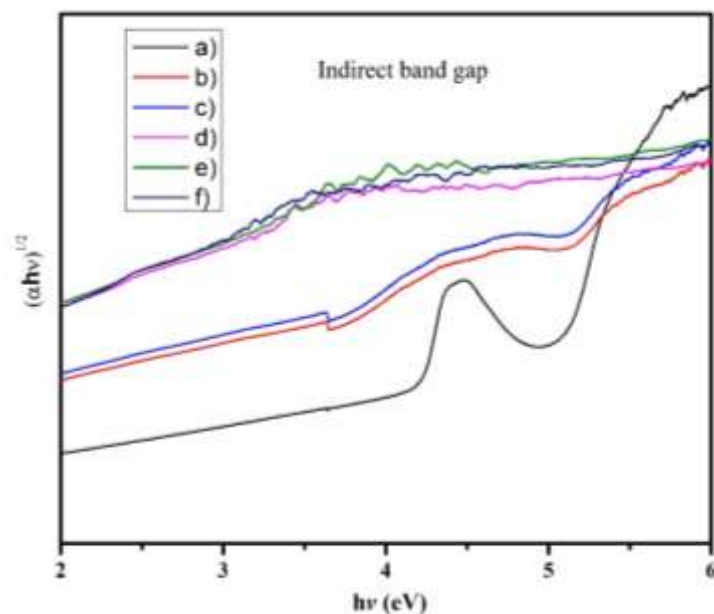


Fig.2 Tauc plots- indirect band gap of a) PS0, b) PS1, c) PS2, d) PS3, e) PS4, and f) PS5.

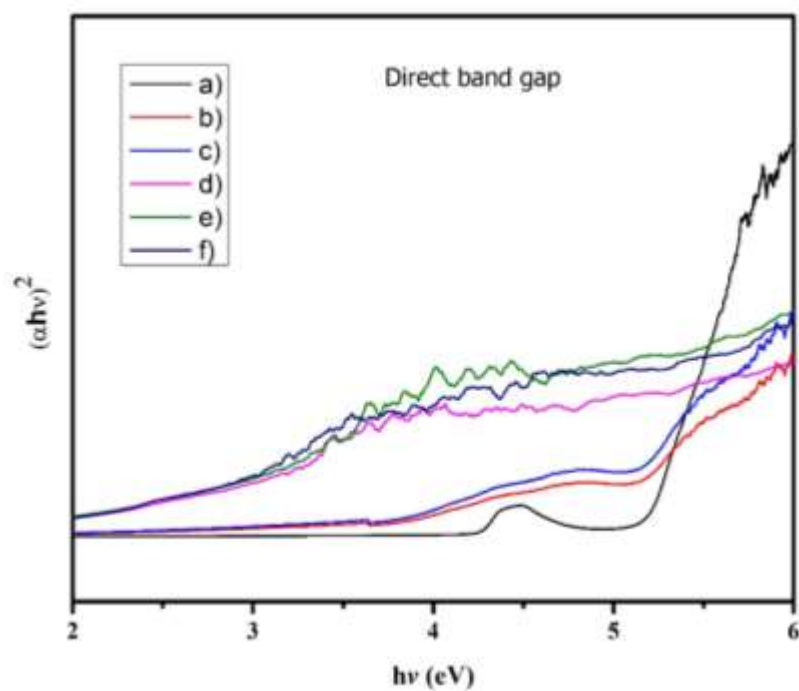


Fig.3 Tauc plots – direct band gap of a) PS0, b) PS1, c) PS2, d) PS3, e) PS4, and f) PS5.

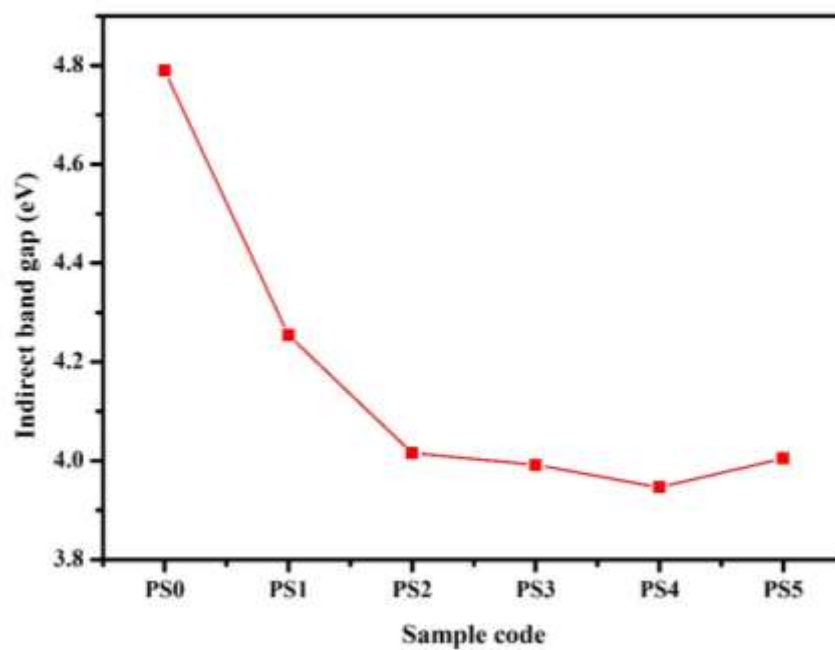


Fig.4 Represents indirect band gap values with concentration.

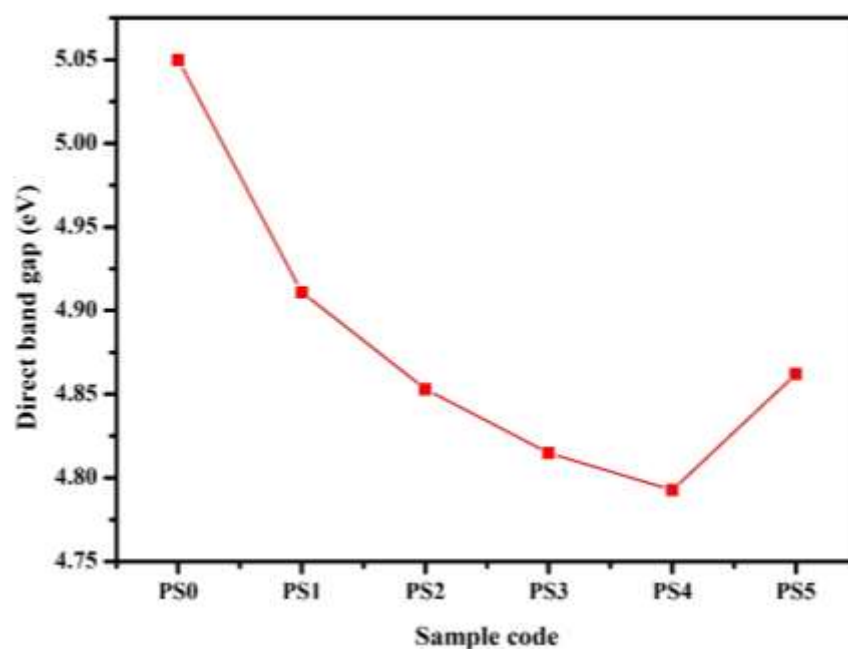


Fig.5 Represents direct band gap values with concentration.

2.3 DSC

The melting point of PVDF-HFP is 147 °C. The pure PVDF-HFP melting point under perfect vacuum condition may also represent 140 °C. PVDF has a T_g (glass transition temperature) below -37 degrees celsius [12], signifying PVDF- is rubbery at room temperature [13], where the polymer chains can take place segmental motion. As a result, due to the effects of Mg (ClO₄)₂ and temperature change, the polymer PVDF-HFP is experiencing a thermic absorption, which represents a reorientation of the PVDF-HFP polymer chain. Additionally, it is reproducing PVDF-HFP's excellent amorphous character. PVDF-HFP polymer electrolytes reach excellent amorphous nature up to a specific weight concentration of Mg (ClO₄)₂ as the weight concentration of Mg (ClO₄)₂ grows in the polymer. For sample PS4, the polymer electrolyte with the highest potential for Mg (ClO₄)₂ salt separation as Mg²⁺ ions and (ClO₄)⁻ ions was discovered. Additionally, these saturated ions interact with the polymer chain and encourage segmental mobility of polymer chains in response to temperature variations. The PVDF-HFP polymer electrolyte's melting point initially rises due to the incorporation of Mg (ClO₄)₂, but it falls with increasing Mg (ClO₄)₂ weight concentration and reaches the lowest melting point among Mg (ClO₄)₂ incorporated polymer electrolytes, the electrolyte that has a good tendency towards amorphousness. The structural alterations brought on by Mg (ClO₄)₂ and temperature may be seen in polymer electrolyte form in fig.6. This is because Mg (ClO₄)₂ and PVDF-HFP may both go through a variety of changes to acquire a stable amorphous nature. The endothermic temperature drops, which represents attainment of amorphous nature due to maximum reorientation of polymer chains. Hence, it exhibits high ionic conductivity. The polymer PVDF-HFP once again demonstrates significant thermic adjustment of polymer attains at higher temperature for the sample PS5 owing to further rising concentration of Mg (ClO₄)₂. But for the PS4 concentration of polymer electrolyte PVDF-HFP: Mg (ClO₄)₂ may lead to no endothermic polymer chain adjustments and no “ α , β , and γ ” transition with a smooth curve, represents good amorphous even at low temperature.

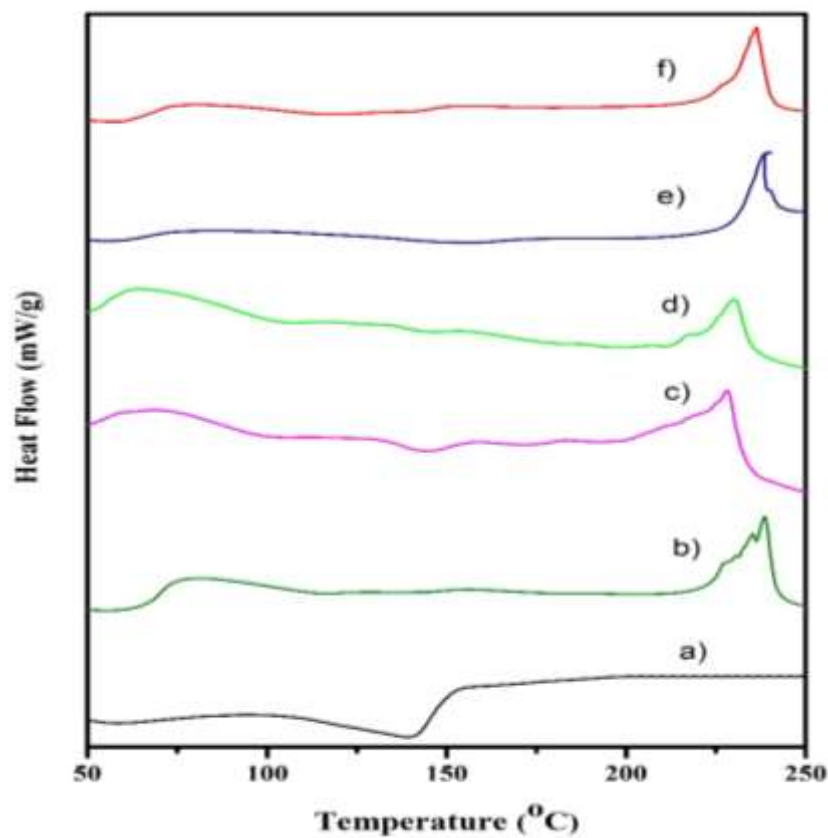


Fig.6 DSC curves represent Heat flow through samples of a) PS0, b) PS1, c) PS2, d) PS3, e) PS4, and f) PS5.

2.4 Electrochemical Impedance Spectroscopy (EIS)

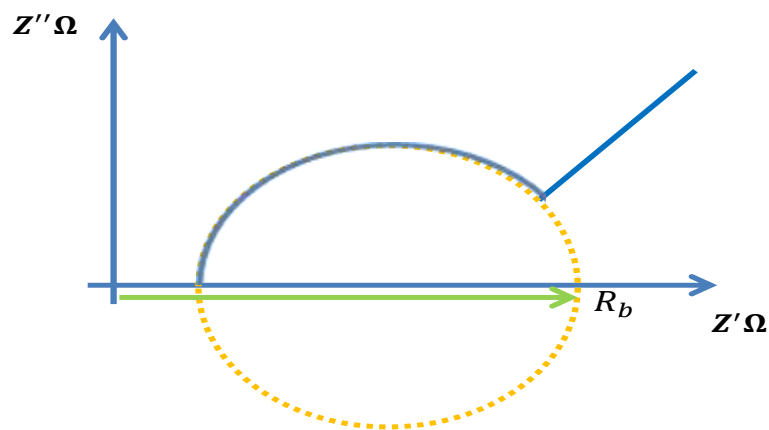


Fig.7 Depicts the bulk resistance of EIS polymer electrolytes.

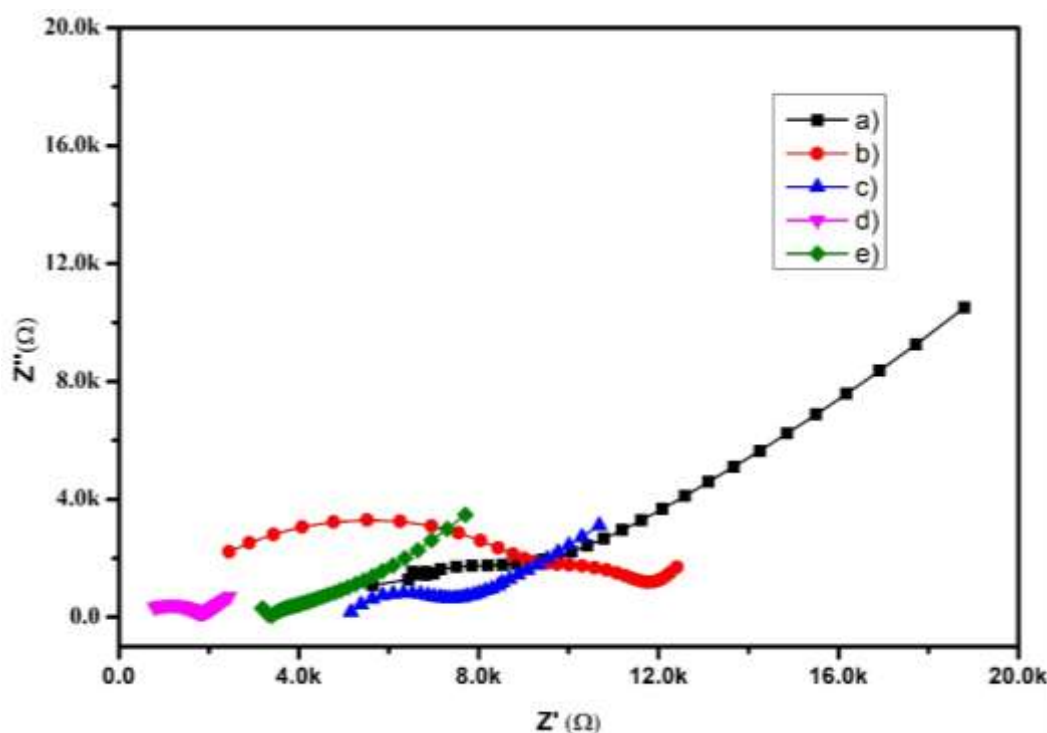


Fig. 8 EIS of a) PS1, b) PS2, c) PS3, d) PS4, and e) PS5.

EIS is a top-of-the-line tool for characterizing the electrical and ionic conductivity of polymer electrolyte, it can be seen in fig.7. It contributes to estimate the bulk resistance (R_b), which is used for measuring dc ionic conductivity. Ionic conductivity can be measured by bulk resistance [14] using the equation (2).

$$\sigma = t/R_b A \text{ -----(2)}$$

Where σ = ionic conductivity

t = thickness of film

A = Area of the electrolyte

R_b = Bulk resistance

The semicircle intersecting point at low frequency of real impedance axis reveals bulk resistance (R_b) of the sample PS4 as shown in Fig.8. The decreasing of bulk resistance may lead to improved conductivity. As the concentration of Mg (ClO_4)₂ raises from sample PS1 to PS4, the bulk resistance is decreasing and eventually it leads to rise in conductivity. This is indicating as the raising of Mg (ClO_4)₂ concentration may lead to reorientation of polymer segment and also Mg²⁺ and (ClO_4)⁻¹ ion disassociation improves to attain amorphous nature. It also represents a good segmental motion of polymer chain and easy migration of Mg²⁺ ion through inter link porous network of PVDF-HFP membrane. The best ionic conductivity was found for the sample PS4, where the polymer represents great amorphous nature compared to all other samples. The highest conductivity can be seen for good amorphous nature SPEs [15].

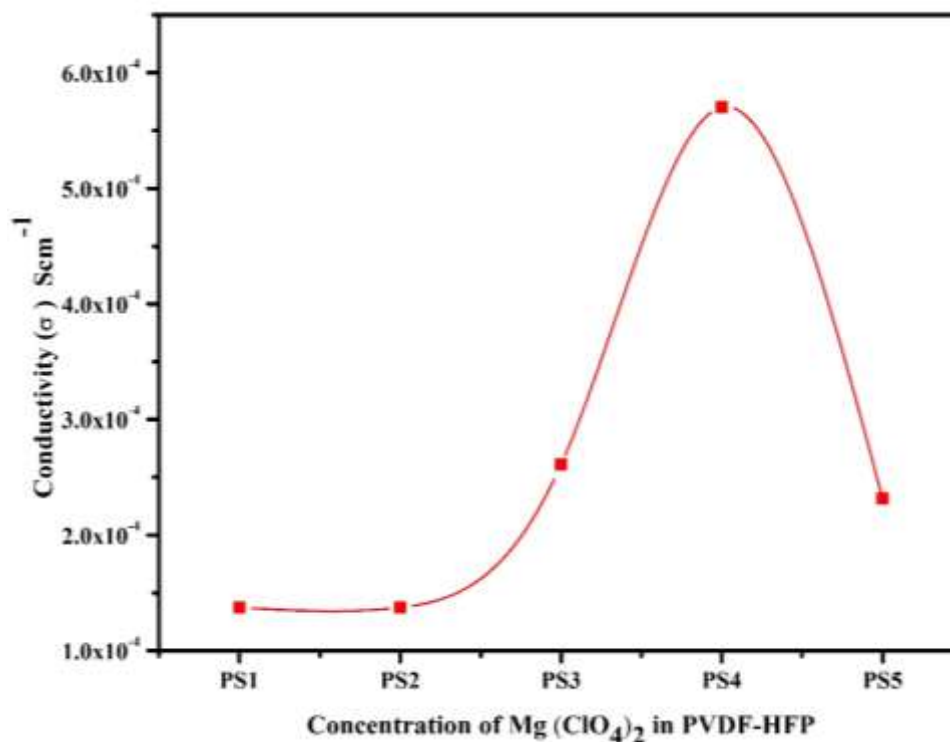


Fig.9 The figure depicts ionic conductivity for different samples of various weight of Mg (ClO₄)₂ in PVDF-HFP

The highest conductivity obtained for the sample PS4 is $\sigma = 5.70 \times 10^{-4} \text{ Scm}^{-1}$. For further raise of Mg (ClO₄)₂ concentration of PS5 sample conductivity is less than PS4. As the larger weight concentration of Mg (ClO₄)₂ may lead aggregation of salt and also it may lead to block the polymer chain segmental motion. And it also blocks the interconnecting porous network which is essential for ion segmental motion and migration. Fig.9 illustrates the modulation of polymer electrolyte ionic conductivity via Mg (ClO₄)₂ slat variation.

3.0 Conclusions

SPEs synthesized by solution casting technique are investigated optical, thermal, conductivity properties by UV-visible spectroscopy, DSC and bulk resistance by EIS spectra. Good optical absorption, and low direct and indirect band gap was noticed by UV-visible spectra for the PS4 sample among the all SPE samples. Low bulk resistance and high conductivity ($\sigma = 5.70 \times 10^{-4} \text{ Scm}^{-1}$) was recorded to the PS4 sample, which is essential for good polymer electrolyte for advanced technical applications.

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