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Proton conducting polymeric electrolytes composed of PVA and H₃PO₄ and metal oxide

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Abstract

Strong organic acids, such as phosphoric acid (H_3PO_4) , have been trapped in a variety of polymeric solids that have been synthesised from the acid solutions. Polyvinyl alcohol (PVA)-based polymer electrolytes comprising with various concentrations of H₃PO₄ are prepared using a solution casting technique. To study conductivity and charge transport in the solid polymer electrolytes (SPEs), measurements of electrical conductivity and transference number were carried out. The frequency dependent AC conductivity at room temperature obeys the modified universal power law and the DC conductivity was obtained from the fitting parameter. The room temperature protonic conductivities of solid polymer electrolytes PVA- H_3PO_4 is higher than 10^{-4} S cm⁻¹. According to the conductivity results, the ionic conductivity of the samples increases when the amount of acid is increased. The results of the transference number measurements agree with this hypothesis. The films' temperature-dependent conductivity appears to follow the Arrhenius principle. The proton transport mechanisms are affected by acid concentrations. The characteristics of these different solid polymer electrolytes have been examined to increase the protonic conductivity and maybe apply these solid polymer electrolytes in electrochemical devices such as batteries, sensors, and electrochromic devices.

Keywords: PVA; polymer electrolyte; proton conduction

Introduction

Due to their potential use in solid electrochemical devices such as energy conversion units (like batteries/fuel cells), electrochromic display devices/smart windows, photo electrochemical solar cells, etc., ion conducting solid polymer electrolytes recently (SPEs) have gained widespread interest in the fields of solid-state electronics and Ionics[2–4]. The fundamental advantages of SPEs are their mechanical characteristics, the flexibility with which thin films of appropriate sizes may be produced, and their ability to create satisfactory electrode-electrolyte interfaces. Numerous extensively researched polymers may dissolve substantial amounts of a wide variety of salts, oxides, nanometals or acids to create SPEs [5]. Because liquid electrolytes have limitations including leakage, corrosion, and packing issues, SPEs recently gained increased have attraction with the emergence of devices electrochemical such as electrochromic and energy storage devices like batteries, supercapacitors, and fuel cells. To overcome these practical problems, SPEs or hydrogel polymer electrolytes have been employed. Therefore, polymer electrolytes such as poly (vinyl alcohol) (PVA), poly (vinyl chloride), poly (ethylene oxide) (PEO), poly (vinylidene carbonate), and poly (vinylidene fluoride) have a distinct advantage over solid electrolytes (10^{-7}) to 10^{-8} S.cm⁻¹).

Due to their ability to produce materials with variety of a advantageous physical, chemical, thermal, and mechanical characteristics of organic and inorganic phases, inorganic-organic hybrid materials are of interest. Conductive proton in the literature, inorganic-organic hybrids with different acid species have been described [6-10].

In addition to filler additives, choosing an appropriate polymer matrix is a key to producing excellent ionic solid polymer electrolytes[11]. The fabrication of ionic solid polymer electrolytes has been described for several synthetic and natural polymers, poly(ethylene including oxide) (PEO)[12–14], cellulose[15], polyvinylidene fluoride (PVDF)[16], polyacrylonitrile (PAN)[17], chitosan [18]. poly(methyl methacrylate) (PMMA)[19], starch [20], and poly(vinylidene fluoridehexafluoropropylene] (PVDF-HFP) [21], poly(vinyl alcohol) (PVA)[22]. The synthetic water-soluble polymer polyvinyl alcohol (PVA), with excellent biocompatibility and biodegradability, as well as chemical resistance, good mechanical behaviour, adhesion, excellent film forming properties, and widespread availability, is the best candidate in the category for creating an ionic solid polymer electrolyte. As a result, considering the characteristics of the previous mentioned materials, the current study aims to develop ionic solid polymer electrolyte films of PVA using H₃PO₄ acid as the filler and investigate their suitability for use as matrix materials in ionic solid polymer electrolyte engineering applications.

Numerous researchers have examined the behaviour of acid-based polymer electrolyte complexes as proton conductors, and it has been suggested that these complexes may be used as gas sensors and electrochromic devices [23, 24].

In the conducted study, solution cast complexes of polyvinyl alcohol (PVA) with orthophosphoric acid (H₃PO₄) in thin film form have been prepared at various stoichiometric ratios. Experimental methods such as X-ray diffraction (XRD) pattern, Infra-red (IR), Scan electron microscopy (SEM), Thermal Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and UV-vis spectroscopy are used to analyse thin films of PVA complexes. Wagner's polarisation and complex impedance techniques. respectively, have been used to measure electrical conductivity and transference number.

Experimental

The PVA-H₃PO₄ solid polymer electrolyte was prepared by vigorously mixing 30 mL of deionized water into 3 g of polyvinyl alcohol (PVA) at a temperature of 95 °C. The 3 g of phosphoric acid (H_3PO_4) was added to the PVA solution after the PVA had completely dissolved, and the mixture was vigorously stirred until it had

produced a homogenous, sticky solution. The mixture was then cooled to room temperature when it solidified as a clear, transparent solid polymer.

Result and discussion



Figure 1 FTIR for PVA-H₃PO₄

The analysis of polymer structures benefits from the use of FTIR spectroscopy because it focuses on the interactions and complexation of the many components found in polymer electrolyte complexes[25]. The FTIR spectra of pure PVA and PVA complexed with various phosphoric acid concentrations are shown in Figure 1. The absorption peaks of virgin PVA are attributed to O-H stretching. C-H stretching. C-O stretching, O-H and C-H bending, and C-O stretching, respectively, at 3240, 2912, 1720, 1446, and 1096 cm⁻¹. For PVA complexed with H_3PO_4 , the

absorption peaks corresponding to wave numbers 3340 and 2910 cm⁻¹ are discovered to be unshifted, but the peaks belonging to wave numbers 1720, 1446, and 1096 cm⁻¹ are shifted to 1700, 1420, and 1085 cm⁻¹, respectively.

Additionally, for PVA complexed with H_3PO_4 , all these peaks can be seen at 2325, 1329, 976, 925, 819, 584 and 476 cm⁻¹ [26]. A unique interaction of the dopant with the polymer matrix is revealed by the shifting of the aforementioned wave numbers for acid doped systems compared to pure PVA, which sufficiently supports the

complexation of the system. Additionally, from pure PVA to the PVA-H₃PO₄ system, there has been a broadening of the steady peak corresponding to C-H stretching. This denotes an increase in the sample's amorphicity, which may be caused by the intermolecular forces that are random in nature and result in slightly variable force fields for each absorbing group. The examination of the DSC and XRD has revealed this sort of behaviour. However. the peak corresponding to 1720 cm⁻¹ has been found to be missing in the complexed PVA in the presence of phosphoric acid. This also implies complexation

and specific interaction of the dopant in the polymer matrix.

The P-O groups[27], which evolved from $(H_2PO_4)^{-}$ and $(VHPO_4)^{2^{-}}$, are represented by the peaks at 986–880 cm⁻¹. While the $(VHPO_4)^{2^{-}}$ peak changes to a lower wavenumber as the acid concentrations increase, the P-O peak can be seen emerging at 828 cm⁻¹. However, this is not the case for the VHPO₄ peak. The O-P-O peak for the PVA doped acid sample, however, moves to a higher wavenumber as the acid concentrations increase. It is possible to see clearly both the vibration modes in $(PO_4)^{-3}$ and the deformation of O-P-O [28].



Figure 2 shows the DSC, TG and its derivative for PVA-H₃PO₄

The glass transition (T_g) , melting (T_m) , and crystallization temperatures (T_c) may be determined using the Differential Scanning Calorimetry (DSC) method. Figure 2 depicts the DSC thermograph for the PVA polymer film and the PVA-H₃PO₄ composite films at concentration ratios in the temperature range of 30-800 °C. In all the electrolytes, the curves exhibit a broad endothermic peak cantered at around 85 °C. This demonstrates that the overlapping between Tg transitions and any remaining water in the electrolytes has evaporated. The melting temperature (T_m) of PVA is 240 °C, where an endothermic peak appears. The T_m of pure PVA powder with a hydrolysis degree of 98-99 % is approximately 225 °C [29]. When H_3PO_4 is doped into PVA polymer at a ratio of 1:1, it is observed that the melting temperature, Tm, of the PVA-H₃PO₄ composite polymer film shifts to a lower temperature ($T_m = 213$ C). With a larger concentration ratio, a lower T_m indicates a transition from а semicrystalline to an amorphous phase. The results for T_g and T_m match those from other publications [30, 31]. [Exothermic peak at 456 °C].

The thermal stability of PVA is an factor in the thermal important processing of PVA. TGA was used to examine the thermal stability of pure PVA and PVA-H₃PO₄ composites. From room temperature to 800 °C, measurements were recorded. The TGA traces were displayed in Figure 2. Water loss may be primarily responsible for the mass loss below 200 °C. The thermal decomposition of pure PVA begins nearly at the same The temperature as T_m. initial decomposition temperature of PVA significantly increases to a higher temperature, around 213 °C, with the addition of phosphoric acid. The decomposition temperature was substantially lower than T_m, which was much higher. It is evident that the phosphoric acid inclusion gave PVA its thermal processing window, or 213 °C. When compared to pure PVA, PVA's thermal stability increased, which indicates a strong interaction between PVA's hydroxyl groups and phosphoric acid. Previous research [32] established a two-step process for the heat degradation of PVA, which is started by the removal of side groups

from the main chain. The elimination of the hydroxyl and acetate side groups is the first stage of PVA's breakdown. The percentage of acetate side groups is quite low in completely hydrolysed PVA. These show that at least hydroxyl groups are involved in the heat degradation of PVA, and that hydroxyl group stability is essential for PVA stabilization. The phosphoric acid could form strong interactions with the hydroxyl groups of PVA, and thus the thermal stability of PVA was improved. It is also likely that the endothermic nature of the melting process in plasticized PVA at about 213 °C would inhibit the degradation process and improve the thermal stability of PVA[33].

The TG and differential gravimetric analysis (DTG) thermographs of the PVA and PVA-H₃PO₄ composite solid polymer electrolyte are shown in Figure 2. The PVA- H₃PO₄ polymer films' TG and DTG curves showed three primary weights loss zones, which were represented by three peaks in the DTG curves. The evaporation of physically weak and chemically strong bound H₂O caused the first region, which was at a temperature of 40-170 $^{\circ}C$ (T_p, 1 at 115 $^{\circ}C$), to form; this caused a weight loss of 6.5-8.7 wt.%. The degradation of the side chain of the PVA- H_3PO_4 solid polymer electrolyte caused the second transitional region to occur at around 170 to 270 °C (T_p , 2 at 213 °C); the overall weight loss at this stage was between 20-24 wt%.

The cleavage of the PVA-H3PO4 solid polymer electrolyte's C-C backbone, or "carbonation," caused the third stage to peak at 460 °C (Tp,3 at 435 °C), with a total weight loss of around 55 wt% at 800 °C.



Figure 3 [34], displays the absorption spectra for films consisting of solid PVA and PVA-H₃PO₄ at mole concentration. In contrast to the reaction between PVA and H₃PO₄, which only exhibits one absorption band at 274 nm because of the interaction of PVA with the phosphate component, pure PVA has absorption bands at 204, 220, 280, and 330 nm [35]. The results of this investigation good agreement [36]. The show production of intra-and intermolecular hydrogen bonds, especially between the H₃PO₄ ions and nearby OH groups, is shown. As a result of changes in crystallinity within the polymer matrix, the bonds reflect changes in the energy band gap.

The samples were subjected to Impedance Spectroscopy (IS) experiments at different temperatures using a sinusoidal signal of 10 mV with a frequency range of 20 Hz–10 MHz. The Nyquist plot from the IS measurement on the SPE samples with 0.1, 0.2, 0.3, and 0.4 wt % of phosphoric acid is shown in Figure 4a. Since the curves in the Nyquist plot initially overlapped, they were offset on a logarithmic scale for a clearer perspective.

To get the bulk conductivity[37], σ_b , using this relation $\sigma_b = \frac{1}{R_b} \frac{t}{A}$ (1), the bulk resistance (R_b) value of the sample was determined from the Nyquist plot in the intercept of the lower frequency region on the Z' axis, where t and A are the thickness, area of the sample, respectively. The high frequency region of the Nyquist plot for the SPE samples shows a semicircle, while the low frequency region shows a spike, showing the typical behavior of a supercapacitor. The increase in acid content causes a decrease in bulk resistance and a prolongation of the spike, and the primary cause of total conductivity is ionic conduction[38].

The relationship between conductivity and the weight fraction of phosphoric acid in the solid polymer electrolytes is displayed in Figure 4b. When 0.1, 0.2, 0.3, and 0.4 wt % of phosphoric acid are added, the conductivity of the solid polymer electrolyte samples is drastically improved by 2 orders of magnitude. The conductivity increases steadily at 0.4 wt % phosphoric acid. It is generally known that the charge (q), charge number (n), and mobility of charges (μ) have an influence on the conductivity of polymer electrolytes, and this relation can be used to explain it [39]:

 $\sigma = \sum qn\mu$ (2) Therefore, an increase in the number of charge carriers and their mobility

be responsible might for the conductivity increasing with increasing acid concentration. When more than 0.3wt % phosphoric acid is introduced, the solid polymer electrolyte samples reach saturation, which reduces the amount of free space in the samples and lowers the ionic conductivity[40]. The number of charge carriers is reduced as a result, which is probably caused by the development of ion aggregates or scattered [41].



Figure 4: (a) Cole-Cole plot for PVA with different concentration of H_3PO_4 , (b) Relation between concentration and σ_b

The subsequent Nyquist plots were investigated using EIS software based on the electrical equivalent circuit observed in the inset of Figure 4a. The high, middle, and low frequency regions mainly consist of the Nyquist plot's frequency range. Based on the equivalent circuit, a sample's non-zero semicircle intersects at high frequencies, which is explained (R_s) . It is the result of the interaction between the polymer electrolyte resistance, the interfacial resistance at the interface of the active material and substrate, and the internal resistance of the electrode material. The obtained R_s value of 0.4 wt % PVA-H₃PO₄ solid polymer electrolyte is 130 Ω . This clearly reveals that R_s appears due to high addition of H_3PO_4 in the polymer.

The frequency dependence of ac conductivity for various concentrations of phosphoric acid in the SPE samples

is shown in Figure 5a. For all SPE samples, a consistent pattern in the variation of the frequency vs ac conductivity is shown. The curves are divided into two separate regions: at lower frequencies, near 10 kHz, the ac conductivity is shown to increase with frequency, indicating the electrode polarization phenomenon [42], and at higher frequencies, from 10 kHz to 1 the frequency independent MHz, plateau region appears. The dispersion region is the third region above 1 MHz. convenient Α formalism Jonscher's universal power law $\sigma(\omega) = \sigma_{dc} + A(\omega)^s$ (3) helps to explain the variation of conductivity in SPE [43,44]. The DC conductivity, includes the frequency- $\sigma_{\rm dc}$, independent ac conductivity. The σ_{dc} of the prepared SPE samples was obtained by extrapolating the plateau region on the s-axis. The computed σ_{dc} values from the conductivity-frequency dependency plots and those derived from the Cole-Cole plot are in good agreement with one another [45]. This study's investigation of conductivityfrequency dependency is quite comparable to earlier work that was published and focused on ionically conducting polymers, glasses, and doped crystalline solids [46,47]. The mechanism of charge transport behavior of charge carriers is supposed to match this.



 $\label{eq:Figure5:(a)} Figure5: (a) \ variation \ of \ the \ frequency \ Vs \ ac \ conductivity, \ (b) \ variation \ of \ the \ frequency \ Vs \ Capacitance \ for \ PVA \ with \ different \ concentration \ of \ H_3PO_4$

In addition, as the concentration of phosphoric acid increased, so did the length of the spike region in the and the frequency Nyquist plot dependence of ac conductivity at low frequencies that correspond to the of capacitance the electrode polarisation. Figure 5b displays the capacitance vs. frequency. As can be observed, the capacitance increased dramatically as the frequency decreased at the low frequency side (f \leq 100 kHz). This increment increased as the ionic concentration level increased, indicating that a higher ionic concentration level is quite effective at increasing the capacitance. Capacitance values are more stable in the high frequency range (f > 100)kHz); all ionic solid electrolytes, glasses, and doped crystalline solid

materials have identical capacitance. This is since a strongly alternating current cannot flow through accumulated ionic charges at the electrode/electrolyte interface.

With increasing frequency[48], the dependent frequency impedance (Figure 6a) decreases in both the lower and higher frequency regions. The middle frequency region's observed frequency independent impedance shows ionic transport from the electrolyte to the electrode. However, spectra show that impedance decreases in the middle frequency range as acid content increases, which may be caused by the electrolyte's increased ionic charge carriers (ionic conductivity/diffusion or frequency dependent ionic diffusion).



of H₃PO₄

The ideal-capacitive character is also revealed by the higher phase angle values (Figure 6a) of-83° and-89° for x = 0.3 and 0.4, respectively, as it is closer to-90°. Even though x = 0.1 and 0.2 have a low phase angle, this may be due to the partial ideal capacitive behaviour or the redox nature of the systems [49] However, the reduced phase angle causes ionic diffusion to take place [50]. According to Figure 5b, which shows a drop in capacitance as frequency increases, a significant amount of capacitance is produced at low frequencies as opposed to high frequencies.

The complex impedance plane plots (Z' vs Z'') are given in Figure 7. Usually a conduction process results in a semicircular arc in a linear complex plane plot. The log-log presentation in Figure 4a enables us to compare two responses with vastly different impedances in one plot. Despite the curved semicircular arcs, the logarithmic plot, moreover, has several positive effects, as Jonscher has noted [51].





Figure 7 Cole-Cole plot for PVA-xH₃PO₄ (x= 0.1, 0.2, 0.3, and 0.4 wt%) at different frequencies



Figure 8 Relation between the frequency and the imaginary part of impedance with different concentration of $\rm H_3PO_4$

In Figure 8 we present the frequency dependence of the imaginary part Z" of the impedance $Z^* = Z'-iZ''$ at different acid concentration. We observe at x= 0.1 a higher peak at about 10⁴ Hz, shifting to higher frequencies with decreased intensity as the acid concentration increases. At x = 0.4 it moves close of the frequency range of our experiment. This implies both electrical responses are thermal activated.

Dielectric studies

It is important to evaluate the dielectric relaxation to analyse the composition, physical characteristics, and electrochemical properties of solid polymer electrolytes and the composites they correspond to. Additionally, investigations of solid polymer electrolytes' dielectric and dipole relaxation over a broad frequency range are required and advantageous [52-54]. One of the effective and efficient methods for studying the mechanism of ion transport is dielectric spectroscopy [52-55]. Complex electric modulus (M*) and complex dielectric constant (ε^*) measurements are required to achieve this aim. The dielectric constant (ϵ') and dielectric loss (ϵ'') are depicted in Figure 9: (a) and (b) compared to electrolyte systems that operate at ambient temperature. The magnitudes of ε' and ε'' utilising the formulae shown below [52-54],[56]:

$$\varepsilon' = \frac{Z''}{\omega C_o(Z'^2 + Z'')} \tag{4}$$

$$\varepsilon'' = \frac{Z'}{\omega C_o(Z^2 + Z^{*2})} \tag{5}$$

Where $C_o = \varepsilon_o A/d$, ε_o is the free space permittivity $(8.854 \times 10^{12} \text{ F m}^{-1})$ and is the angular frequency. In contrast, it is nearly a plateau at a higher frequency. The value of ε' and ε'' is very large inside the low-frequency range. It's interesting to note that at low frequencies. electrode polarisation causes charge build-up from free mobile ions at the electrode-electrolyte interfacial region, resulting in a thin layer of capacitance [57-58]. The applied electric field, on the other hand, quickly restores, and the majority of the ions may continue to exist in the majority of the sample. As a result, the electrode polarisation is reduced, which lowers the values of ε' and ε " [52-54],[59].

It is observed that the ε' increases as the acid content increases. This is because there are more charge carriers, which results in more polarisation [60-63]. These results indicate that the dielectric constant may be used to easily control the conductivity of polymer electrolytes. The mathematical formula $n_i = n_o \exp (U/\epsilon')$ K_BT) (6), where U is the energy of dissociation, has already been used to demonstrate the significant correlation between and the density of charge carriers (n_i) [52,54,62-63]. In other words, a reduction in causes a reduction in DC conductivity. Two polymer factors that govern the DC ionic conductivity of polymer ionconducting electrolytes are the density of charge carriers (n_i) and their mobility (μ_i) ($\sigma = \sum q n_i \mu_i$), where q is the charge on the ion carriers [52,54]. A precise study of ε' is useful in that achieve complete one can a understanding the electrical of properties of polymer electrolytes, particularly the conductivity.



Figure 9 (a) Dielectric constant and (b) dielectric loss versus log (f) for PVA-xH₃PO₄ (x= 0.1, 0.2, 0.3, and 0.4 wt %)



Figure 10 Tan δ versus log (f) for PVA-xH₃PO₄ (x= 0.1, 0.2, 0.3, and 0.4 wt %)

This formula, $Z^* = R - jX_C$ (7), where R and X_C are the resistor element and the capacitive element, respectively, mathematically defines the complex impedance function [63]. According to the impedance's above mathematical function, a significant amount of current flows through the resistor element at low frequencies because the capacitive component is prominent. It is noticed that from the tan $\delta = \varepsilon''/\varepsilon'$ (8) relationship, the tan δ is directly proportional to ε'' .

There are two types of dipoles that can create peaks in highly electrically conductive polymer electrolyte induced systems: and permanent. low-frequency The relaxation peaks may disappear as a result of these dipoles being hidden by the polarisation relaxation of mobile charged species that are present in the material [64-65]. The dielectric loss tangent (tan δ) versus frequency is shown in Figure 10 and can be used to understand the relaxation process. Koop's phenomenological model is

used in the interpretation of the shape of tan δ [63,66]. The model's guiding principles state that tan δ increases with increasing frequency until it reaches a maximum value, at which point it begins to decrease. The explanation is since the Ohmic component of the generated current noticeably relative grows to its capacitive component in a lowfrequency region where tan δ increases. In contrast, the Ohmic component is essentially frequency independent in the high-frequency region, where tan δ drops and the capacitive component grows, resulting in a modest value of capacitive reactance[63,66-67]. Additionally, the wide nature of the tan δ peaks[68-69] is proof of the relaxation process' non-Debye type behaviour.

One can study the dielectric response that results from ion relaxation in which the electrode polarisation effects can be suppressed; in other words, small features in the high-frequency region are recognised[70]. Through the equations shown below[71-72], the impedance data correlate the real and imaginary parts of the electric modulus.

$$M' = \frac{\varepsilon'}{{\varepsilon'}^2 + {\varepsilon'}^2} \tag{9}$$

$$M'' = \frac{\varepsilon}{\varepsilon'^2 + \varepsilon''^2}$$
(10)



Figure 11 the electric modulus versus log (f) for PVA-xH₃PO₄ (x= 0.1, 0.2, 0.3, and 0.4 wt %) (a) Real component and (b) imaginary component.

Figure 11: (a) and (b) shows that the real and imaginary components of the electrical modulus plot, which and correspond to M' М", are frequency dependent. The lowfrequency region is where the data points for the real component of the modulus spectra are situated. This could be caused by the electrodes' high capacitance, which helps the ion conduction process' migration. It can be shown that in the high-frequency range, M' approaches its maximum saturation level. The ε' decreases to a minimum, whereas M' increases to a maximum $(M_{\infty} = 1/\epsilon_{\infty})$ [73]. The samples are non-Debye because the frequency increases cause dispersion in [74]. Figure 11b displays the M' imaginary component of the modulus spectra. It is seen that; the conductivity relaxation peaks appear at low phosphoric acid concentration. It also is notable that there is decrease of peak and a shift of peak position to the higher frequency region with the addition of further acid concentration.

In addition, the translational ion dynamics and conductivity relaxation of the mobile ions are likely to be connected to some of the peaks in the M" spectra. The segmental mobility of the polymeric chain reduces the relaxation time and accelerates ion transport during the amorphous phase. To be accurate, the ionic charge carriers' relaxation time τ is indicated by the mathematical relationship $\tau =$ $1/2\pi f_{max}$ [75]. The relaxation peaks are shown to have shifted to the lower frequency side in Figure 11b. This is because the presence of phosphoric acid increases ionic conductivity, which reduces the relaxation time.

Conclusion

In this study, we have introduced the noble of the pure solid polymer electrolyte at room temperature used as an electrolyte as well as a separator from the piece of PVA and H₃PO₄ such that, the PVA samples were kept constant while the phosphoric acid was varied at 0.1, 0.2, 0.3 and 0.4. the PSPE results in higher conductivity of 2x10⁻⁴ Scm⁻¹ at the compositions of 0.4. in addition to that, we also observed that, the bulk modulus R_b decreases with increasing concentration, recording 100 Ω at the highest compositions of 0.4.

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