Limiting Molar Conductivity Value for Binary and Ternary Electrolyte System Using Power Law

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A new mathematic equation (Power Law) has been proposed by Hanibah *et al.* to determine the limiting molar conductivity (Λ_0) value with a better accuracy for the liquid electrolyte system especially in an organic solvent. The proposed Power law is fulfilled to the basic linear graph equation for certain (finite) range of salt concentration ($C_{salt} = 10^{-8}–10^{-6}$ mol cm^{-3}). It is observed that, reference salt concentration (C_{ref}) for each system that corresponds to the Λ_0 is approximately half that of the lowest C_{salt} and it still obeys the Power law before the data starts to divert from the linearity of the Power law. By using the proposed Power law equation, the Λ_0 and ion mobility (K') value for liquid polymer electrolyte (LPE) has been estimated. In order to estimate Λ_0 value at 25 ºC for LiClO$_4$ in liquid polymer electrolytes [poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), poly(methylmethacrylate-*co*-methacrylic acid) (PMMA-*co*-MA)–binary system], [PEO$_5$ blend with PMMA and PEO$_5$ blend with PMMA-*co*-MA–ternary system], the $C_{ref} = 1.89 \times 10^{-9}$ mol cm^{-3} is adopted. The κ value of the LiClO$_4$ in polymer solutions was measured as a function of C_{salt}. The polymer solutions comprised of fixed polymer concentrations (C_{poly}) for each electrolyte system. Consistent with C_{poly} and the increasing values of M_w in the electrolyte system, Λ_0 values tend to show a descending trend that indicates a better salt solubility in a binary system compared to a ternary system. In general, the K' and κ values showed an increasing trend in the ternary electrolyte system as the polarity increases.

Keywords: Power law, Liquid polymer electrolyte, Limiting molar conductivity, Ionic conductivity, Ion mobility.

INTRODUCTION

Polymer electrolyte is a system comprising of inorganic salt as a solute dissolved in a polymer solution [1]. Normally, the added salt provides ions for conduction and the polymer helps dissolution of salt and act as a backbone for ion conduction [2]. In a polymer electrolyte system, it is commonly understood that ions coordinate with the polymer chain and are transported through the polymer medium by the extensive segmental motion of the polymer chains [3].

Liquid polymer electrolyte (LPE) generally a combination of inorganic salt–polymer–solvent hybrid systems, which the salt is solvated in suitable dilute polymer solution [4,5]. Normally, at room temperature LPE displays a relatively high value of conductivity (~10^2 S cm^{-1}) [6-8]. On top of it, the preparation of LPE is comparatively easy [4,9]. The conductivity of the LPE is enhanced by the good contact between the electrolyte and the electrode [10-12]. However, most of LPE systems suffer low thermal at ambient temperature [13,14], poor mechanical

stabilities [4] and low electrochemical stability [5]. The high potential for leakage in for LPE requires special sealing in the battery systems. Furthermore, the solvent employed in LPE might gradually interact with the electrodes, potentially resulting in their deterioration over time [15,16].

However, it is observed that the strength of this electrolyte at any solute concentration depends on its degree of dissociation. Therefore, the strength of the electrolyte can be monitored by measuring total free ions presence in the electrolyte system. Therefore, the fundamental measurement for investigating this is the electrical resistance of the LPE solution. This value can be used to correlate the ion mobility (K') in an electrolyte system. The conventional method for measuring electrical resistance involves utilizing a conductivity cell composed of two parallel electrodes with identical geometric surface areas, separated by fixed dimensions [17,18]. In the following section, a much-detailed explanation of the theory and measurement of the conductivity are presented.

The ionic conductivity (κ) measurements for LPE (the dilute solutions of salt-polymer systems) might serve as a powerful tool in the elucidation of the ion-ion and ion-polymer inter-actions and the salt solubility behaviour in a total amorphous phase. In addition, the conductivity measurements for LPE take a much shorter time scale to be measured as compared to the measurements in solid polymer electrolyte (SPE). This system also gives a better accuracy in conductivity measurement compared to measurements in solvent-free systems. The information extracted gives an added knowledge and could serve as a foundation for understanding ionic conduction in amorphous regions for the SPE of salt-polymer systems.

In present study, the salt solubility behaviour of molar conductivity (Λ) for different liquid electrolyte systems been discussed. The effect of semicrystalline polymers in ion mobility (K′) is further discussed in detail. The study also expanded to focus on several factors such as the use of different molecular weight, the presence of the co-polymer and the effect of the blends of different semicrystalline polymer. Lithium perchlorate ($LiClO_4$) was used as the inorganic salt to prepare the electrolyte system. It was dissolved in poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), poly(methylmethacrylate -*co*-methacrylic acid) (PMMA-*co*-MA), PEO blend with PMMA and PEO blend with PMMA-*co*-MA, in good solvent like acetonitrile at 25 ºC.

The use of different molecular mass of the PEO allows for variation of viscosity of the electrolyte system. Variation in viscosity, in turn, is strongly related to electrolytic conductivity (κ). The stability of the polymer electrolyte requires an optimized balance of its viscosity and electrolytic conductivity. Establishing of this balance for $LiClO_4$ in different liquid polymer electrolytes will be the main focus of these studies. A variation of the molecular mass of the polymer, polymer concentration, the presence of the co-polymer and the blends system serves to adjust the optimized balance.

Power law: The double-logarithmic plot of *versus* C_{salt} in eqn. 1 been proposed by Hanibah *et al.* [19] is adapted in this study to calculate limiting molar conductivity (Λ₀) for the binary and ternary electrolyte system at 25 ºC. Accurate calculation of Λ₀ for the binary and ternary polymer electrolyte system after the proposed Power law might investigate the salt dissociation behaviour at a specific temperature. This calculated Λ₀ can be further used to estimate the degree of salt dissociation and conductivity behaviour of $LiClO_4$ in different polymer solutions system in a various polymer concentrations, salt concentrations, M_ws of PEO and in a blends system.

$$\log \kappa = K' + \gamma \log C_{salt} \tag{1}$$

where K′ is the intercept and γ is the slope of the double-logarithmic plot.

Upon rearranging eqn. 1, it becomes:

$$\kappa = K'\left(\frac{C_{salt}}{C^\theta}\right)^\gamma \tag{2}$$

In term of molar conductivity (Λ), we obtained eqn. 3 as:

$$\Lambda = K'\left(\frac{C_{salt}}{C^\theta}\right)^{\gamma-1} \tag{3}$$

where $C^\theta = 1$ mol cm⁻³, it is introduced to keep the exponential expression; K′ denotes as ion mobility value for a particular electrolyte system at a fixed temperature.

It is always convenient to discuss the conductivity behaviour of a liquid electrolyte in the term of molar conductivity (Λ), because this term is interrelated to the total free moving ions present in an electrolyte system at a specified temperature. It is also observed that the flow of electricity in an electrolyte will result in the ions movement and the measurement of its resistivity will give the κ value at the specific condition. Therefore, the quantity κ of an electrolyte depends on several factors such as (i) total ions concentration [20]; (ii) solvent temperature [21,22]; (iii) solvent dielectric properties (ε) [23,24]; and (iv) solvent polarity [25,26].

These factors interrelate one another which will affect ion dissociation in an electrolyte. As mentioned earlier, unless specified, the term κ refers to electrolytic conductivity at 25 ºC. For an electrolyte in a solvent, the κ value of a solution containing one electrolyte depends on the concentration of electrolyte (C). Therefore, it is convenient to divide the electrolytic conductivity by concentration. This quotient is termed as molar conductivity (Λ) as shown in eqn. 4:

$$\Lambda = \frac{\kappa}{C} \tag{4}$$

The term molar conductivity for an electrolyte solution at a specific dilution can be defined as a resistivity of a solution that contains free mobile ions that has been placed between two electrodes with one cm apart between each other [27]. Quantity Λ is normally expressed in the unit of S m² mol⁻¹ or S cm² mol⁻¹.

Hence, from eqn. 3, the value of Λ of binary and ternary electrolyte systems is calculated. Hence, the Λ₀ for the system is also calculated after eqn. 3 at a selected salt concentration known as reference salt concentration (C_{ref}). Thus, by using the electrolytic conductivity (κ) data, quantity Λ₀, the K′ value can be determined using the Power law been proposed for an electrolyte system.

From the proposed method, this study may contribute to a simple alternative and yet with acceptable accuracy in the determination of quantity limiting molar conductivity (Λ₀) and K′ of $LiClO_4$ in binary and ternary electrolytes system at a fixed temperature is reviewed. Thus, from the estimated quantity of Λ₀ and ion mobility (K′) values for a liquid polymer electrolyte can be the fundamental knowledge to design a more efficient secondary battery systems.

EXPERIMENTAL

Poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA) and poly(methyl methacrylate-*co*-methacrylic acid) (PMMA-*co*-MA) with purity ≥ 99% were purchased from Sigma-Aldrich Chemical Company, USA. All the polymers were utilized after purification. PEO_1, PEO_2, PEO_3, PEO_4 and PEO_5 denote PEO with $M_w = 1 \times 10^5$, 3×10^5, 6×10^5, 1×10^6 and 4×10^6 g mol⁻¹, respectively.

Purification of materials: All the polymers were purified by using a re-precipitation method. It was done by dissolving

the polymer in a polar organic solvent and re-precipiting in a non-polar organic solvent. Therefore, to purify PEO, an appropriate amount of polymer (2 g) was dissolved in 98 mL of chloroform (polar organic solvent) to make a stock solution of 2 (w/w) %. Afterwards, it was stirred continuously using a magnetic stirrer for 24 h at 50 ℃ to ensure a complete dissolution of the polymer.

The stock solution was concentrated to a half of its initial volume using a rotary evaporator (IKA-WERKE, Staufen, Germany) at 50 ℃. After the evaporation process, the final solution was quite viscous. When the viscous solution was poured into analytical reagent grade *n*-hexane (non-polar organic solvent) (Fisher Scientific, Leicestershire, UK) at a ratio of 1:5 for a polymer solution:*n*-hexane with mixture continuous stirring. During the stirring process, a gel-like precipitate of pure PEO was formed. The gel-like PEO was left in the solvent for 1 h for a complete re-precipitation process to take place. After decanting off the solvent, the precipitate was fished out with a glass rod onto a Petri dish, squeezed to remove excess solvent and left to dry overnight in the fume hood.

Further drying was carried out in a conventional oven (JEIO-TECH, Seoul, Korea) for 24 h, then transferred to a vacuum oven (JEIO-TECH, Seoul, Korea) for another 24 h at 50 ℃ before being kept in the electronic desiccators (Secador, New Jersey, USA) (with relative humidity around 40%) under nitrogen gas condition to avoid absorption of gas from the atmosphere. The purified sample will only be taken out from the desiccator during the sample preparation and immediately after the use, the polymer sample will be transferred back into the desiccator. The purification steps were also repeated for PMMA and PMMA-*co*-MA polymer samples. This purification step appears to have removed added 2,6-di-*tert*.-butyl-4-methylphenol (BHT) (200-500 ppm) inhibitor by the manufacturer from the polymer samples.

Inorganic salt (LiClO₄), acetronitrile (ACN) and water: The inorganic salt, anhydrous $LiClO_4$ with purity ≥ 99 was purchased from Acrōs Organics (Geel, Belgium). Since, $LiClO_4$ is water sensitive, it was only used after drying in vacuum oven for 48 h at 120 ℃ to eliminate trace amounts of water that may trap in the salt. After the drying process, $LICIO_4$ was carefully transferred into the electronic desiccators with the relative humidity < 40 % under nitrogen gas condition to avoid any re-absorption of water from the environment [19].

Only HPLC grade of organic solvents with purity ≥ 99.99% ACN (Fisher Scientific, Leicestershire, UK) was used in this analysis for the preparation of electrolyte. And the organic solvent was used as supplied without further purification process. However, the organic solvents were kept dry by the addition of the molecular sieves (Merck, Darmstadt, Germany) with pore diameter of 3 Å. This step is carried out to prevent any potential water reabsorption that may occur during the solvent consumption process [28].

Since the accuracy of the conductivity measurement is an important factor in this study, only a high-quality solvent is used for the preparation of the electrolyte solution. Ultrapure water was used to rinse the glasswares before drying the glasswares in this analysis. The water used in this study was prepared by passing through the double distilled water to water deionizing system Arium® 611D1 (Sartorius, Goettingen, Germany) that generally has electrolytic conductivity less than 18×10^6 Ω cm at 25 ℃. Afterwards, the deionized water was kept in a fluorinated high-density polyethylene (FLPE) container (Nalgene Labwere, Rochester, USA) before further use [29].

Sample preparation

PEO in acetonitrile: A liquid polymer solution was prepared in advance and will be used as solvent to dissolve $LiClO_4$ for the preparation of liquid polymer electrolyte system. The stock solution of PEO_1 in ACN at a fixed polymer concentration (C_{Poly}) at 0.0010 g cm⁻³ was prepared. Therefore, the preparation of polymer stock solution is been prepared pecisely by dissolving 0.5000 g of PEO in a 1 L blue cap solvent bottle. The organic solvent was filled to almost to the fiduciary mark by slowly adding acetonitrile. Then by using a disposable Pasteur pipettes, the meniscus level of the solution was made parallel to the fiduciary mark of the volumetric flask. Then, the organic solvent was quickly transferred into the solvent bottle that contains the polymer sample.

The cap solvent bottle which contains both polymer and organic solvent was firmly closed and swirled repeatedly to ensure thorough mixing. Subsequently, the polymer solution was stirred for 24 h at 50 ℃ to ensure a complete dissolution of the polymer before further used. The concentration of PEO in this stock solution is noted as $C_{Poly} = 0.0010$ g cm⁻³.

Stock solutions of PEO_1 to PEO_5 in ACN were prepared (0.0010-0.0030 g cm⁻³) in a 0.0005 g cm⁻³ interval. ACN serves as a theta solvent for PEO, anticipated to effectively dissolve PEO without phase separation, resulting in a homogeneous solution, while also facilitating improved interaction with $LiClO_4$ salt. For the concentrations of PEO in ACN prepared in this study, transparent or clear solutions were observed. Thus, these stock solutions of PEO in ACN were used as a polymer solution to be added with $LiClO_4$ in the subsequent steps for the preparation of liquid polymer electrolyte.

Since, PEO dissolved well in ACN to form a homogeneous solution at all the polymer concentrations, hence ACN was used to dissolve PMMA, PMMA-*co*-MA and for the preparation of polymer blends in this study. It is observed that ACN also acts as a good solvent for the remaining polymer system by forming a transparent solution at all concentration ratios. The same 0.0010-0.0030 g cm⁻³ polymer concentration in a 0.0005 g cm⁻³ interval was also applied to prepare the remining stock solution of PMMA, PMMA-*co*-MA and blends polymer in ACN.

Preparation of liquid polymer electrolyte-LiClO₄ in polymer solution: The stock solution of $LiClO_4$ in polymer solution ($C_{Poly} = 0.0010$ g cm⁻³) at precisely 1.00×10^{-3} mol cm⁻³ was prepared. This polymer electrolyte stock solution was prepared by transferring the precisely amount of $LiClO_4$ into the polymer stock solution. Now the polymer solution will act as solvent to dissolve $LiClO_4$. Next, utilizing a disposable Pasteur pipette, adjust the meniscus level of the solution to align with the fiduciary mark of the volumetric flask. The volumetric flask was firmly closed with glass stopper and

inverted it repeatedly to ensure thorough mixing. Subsequently, the solution was stirred for 24 h at 50 ºC before further used. This solution was used as a stock solution (liquid polymer electrolyte stock solution). Then, a series of dilution (C_{salt} = 10^{-3} – 10^{-7} mol cm^{-3}) from the polymer stock solution was carried out by adding up the polymer solution up to the fiduciary mark of 50 mL volumetric flask.

All salt solutions were thermally equilibrated at 25 ± 2 ºC at least for 10 min before the conductivity measurement. The same procedure was adopted to prepare the various concentrations of LiClO$_4$ in PEO$_1$–PEO$_5$, PMMA, PMMA-*co*-MA, blends of PEO$_5$/PMMA and PEO$_5$/PMMA-*co*-MA solutions (at 50:50 wt.% ratio, respectively).

AC conductivity: The electrolytic conductivity measurement (κ) for diluted solutions of salt-polymer solutions (for different polymer system at different C_{Poly}) were carried out using Mettler-Toledo SevenCompact S230 AC conductivity meter (Schwerzenbach, Switzerland) with its probes InLab® 741 (with different cell constant) (Mettler-Toledo, Switzerland) at 25 ºC.

InLab® 741 conductivity probe was used to measure the electrolytic conductivity (κ) for systems comprising of organic solvents (weak electrolyte). Since this probe is much suitable for organic system and from steel to avoid any chemical reaction between the probe that might affect the conductivity value of the electrolyte system. This probe has a measurement range of 0.001-500 μS cm^{-1} and the temperature range of 0-70 ºC. The mean ($\bar{\kappa}$) and standard deviation (S) of electrolytic conductivity were calculated for fixed electrolytic conductivity measurements for each sample. These quantities are needed to calculate the error of electrolytic conductivity in this study. The error for electrolytic conductivity for all systems in this study only lies between ± 0.3% ± 0.5%. It is also observed that the error bars for all the conductivity value are within the size of the experimental points.

The cell constant (K_{cell}) of SevenCompact S230 AC conductivity meter was estimated by automatic calibration on a daily basis. The aqueous solution of KCl at concentrations 0.01 and 0.0005 mol L^{-1} with the κ at 1413 and 84 μS cm^{-1}, respectively at 25 ºC were used for the calibration when the conductivity meter attached to InLab® 741. After the calibration process of the conductivity meter, the measurement of electrolytic conductivity at reference temperature of 25 ºC for sample solutions were carried out. At least six measurements of κ values for each solution were performed. The reported electrolytic conductivity (κ) value for a particular sample solution is the average value of six quantities κ at reference temperature 25 ºC.

In the following section, all the conductivities were recorded at reference temperature 25 ºC. In addition, all the preparation steps of the solution and conductivity measurements were carried out in a glove box under nitrogen gas atmosphere to avoid absorption of CO$_2$ gas into the salt solution that might form carbonic acid in the solution. The formation of carbonic acid need to be avoided in an electrolyte system, since formation of carbonic acid in the solution significantly affects the electrolytic conductivity value particularly at low salt concentration which causes a large error in the conductivity measurement. The experimental electrolytic conductivity value were

analyzed according to the respective equation in this study to determine the value of Λ_0.

RESULTS AND DISCUSSION

Determination of Λ_0 for liquid polymer electrolyte (polymer + solvent + salt) using Power law: Hanibah *et al.* [19] have highlighted that the workability of the proposed Power law in determination of Λ_0 at C_{ref} for strong and weak electrolyte systems. It is also observed that the proposed Power law fits well with high accuracy as compared to the extrapolation method that subjects to large discrepancy in the determination of the limiting value of an electrolyte system particularly for an organic electrolyte system. An accurate of the determination of Λ_0 for a liquid polymer electrolyte system will serve as an important point to analyze the strength of solution in enhancing the salt dissociation (solubility) behaviour upon the addition of polymer into an electrolyte system.

It is well-known that LiClO$_4$ in ACN system serves as a weak electrolyte that indicated a much lower amount of free ions present in the solution due to its natural behaviour of the solvent that only partially dissociated LiClO$_4$ in the solution. Therefore, the solubility effect of LiClO$_4$ in polymer solution will be investigated. It is suggested that the addition of polymer into an electrolyte system will further enhance the salt solubility and conductivity mainly due to a stronger interaction between the reactive side of the polymer and the inorganic salt. This attraction primarily as a result of different in electrostatic attraction.

Therefore, the same approach as discussed by Hanibah *et al.* [19] is adopted to determine the Λ_0 value for LiClO$_4$ in polymer solution at 25.0 ºC for different C_{Poly}, as a function of different M_ws of PEO and for different polymer type. Now, the solvent used for LiClO$_4$ is a polymer solution (polymer dissolved in ACN). The parameter C_{ref} for LiClO$_4$ in ACN is 1.89×10^{-9} mol cm^{-3} as determined by Hanibah *et al.* [19], the same value is adopted in this work to estimate Λ_0 values for LiClO$_4$ in polymer solutions (polymer in ACN). This is done with the assumption that C_{ref} will remain unchanged with the addition of polymer. It is important to take same C_{ref} value in the estimation of limiting molar conductivity values for LiClO$_4$ in polymer solution. Only under this condition, one obtains the pristine condition of addition LiClO$_4$ to polymer solution. The degree of dissociation (α) of LiClO$_4$ in polymer solution can be indicated and subsequently.

Table-1 summarizes the concentration range of C_{Poly} for different polymer in ACN to dissolve LiClO$_4$. The solvent with different C_{Poly} were prepared in increasing C_{Poly}s, where the visual inspection of the solution to check that no phase separation was be observed. The electrolytic conductivity (κ) were measured at various C_{salt} by series of dilution until a constant κ values were obtained. This constancy in κ is an indication of measurements, which start to deviate from the linearity of the Power law.

Table-2 shows the κ for C_{Poly} = 0.0010 and 0.0030 g cm^{-3}, respectively as a function of C_{salt} at 25.0 ºC for PEO$_1$ electrolyte system. Thus, data from Table-1 was used to plot double-logarithmic plot in polymer solution (PEO$_1$ in ACN) C_{Poly} = 0.0010 and 0.0030 g cm^{-3}, respectively in ACN at 25 ºC (Fig. 1). This

TABLE-2
LIMITING MOLAR CONDUCTIVITY (Λ_0) C_{salt}, κ AND Λ VALUES OF LiClO$_4$ IN 0.0010 AND 0.0030 g cm^{-3} FOR PEO$_1$ SOLUTION AT 25 ºC

C_{Poly} = 0.0010 g cm^{-3}			C_{Poly} = 0.0030 g cm^{-3}		
10^6 C_{salt} (mol cm^{-3})	10^4 κ (S cm^{-1})	Λ (S cm^2 mol^{-1})	10^6 C_{salt} (mol cm^{-3})	10^4 κ (S cm^{-1})	Λ (S cm^2 mol^{-1})
1100	245	23.33	1050	255	24.29
21.1	26.3	124.9	21.1	23.7	112.4
0.421	0.712	169.1	0.422	5.71	135.4
0.842	1.44	170.9	0.844	1.16	137.3
1.26	2.11	167.0	1.27	1.71	135.4
1.68	2.77	164.5	1.69	2.19	129.8
2.11	3.42	162.4	2.11	2.83	134.2
2.53	4.07	161.1	2.53	3.41	134.7
2.95	4.71	159.8	2.95	3.95	133.8
3.37	5.34	158.5	3.37	4.53	134.2
3.79	5.97	157.5	3.80	4.77	125.6
4.21	6.60	156.7	4.22	5.36	127.1
6.32	9.68	153.3	6.33	7.88	124.5
8.42	12.7	150.8	8.44	10.4	123.3

TABLE-1
C_{Poly} RANGE FOR DIFFERENT POLYMER IN ACN AT 25 ºC

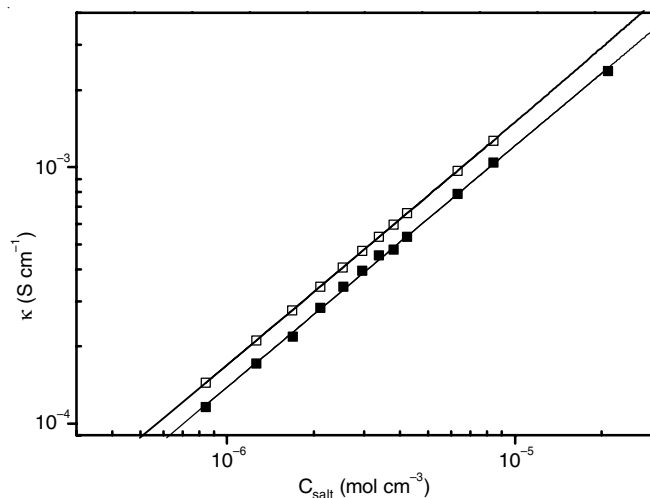| Polymer	C_{Poly} (g cm^{-3})
PEO$_1$	0.0010-0.0030
PEO$_2$	0.0010-0.0030
PEO$_3$	0.0010-0.0030
PEO$_4$	0.0010-0.0030
PEO$_5$	0.0010-0.0030
PMMA	0.0010-0.0030
PMMA-*co*-MA	0.0010-0.0030
PEO$_5$/PMMA (50:50)	0.0010-0.0030
PEO$_5$/PMMA-*co*-MA (50:50)	0.0010-0.0030

Fig. 1. Double-logarithmic plot of κ *versus* C_{salt} of LiClO$_4$ in PEO and ACN solution (binary electrolyte system) at 25 ºC. C_{Poly} = (□) 0.0010 g cm^{-3} and (■) 0.0030 g cm^{-3}. Solid curves represent the regression curve after eqns. 5 and 6. Error bars are within the size of the experimental points

graph is plotted by taking the experimental data as tabulated in Table-2.

Regression functions for Fig. 1.

C_{Poly} = 0.0010 g cm^{-3} (PEO$_1$ in ACN)
$$\log \kappa = 1.9068 + 0.9464 \log C_{salt} \quad (\text{correlation: } 0.9999) \quad (5)$$

C_{Poly} = 0.0030 g cm^{-3} (PEO$_1$ in ACN)
$$\log \kappa = 1.78777 + 0.9409 \log C_{salt} \quad (\text{correlation: } 0.9991) \quad (6)$$

Upon rearranging eqns. 5 and 6 in the molar conductivity (Λ) form:

$$\Lambda \ (\text{S cm}^2 \text{ mol}^{-1}) = 80.7 \left(\frac{C_{salt}}{C^\theta} \right)^{-0.054} \quad (7)$$

$$\Lambda \ (\text{S cm}^2 \text{ mol}^{-1}) = 61.3 \left(\frac{C_{salt}}{C^\theta} \right)^{-0.059} \quad (8)$$

We get 0.0010 g cm^{-3} PEO$_1$ in ACN (eqn. 7) and 0.0030 g cm^{-3} PEO$_1$ in ACN (eqn. 8), respectively.

Hence, the Λ_0 value of the above systems was calculated after eqn. 9 has been proposed by Hanibah *et al.* [19].

$$\Lambda_0 = K'\gamma C_{ref}^{\gamma-1} \quad (9)$$

Eqn. 9 is known in these systems except L$_0$; K′ and γ from the Power law [eqns. 7 and 8]. Thus, by using the relevant parameters for C_{Poly} = 0.0010 g cm^{-3} (K′ = 80.7 and γ = 0.9464) and C_{Poly} = 0.0030 g cm^{-3} (K′ = 61.3 and γ = 0.9409) at C_{ref} = 1.89 × 10^{-9} mol cm^{-3} into eqn. 9, the result for quantity Λ_0 for PEO$_1$ in ACN solution at 0.0010 and 0.0030 g cm^{-3} were 225.9 and 188.7 S cm^2 mol^{-1}, respectively.

Tables 3 and 4 summarizes the regression function after eqn. 9 and quantity Λ_0 for LiClO$_4$ in polymer solution at 25.0 ºC that has been calculated at C_{ref} = 1.89 × 10^{-9} mol cm^{-3}. For all the electrolyte system, it is observed that it fitted well with the proposed Power law with a high correlation (r^2) value for each system within the working concentration range (C_{salt} = 10^{-6}-10^{-4} mol cm^{-3}).

Fig. 2 depicts the quantity Λ_0 as a function of C_{Poly} for different M$_w$s PEO, PMMA, PMMA-*co*-MA, PEO$_5$/PMMA and PEO$_5$/PMMA-*co*-MA electrolyte systems at 25 ºC. Fig. 2a shows the Λ_0 values for LiClO$_4$ in different C_{Poly}s at 25.0 ºC. The value Λ_0 decreases at higher C_{Poly}.

Fig. 2 suggests the addition of polymer into an electrolyte system causes a linear decrease in quantity Λ_0 respective to Λ_0 of LiClO$_4$ in ACN at different C_{Poly} concentrations. A

TABLE-3
REGRESSION FUNCTIONS AFTER POWER LAW AND LIMITING MOLAR CONDUCTIVITY (Λ_0) FOR LiClO$_4$ IN WATER, ACN AND PEO$_x$ SOLUTIONS (BINARY ELECTROLYTE SYSTEM) AT 25 ºC (C$_{ref}$ = 1.89 × 10^{-9} mol cm^{-3})

System (g cm^{-3})	$\Lambda = K'\left(\dfrac{C_{salt}}{C^\theta}\right)^{\gamma-1}$	$\Lambda_0 = K'\gamma C_{ref}^{\gamma-1}$ (S cm^2 mol^{-1})	r^2
ACN*	68.90 C$_{salt}^{-0.065}$	177.4	0.9993
PEO$_1$ (100 Kg mol^{-1})			
0.0010	80.7 C$_{salt}^{-0.054}$	225.9	0.9999
0.0015	73.3 C$_{salt}^{-0.060}$	230.0	0.9996
0.0020	72.3 C$_{salt}^{-0.055}$	206.2	0.9999
0.0025	62.9 C$_{salt}^{-0.059}$	193.6	0.9983
0.0030	61.3 C$_{salt}^{-0.059}$	188.7	0.9991
PEO$_2$ (300 Kg mol^{-1})			
0.0010	80.0 C$_{salt}^{-0.057}$	240.1	0.9982
0.0015	71.2 C$_{salt}^{-0.060}$	223.4	0.9994
0.0020	70.4 C$_{salt}^{-0.055}$	200.8	0.9999
0.0025	60.9 C$_{salt}^{-0.065}$	210.1	0.9990
0.0030	57.1 C$_{salt}^{-0.069}$	212.6	0.9980
PEO$_3$ (600 Kg mol^{-1})			
0.0010	79.2 C$_{salt}^{-0.057}$	234.7	0.9999
0.0015	68.9 C$_{salt}^{-0.063}$	228.8	0.9999
0.0020	66.6 C$_{salt}^{-0.065}$	229.8	0.9999
0.0025	59.9 C$_{salt}^{-0.071}$	231.6	0.9987
0.0030	56.9 C$_{salt}^{-0.065}$	196.3	0.9996
PEO$_4$ (1000 Kg mol^{-1})			
0.0010	78.9 C$_{salt}^{-0.053}$	216.7	0.9998
0.0015	59.3 C$_{salt}^{-0.070}$	225.0	0.9994
0.0020	54.9 C$_{salt}^{-0.074}$	227.1	0.9991
0.0025	51.7 C$_{salt}^{-0.075}$	215.7	0.9996
0.0030	51.4 C$_{salt}^{-0.073}$	206.5	0.9991
PEO$_5$ (4000 Kg mol^{-1})			
0.0010	77.7 C$_{salt}^{-0.058}$	242.5	0.9995
0.0015	58.2 C$_{salt}^{-0.071}$	225.1	0.9999
0.0020	54.0 C$_{salt}^{-0.074}$	221.1	0.9984
0.0025	50.4 C$_{salt}^{-0.077}$	218.4	0.9980
0.0030	49.1 C$_{salt}^{-0.081}$	229.6	0.9983

Data from*; *C$^\theta$ = 1 mol cm^{-3}

TABLE-4
REGRESSION FUNCTIONS AFTER POWER LAW AND LIMITING MOLAR CONDUCTIVITY (Λ_0) FOR LiClO$_4$ IN PMMA, PMMA-*co*-MA (BINARY ELECTROLYTE SYSTEM), PEO$_5$/PMMA AND PEO$_5$/PMMA-*co*-MA (TERNARY ELECTROLYTE SYSTEM) SOLUTIONS AT 25 ºC (C$_{ref}$ = 1.89 × 10^{-9} mol cm^{-3})

System (g cm^{-3})	$\Lambda = K'\left(\dfrac{C_{salt}}{C^\theta}\right)^{\gamma-1}$	$\Lambda_0 = K'\gamma C_{ref}^{\gamma-1}$ (S cm^2 mol^{-1})	r^2
PMMA			
0.0010	71.5 C$_{salt}^{-0.063}$	237.5	0.9999
0.0015	70.9 C$_{salt}^{-0.061}$	226.7	0.9998
0.0020	62.0 C$_{salt}^{-0.070}$	227.6	0.9995
0.0025	61.7 C$_{salt}^{-0.067}$	221.1	0.9995
0.0030	54.8 C$_{salt}^{-0.073}$	220.1	0.9990
PMMA-*co*-MA (34 kg mol^{-1})			
0.0010	67.3 C$_{salt}^{-0.073}$	270.3	0.9998
0.0015	60.3 C$_{salt}^{-0.081}$	282.0	0.9996
0.0020	55.3 C$_{salt}^{-0.086}$	284.4	0.9998
0.0025	53.2 C$_{salt}^{-0.087}$	278.8	0.9998
0.0030	51.7 C$_{salt}^{-0.086}$	265.9	0.9996
PEO$_5$/PMMA (50:50)			
0.0010	58.1 C$_{salt}^{-0.072}$	229.0	0.9985
0.0015	62.4 C$_{salt}^{-0.062}$	203.4	0.9989
0.0020	65.2 C$_{salt}^{-0.053}$	179.0	0.9999
0.0025	68.1 C$_{salt}^{-0.047}$	166.8	0.9988
0.0030	73.7 C$_{salt}^{-0.037}$	149.2	0.9993
PEO$_5$/PMMA-*co*-MA (50:50)			
0.0010	62.6 C$_{salt}^{-0.064}$	211.9	0.9998
0.0015	67.5 C$_{salt}^{-0.057}$	200.0	0.9985
0.0020	77.1 C$_{salt}^{-0.041}$	168.5	0.9984
0.0025	89.6 C$_{salt}^{-0.028}$	152.8	0.9999
0.0030	123.7 C$_{salt}^{-0.0028}$	130.5	0.9998

**C$^\theta$ = 1 mol cm^{-3}

Λ_0 = 106 S cm^2 mol^{-1}) dissociation might be achieved upon the addition of polymer into the LiClO$_4$ in ACN electrolyte system. Therefore, it can be suggested that the addition of polymer into an electrolyte has proven to improve the lithium salt dissociation and increase the total free ions in the electrolyte that might enhanced the ionic conductivity of the system.

The determination of limiting value of an electrolyte is approximately half of the lowest C$_{salt}$ concentration that still obeys the proposed Power law. Therefore, a normalization step will be conducted in order to determine the Λ_0 value for the liquid polymer electrolyte system at a much specific C$_{ref}$ to

decreasing trend of Λ_0 is an indication for a much closer behaviour of the electrolyte approaching to a strong electrolyte system particularly at higher C$_{Poly}$ concentration. Smaller limiting values causes a better solute solubility in the electrolyte solution. This direct to almost a 100% of LiClO$_4$ (LiClO$_{4aq.}$);

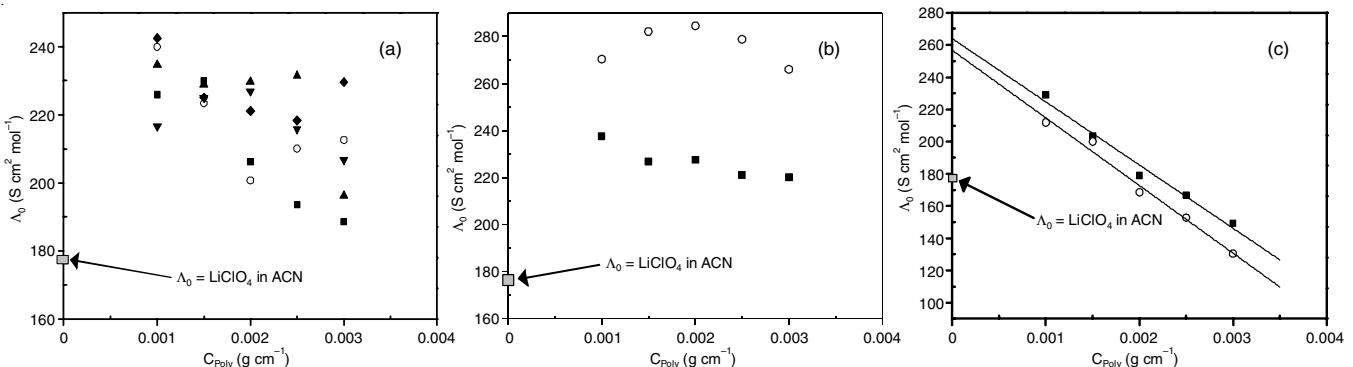Fig. 2. The regression curves for limiting molar conductivity (Λ_0) *versus* (a) C$_{PEO_1}$ (■), C$_{PEO_2}$ (○), C$_{PEO_3}$ (▲), C$_{PEO_4}$ (▼) and C$_{PEO_5}$ (◆) in ACN (binary electrolyte system) at 25 ºC; (b) PMMA (■) and PMMA-co-MA (○) in ACN (binary electrolyte system) at 25 ºC and (c) PEO$_5$/PMMA (50:50) (■) and PEO$_5$/PMMA-co-MA (50:50) (○) in ACN (ternary electrolyte system) at 25 ºC

avoid the discrepancy in the Λ_0 value as reported in Fig. 2. Procedure for determination of C_{ref} for $LiClO_4$ in polymer solution is as follow:

$$\Lambda_0(ACN) = 177.4 \text{ cm}^2 \text{ mol}^{-1} \tag{10}$$

Apparently eqn. (4.26) determined with

$$C_{ref}^{ACN} = 1.89 \times 10^{-9} \text{ mol cm}^{-1} \tag{11}$$

Next determination of Λ_0 for ACN solutions with varying polymer content for binary; PEO_1 to PEO_5, PMMA, PMMA-*co*-MA and ternary electrolyte system; PEO_5/PMMA (50:50) and PEO_5/PMMA-*co*-MA (50:50) electrolyte system (Tables 3 and 4). It is obvious that $\Lambda_0(C_{Poly})$ varies linearly with polymer concentration C_{Poly} in the range of sufficiently low polymer concentration:

$$\Lambda_0(C_{PEO}) = \Lambda_0^{ACN} + Y * C_{PEO} \tag{12}$$

where Λ_0^{ACN} is given by eqn. 10 C_{PEO} refers to the PEO concentration in the electrolyte solution.

The regression curves read after Fig. 2b:
PEO_1 in ACN at 25 °C

$$\Lambda_0(C_{PEO}) = 244.1 \text{ S cm}^2 \text{ mol}^{-1} - 18600 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{13}$$

PEO_2 in ACN at 25 °C

$$\Lambda_0(C_{PEO}) = 256.0 \text{ S cm}^2 \text{ mol}^{-1} - 18985.7 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{14}$$

PEO_3 in ACN at 25.0 °C

$$\Lambda_0(C_{PEO}) = 256.2 \text{ S cm}^2 \text{ mol}^{-1} - 19769.2 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{15}$$

PEO_4 in ACN at 25 °C

$$\Lambda_0(C_{PEO}) = 267.0 \text{ S cm}^2 \text{ mol}^{-1} - 20200.0 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{16}$$

PEO_5 in ACN at 25 °C

$$\Lambda_0(C_{PEO}) = 261.7 \text{ S cm}^2 \text{ mol}^{-1} - 21400 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{17}$$

Assume that the shift in Λ_0^{ACN} in eqns. 13-17 are solely caused by imprecise selection of C_{ref} and independent of C_{PEO}. Accepting this assumption, the corrected or true functions $\Lambda_0(C_{PEO})$ read;

$$PEO_1 \ L_0(C_{PEO}) = 177.4 \text{ S cm}^2 \text{ mol}^{-1} - 18600.0 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{18}$$

$$PEO_2 \ L_0(C_{PEO}) = 177.4 \text{ S cm}^2 \text{ mol}^{-1} - 18985.7 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{19}$$

$$PEO_3 \ L_0(C_{PEO}) = 177.4 \text{ S cm}^2 \text{ mol}^{-1} - 19769.2 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{20}$$

$$PEO_4 \ L_0(C_{PEO}) = 177.4 \text{ S cm}^2 \text{ mol}^{-1} - 20200.0 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{21}$$

$$PEO_5 \ L_0(C_{PEO}) = 177.4 \text{ S cm}^2 \text{ mol}^{-1} - 21400.0 \text{ S cm}^5 \text{ g}^{-1} \text{ mol}^{-1} C_{PEO} \tag{22}$$

In combination with the second column of Table-3 and eqns. (4.34-4.38) allow for estimation of C_{ref} for $LiClO_4$ in PEO solution.

As Fig. 1 shows for higher concentrations C_{PEO} deviations from eqns. 5-8 occur. As a result, no adequate determination of C_{ref} is possible anymore. Therefore, the average of the Λ_0 data used in regression in Table-5 as suitable C_{ref} for PEO_1

$$\overline{C_{ref}}(PEO_1) = 5.91 \times 10^{-6} \text{ mol cm}^{-1} \tag{23}$$

TABLE-5
LIMITING MOLAR CONDUCTIVITY (Λ_0) AND RESPECTIVE C_{ref} VALUES AFTER EQN. 18 FOR $LiClO_4$ IN PEO_1 AT 25 °C

C_{Poly} (g cm^{-3})	Λ_0 (S cm^2 mol^{-1})	C_{ref} (mol cm^{-3})
1.0×10^{-3}	158.8	3.60×10^{-6}
1.5×10^{-3}	149.5	6.93×10^{-6}
2.0×10^{-3}	140.2	5.90×10^{-6}
2.5×10^{-3}	130.9	4.03×10^{-6}
3.0×10^{-3}	121.6	9.08×10^{-6}

There is a difference between eqns. 11 and 23. Using this new reference concentration, the Λ_0 is recalculated for C_{PEO_1} system as shown in Table-6.

TABLE-6
LIMITING MOLAR CONDUCTIVITY (Λ_0) AFTER EQN. 23 FOR $LiClO_4$ IN PEO_1 AT 25 °C

C_{Poly} (g cm^{-3})	Λ_0 (S cm^2 mol^{-1})
1.0×10^{-3}	146.3
1.5×10^{-3}	141.9
2.0×10^{-3}	132.5
2.5×10^{-3}	120.4
3.0×10^{-3}	117.4

Eqns. 19-22 and 7 are the repeated for PEO_2-PEO_5, PMMA, PMMA-*co*-MA, PEO_5/PMMA (50:50) and PEO_5/PMMA-*co*-MA (50:50) to determine Λ_0 at a new C_{ref}. Tables 7 and 8 summarize the regression function after eqn. 9 and the Λ_0 for $LiClO_4$ in PEO_X, PMMA and PMMA-*co*-MA polymer solution at 25 °C.

In general, for binary electrolyte ($LiClO_4$ in PEO_X, PMMA or PMMMA-*co*-MA) system the addition of polymer into a monoelectrolyte system ($LiClO_4$ in ACN) causes a decrease in Λ_0 respective to Λ_0 of $LiClO_4$ in ACN. It is also observed that for higher M_w of PEO at a constant polymer concentration a descending Λ_0 was demonstrated. This indicates that the binary polymer electrolyte system is approaching to the behaviour of strong electrolyte ($LiClO_{4aq.}$) upon the addition of polymer and the result becomes much more significant at higher C_{Poly}. This suggested that use of high molecular weight polymer (PEO) have further enhanced the solubility of $LiClO_4$ and increases the total free ions in the solution that simultaneously increases the total charge carrier and ionic conductivity.

Table-9 summarizes the regression function after eqn. 9 and the value of Λ_0 for $LiClO_4$ in ternary polymer blends of PEO_5/PMMA and PEO_5/PMMA-*co*-MA polymer solution at 25 °C.

From Table-9, the calculation of limiting molar conductivity (Λ_0) value after $\overline{C_{ref}}$ was not preceded further for the ternary electrolyte system. This is mainly due to an exponential increase in the calculated C_{ref} value as the concentration of polymer increases was observed. This exponential increase in

TABLE-7
LIMITING MOLAR CONDUCTIVITY (Λ_0) FOR
LiClO$_4$ IN PEO$_x$ SOLUTIONS AT 25 ºC

System (g cm^{-3})	$\Lambda = K'\left(\dfrac{C_{salt}}{C^\theta}\right)^{\gamma-1}$	$\Lambda_0 = K'\gamma C_{ref}^{\gamma-1}$ (S cm^2 mol^{-1})
PEO$_1$ (100 Kg mol^{-1})		
0.0010	80.7 C$_{salt}^{-0.054}$	146.3
0.0015	73.3 C$_{salt}^{-0.060}$	141.9
0.0020	72.3 C$_{salt}^{-0.055}$	132.5
0.0025	62.9 C$_{salt}^{-0.059}$	120.4
0.0030	61.3 C$_{salt}^{-0.059}$	117.4
PEO$_2$ (300 Kg mol^{-1})		
0.0010	80.0 C$_{salt}^{-0.057}$	146.3
0.0015	71.2 C$_{salt}^{-0.060}$	134.4
0.0020	70.4 C$_{salt}^{-0.055}$	126.0
0.0025	60.9 C$_{salt}^{-0.065}$	121.1
0.0030	57.1 C$_{salt}^{-0.069}$	118.5
PEO$_3$ (600 Kg mol^{-1})		
0.0010	79.2 C$_{salt}^{-0.057}$	142.3
0.0015	68.9 C$_{salt}^{-0.063}$	131.7
0.0020	66.6 C$_{salt}^{-0.065}$	129.9
0.0025	59.9 C$_{salt}^{-0.071}$	124.3
0.0030	56.9 C$_{salt}^{-0.065}$	111.0
PEO$_4$ (1000 Kg mol^{-1})		
0.0010	78.9 C$_{salt}^{-0.053}$	141.7
0.0015	59.3 C$_{salt}^{-0.070}$	128.5
0.0020	54.9 C$_{salt}^{-0.074}$	124.3
0.0025	51.7 C$_{salt}^{-0.075}$	118.3
0.0030	51.4 C$_{salt}^{-0.073}$	115.1
PEO$_5$ (4000 Kg mol^{-1})		
0.0010	77.7 C$_{salt}^{-0.058}$	141.6
0.0015	58.2 C$_{salt}^{-0.071}$	121.2
0.0020	54.0 C$_{salt}^{-0.074}$	116.0
0.0025	50.4 C$_{salt}^{-0.077}$	111.7
0.0030	49.1 C$_{salt}^{-0.081}$	113.4

**C$^\theta$ = 1 g cm^{-3}

TABLE-8
LIMITING MOLAR CONDUCTIVITY (Λ_0) FOR LiClO$_4$
IN DIFFERENT POLYMER SOLUTIONS AT 25 ºC

System (g cm^{-3})	$\Lambda = K'\left(\dfrac{C_{salt}}{C^\theta}\right)^{\gamma-1}$	$\Lambda_0 = K'\gamma C_{ref}^{\gamma-1}$ (S cm^2 mol^{-1})
PMMA		
0.0010	71.5 C$_{salt}^{-0.063}$	158.1
0.0015	70.9 C$_{salt}^{-0.061}$	152.9
0.0020	62.0 C$_{salt}^{-0.070}$	149.7
0.0025	61.7 C$_{salt}^{-0.067}$	143.5
0.0030	54.8 C$_{salt}^{-0.073}$	137.4
PMMA-*co*-MA (34 kg mol^{-1})		
0.0010	67.3 C$_{salt}^{-0.073}$	135.7
0.0015	60.3 C$_{salt}^{-0.081}$	131.3
0.0020	55.3 C$_{salt}^{-0.086}$	126.3
0.0025	53.2 C$_{salt}^{-0.087}$	122.7
0.0030	51.7 C$_{salt}^{-0.086}$	118.1

**C$^\theta$ = 1 g cm^{-3}

C_{ref} is very much different as compared to the binary electrolyte system (increase linearly). Therefore, the calculation of Λ_0 value at different polymer concentration for the ternary electrolyte system is invalid and a new approach is recommended to re-estimated the Λ_0 for the ternary electrolyte system. It is proposed,

TABLE-9
LIMITING MOLAR CONDUCTIVITY (Λ_0) AFTER THE
NORMALIZATION STEPS FOR LiClO$_4$ FOR TERNARY
POLYMER BLENDS SOLUTIONS AT 25 ºC

System (g cm^{-3})	$\Lambda = K'\left(\dfrac{C_{salt}}{C^\theta}\right)^{\gamma-1}$	Λ_0 (S cm^2 mol^{-1})	C_{ref} (mol cm^{-3})
PEO$_5$/PMMA (50:50)			
0.0010	58.1 C$_{salt}^{-0.072}$	138.2	5.93 × 10^{-6}
0.0015	62.4 C$_{salt}^{-0.062}$	118.5	3.22 × 10^{-6}
0.0020	65.2 C$_{salt}^{-0.053}$	98.92	3.84 × 10^{-4}
0.0025	68.1 C$_{salt}^{-0.047}$	79.30	0.0392
0.0030	73.7 C$_{salt}^{-0.037}$	59.68	300
PEO$_5$/PMMA-*co*-MA (50:50)			
0.0010	62.6 C$_{salt}^{-0.064}$	135.4	5.82 × 10^{-6}
0.0015	67.5 C$_{salt}^{-0.057}$	114.4	9.56 × 10^{-5}
0.0020	77.1 C$_{salt}^{-0.041}$	93.40	9.30 × 10^{-3}
0.0025	89.6 C$_{salt}^{-0.028}$	72.43	2023.3
0.0030	123.7 C$_{salt}^{-0.0028}$	51.42	∞

**C$^\theta$ = 1 g cm^{-3}

the Λ_0 for ternary electrolyte system is a result of the sum of its individual limiting molar conductivity in its binary electrolyte system as proposed in eqns. 24 and 25:

$$\Lambda_0\left(\frac{PEO_5}{PMMA}\right) = \Lambda_{0_{PEO_5}} + \Lambda_{0_{PMMA}} \tag{24}$$

$$\Lambda_0\left(\frac{PEO_5}{PMMA\text{-}co\text{-}MA}\right) = \Lambda_{0_{PEO_5}} + \Lambda_{0_{PMMA\text{-}co\text{-}MA}} \tag{25}$$

Table-10 summarizes the regression function after eqns. 24 and 25 for estimation of Λ_0 for LiClO$_4$ in ternary polymer blends of PEO$_5$/PMMA and PEO$_5$/PMMA-*co*-MA polymer electrolyte solution at 25 ºC.

TABLE-10
LIMITING MOLAR CONDUCTIVITY (Λ_0) AFTER THE
EQNS. 24 AND 25 AND CORRESPONDING C_{ref} FOR LiClO$_4$
FOR TERNARY POLYMER BLENDS SOLUTIONS AT 25 ºC

System (g cm^{-3})	$\Lambda = K'\left(\dfrac{C_{salt}}{C^\theta}\right)^{\gamma-1}$	Λ_0 (S cm^2 mol^{-1})	C_{ref} (mol cm^{-3})
PEO$_5$/PMMA (50:50)			
0.0010	58.1 C$_{salt}^{-0.072}$	299.7	1.27 × 10^{-10}
0.0015	62.4 C$_{salt}^{-0.062}$	274.1	4.30 × 10^{-11}
0.0020	65.2 C$_{salt}^{-0.053}$	265.7	3.08 × 10^{-12}
0.0025	68.1 C$_{salt}^{-0.047}$	255.2	6.21 × 10^{-13}
0.0030	73.7 C$_{salt}^{-0.037}$	250.8	4.22 × 10^{-15}
PEO$_5$/PMMA-*co*-MA (50:50)			
0.0010	62.6 C$_{salt}^{-0.064}$	277.3	7.95 × 10^{-11}
0.0015	67.5 C$_{salt}^{-0.057}$	252.5	8.87 × 10^{-11}
0.0020	77.1 C$_{salt}^{-0.041}$	242.3	7.42 × 10^{-13}
0.0025	89.6 C$_{salt}^{-0.028}$	234.4	1.21 × 10^{-15}
0.0030	123.7 C$_{salt}^{-0.0028}$	231.5	≈ 0

The molar conductivity of the ternary electrolyte system (PEO$_5$/PMMA and PEO$_5$/PMMA-*co*-MA) only weakly depended on the total salt concentration in the electrolyte solution. Hence, the conductivity due to the ion mobility of the ternary electrolyte system is mostly proposed due the segmental motion of the polymer chain in the system. This recommendation is

further supported with the observation that conductivity dependent factor $(\gamma-1)$ value shows a decreasing trend as the polymer concentration increases, which indicated the electrolyte does not depend on the total salt concentration. The calculation of C_{ref} for corresponding Λ_0 (Table-10) have further proved that the ternary electrolyte system only contains a small amount of dissociated $LiClO_4$ salt and agrees with the present assumption.

Conclusion

After the calibration of the Power law, it is observed the C_{salt} that corresponded to $\Lambda_0 = 177.4$ S cm^2 mol^{-1} for $LiClO_4$ in ACN electrolyte system is at 1.89×10^{-9} mol cm^{-3}. This salt concentration is known as reference salt concentration (C_{ref}) and this value is further adopted (first stage) in the estimation of quantity Λ_0 for $LiClO_4$ in binary and ternary electrolyte system at 25 ℃. However, a re-estimation of C_{ref} was carried out for each electrolyte system after the normalization steps. Afterwards, the estimation of quantities Λ_0 is done once more. In general, as the polymer concentration increases, quantity Λ_0 tends to show a descending trend at $M_w = $ const. This might indicate a more positive correlation between the C_{Poly} and ionic conductivity. In addition, the decreasing trend of Λ_0 might suggest an enhancement of the degree of $LiClO_4$ dissociation upon the addition of polymer into the ACN electrolyte system. At $C_{Poly} = $ constant, the limiting molar conductivity (Λ_0) value decrease as the M_w of PEO increases. Lower value of Λ_0 which is approaching the value of Λ_0 of $LiClO_4$ in water (106 S cm^2 mol^{-1}). The same observation has also been noted for PMMA, PMMA-co-MA, PEO5/PMMA and PEO5/PMMA-co-MA electrolyte system that may suggest that the system are turning from weak electrolyte to strong electrolyte. In addition, it is also observed that $LiClO_4$ in PEO5 electrolyte system have a better $LiClO_4$ solubility behaviour compared to PMMA and PMMA-co-MA electrolyte system due to a much stronger electrostatic interaction between the lone pair electrons of the ether oxygen atom in the monomer unit of PEO. The $LiClO_4$ in PEO5/PMMA-co-MA is observed to be the best electrolyte system in this study that have a relatively high salt dissociation and lithium ion mobility compared to $LiClO_4$ in PEO5/PMMA.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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