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ELECTRICAL AND INFRARED SPECTROSCOPIC ANALYSIS OF SOLID POLYMER ELECTROLYTE BASED ON POLYETHYLENE OXIDE AND GRAPHENE OXIDE BLEND

(Kajian Elektrik dan Spektroskopik Inframerah kepada Elektrolit Polimer Pepejal Campuran Polietilena Oksida dan Grafena Oksida)

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Abstract

Poly(ethylene oxide) (PEO), polyvinyl alcohol (PVA), and poly(ethylene carbonate) are synthetic polymers that have been widely used as polymer host in solid polymer electrolyte (SPE). A proton source, for example, lithium triflate ($LiCF_3SO_3$), ammonium bromide (NH_4Br), and ammonium fluoride (NH_4F) are doped in the polymer blend to provide the mobile Li^+ or H^+ ions. Polymer blending has been introduced to improve the properties of SPEs due to the easy preparation and excellent physical properties. In the present work, SPEs hosted by poly(ethylene oxide) (PEO) - graphene oxide (GO) blend doped with ammonium triflate ($NH_4CF_3SO_3$) has been prepared *via* solution casting technique. The highest room temperature conductivity of the PEO-GO polymer electrolytes containing 35 wt.% $NH_4CF_3SO_3$ was found to be $(2.48 \pm 0.83) \times 10^{-6}$ S cm^{-1}. This conductivity is comparable to our previous work for the system of PEO-GO-$LiCF_3SO_3$ at $(3.84 \pm 0.83) \times 10^{-6}$ S cm^{-1}. Fourier transmission infrared (FTIR) analysis exhibits the complexation between ammonium salt and polymer host. The FTIR spectra have been deconvoluted in the wavenumber region between 1010 and 1100 cm^{-1} to determine the percentage of free triflate ion and ion aggregations. The results show that the number of free ions increases and attains maximum at 35 wt.% $NH_4CF_3SO_3$. The relaxation time of the electrolytes was found to decrease as the ionic conductivity at room temperature increased. Dielectric studies show that all electrolytes obeyed non-Debye behavior.

Keywords: polymer electrolyte, PEO-GO blend, ammonium triflate, ionic conductivity, dielectric constant

Abstrak

Poli (etilena oksida) (PEO), polivinil alkohol (PVA), dan poli (etilena karbonat) merupakan polimer sintetik yang banyak digunakan sebagai polimer asas dalam elektrolit polimer pepejal (SPE). Sebagai sumber proton seperti litium triflate ($LiCF_3SO_3$), amonium bromida (NH_4Br), dan amonium fluorida (NH_4F) ditambah ke dalam campuran polimer untuk memberi ion Li^+ atau H^+.

Pengadun polimer telah diperkenalkan untuk meningkatkan sifat-sifat SPE kerana penyediaannya yang mudah dan sifat fizikal yang sangat baik. Dalam kajian ini, SPE yang berasaskan campuran poli (etilena oksida) (PEO) - grafena oksida (GO) yang dengan tambahan amonium triflate ($NH_4CF_3SO_3$) telah disediakan melalui teknik pengacuan larutan. Kekonduksian pada suhu bilik tertinggi ialah bagi elektrolit polimer PEO-GO yang mengandungi 35% berat $NH_4CF_3SO_3$ iaitu pada $(2.48 \pm 0.83) \times 10^{-6}$ S cm^{-1}. Kekonduksian ini adalah setanding dengan kajian kami sebelum ini bagi sistem PEO-GO-$LiCF_3SO_3$ pada $(3.84 \pm 0.83) \times 10^{-6}$ S cm^{-1}. Analisis spektrometer inframerah (FTIR) mempamerkan kompleks antara garam ammonium dan polimer asas. Spektrum FTIR telah didikonvolutkan di antara 1010 dan 1100 cm^{-1} untuk menentukan peratusan agregat ion dan ion triflat bebas. Keputusan menunjukkan bahawa bilangan ion bebas meningkat dan mencapai maksimum pada 35% berat $NH_4CF_3SO_3$. Masa kelonggaran elektrolit didapati berkurangan apabila kekonduksian ionik meningkat pada suhu bilik. Kajian dielektrik menunjukkan bahawa semua elektrolit mematuhi tingkah laku bukan Debye.

Kata kunci: elektrolit polimer, campuran PEO-GO, amonium triflate, kekonduksian ionik, pemalar dielektrik

Introduction

Polymer electrolyte is a vital component that is used in electrochemical devices such as proton batteries and electrochemical double layer capacitors (EDLCs). The development of solid polymer electrolyte (SPE) first began in 1979 by applying lithium batteries [1]. Liquid electrolytes are well known due to their high performance in various energy devices [2, 3]. However, liquid electrolytes are easy to evaporate and damage the equipment due to leaking and corrosive problems [4]. SPEs have good potential to replace liquid electrolyte due to their safe and easy fabrication as well as having long shelf life [5]. Lithium batteries provide high conductivity and overall good performance. However, their characteristics which include not being able to naturally degrade may lead to environmental pollutions [6]. Hence, researchers have started to replacing Li-ion provider with other alternatives to replace the H^+ ion including Mg^{2+} ion and NH_4^+ ion [2, 7].

Blending two or more different polymers in producing a polymer electrolyte system is a technique that can assist in increasing the sites availability for ion hopping and exchange [8]. Rather than a single polymer, a mixture of polymers can enhance the thermal stability and mechanical strength [9]. Polymer electrolyte hosted by poly(ethylene oxide) (PEO) has the potential for the development of ion conduction because it is naturally semi crystalline, has high tensile strength, and flexible due to non-hazardous and easy preparation of electrolyte [10, 11]. The high molecular weight of PEO based polymer electrolytes shows the movement of ions *via* their amorphous phase [12]. Thus, the selection of PEO as polymer host for the designing of SPE is significant due to their ability to form complexation with other components as well as improving the transport mechanism [13]. Meanwhile, graphene oxide (GO) has the ability to be used as an active nanofiller [14]. Mohanta et al. stated that GO has high surface area, able to disperse in organic solvents, and is stable thermally and chemically. Polymer nanocomposites of GO based have better mechanical and electrical properties compared to other clay or carbon filler based [15]. GO can be modified and functionalized for the preparation of polymer host, and it is also a pioneer material for the preparation of large quantities of graphene nanosheets for various functions such as sensors and transparent conductive films [16, 17].

The addition of salt into polymer blend has been proven to increase the ionic conductivity. Anuar et al. reported that addition of ammonium triflate ($NH_4CF_3SO_3$) salt into poly(ethyl methacrylate) (PEMA) based polymer electrolyte had increased the conductivity from 8.60×10^{-11} S cm^{-1} to 1.02×10^{-5} S cm^{-1} [18]. The incorporation of ammonium salt was more cost-effective and had been reported as a suitable proton donor to the polymer electrolyte salted system which was comparable with a lithium salt-doped system [19, 20]. Rodi et al. reported that the incorporation of 20 wt.% $LiCF_3SO_3$ in PEMA based electrolyte had obtained an ionic conductivity of 7.20×10^{-8} S cm^{-1} at room temperature [21].

Our previous work showed that the X-ray diffraction (XRD) analysis of 90 wt.% PEO - 10 wt.% GO blend was suitable to act as polymer host since it exhibited the

most amorphous blend [22]. In the present work, attention was given to develop the same ratio of PEO-GO blend polymer host with the incorporation of $NH_4CF_3SO_3$ salt as proton provider for the system. The effect of salt concentration on the ionic conductivity at room temperature was studied based on the electrical properties via electrical impedance spectroscopy (EIS) and Fourier transform infrared (FTIR) spectroscopy. The transport and dielectric properties of the electrolytes are further discussed.

Materials and Methods

Preparation of graphene oxide (GO)

GO nanosheets were prepared by a modified Hummers method [23]. The impurities such as sulfuric acid and phosphoric acid traces from the Hummers method were removed through the washing process by using distilled water. Mild sonication was applied to the suspension for about 10 minutes to exfoliate graphite oxide that remained in the GO suspension. Finally, GO suspension was put into the oven for 48 hours at 60ºC to discard water present, thus obtaining dark brown GO nanosheets.

Preparation of PEO-GO-$NH_4CF_3SO_3$ (salted) system

The polymer blend electrolyte system was prepared by homogenizing 10 wt.% of GO nanosheets in 50 mL distilled water from a total of 0.5 g polymer blend by using ultrasonicator XO-650D (Nanjing Xianou Instruments Co. Ltd.) for about 15 minutes at 50% crusher capacity. After the solution was cooled to room temperature, 90 wt.% of PEO (Aldrich Chemistry) was then added to the GO solutions and stirred until a homogeneous solution was obtained. Before the preparation of salted electrolytes, $NH_4CF_3SO_3$ (Aldrich Chemistry) was dried at 100 ºC for 1 hour to eliminate trace amounts water. Different amount of $NH_4CF_3SO_3$ between 5 to 45 wt.% was added to the PEO-GO solutions and stirred until complete dissolution. The composition and designation of various PEO-GO-$NH_4CF_3SO_3$ blends are listed in Table 1. All homogeneous solutions were cast onto plastic Petri dishes and left to dry at room temperature for 4 to 5 days to form a film. The dry films were then kept in desiccators filled with silica gel desiccants for 2 to 3 hours before being characterized to avoid any trace of moisture.

Characterization of electrolytes

Impedance measurements were conducted using HIOKI 3532-50 LCR HiTESTER at room temperature in the frequency range of 50 Hz to 5 MHz. The electrolyte films were sandwiched between two stainless steel electrodes of a conductivity holder with a diameter of 1.9 cm. The value of bulk resistance (R_b) determined from the Cole-Cole plots. Conductivity (σ) was calculated using the equation below;

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$$\sigma = \frac{d}{R_b A} \quad (1)$$

where d is the thickness of the electrolyte samples, and A is the electrode-electrolyte contact area. A digital thickness gauge (Mitutoyo Corp.) was employed to measure the thickness of the electrolytes.

The Fourier transform infrared spectroscopy (FTIR) studies were performed using attenuated total reflection infrared spectroscopy (ATR-IR) Perkin Elmer Spectrum 400 GladiATR in the wavenumber range of 600 - 4000 cm^{-1}. The purpose of FTIR analysis was to confirm the complexation between polymer and salt. Deconvolution technique was used to extract any overlapping peaks. Correction of baseline and fitting curve was implemented via Gaussian-Lorentzian function. From FTIR deconvolution, number density (n), ionic mobility (μ), and diffusion coefficient (D) of charges carriers were calculated the following Eq. 2 to Eq. 4.

$$n = \frac{M \times N_A}{V_{Total}} \times (free\ ion\%) \quad (2)$$

$$\mu = \frac{\sigma}{ne} \quad (3)$$

$$D = \frac{\mu kT}{e} \quad (4)$$

In Eq. 2, M is the number of moles of $NH_4CF_3SO_3$ salt used, N_A is Avogadro's number (6.02×10^{23} mol^{-1}), and V_{Total} is the total volume (cm^3) of polymer electrolyte. In Eq. 3, e is the elementary charge (1.602×10^{-19} C) while k and t in Eq. 4, is a Boltzmann constant (1.38×10^{-23} JK^{-1}) and absolute temperature, respectively.

Table 1. The composition and designation of electrolytes in salted system

Poly(ethylene oxide) : Graphene oxide : $NH_4CF_3SO_3$ composition (wt.%)	**Designation**
90 wt.% PEO - 10 wt.% GO	PG9
90 wt.% PEO - 10 wt.% GO - 5 wt.% $NH_4CF_3SO_3$	S5
90 wt.% PEO - 10 wt.% GO - 15 wt.% $NH_4CF_3SO_3$	S15
90 wt.% PEO - 10 wt.% GO - 25 wt.% $NH_4CF_3SO_3$	S25
90 wt.% PEO - 10 wt.% GO - 35 wt.% $NH_4CF_3SO_3$	S35
90 wt.% PEO - 10 wt.% GO - 45 wt.% $NH_4CF_3SO_3$	S45

Results and Discussion

Figure 1 shows the ionic conductivity of the polymer electrolyte with different concentration of $NH_4CF_3SO_3$ at room temperature. The conductivity for an un-doped sample (PG9) is $(4.10 \pm 1.12) \times 10^{-11}$ S cm^{-1}, which is relatively low since there is no mobile ions presence within the film. However, the conductivity increases to $(1.30 \pm 0.32) \times 10^{-8}$ S cm^{-1} for S5. Anuar et al. also reported that addition of $NH_4CF_3SO_3$ salt into PEMA would increase the conductivity of the polymer electrolyte. On the addition of 35 wt.% of $NH_4CF_3SO_3$ into PEO-GO polymer blend, the conductivity is further increased to $(2.48 \pm 0.83) \times 10^{-6}$ S cm^{-1}. The conductivity with the order of ~10^{-6} S cm^{-1} is comparable with other reports on polymer host containing triflate salt [24, 25]. The conductivity is then decreased to $(3.64 \pm 3.67) \times 10^{-7}$ S cm^{-1} with the addition of 45 wt.% of $NH_4CF_3SO_3$. It clearly explains that the addition of $NH_4CF_3SO_3$ more than 35 wt.% will reduce the ionic conductivity due to the formation of overcrowded ions in the system. Samsudin et al. had reported a 35 wt.% of dodecyltrimethyl ammonium bromide salt in carboxymethylcellulose-based electrolyte resulted the highest ionic conductivity which also proved that the ion mobility is lower at higher salt concentration due to the aggregation of ion clusters [26].

In this work, the focus has been given to study the interaction of the polymer blend with ammonium salt based on the FTIR analysis. The band assignments for the polymer electrolyte system are listed in Table 2. Figure 2 shows the FTIR spectra for regions at 600 - 4000 cm^{-1}.

The appearance of a peak at (i) 638 cm^{-1} for S5 could be assigned to asymmetric SO_3 bending due to the incorporation of $NH_4CF_3SO_3$ salt into the PEO-GO polymer host. Besides, the peak at (v) 1031 cm^{-1} and (ix) 1242 cm^{-1} are assigned to symmetric SO_3, $\upsilon_s(SO_3)$ and asymmetric SO_3, $\upsilon_{as}(SO_3)$ vibrations of $NH_4CF_3SO_3$ for S5 respectively. The peaks are then shifted to 1024 cm^{-1} and 1252 cm^{-1} as the salt concentration rises to 45 wt.%. Asmara et al. mentioned that free triflate ion should peak at 1032 cm^{-1} [31]. However, according to Wendsjö et al., the peak may shift to 1020 - 1026 cm^{-1} for higher salt concentration [32]. The triflate ion peaks may produce various FTIR active bands when the salt concentration

is increased due to sensitive vibrational spectrum to the coordination state [39].

Peaks located at (iii) 843 cm^{-1} and (iv) 960 cm^{-1} are recognized to CH_2 rocking and twisting, respectively. These peaks are shifted to 840 cm^{-1} and 952 cm^{-1} as the concentration of salt increases to 45 wt.%. Moreover, for CH_2 wagging and scissoring bands, the peaks are located at 1344 cm^{-1} and 1471 cm^{-1} and then shifted consequently to (x) 1360 cm^{-1} and (xi) 1446 cm^{-1}. Hence, this indicates that there is an interaction of salt in PEO/GO polymer blend [40]. The peak at (vi) 1100 cm^{-1} fits for the C-O-C stretching band and is relocated to 1090 cm^{-1} upon the addition of salt. Since the cation of $NH_4CF_3SO_3$ is coordinated with the ether oxygen of PEO, the spectral changes are believed to be due to the influence of salt or the C-O-C stretching mode and deformation [34].

Another band is observed at lower wavenumbers that is symmetric CF_3 deformation at (ii) 760 cm^{-1}. The appearance of this peak indicates the complexation of salt addition into the polymer host has occurred and the intensity of the peak increases as the concentration of salt increases. The CF_3 deformation has appeared at 755 - 765 cm^{-1} in the system of propylene carbonate (PC) with $NH_4CF_3SO_3$ salt [41]. Other transmittance bands were also reported by Kumar et al. that are for symmetric and asymmetric CH stretching vibrations at 2700 - 3800 cm^{-1} and 2962 - 2695 cm^{-1}, respectively. Symmetric and asymmetric CH stretching bands are located at (xii) 2897 cm^{-1} and (xiii) 3102 cm^{-1} for S45 [29].

The FTIR spectroscopy is also an analytical technique that can further be used to analyze the transport properties of an electrolyte. This study was performed for further understanding of the ionic conductivity (σ) and its relationship with the number density of mobile ion (n), ionic mobility (μ) and diffusion coefficient (D) [42]. The overlapping bands can be solved through FTIR deconvolution by compensating the essential line widths of a particular band. This technique yields spectra that have much narrower bands and can distinguish space features closely.

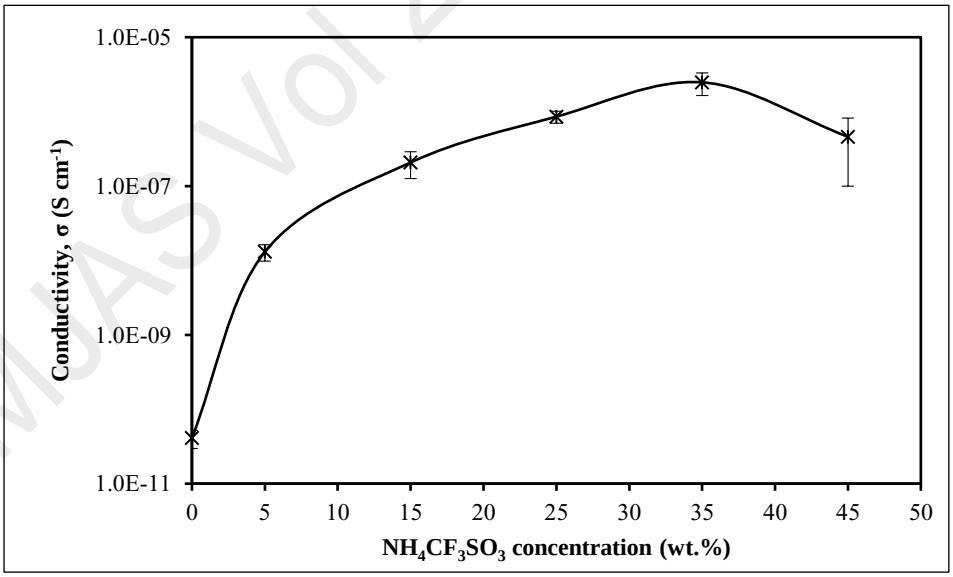

Figure 1. Ionic conductivity at room temperature for PEO-GO-$NH_4CF_3SO_3$ system

Table 2. Vibrational assignments of salted system for PEO-GO-$NH_4CF_3SO_3$ system

Wavenumber (cm^{-1})		Assignments	Reference
(i)	638	Asymmetric SO_3 bending	[27]
(ii)	760	Symmetric CF_3 deformation	[25, 28]
(iii)	843	CH_2 rocking	[27–30]
(iv)	960	CH_2 twisting	[28, 30]
(v)	1031	Symmetric SO_3 stretching	[27, 30–33]
(vi)	1100	C-O-C stretching	[34]
(vii)	1152	Asymmetric CF_3 stretching	[28, 35, 36]
(viii)	1225	Symmetric CF_3 stretching	[36, 37]
(ix)	1242	Asymmetric SO_3 stretching	[27, 30, 33]
(x)	1360	CH_2 wagging	[29, 38]
(xi)	1446	CH_2 scissoring	[27, 28, 30]
(xii)	2897	Symmetric CH stretching	[29, 30, 38]
(xiii)	3102	Asymmetric CH stretching	[29]

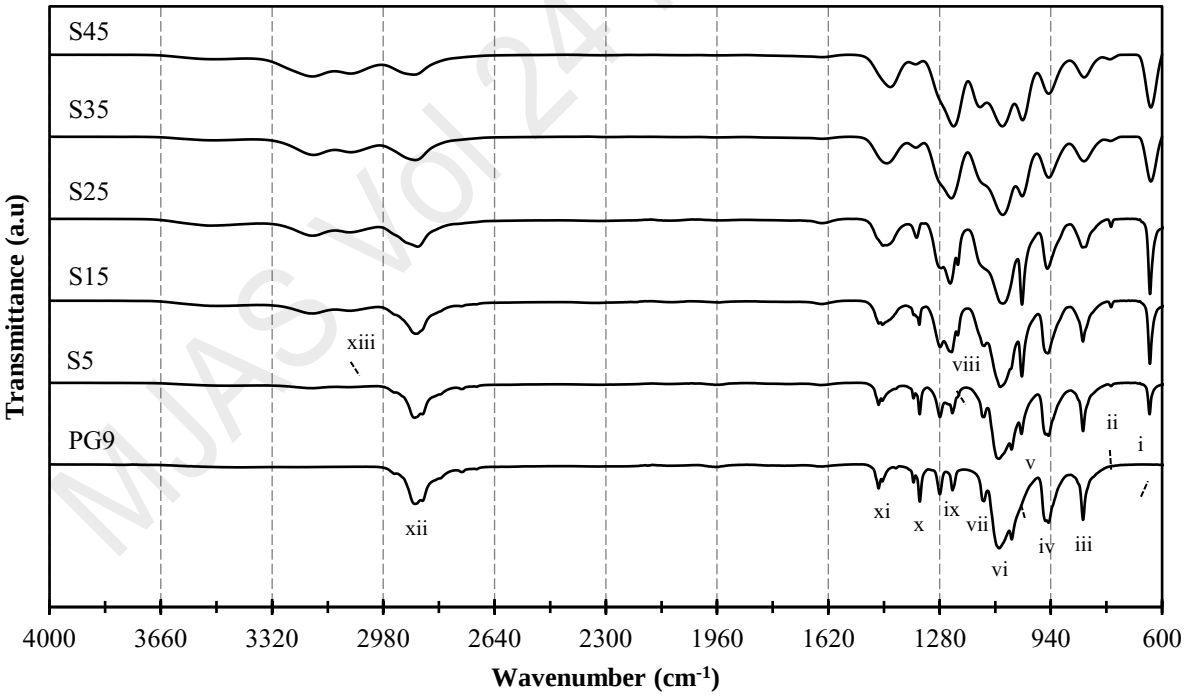

Figure 2. FTIR spectra for PEO-GO-$NH_4CF_3SO_3$ system

In this study, FTIR spectra of 1010 cm^{-1} to 1100 cm^{-1} was deconvoluted by using Gaussian-Lorentzian function, as shown in Figure 3 where the significant interaction of several peaks can be spotted. The deconvoluted area of FTIR peak will show the transport parameters. According to Asmara et al., a study on the poly(methyl methacrylate) (PMMA) gel polymer electrolytes with magnesium triflate ($Mg(CF_3SO_3)_2$), free triflate ion should peak at 1032 cm^{-1} due to decomposition of the SO_3 bands; and bands due to ion pairs and large ion aggregates should peak at 1051 cm^{-1} and 1062 cm^{-1} respectively. The peak of free triflate ion at 1032 cm^{-1} is agreeable to the previous literatures stated in Table 2. However, the free triflate ion peak may shift to 1020 - 1026 cm^{-1} for the higher salt concentration [32]. The bands that peak at 1070 cm^{-1} and 1080 cm^{-1} were also mentioned by Asmara et al. that is corresponding to ring breathing and skeletal stretching of the carbonate compound.

From Figure 3, two main peaks of free triflate ion (1026 - 1033 cm^{-1}) and ion aggregates (1058 - 1064 cm^{-1}) can be observed. Besides, ring breathing and skeletal stretching peaks from carbonate compound are located respectively between 1074 to 1079 cm^{-1} and 1087 to 1093 cm^{-1}. Meanwhile, a peak is found between 1018 to 1023 cm^{-1} which is ascribed to band of $\upsilon_s(SO_3)$. Bergstroem & Frech reported that the additional band of $\upsilon_s(SO_3)$ could be detected at wavenumber 1020 cm^{-1} to 1026 cm^{-1} [35].

The percentage of free triflate ion and ion aggregate was calculated and plotted in Figure 4. The percentage of free triflate ion increases as the $NH_4CF_3SO_3$ concentration increases but the trend is vice versa with the ion aggregates. Highest conducting electrolyte has the highest free triflate ion percentage (93.34%) that can be related to the hypothesis that the ionic conductivity of a polymer electrolyte will increase as the percentage of free ions increases. This trend of results is similar to the study by Aniskari & Mohd Isa that had 95.45% of free ion for the highest conducting sample of the 2-hydroxyethyl cellulose doped with glycolic acid polymer electrolyte system [37]. However, further addition of $NH_4CF_3SO_3$ reduces the intensity of the free triflate ion peaks which caused the ions to recombine. The recombination of ions may lead to the formation of ion pairs and caused the number of movable ions to reduce. The intensity of $\upsilon_s(SO_3)$ band is found to increase in S45 electrolyte that explains the reduction of mobile charge carriers hence decreasing the conductivity [43].

The calculated ionic transport parameters based on the percentage of free triflate ion (Eq. 2-Eq. 4) for PEO-GO polymer electrolyte with different $NH_4CF_3SO_3$ concentration are tabulated in Table 3 and plotted in Figure 5. The graphs follow the trend of ionic conductivity at room temperature are plotted in Figure 1. From the graphs, the addition of salt into the system causes the number density of mobile ion in the polymer electrolytes increases. It is believed that doping the parental host polymer leads to the increment of free ions that can contribute to the rise of ionic conductivity [37]. This is proven when the highest conducting electrolyte (S35) resulted on the highest n, μ and D values compared to other electrolytes as shown in Figure 5(a) to (c). It can be seen that after the addition of 35 wt.% $NH_4CF_3SO_3$, the ionic mobility and diffusion coefficient have decreased, which explains that the optimum value of number density was obtained at the highest conducting sample. Higher composition of salt form ion clouds where the overcrowding situation blocks most of the free ions present in the sample hence the ionic mobility and diffusion coefficient have decreased [44].

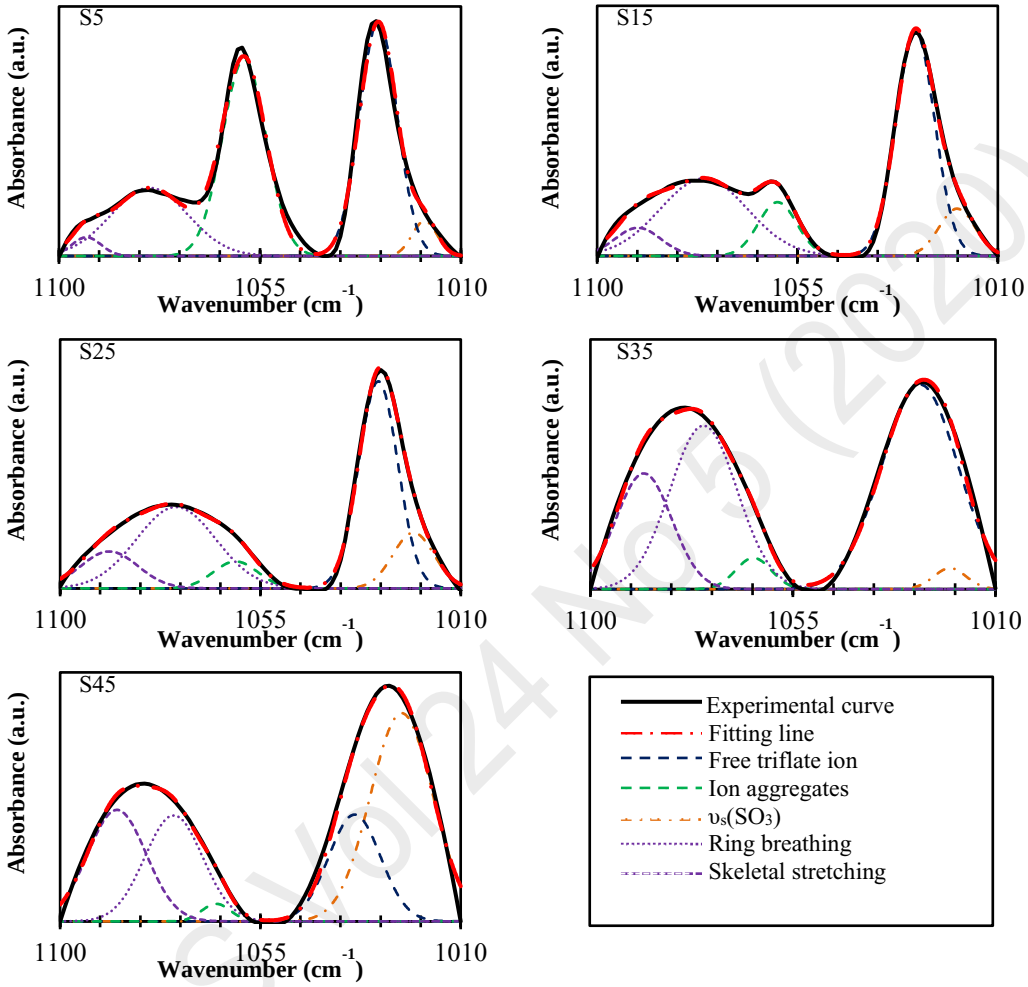

Figure 3. FTIR deconvolution for PEO-GO-$NH_4CF_3SO_3$ salted system between 1010 to 1100 cm^{-1}

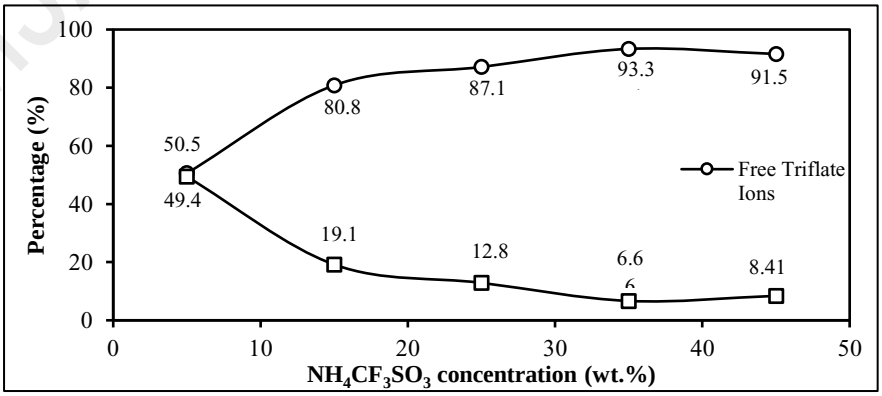

Figure 4. Percentage of free triflate ion and ion aggregates of PEO-GO-$NH_4CF_3SO_3$ salted system

Table 3. Transport parameters for PEO-GO-$NH_4CF_3SO_3$ salted system

Sample	Ionic Conductivity, σ (S cm^{-1})	Number of Density, n (cm^{-3})	Ionic Mobility, μ (cm^{2}V^{-1}s^{-1})	Diffusion Coefficient, D (cm^{2}s^{-1})
S5	$(1.30 \pm 0.32) \times 10^{-8}$	4.50×10^{23}	1.81×10^{-13}	4.64×10^{-15}
S15	$(2.07 \pm 0.81) \times 10^{-7}$	2.00×10^{24}	6.48×10^{-13}	1.66×10^{-14}
S25	$(8.56 \pm 1.57) \times 10^{-7}$	3.67×10^{24}	1.46×10^{-12}	3.74×10^{-14}
S35	$(2.48 \pm 0.83) \times 10^{-6}$	5.06×10^{24}	3.05×10^{-12}	7.84×10^{-14}
S45	$(4.60 \pm 3.60) \times 10^{-7}$	4.63×10^{24}	6.20×10^{-13}	1.59×10^{-14}

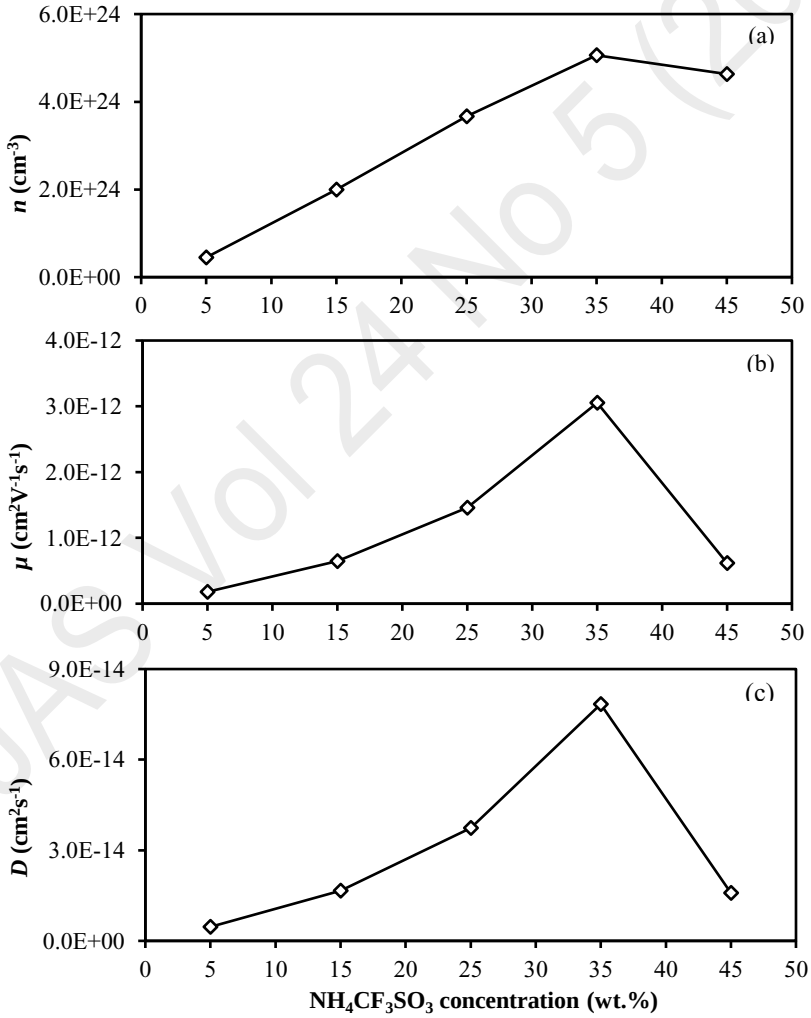

Figure 5. The transport parameter of (a) number of densities, (b) ion mobility and (c) diffusion coefficient for PEO-GO-$NH_4CF_3SO_3$ salted system

Dielectric study is useful to further verify the conductivity trend of PEO-GO polymer electrolyte with the addition of $NH_4CF_3SO_3$. The dielectric constant (ε_r) represents the charges stored in materials and dielectric loss (ε_i) stands for the loss of energy to move ions and align dipoles when the electric field polarity reverses rapidly [45]. Studies on dielectric properties help to understand the behavior of conductivity and also further support the hypothesis that the increase in the charge or the number of free mobile ions will increase the conductivity. Moreover, a detailed study of polarization and relaxation phenomena is conducted because the transport mechanism in the electrolyte is strongly correlated to the properties of the polymer matrix [46]. Both ε_r and ε_i can be expressed as in the equation below;

$$\varepsilon_r = \frac{Z_i}{\omega C_o (Z_r^2 + Z_i^2)} \quad (5)$$

$$\varepsilon_i = \frac{Z_r}{\omega C_o (Z_r^2 + Z_i^2)} \quad (6)$$

From Eq. 5 and Eq. 6, the Z_i is the imaginary part of impedance, Z_r is the real part of impedance, ω stands for the angular frequency and C_o representing the vacuum capacitance. Figure 6 shows the dependence of dielectric properties on $NH_4CF_3SO_3$ salt content. It can be observed that the highest conducting electrolyte has a higher value of ε_r and ε_i, especially at lower frequency. The increasing charge stored in the electrolyte shows that the number density of mobile ions has increased, hence increasing the conductivity [47]. Shukur et al. reported that the dielectric constant result is agreeable with the conductivity [48]. Besides, both ε_r and ε_i rise towards lower frequencies due to the electrode polarization and space charge effects, therefore obey the non-Debye behavior [7]. However, the ε_r and ε_i have decreased and become almost constant values towards higher frequencies due to the rapid periodic reversal of the electric field where there is no excess ion diffusion following the direction of the field. The polarization from the decrease of charge accumulation will lead to the a decrease in the value of ε_r and ε_i [49]. Figure 7 exhibits the $NH_4CF_3SO_3$ salt dependence of ε_r and ε_i at selected frequencies to support the trend.

The loss tangent (tan δ) graph is plotted to determine the relaxation behavior in the polymer electrolytes. It is a ratio of energy loss to energy stored in a periodical field which is also called as dissipation factor [50]. The value of tan δ can be calculated using the Eq. 7 below;

$$\tan \delta = \frac{\varepsilon_i}{\varepsilon_r} \quad (7)$$

The frequency dependence of tan δ for PEO-GO with different concentration of $NH_4CF_3SO_3$ salt at room temperature is shown in Figure 8. It illustrates that the tan δ consists of a well-defined curve at a characteristic frequency. At low frequency, tan δ increases with frequency due to the active component (ohmic) presence is more dominant than the reactive component (capacitive) while tan δ decreases at higher frequency because the amount of active component is frequency independent and the reactive component rises proportionally to the frequency [51]. The maximum of tan δ (tan δ_{max}) represents the relaxation peak that is located at a higher frequency for higher conducting electrolyte. The relaxation time (t_r) for each electrolyte can be obtained from the Eq. 8.

$$t_r \, \omega_{peak} = 1 \quad (8)$$

where ω_{peak} is the angular frequency of the relaxation peak. The values of t_r are tabulated in Table 4. The highest conducting electrolyte with the incorporation of 35 wt.% of $NH_4CF_3SO_3$ exhibits the lowest t_r value of 1.22×10^{-5} s while the lowest conducting electrolyte with 5 wt.% of $NH_4CF_3SO_3$ shows the highest value of relaxation time. The reduction in the value indicates that the polymer chain can easily orient through the increased amorphous region and/or empty room by incorporating more concentration of salts [52]. Idris et al. also reported that the lowest relaxation time possessed by the highest conducting electrolyte [53].

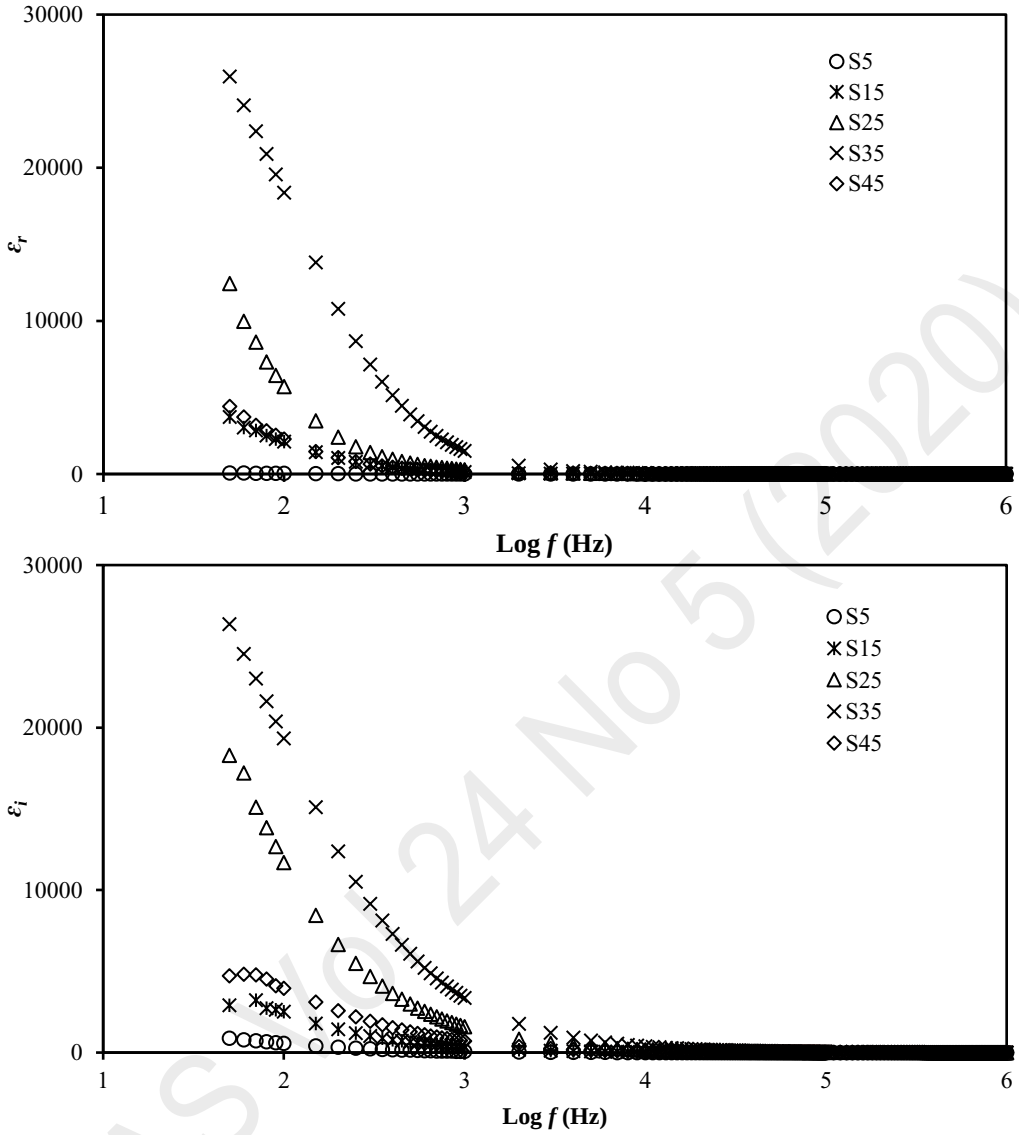

Figure 6. Frequency dependence of (a) ε_r and (b) ε_i for PEO-GO-$NH_4CF_3SO_3$ salted system at room temperature

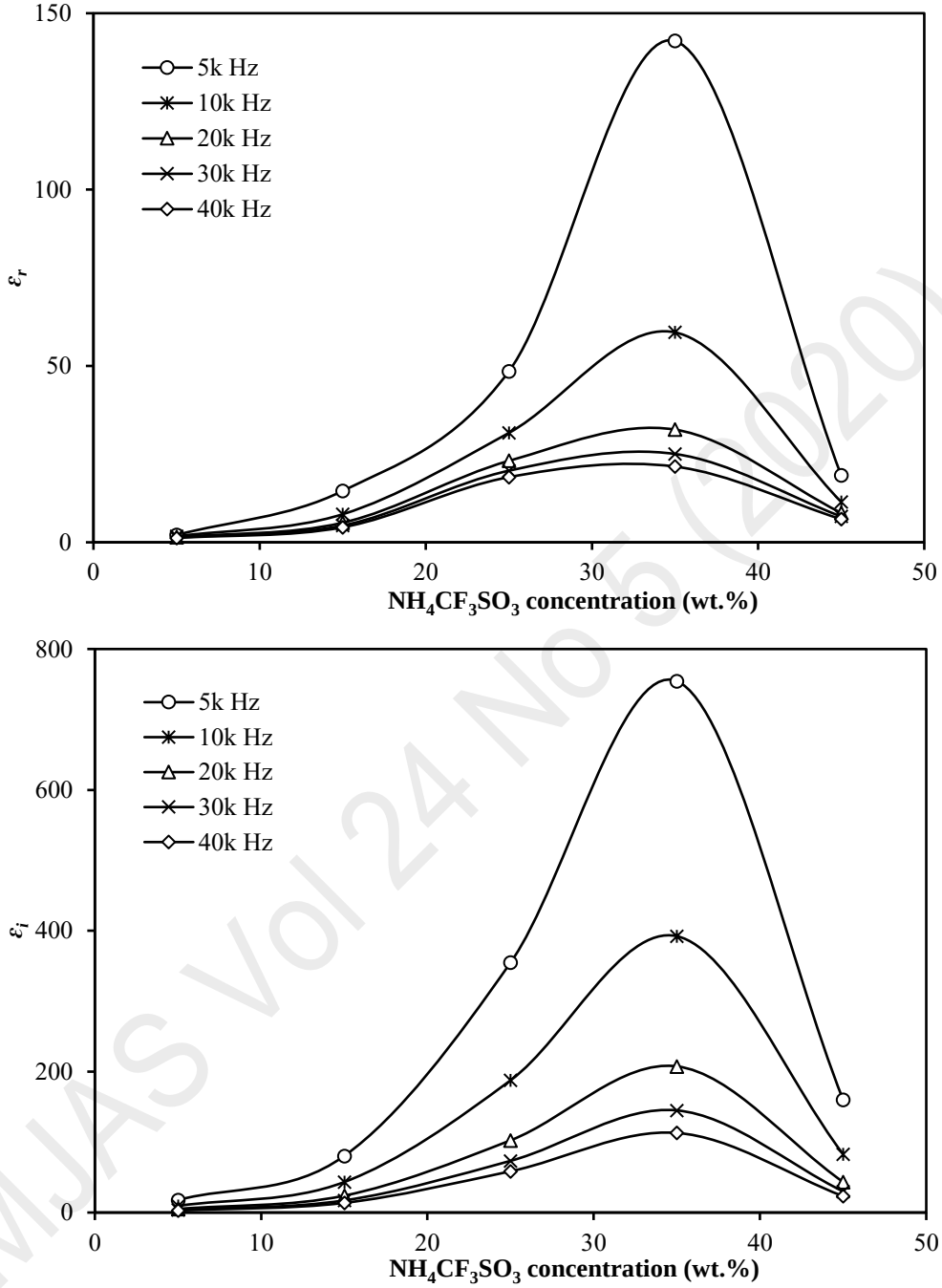

Figure 7. NH4CF3SO3 salt dependence of (a) εr and (b) εi at room temperature for selected frequencies

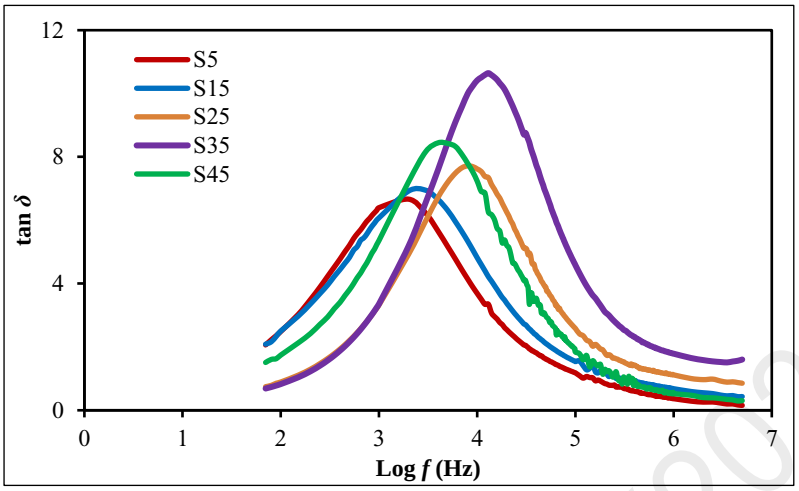

Figure 8. The frequency dependence of tan δ for PEO-GO-$NH_4CF_3SO_3$ salted system at room temperature

Table 4. Relaxation time (t_r) for PEO-GO-$NH_4CF_3SO_3$ salted system

Concentration of $NH_4CF_3SO_3$ (wt.%)	**t_r (s)**
5	$7.96. \times 10^{-5}$
15	$5.31. \times 10^{-5}$
25	$1.99. \times 10^{-5}$
35	1.22×10^{-5}
45	$3.98. \times 10^{-5}$

Conclusion

Solid polymer electrolytes hosted by PEO-GO polymer blend with varied composition of $NH_4CF_3SO_3$ salt were successfully prepared *via* solution casting technique. The conductivity studies at room temperature showed that there is an increment of ionic conductivity from $(4.10 \pm 1.12) \times 10^{-11}$ S cm^{-1} for an un-doped PEO-GO polymer blend to $(2.48 \pm 0.83) \times 10^{-6}$ S cm^{-1} with the incorporation of 35 wt.% of $NH_4CF_3SO_3$. FTIR study showed the interactions between PEO-GO polymer host blend with the addition of ammonium salt into the system occurring at certain observed peaks. FTIR deconvolution in the wavenumber region between 1010 and 1100 cm^{-1} was carried out to determine the percentage of free triflate ion and confirmed the dependence of ionic conductivity on the number density of mobile ion (n), ionic mobility (μ) and diffusion coefficient (D) of the solid polymer electrolyte. The relaxation time of the electrolytes is found to decrease as the ionic conductivity at room temperature increases. Dielectric studies show that all the electrolytes obey non-Debye behavior. The characteristics exhibited by the electrolyte in this study shows that this system has a great potential to be applied in the application of low-energy density devices such as electrical double layer capacitors (EDLCs) and proton batteries.

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