*Iraqi Journal of Physics, 2019* *Vol.17, No.42, PP. 42-50*

*DOI: 10.20723/ijp.17.42.42-50*

# Investigate salts type and concentration on the conductivity of polymer electrolyte

**Shaimaa Mohsen Abdelcareem and Mohammed Kadhim Jawad**

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

E-mail: mohamedkadhom66@gmail.com

## Abstract

Polymer electrolytes compose of {polyethylene oxide (PEO)+ potassium iodide (KI)+iodine ($I_2$)} and {PEO+ rubidium iodide (RbI)+$I_2$} with different weight ratio of salts, and a fixed amount of ethylene carbonate (EC) and propylene carbonate (PC) has prepared by solution casting method. The conductivity and dielectric constant of the gel electrolytes were studied over temperatures range (293-343) K. The conductivity of the electrolytes increases steadily with increased concentration of salts KI and RbI. The higher value of conductivity of ($4.7\times 10^{-3}$ at RT) $S.cm^{-1}$ for electrolyte contains (KI 50%). Whereas the maximum amount of conductivity of ($5.4\times 10^{-3}$ at RT) $S.cm^{-1}$ for electrolyte includes (RbI 50%) the ionic conductivity depends on the ionic radii of the migrating species effect on it. As the temperature increase, the number of free ions also increases, thus increases the diffusion of ions through their free volume of the polymer. The dielectric constant decrease at higher frequencies due to the inability of dipoles to align quickly with the change of applied field. The dielectric constant proportional positively with variation temperature causes an increase in the dielectric constant. The higher the value of real dielectric constant ($\varepsilon_r$), the better is the electrical conductivity.

**Key words**

*Polymer electrolyte, electric conductivity, salts, dielectric constant.*

**Article info.**

*Received: Apr. 2019*
*Accepted: May. 2019*
*Published: Sep. 2019*

# بحث تركيز ونوع الملح على التوصيلية للبوليمر الالكتروليتي

**شيماء محسن عبدالكريم و محمد كاظم جواد**

قسم الفيزياء، كلية العلوم، جامعة بغداد

## الخلاصة

الالكترولايتات البوليمرية المتكونة من (البولي اثلين اوكسايد+بوتاسيوم ايوديد+ايودين) و(بولي اثلين اوكسايد+روبديوم ايوديد+ايودين) مع نسب وزنية مختلفة من الاملاح وكمية ثابتة من الاثلين كاربونيت والبروبلين كاربونيت قد حضرت بطريقة صب السائل. درست التوصيلية وثابت العزل الكهربائي للالكترولايتات الهلامية لمدى درجات حرارة (293-343) كلفن. زادت التوصيلية للالكترولايتات بشكل ثابت مع زيادة تركيز الاملاح. . اعلى قيمة للتوصيلية (سيمنس/سم $4.7*10^{-3}$) عند درجة حرارة الغرفة للالكترولايت الذي يحتوي 50% بوتاسيوم ايوديد. في حين اقصى قيمة للتوصيلية ($5.4*10^{-3}$ سيمنس/سم) للالكترولايت الذي يحتوي 50% روبديوم ايوديد، ان التوصيلية تعتمد على نصف القطر الايوني للاجزاء المرتحلة التي تؤثر عليه. كلما زادت درجة الحرارة سيزداد ايضا عدد الايونات الحرة وهكذا سيزداد انتشار الايونات خلال الحجم الحر للبوليمر. قل ثابت العزل الكهربائي نتيجة لعدم قدرة الدايبولات للاصطفاف بسرعة مع تغير المجال المسلط. ثابت العزل الكهربائي يتناسب مع درجة حرارة التباين يسبب زيادة في ثابت العزل الكهربائي. كلما زادت قيمة ثابت العزل الكهربائي الحقيقي ، كلما كانت التوصلية الكهربائية أفضل.

## Introduction

The electrolytes are a solution of acids, bases, or salts. The electrolyte is an essential component of an electrochemical cell, a battery or fuel cell for producing electrical energy. It can also define as an electrically conductive substance containing free ion [1]. Polymer electrolyte is flexible and lightweight [2]. Polymer electrolytes mechanically behave like solids, but their internal structure and, consequently, the conductivity behavior closely resembles the liquid state [3]. They have emerged as potential ionic materials for application in different electrochemical devices due to some unique properties like proper electrode–electrolyte contact and adherence, their high compliance, ease of preparation in various forms, excellent mechanical and adhesive properties [4]. They have gained significant attention due to the potential applications in rechargeable lithium-ion batteries, electrochemical devices, electrochromic windows and sensors, electrochromic display devices, smart windows, and other utilization [5-8]. The development of polymer electrolytes has gone through three stages, which are dry solid-state polymers, gel/plasticizer polymer electrolytes systems, and composite polymer electrolytes system [9,10]. The dielectric and electrical properties of the materials are essential for its applications in devices like supercapacitors, field effect transistors, and other components [11]. The goal of the present work is to investigate electrical properties. The effect of variation of single salt weight ratio on ionic conductivity of polymer gel electrolytes with temperature investigated and its possible application in electronic devices.

## Experimental part

PEO with a molecular weight 100,000 g/mol, ethylene carbonate (EC) and propylene carbonate (PC) used as a solvent has a molecular weight of (88.06, 102.09 g/mol) respectively. Potassium iodide (KI), rubidium iodide (RbI) and iodine ($I_2$) with a molecular weight of (166, 212.37 and 253.81 g/mol) respectively. All above materials purchased from Sigma Aldrich.

Two systems of gel polymer electrolytes samples {(PEO)+KI+$I_2$}, and {(PEO)+RbI+$I_2$ } were prepared using the solution-cast technique and assigned as S and H electrolytes, respectively. The weight ratio of the salts RbI and KI changed according to Table 1. In the first stage, each salt was dissolved separately into the polymer solvent using a mixture of EC and PC with fixed ratio 1:1. After dissolving the salt completely then add the appropriate amount of PEO; the mixture was then stirred continuously for 1h until became homogenous. The electrolyte was allowed to cool to room temperature then added iodine ($I_2$ =10%) and stirred for 1h till gating a homogenous gel electrolyte. However, the samples are allowed to evaporate slowly inside the fume hood for 24 hours and then transferred into a desiccator for further drying. The gel electrolytes were prepared and studied under controlled temperature and humidity conditions (20 °C and RH~50%). The prepared electrolytes subjected to frequency dependent behavior recorded range between 100 Hz and 1MHz by using HIOKI LCR Hi Tester 8110G/8105G impedance analyzer. The conductivity has calculated by the following Eq. (1) [9]:

$$\sigma = L/AR_b \qquad (1)$$

where L is thickness for the sample, A is the area of the electrode, and $R_b$ is the bulk resistance of the gel electrolyte measured by impedance analyzer. The dielectric constant ($\varepsilon_r$)values were calculated using the following Eq. (2) [9]:

$$\varepsilon_r = Z_i / \omega C_o[Z_r^2 + Z_i^2] \quad (2)$$

where ω is the angular frequency (ω=2πf) being the frequency in Hertz (Hz), $C_o$ is vacuum capacitance, and $Z_r$ and $Z_i$ are real and imaginary parts of impedance.

***Table 1: Illustrate the composition of electrolytes S and H and weight ratio of salts.***

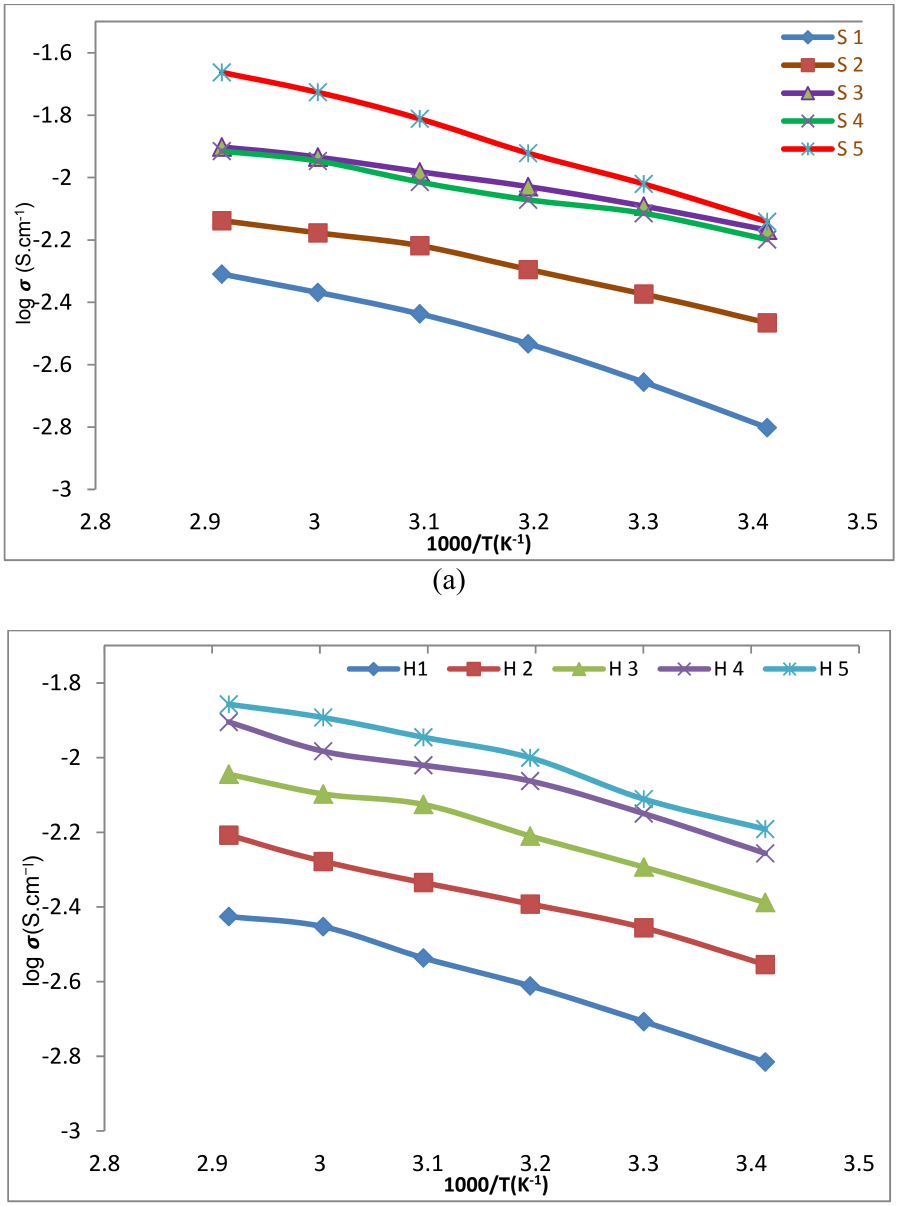
| Assignments | KI% | Composition | Assignments | RbI% | Composition |
|---|---|---|---|---|---|
| S1 | 10 | 90%PEO+10%KI | H1 | 10 | 90%PEO+10%RbI |
| S2 | 20 | 80%PEO+20%KI | H2 | 20 | 80%PEO+20%RbI |
| S3 | 30 | 70%PEO+30%KI | H3 | 30 | 70%PEO+30%RbI |
| S4 | 40 | 60%PEO+40%KI | H4 | 40 | 60%PEO+40%RbI |
| S5 | 50 | 50%PEO+50%KI | H5 | 50 | 50%PEO+50%RbI |

## Results and discussion

The ionic conductivity of polymer electrolytes is assumed to occur by Lewis acid-base interaction between cation and polymer. The conductivity of electrolytes Ss and Hs were investigated over temperatures range 293-343 K, with a different weight ratio of the single salts KI and RbI. The resulting conductivity is mainly due to the overall mobility of ions and polymer, which is determined by the free volume, and this leads to an increase in ionic conductivity and segmental mobility. That assists ion transport and compensates the retarding effect of the ionic clouds [12]. EC and PC solution with equal wt.% has used as the solvent because of its high dielectric constant, and its role as a suitable plasticizer. It is an excellent electron donor and therefore, expected to coordinate the cations and consequently enhances the conductivity fully.

The conductivity of both gel electrolytes Ss and Hs illustrated in Fig. 1(a and b) it can be noted to affect a positive linear relationship by temperature. This increase in ionic conductivity was corresponding to the rise in the temperature obeyed the Arrhenius type thermally activated process. That can understand with the emphasis that as temperature increases, the vibrational energy of segmental motion operates against the hydrostatic pressure imposed by its neighboring atoms. Consequently, it creates a small amount of space surrounding its volume in which vibrational motion can occur. Therefore, free size around the polymer chain causes augmentation in the mobility of ions and hence enhances the conductivity [13].

Fig. 1(a) shows gradually increases of ionic conductivity for gel polymer electrolyte Ss with different wt.% of single salt KI by raising the temperature in range (293-343)K. It confirmed that as temperature increases, the polymer could expand readily and produce a free volume, which leads to an increase in the conductivity values for all electrolytes. Thus ions, solvated molecules or polymer segments may move into the open size, which is for the motion of ions through the polymer backbone [14]. The increase in full size leads to the increase in ion mobility and segmental mobility that will assist the ion transport til reaches the maximum value of ($7.22\times 10^{-3}$ at RT to $2.1 \times10^{-2}$ at 343 K) ($S.cm^{-1}$) for S5 electrolyte which contains (KI 50%).



(a)

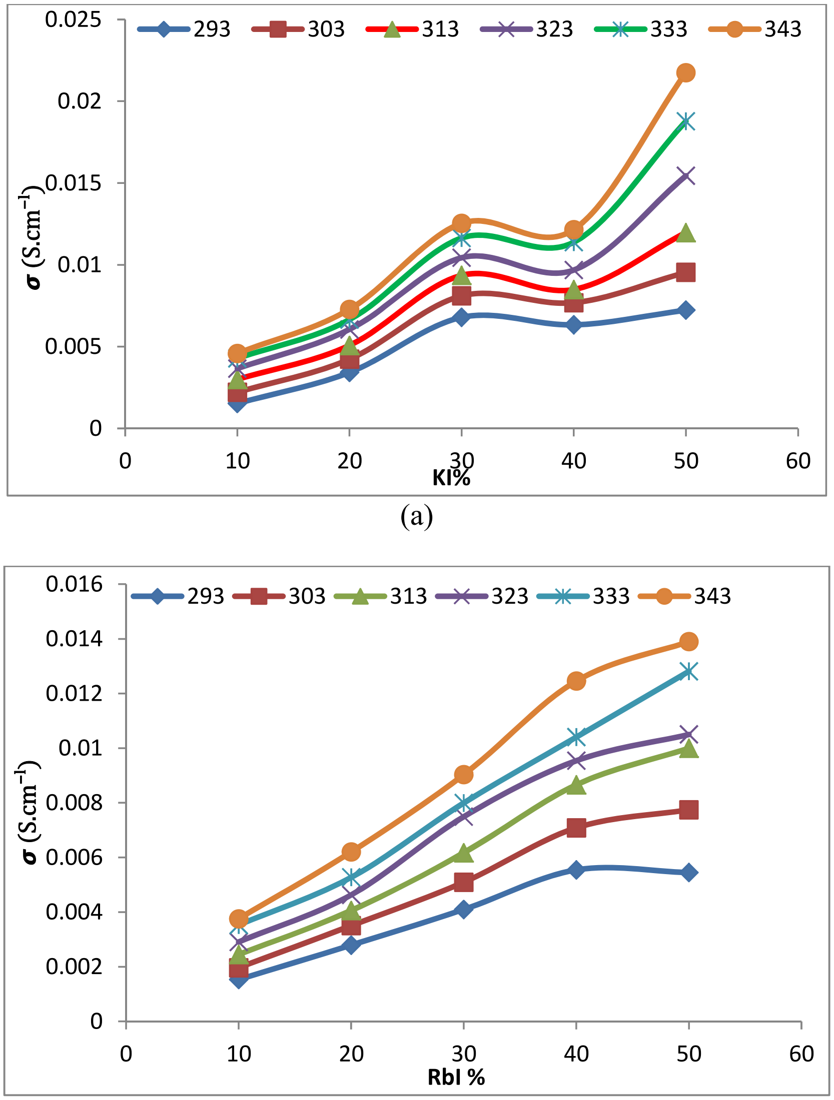
(b)

***Fig. 1: Temperature dependence of the ionic conductivity of the gel polymer electrolytes (a) S and (b) H.***

Fig.1(b) also shows gradually increases of ionic conductivity for gel polymer electrolyte Hs with different wt.% of single salt RbI with increasing temperature in range (293-343 K). The maximum value of $(6.4\times 10^{-3}$-$1.39 \times10^{-2})$ $S.cm^{-1}$ for H5 electrolyte which contains (RbI 50%), as the temperature increase, the number of free ions also increases, thus increases the diffusion of ions through their free volume [15]. But when compare between both electrolytes (Ss and Hs) find that the Ss has better ionic conductivity values than the Hs, this enhancement in the influence of the ionic conductivity depends on the ionic radii of the migrating species (cation $K^+$, $Rb^+$) effect on it [16, 17]. The mobility of the ions become more excellent capability to decrease in viscosity and hence, increased chain flexibility of polymer [9]. The conductivity of the electrolytes Ss increases steadily with increased concentration of salt KI as shown in Fig. 2(a) which can further affirm related to the rise in the number of mobile charge carriers [18], then curve acquires small peaks at concentration 30% of KI salt then decreases. However, the possible decrease in the ionic conductivity attributed to the formation of ionic multiples. This behavior clarify in terms of the ion (association theory) as the concentration of the salt and ion aggregates was increased, due to dipole-dipole interaction, immobile charge multiples formed. The mutual distance between ions reduces significantly, and ion-ion interactions become dominant and the obstructed segmental motion that inhibits migration of the electrons/ions, causing more difficulties in the transportation of charge carriers [3]. At higher salt weight ratio after 30% reach saturation state. Therefore, which do not contribute to the ionic conductivity. With increased concentration of KI salt about 50% conductivity increasing one more time electrostatic crosslinking of the polymer and substantially reduces the diffusion coefficients. However, above a limiting high salt concentration, the segmental motion of the polymer chains is diminished due to an ionic cross-linking, which decreases ionic conductivity. The conductivity of the electrolytes originates from two types of ions, namely $K^+$ ions and $I^-$ ions and both these ions contribute to the highest conductivity seen for this electrolyte [19].

The conductivity of plasticized polymer electrolytes Hs as a function of temperature and RbI wt.% shown in Fig.2(b) which describe the increase of ionic conductivity with increasing content of RbI, reaching a high value at 50 wt.% RbI over temperatures range (293-343) K of ($6.4 \times 10^{-3}$-$1.39\times 10^{-2}$) $S.cm^{-1}$. That lead to a product of more conducting channels for charge transfer constructed and the conductivity of the gel electrolyte is hence enhanced. But it can be observed from the limitation of the curve after 40% wt. of RbI its slope is less more smooth, it can interpretation the conductivity almost saturates, and the rate of increase in conductivity becomes slower upon further addition of RbI salt after due to dipole-dipole interaction.

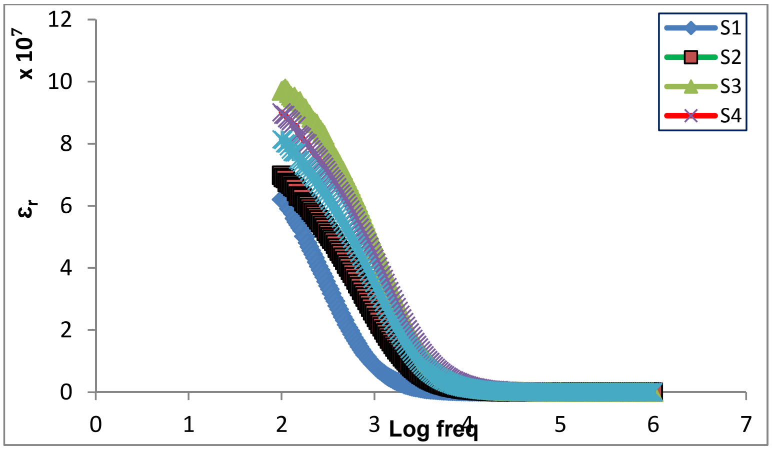
The high dielectric constant of PEO (~ 4–5) evidences its suitability to dissolve various salts [20]. The dielectric relaxation refers to the relaxation response of a dielectric medium to an external, oscillating electric field [21]. Figs. 3 (a and b) shows, the dielectric at room temperature response decreases with the increase of frequency. High dielectric permittivity of the polymer at lower frequencies may be because the dipoles have sufficient time to get aligned to the electric field thus results in higher polarization. That leads to an increase in dielectric constant (ε) effect, which also known as Maxwell-Wagner-Sillars (MWS) dielectric polarization process as known in most of the composite materials [22]. The decrease in dielectric permittivity at higher frequencies may be associated with the inability of dipoles to align quickly with the change of applied field. Hence the polarization due to charge accumulation decreases and results in a decrease in both the dielectric constant and dielectric loss [9, 23, 24].



(a)

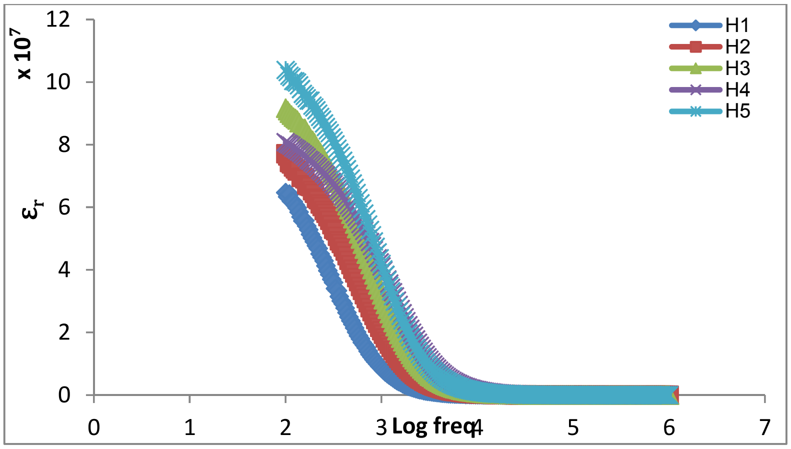
(b)

***Fig.2: Dependence of ionic conductivity on KI & RbI weight ratio in the gel polymer electrolytes (a) S and (b) H.***



(a)

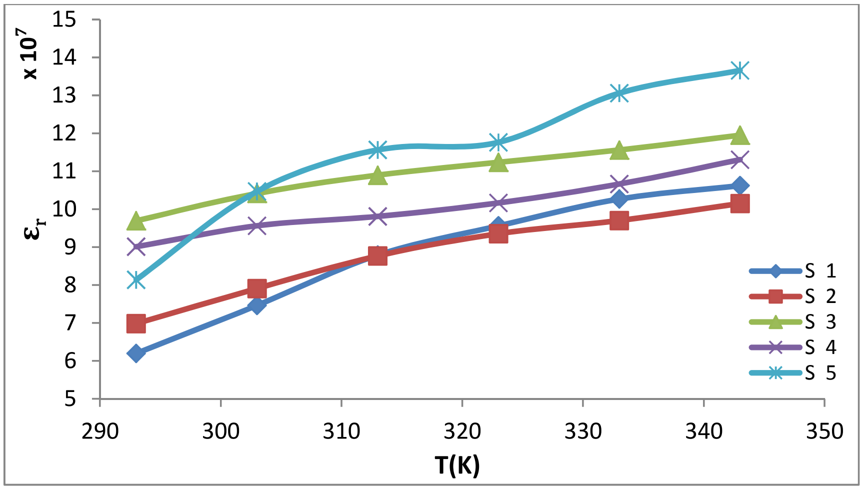
***Fig.3: Dielectric constant vs. Log frequency at RT with different salts concentration for electrolytes, (a) S.***



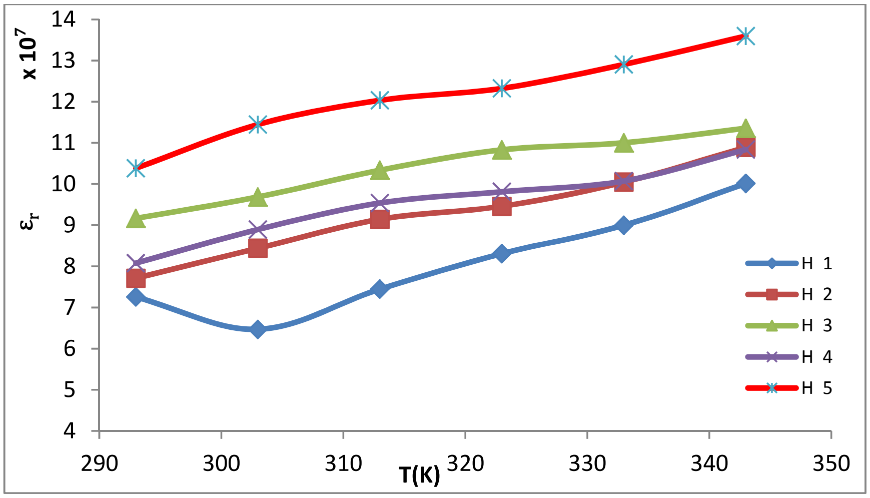
(b)

***Fig.3: Dielectric constant vs. Log frequency at RT with different salts concentration for electrolytes, (b) H.***

Fig.4 (a and b) illustrates the effect of temperature and salts concentration on dielectric constant. The dielectric constant proportional positively with variation temperature causes an increase in the dielectric constant. That is because, the dipoles remain frozen at lower temperatures, [21], while at higher temperatures, the dipoles become relatively free to respond to the applied electric field. That results in higher polarization and consequently raised a dielectric response. High dielectric constant may due to higher hydrolysis degree as hydroxyl groups function as strong permanent dipoles that align themselves to the applied field, resulting in increased polarization and thus dielectric constant [23]. Besides, the dielectric constant values are complex and depend on the frequency of applied electromagnetic radiation. Dielectric analysis of all the samples was performed using the real ($\varepsilon_r$) and imaginary ($\varepsilon_i$) parts of the dielectric function extracted from high-frequency impedance data [24]. The real part of dielectric permittivity ($\varepsilon_r$) has the same significance as that of ordinary dielectric constant it measures the elastically stored energy in the material during each cycle of applied alternating field, and the power returned to the area at the end of each period. The higher the value of ($\varepsilon_r$), the better is the electrical conductivity. When an electrical field applied to a material, the dipoles show the tendency to orient them in the direction of the affected area. However, the mobilization of the dipole depends on the flexibility of the materials. The imaginary part of dielectric permittivity ($\varepsilon_i$) corresponds to the dielectric loss factor due to the conduction of ionic species in the mater when an electrical field is applied. At higher temperatures, dipoles can orient readily, whereas a highly cross-linked material finds difficulty in orientation. The delayed response to a stimulus in a system is the called relaxation. The tendency involves appropriate time called relaxation time [25].



(a)



(b)

***Fig. 4: Dielectric constant vs. Temperature with different salts weight ratio for electrolytes (a) S and (b) H.***

## Conclusions

Conductive polymer electrolytes composed of PEO as host polymer was prepared by introducing single salts (KI and RbI) using solution cast technique and characterized using AC impedance spectroscopic techniques. The results indicate that the conductivity raises as the salts concentration increase up to 50%. The highest value of conductivity of $(7.22\times 10^{-3})$S.cm$^{-1}$ for electrolyte with 50 %KI, whereas for electrolyte with 50 % RbI of $(6.4\times 10^{-3}$-$1.39\times10^{-2})$ S.cm$^{-1}$. High dielectric permittivity of the polymer at lower frequencies may be because the dipoles have sufficient time to get aligned to the electric field thus results in higher polarization. The constant dielectric increase with variation temperature causes an increase in the dielectric constant.

## References

[1] K. W. Chew, T. C. Ng, Z. H. How, Int. J. Electrochem. Sci., 8, 5 (2013) 6354-6364.

[2] J. L. Schaefer, Y. Y. Lu, S. S. Moganty, P. Agarwal, N. Jayaprakash, L. A. Archer, Applied Nanoscience, 2, 2 (2012) 91-109.

[3] A. Annu, A. Singh, P. K. Singh, B. Bhattacharya, J. Mater. Sci. Mater. Electron., 29, 11 (2018) 9709-9716.
[4] S. L. Agrawal and A. Awadhia, Bull. Mater. Sci., 27, 6 (2004) 523-527.
[5] S. Rajendran, O. Mahendran, K. Krishnaveni, J. New Mater. Electrochem. Syst., 6, 1 (2003) 25-28.
[6] Z. Osman, N. M. Ansor, K. W. Chew, N. Kamarulzaman, Ionics (Kiel)., 11, 5–6 (2005) 431-435.
[7] A. Dey, S. Karan, S. K. De, Solid State Commun., 149, 31–32 (2009) 1282-1287.
[8] C. S. Transactions, S. Sarojini, C. Anjalai, Chem. Sci. Trans., 5, 3 (2016) 711-719.
[9] S. K. Tripathi, A. Gupta, M. Kumari, Bull. Mater. Sci., 35, 6 (2012) 969-975.
[10] C. C. Sun, A. H. You, L. L. Teo, L. W. Thong, AIP Conf. Proc., 1958 (2018) 020028-1_ 020028-7.
[11] Rakhi Nangia, Neeraj K Shukla Ambika Sharma, High-Performance Polymers, 30, 8 (2018) 918-926.
[12] A. Dey, S. Karan, S.K. De, Solid State Communications, 149 (2009) 1282-1287.
[13] G.K. Prajapati, R. Roshan, P.N. Gupta, Journal of Physics and Chemistry of Solids, 71 (2010) 1717-1723.
[14] S. Rajendran, O. Mahendran, K. Krishnaveni, J. New Mater. Electrochem. Syst., 6, 1 (2003) 25-28.
[15] A. H. A. Mohd Noor Zairi Mohd Sapri, Sci. Lett., 10, 1 (2016) 11-13.
[16] A. Arya and A. L. Sharma, J. Solid State Electrochem., 24, 4 (2019) 997-1059.
[17] T. M. W. J. Bandara, Hdns Fernando, Maurizio Furlani, Ingvar Albinsson, J. L. Ratnasekera, L. Ajith DeSilva, MAKL Dissanayake, Bengt-Erik Mellander, Electrochim. Acta, 252 (2017) 208-214.
[18] K. S. Perera and K. P. Vidanapathirana, Ceylon Journal of Science, 46, 4 (2017) 15-19.
[19] M.A.K.L. Dissanayakea, C.A. Thotawatthagea, G.K.R. Senadeera, T.M.W.J. Bandara, W.J.M.J.S.R. Jayasundera, B. E. Mellander, Journal of Photochemistry and Photobiology A: Chemistry, 246 (2012) 29-35.
[20] A. Arya and A. L. Sharma, J. Phys. D. Appl. Phys., 50, 44, 2017.
[21] R. Nangia, N. K. Shukla, A. Sharma, 2009,1 (2018) 2-7.
[22] R. J. Sengwa, S. Choudhary, P. Dhatarwal, Adv. Compos. Hybrid Mater., 2, 1 (2019) 162–175.
[23] R. Nangia, N. K. Shukla, A. Sharma, IOP Conf. Ser. Mater. Sci. Eng., 225 (2017) 1-6.
[24] T. M. W. J. Bandara, D. G. N. Karunathilaka, J. L. Ratnasekera, L. Ajith De Silva, A. C. Herath, B. E. Mellander, Ionics (Kiel)., 23, 7 (2017) 1711-1719.
[25] D. Singh, D. Kanjilal, G. V. S. Laxmi, P. K. Singh, S. K. Tomar, B. Bhattacharya, High Perform. Polym., 30, 8 (2018) 978-985.