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Mobile charge carrier concentration and mobility of a polymer electrolyte containing PEO and $Pr_4N^+I^-$ using electrical and dielectric measurements

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ABSTRACT

For the characterization and development of new electrolytes it is important to know the number of free charge carriers and their mobility. A new method has been developed to estimate the charge carrier density, *n*, and mobility, μ , for an electrolyte using dielectric measurements and a space charge relaxation model. In order to verify the applicability of this method, it has been tested with an aqueous KI solution electrolyte. The method was then applied to a polyethylene oxide (PEO) based polymer electrolyte. In the case of the polymer electrolyte, plasticized and non plasticized electrolytes intended for photo-electrochemical solar cells containing $Pr_4N^+I^-$ salt which is an iodide ion conductor at room temperature was used. The significant conductivity increase that occurs during the PEO crystallite melting is shown to be due to a large and abrupt increase of the concentration of the plasticizer results in an increased mobility. Results from the solution electrolyte show good agreement with known values.

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1. Introduction

lonic conductors are key components for many applications, mainly in the field of energy conversion, for example, in batteries, super-capacitors and also in photo-electrochemical (PEC) solar cells [1,2]. In fact, in recent years there has been an intense effort to develop high performance ion-conducting solid-state membranes for these types of applications. The conductivity is one of the key properties that needs to be optimized. Thus, the estimation of mobility (μ) and carrier density (n) is extremely important for the characterization and development of ionic conductors.

The ionic conductivity, σ , of an electrolyte containing two types of ions can be described by

$$\sigma = n_{-}e|Z^{-}|\mu_{-} + n_{+}e|Z^{+}|\mu_{+}$$
(1)

where n_+, n_- are the number of positive and negative charge carriers per unit volume, e is the electronic charge, μ_+ and μ_- are the mobility of the cation and anion and Z^+ and Z_-^- are the valence of the positive and negative charge carriers. In order to obtain a high ionic conductivity the charge carrier density, n, and mobility, μ , should thus be as large as possible. However, the determination of n and μ is not an easy task although desirable in order to optimize the performance of the material.

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The study of these parameters is not only important for the characterization and development of good quality electrolytes but also for other applications such as in bacteria counting [3].

The literature reveals a number of approaches that have been made to determine ion mobility under an applied electric field, including impedance spectroscopic methods. Transient ionic direct current measurements have also been used to determine ion mobility [4,5]. This method employs a *dc* voltage until a steady state is reached after that the voltage is reversed and the current as a function of time is measured, from which the mobility is calculated. Nuclear Magnetic Resonance spectroscopy, NMR, has also been used to obtain this type of information and has been applied to polymer electrolytes [6]. However, despite numerous efforts, the mechanisms of ion conduction are still not well understood in many systems [7,8] and in particular there is uncertainty about the values of ion mobility in solid-state electrolytes. Therefore this field would benefit from reliable models describing ion transport.

Impedance analysis has advantages compared to potentiometric and amperometric electrochemical analysis in that a small perturbation potential is applied across the cell or electrolyte minimizing possible charge carrier concentration changes during the measurements. In impedance analysis, the applied voltage is very small and the time average of the changes, due to the applied sinusoidal potential, is zero. Several approaches to determine the mobility and charge carrier concentration based on impedance spectroscopic methods have been reported in the literature [3,8–10]. The method used in reference [10] is interesting in that the frequency selected for the calculations is the one

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where the real part of the dielectric constant is ten times that of the high frequency plateau (ε'^{∞}) value. Another recently developed model uses the frequency dependence of complex dielectric loss, ε'' , and loss tangent, tan(ϕ), in order to extract both the ion mobility and the mobile ion concentration [8]. This method is based on an analysis of electrode polarization at low frequency electric fields. However, the values obtained for mobile charge carrier concentrations are very low, nearly four orders of magnitude lower than that of the total number of ionic species available from the salt. As a consequence, this analysis leads to very high mobility values for such solid electrolytes.

The present work is aimed at developing a reliable method to deduce the mobile charge carrier concentration and the mobility using impedance and dielectric spectroscopic data by modeling the space charge relaxation of an electrolyte sandwiched between two blocking electrodes. The method is primarily based on the models proposed by Schütt [11,12] and Coelho [13] for ion conducting glasses and generalized by Jönsson et al. [3]. In the present work, new equations were derived to model the real and the imaginary parts of the dielectric constant. The relevant parameters for measured electrolytes were determined by fitting the data to the real part of the dielectric constant according to the model enabling the determination of the charge carrier concentration n, and the mobility μ . It has been shown that iodide ion conductors are suitable for PEC solar cells [1,14]. In a previous study by us PEO/Pr₄N⁺I⁻ based electrolytes have been suggested for solar cells due to the predominant iodide ion conductivity in these materials [14]. The $PEO/Pr_4N^+I^-$ electrolyte with and without plasticizer is selected to test this method to determine the n and μ values as it is more or less a single ionic conductor at room temperature [14].

2. Experimental

For the sample preparation PEO, $Pr_4N^+I^-$, KI, iodine chips (I2), and ethylene carbonate (EC), all with purity greater than 98% purchased from Aldrich, were used as starting materials. The PEO, Pr₄N⁺I⁻ and KI were vacuum dried for 24 h in a vacuum oven prior to use. KI solution electrolytes were prepared by dissolving relevant amounts of KI in distilled and deionised water. Polymer electrolyte samples were prepared using a solvent casting method [14]; A mixture of 0.065 g of $Pr_4N^+I^-$, 0.005 g of I2 and 0.63 g of PEO was dissolved in anhydrous acetonitrile solvent and then stirred at room temperature for 24 h, until a homogeneous viscous solution was obtained. The resulting slurry was cast on a Teflon plate and kept inside a fume box for 24 h in order to gradually evaporate the solvent. This procedure yielded visually homogeneous polymer electrolyte films which were vacuum dried for 24 h prior to measurements. Complex impedance measurements were performed using a Schlumberger SI-1260 impedance-gain phase analyzer in the frequency range of 10 Hz-10 MHz and in the temperature range of 30 °C to 100 °C in a temperature regulated oven. Disc shaped electrolyte films of 13 mm diameter and 0.1-0.3 mm thickness were sandwiched between two polished stainless steel blocking electrodes and ac-impedance measurements were made in order to obtain the dielectric data for the sample.

3. Theory

If we consider the case where the valency of the cation and anion are the same and the mobility of both ions are approximately the same Eq. (1) can be written as;

$$\sigma_{dc} = ne|Z|\mu. \tag{2}$$

If this is not the case, a mean mobility (μ) can be obtained from the equation, $\mu = ((n_{-}\mu_{-} + n_{+}\mu_{+})/n)$ where n ($n = n_{-} + n_{+}$) is the total charge carrier density. In case we have a single ion conductor that is

only one type of ion is mobile, Eq. (2) is still valid, and the values refer to the mobile ion.

The Nernst–Einstein relation gives the link between the mobility and the diffusion coefficient, *D*,

$$\mu = \frac{|Z|eD}{k_B T} \tag{3}$$

where, k_B is the Boltzmann constant and *T* is the absolute temperature. For a single ion conductor, $D = D_{ion}$ can be used and in the case where both cations and anions are mobile, an effective *D* value may be used [15,16]. From Eqs. (2) and (3) one can derive,

$$n = \frac{\sigma k_B T}{(|Z|e)^2 D}.$$
(4)

Thus, if *D* is known then *n* and μ can be calculated using Eqs. (3) and (4).

3.1. Determination of D

The effective permittivity of an ionic conductor sandwiched between two blocking electrodes can be described by [12,13],

$$\tilde{\varepsilon}^* = \varepsilon'_{\infty} \left\{ \left(1 + \frac{\delta}{1 + (\omega\tau\delta)^2} \right) - i \left(\frac{\omega\tau\delta^2}{1 + (\omega\tau\delta)^2} \right) \right\}$$
(5)

where, ε'_{∞} is the high frequency permittivity, $\tilde{\varepsilon}^*$ is the effective complex dielectric constant, ω is the angular frequency of the signal and τ is the dielectric relaxation time given by,

$$\tau = \frac{\varepsilon}{\sigma} = \frac{\varepsilon_{\rm s}\varepsilon_{\rm s}'}{\sigma}.\tag{6}$$

 δ is given by

$$\delta = \frac{d}{(D\tau)^{1/2}} = \frac{d}{\lambda} \tag{7}$$

where 2*d* is the sample thickness, ε_{\circ} is the permittivity of free space and λ is the Debye length. The frequency dependence of the real part of the apparent dielectric constant (ε') can be obtained from Eq. (5).

$$\varepsilon' = \varepsilon'_{\infty} \left(1 + \frac{\delta}{1 + (\omega \tau \delta)^2} \right) \tag{8}$$

If $\omega \tau \delta > 1$ then $(\omega \tau \delta)^2 >> 1$. In such a case Eq. (8) can be simplified to,

$$\varepsilon' = \varepsilon'_{\infty} \left(1 + \frac{1}{(\omega\tau)^2 \delta} \right). \tag{9}$$

Hence, according to Eq. (9), δ is given by,

$$\delta = \varepsilon'_{\infty} \left(\frac{1}{(\omega \tau)^2 (\varepsilon' - \varepsilon'_{\infty})} \right) \tag{10}$$

From Eqs. (7) and (10) one can obtain;

$$D = \frac{d^2}{\tau \delta^2} = \frac{d^2 \omega^4 \tau^3 (\varepsilon' - \varepsilon_{\infty}')^2}{(\varepsilon_{\infty}')^2}.$$
(11)

 τ in Eq. (11) can be substituted from Eq. (6), thus the diffusion coefficient is given by;

$$D = \left(d^2 \omega^4 \varepsilon'_{\infty} (\varepsilon' - \varepsilon'_{\infty})^2\right) \left(\frac{\varepsilon_0}{\sigma}\right)^3.$$
(12)

In order to obtain *n*, *D* in Eq. (4) is substituted by Eq. (12);

$$n(\varepsilon') = \frac{\sigma^4 k_B T}{(|Z|ed)^2 \varepsilon_0^3 \varepsilon_{\omega}' (\omega^4 (\varepsilon' - \varepsilon_{\omega}')^2).}$$
(13)

This equation has been used in some recent research articles [3,9] by introducing a parameter *x* which is given by,

$$\varepsilon' = x\varepsilon'_{\infty}$$
 (14)

whereas in some articles [11,12] x = 10 have been used.

3.2. New method

Attempts made by us to deduce charge carrier density and mobility based on Eq. (13) for well known systems such as aqueous KI solutions were unsuccessful. The efforts to use curve fitting to determine parameters τ and δ using the equations in the method suggested by Schütt and Gerdes [12] for other systems also failed as the fitted curves have deviated from the measured data. The problems seem to originate from the difficulty to obtain proper values for the two parameters τ and δ . For example, using τ values corresponding to the maximum in the imaginary part of the electrical modulus, $M''(\omega)$, as in reference [11] gives inappropriate values for our samples resulting in poor curve fitting. An alternative is to use the time constant corresponding to the maximum dielectric loss tangent, τ_m . The relaxation time τ in Eq. (7) is actually τ_m [13,17]. Since $\tau_m = \tau \sqrt{\delta}$ as described in cydix A, Eq. (5) may be modified as;

$$\tilde{\varepsilon}^* = \varepsilon'_{\infty} \left\{ \left(1 + \frac{\delta}{1 + (\omega \tau_m)^2 \delta} \right) - i \left(\frac{\omega \tau_m \delta^{3/2}}{1 + (\omega \tau_m)^2 \delta} \right) \right\}.$$
(13)

Thus, ε' can be written as,

$$\varepsilon' = \varepsilon'_{\infty} \left(1 + \frac{\delta}{1 + (\omega \tau_m)^2 \delta} \right). \tag{14}$$

It is noteworthy that this frequency (at the maximum dielectric loss tangent) corresponds to the frequency where the dc resistance is usually obtained from complex impedance plots and thus the real part of the impedance as well as the ac conductivity remains relatively unchanged close to this frequency.

In the present work, the graph of ε' versus the logarithm of the frequency was chosen to determine τ_m and δ . Curve fitting was used for the determination of δ and τ_m , first assuming a our Eq. (13) for Debye type relaxation. However, to widen the applicability of the method for other electrode effects that leads to inclination of low frequency plateau and to take these effects into account as inspired by Cole–Cole type [18] following modification is used for the Eq. (14);

$$\varepsilon' = \varepsilon'_{\infty} \left(1 + \frac{\delta}{1 + (\omega \tau_m)^{2(1-\alpha)} \delta} \right)$$
(15)

where α is a constant.

Thus, n can be determined using Eqs. (4) and (7) giving;

$$n = \frac{\sigma k_B T \tau_m \delta^2}{(|Z|e)^2 d^2} \tag{16}$$

and μ can be determined using Eqs. (3) and (7) giving;

$$\mu = \frac{ed^2}{k_B T \tau_m \delta^2}.$$
(17)



Fig. 1. Imaginary part vs. real part of complex impedance at 25 $^\circ C$ for 10^{-2} M, 10^{-3} M and 10^{-4} M KI solutions.

4. Results and discussion

The complex impedance measurements are the basis for the evaluation of μ and n. Hence, impedance measurements were made on aqueous solutions of KI as a test of the model. The graph of the imaginary part of the complex impedance Z'' versus the real part, Z', showed a semicircle with a spike or a spike only as shown in Fig. 1 and such plots were used to determine σ of the KI solutions. The relaxation time, τ_m , and δ were obtained by curve fitting to Eq. (15). In principle, this τ_m value is analogous to the time constant corresponding to the frequency of the maximum in tan(ϕ). Therefore, τ_m can equally well be obtained from the tan(ϕ) vs. frequency plots.

The graphs given in Fig. 1 show the real part of *ac* conductivity obtained using impedance measurements [11] as a function of frequency for 10^{-2} M and 10^{-3} M KI solutions at 25 °C. The curves have the expected appearance and σ may be extracted from the plateau values of the graphs in Fig. 2 [10,11]. However, in this study the σ_{dc} values were extracted using the plots of Z'' versus Z' which is the conventional method (not shown). According to Fig. 2 the *ac* conductivity, σ_{ac} , remains unchanged at frequencies close to the maximum in tan(ϕ).

4.1. Determination of n and μ for an aqueous KI solution

The ε' vs. frequency graphs for 10^{-2} M KI and 10^{-3} M KI solutions are shown in Fig. 3. For KI solutions with lower concentrations (less than 10^{-4} M KI) the low frequency plateau appears outside the



Fig. 2. Variation of ac conductivity, σ , and the dielectric loss tangent, $tan(\phi)$, as a function of frequency at 25 °C for 10^{-2} M and 10^{-3} M KI solutions.



Fig. 3. The ε' versus frequency for 10^{-2} M and 10^{-3} M KI solutions at temperatures 25 °C. The solid lines represent the fitted curves according to Eq. (15).

measured frequency window. KI concentrations 10⁻² M and 10⁻³ M KI solutions gave more or less sigmoidal curves within the measured frequency window. The data in Fig. 3 were fitted to Eq. (15) and were used for calculations. An appropriate ε'_{∞} value was determined using the plots in Fig. 3 prior to the curve fitting. During the fitting an appropriate α value was selected. This value was in the range 0.15 to 0.45 for both KI solutions. The fitted curves are also shown in Fig. 3 and the obtained parameters au_m and δ are given in Table 1. The low frequency plateaus of the experimental data are slightly inclined probably due to contribution from other low frequency relaxations apart from space charge relaxation. To take other relaxations into account the model will require modifications but in this study our major concern is the determination of the charge carrier density and the mobility by modelling the space charge relaxation. However, by using this method, the accuracy of the results can be improved by selecting an appropriate frequency region dominated by the space change relaxation. Accordingly the low frequency region in the Fig. 3 was omitted from fitting in order to minimise the errors.

The parameters τ_m and δ extracted from curve fitting were used in Eqs. (7), (19) and (20) to determine the *D*, *n*, and μ values shown in Table 1. The obtained mobile charge carrier concentration values were compared with the known concentration of ionic species in the solution, which is given as n_d in Table 1. The values in Table 1 are reasonable compared to standard values reported in literature [19,20]. The standard deviation of τ_m and δ values from the curve fitting remained less than 10% and the error in σ and *T* can be maintained less than 5%. Based on this, the error limit of the *n* and μ values obtained in this method is estimated to be $\pm 20\%$. This is thus better than the accuracy limit for the carrier density (50%), given for the method in reference for other system [12].

4.1.1. Using the method for a solid polymer electrolyte

The ionic conductivity of the (PEO)₆₈Pr₄N⁺I⁻/I₂ polymer electrolyte as well as the plasticized (PEO)₆₈Pr₄N⁺I⁻/I₂/EC electrolyte containing 33% mass fraction of EC is shown in Fig. 4. At low temperatures the plasticized electrolyte has a higher conductivity while at temperatures above ~60 °C the plasticized and unplasticized samples reach almost similar values. Around the PEO crystallite



Fig. 4. The conductivity versus 1000/T for $(\text{PEO})_{68}\text{Pr}_4\text{N}^+\text{I}^-/\text{I}_2$ electrolyte with and without EC.

melting temperature, $T_{\rm m}$ [21] (about 60 °C), a steep conductivity increase can be observed. A proper estimation of the mobility and the carrier concentration would facilitate the understanding of whether the conductivity enhancement is due to an increase of the mobility or/ and the charge carrier concentration.

The frequency dependence of the real part of the *ac* conductivity extracted from impedance measurements of $(\text{PEO})_{68}\text{Pr}_4\text{N}^+\text{I}^-/\text{I}_2$ electrolyte for different temperatures is shown in Fig. 5. The curves have the expected appearance to motivate the use this model.

The curves of ε' vs. frequency for the polymer electrolyte (PEO)₆₈Pr₄N⁺I⁻/I₂ are plotted in Fig. 6 using a logarithmic scale and the solid lines represent the curves fitted to Eq. (15). These data fit better to the measured values than the fits for aqueous KI solutions. However, some of the measured curves slightly deviate from the fitted curves close to the bulk relaxation. This may possibly be due to effects of other relaxations such as the ion pair relaxation described in [22] or relaxations of other dipoles or triple ions in the electrolyte [23]. However, as these deviations are small compared to bulk space charge relaxation, their effect on the fitted curves will be negligible. The parameters τ_m and δ obtained by curve fitting are used to determine the diffusion coefficient, charge carrier density and mobility, are listed in Table 2.

The curves of ε' vs. frequency for the plasticized polymer electrolyte (PEO)₆₈Pr₄N⁺I⁻/I₂ containing 33.3% EC are shown in Fig. 7. The fitted curves (solid lines) to Eq. (15) deviate somewhat from the measured values, especially for higher temperatures. This deviation may be understood considering effects of dipolar species, for example, ion pairs and larger ionic aggregates that form mainly after the melting of PEO crystallites. The parameters τ_m and δ obtained by curve fitting are used to determine *D*, *n* and μ and the values are given in Table 3.

The *n* and μ values for the solid polymer electrolytes are shown in Fig. 8. The steep conductivity increase observed at about 60 °C in Fig. 4 shifts towards lower temperatures with incorporation of EC as

Table 1

The conductivity (σ), fitting parameters (τ_m , δ), diffusion coefficient (D), charge carrier density (n) and mobility (μ) determined for 10⁻² M and 10⁻³ M KI solutions at 25 °C. The obtained n value is compared with the known concentration of ionic species in the solution, which is given as n_d .

KI concentration	$\sigma/{ m mS~cm^{-1}}$	$ au_m/{ m s}$	δ	$D/m^{2} s^{-1}$	n/m^{-3}	$n_{\rm d}/{\rm m}^{-3}$	$\mu/{ m m}^2~{ m V}^{-1}~{ m s}^{-1}$
10 ⁻² M	1.34	5.09×10^{-7}	46341.33	$\begin{array}{c} 2.0\!\times\!10^{-9} \\ 2.2\!\times\!10^{-9} \end{array}$	1.09×1025	1.2×1025	7.7×10^{-8}
10 ⁻³ M	0.15	27.0 × 10 ⁻⁷	9014.65		1.11×1024	1.2×1024	8.6×10^{-8}



Fig. 5. Frequency dependence of the real part of the ac conductivity for the polymer electrolyte $(PEO)_{68} Pr_4 N^{+} I^{-}/I_2$ for temperatures between 29 and 100 °C .

evidenced from differential scanning colorimetric and conductivity data described in reference [21], which can be correlated to the increase of free charge carrier density shown in Fig. 8. This increase of conductivity and concentration of free charge carriers is due to the structural and morphological changes that occur at the crystallite melting temperature of PEO [24]. Fig. 8 also illustrates that when this increase of the concentration of charge carriers takes place there is actually a decrease in the mobility. However, a slight increase in mobility with increasing temperature can be observed above the melting temperature especially for the EC containing sample. Although the increasing trend in mobility with increasing temperature is not very visible in Fig. 8, detailed analysis of numerical values clearly shows the increasing trend. The data showed that a majority of the ions are dissociated for temperatures higher than the polymer crystallite melting temperature. The rather moderate increase of the conductivity at these temperatures is caused by increasing mobility and charge carrier concentration. Comparing plasticized and unplasticized samples at high temperatures shows that the mobility is significantly higher for the plasticized sample, as expected. At these temperatures the charge carrier concentration is lower for the plasticized sample; however this may be due to the dilution of the charge carriers owing to the incorporation of EC. Thus, the very moderate increase of conductivity with EC content can at these temperatures be explained by the increase of the mobility [25] balanced by a decrease of the charge carrier concentration.



Fig. 6. Frequency dependence of ε' for temperatures between 29 and 100 °C for the polymer electrolyte (PEO)₆₈Pr₄N⁺I⁻/I₂. The solid line represents the fitted curves.

Table 2

The conductivity (σ), τ_m , δ , diffusion coefficient (D), carrier density (n) and mobility (μ) for the polymer electrolyte (PEO)₆₈Pr₄N ⁺I⁻/I₂ at different temperatures.

T/°C	$\tau \times 10^{-6}$ /s	δ	$D/\mathrm{m}^2\mathrm{s}^{-1}$	$\sigma/\mathrm{S}~\mathrm{m}^{-1}$	n/m^{-3}	$\mu\!/m^2{\rm V}^{-1}{\rm s}^{-1}$
29	416.98	81.48	3.98×10^{-09}	7.64×10^{-7}	3.07×1019	1.53×10^{-7}
40	170.29	212.08	1.44×10^{-09}	2.72×10^{-6}	3.03×1020	5.33×10^{-8}
50	15.91	1578.82	2.77×10^{-10}	5.22×10^{-5}	3.01 imes 1022	9.98×10^{-9}
60	3.18	18804.88	9.79×10^{-12}	1.48×10^{-3}	2.42×1025	3.41×10^{-10}
70	1.59	57282.79	2.11×10^{-12}	5.47×10^{-3}	4.15×1026	7.14×10^{-11}
80	1.59	62151.68	1.79×10^{-12}	5.53×10^{-3}	4.94×1026	5.89×10^{-11}
90	1.43	66213.88	1.75×10^{-12}	5.60×10^{-3}	5.11×1026	5.61×10^{-11}
100	1.21	70156.62	1.85×10^{-12}	5.97×10^{-3}	$5.16\!\times\!1026$	5.76×10^{-11}

It can be inferred from the data shown in Fig. 8 that the charge carriers have different transport mechanisms below and above the crystallite melting temperature (~60 °C). At the temperatures bellow ~60 °C, (crystalline phase) the free charge carriers have a high mobility compared to that at higher temperatures (amorphous phase). This may seem surprising but is related to the structural differences between the crystalline and amorphous forms of PEO and/or the increasing ion-ion interactions with increasing number of change carriers. In fact, the conductivity reported in some ordered or crystalline polymer electrolytes may actually be due to a very high mobility in the crystalline phase [26–28]. In the crystallite molten phase of PEO electrolyte, the mobility increases with addition of plasticizer or by increasing the temperature. which is expected and related to the reduction of viscosity. Considering this, the increase in conductivity of the low temperature phase appears to be largely due to the increase in the concentration of mobile charge carriers.

5. Conclusions

A new method has been developed to calculate the charge carrier density, *n*, and the mobility, μ , for an electrolyte using dielectric data with a space charge relaxation model. The mobile charge carrier density can be obtained from the expression $\frac{\sigma k_B T \tau \delta^2}{(|Z|e)^2 d^2}$ and the mobility from $\frac{ed^2}{k_B T \tau \delta^2}$ for an electrolyte with blocking electrodes. The applicability of the method was tested using aqueous KI electrolytes and applied to plasticized and non-plasticized solid polymer electrolytes.

Curve fitting ensured the appropriateness of the model. For the polymer electrolytes good fits could be obtained while for aqueous KI



Fig. 7. Frequency dependence of ε' for temperatures between 29 and 100 °C for the polymer electrolyte, (PEO)₆₈Pr₄N⁺l⁻/l₂ containing 33.3% EC. The solid lines represent the fitted curves.

68 Table 3

The conductivity (σ), fitting parameters (τ_m , δ), diffusion coefficient (D), carrier density (n) and mobility (μ) for the polymer electrolyte, (PEO)₆₈Pr₄N⁺I⁻/l₂ containing 33.3% EC at different temperatures.

-							
	T/°C	$\tau \times 10^{-6}$ /s	δ	$D/m^{2} {\rm s}^{-1}$	$\sigma/\mathrm{S}\mathrm{m}^{-1}$	n/m^{-3}	$\mu\!/m^2{\rm V}^{-1}{\rm s}^{-1}$
	29	17.51	677.04	1.65×10^{-9}	1.75×10^{-5}	1.70×10^{21}	6.33×10^{-8}
	40	7.96	2388.81	2.91×10^{-10}	6.90×10^{-5}	3.79×10^{22}	1.08×10^{-8}
	50	3.18	11285.83	3.26×10^{-11}	3.77×10^{-4}	1.85×10^{24}	1.17×10^{-9}
	60	1.28	48780.98	4.34×10^{-12}	2.49×10^{-3}	9.18×10^{25}	1.51×10^{-10}
	70	1.07	56561.24	3.87×10^{-12}	3.94×10^{-3}	1.63×10^{26}	1.31×10^{-10}
	80	0.78	60062.76	4.67×10^{-12}	4.81×10^{-3}	1.65×10^{26}	1.54×10^{-10}
	90	0.63	62156.35	5.44×10^{-12}	5.95×10^{-3}	1.75×10^{26}	1.74×10^{-10}
	100	0.48	71089.43	5.47×10^{-12}	7.00×10^{-3}	2.05×10^{26}	1.70×10^{-10}

electrolytes the fits deviated somewhat more from the measured values, especially at low frequencies. Hence, a modification to the model is needed to incorporate all relaxations present in aqueous solutions. However, the advantage of this relaxation model is that the parameters in the model have direct relationship to actual physical quantities such as the diffusion coefficient, the charge carrier density and the mobility.

The obtained values for charge carrier density and mobility for the aqueous electrolyte were within 20% of the expected values. The temperature dependence of σ , n and μ investigated for polymer electrolyte revealed that the abrupt increase of conductivity around the crystallite melting temperature of the polymer is dominated by an increase of the charge carrier density n. The mobility in the predominantly crystalline low temperature phase was surprisingly high. However, at these temperatures, the n value was low resulting in a low conductivity. The effect of adding the plasticizer was most pronounced in the low temperature region, increasing the charge carrier concentration considerably. In conclusion, this model represents a useful tool for studying polymer electrolytes.

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Fig. 8. The variation of the charge carrier density (n) and the mobility with inverse temperature for the polymer electrolyte $(PEO)_{68}Pr_4N^+l^-/l_2$ with 33.3% EC and without EC. The mobility for 10^{-2} M KI aqueous solution at 25 °C is shown by a horizontal line for comparison.

Appendix A

 τ_m is the relaxation time corresponding to the frequency where tan (ϕ) shows a maximum. According to Eq. (5) the dielectric loss tangent can be derived as

$$\tan(\phi) = \frac{\varepsilon}{\varepsilon'} = \frac{\omega\tau\delta^2}{1+\delta+(\omega\tau\delta)^2} \approx \frac{\omega\tau\delta}{1+\omega^2\tau^2\delta}$$
(18)

When $tan(\phi)$ is maximum

$$\frac{d}{d\omega}\tan(\phi) = 0 = \frac{\tau\delta((1+\omega^2\tau^2\delta) - 2\omega^2\tau^3\delta^2}{(1+\omega^2\tau^2\delta)}$$
(19)

thus

$$\omega_m^2 \tau^2 \delta = 1. \tag{20}$$

Therefore

$$\tau_m = \tau \sqrt{\delta} \tag{21}$$

thus

$$\tan(\phi)_{Max} = \frac{\sqrt{\delta}}{2}.$$
(22)

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