

Distribution of Relaxation Times: Debye Length Distribution vs Electrode Polarization by a Cole–Cole Relaxation Model

To cite this article: Vicente Compañ *et al* 2022 *J. Electrochem. Soc.* **169** 013506

View the [article online](#) for updates and enhancements.

You may also like

- [Techniques for measuring the microwave dielectric properties of materials](#)
Udo Kaatzke

- [The Temperature Jump Method and Its Application in the Study of Complex Formation](#)
V I Pogonin and Aleksandr K Chibisov

- [Rheological properties of amorphous alloys and their description on the base of linear viscoelastic theory](#)
N O Gonchukova and S L Ratushniak

Investigate your battery materials under defined force!
The new PAT-Cell-Force, especially suitable for solid-state electrolytes!



- Battery test cell for force adjustment and measurement, 0 to 1500 Newton (0-5.9 MPa at 18mm electrode diameter)
- Additional monitoring of gas pressure and temperature

www.el-cell.com +49 (0) 40 79012 737 sales@el-cell.com

EL-CELL[®]
electrochemical test equipment





Distribution of Relaxation Times: Debye Length Distribution vs Electrode Polarization by a Cole–Cole Relaxation Model

Vicente Compañ,^{1,z} Ricardo Diaz-Calleja,² Joaquín Diaz-Boils,³ and Jorge Escorihuela⁴

¹Departamento de Termodinámica Aplicada, Universitat Politècnica de Valencia, 46020 Valencia, Spain

²Departamento de Termodinámica Aplicada, Instituto de Tecnología Eléctrica, Universitat Politècnica de Valencia, 46020 Valencia, Spain

³Universidad Internacional de la Rioja, Logroño, 26006 La Rioja, Spain

⁴Departamento de Química Orgánica. Facultat de Farmàcia. Universitat de Valencia, Burjassot, 46100 Valencia, Spain

Mobility, diffusivity and charge density in polyelectrolytes, are generally determined from electrochemical impedance spectroscopy following the electrode polarization analysis, in which at a given temperature the peaks in $\tan \delta$ are fitted based on a model. These results can be different depending on the model used in the fitting of the curves. Generally, the models are based on a single Debye model or on the existence of an overlap in relaxation times (Cole–Cole model). In this work, we propose the alternative use of the distribution of the relaxation times by a distribution of the Debye length (L_D), which allows the calculation of parameters such as mobility, diffusivity, and charge density as a function of L_D in a more concise approach.

© 2022 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: 10.1149/1945-7111/ac4bf9]

Manuscript submitted November 19, 2021; revised manuscript received January 10, 2022. Published January 27, 2022.

Supplementary material for this article is available [online](#)

The study of mobility, diffusivity and carrier charge density in polymeric electrolytes and composite membranes is of utmost importance to characterize polymeric composites with potential applications as ionic conductors which can be used in energy conversion, as super-capacitors, batteries, solar cells, polymer electrolytes in fuel cells, among others.^{1,2} The determination of these parameters has been addressed by several approaches in the scientific literature focused. One of the most widely used alternatives is based on measurements using electrochemical impedance spectroscopy (EIS) under an applied electric field.^{3–12} The use of EIS has been widely established in the last years in polymer science and in particular as powerful characterization method for fuel cells because it is non-destructive and provides useful information about fuel cell performance as demonstrated in our recent publications.^{13–17} The experimentally obtained spectra can be modeled using the electrode polarization (EP) model initially proposed by Coelho,^{18,19} where EP is characterized by a single Debye relaxation. In this model, also known as Coelho model, the dependence of the complex permittivity on frequency is represented by a single Debye,^{6–8} following Eq. 1:

$$\epsilon^* = \epsilon_s + \frac{\Delta\epsilon_{EP}}{1 + j\omega\tau_{EP}} \quad [1]$$

where $\Delta\epsilon_{EP} = \epsilon_{s,EP} - \epsilon_s$, being $\epsilon_{s,EP}$, the low frequency dielectric constant in the presence of EP and is given by $\epsilon_{s,EP} = M \cdot \epsilon_s$, and $\tau_{EP} = M \cdot \tau$, represents the electrode polarization relaxation time, where M is the ratio of the sample thickness divided by twice the Debye length (L_D), $M = L/2L_D$, and represents the number of rms Debye lengths L_D contained in the thickness L of the sample sandwiched between the two electrodes. Finally, the diffusion relaxation time τ is defined from Einstein-Poisson relations as $\tau = \frac{\epsilon}{\sigma_{dc}} = \frac{\epsilon_s \cdot \epsilon_0}{\sigma_{dc}}$,^{19–21} ω is the angular frequency, σ_{dc} represents the total dc conductivity and j the imaginary unity.

From Eq. 1, the real and imaginary parts of the permittivity (ϵ' , ϵ'') and the loss tangent ($\tan \delta$) can be obtained, and the values of the parameters M , τ_{EP} , τ , ϵ_s , $\Delta\epsilon_{EP}$ and ϵ_{EP} , can be estimated by fitting the experimental data. The plot of loss $\tan \delta = (\epsilon''/\epsilon')$ vs frequency, for conductive systems, displays a peak with a shifting to higher frequencies as a function of the temperature. From this plot, the mobility, diffusivity, and free charge density of the sample can be

calculated. The analysis of experimental data in terms of Coelho model analyzed EP by a Debye relaxation. Following the procedure described by Klein et al.,³ when $\tan \delta$ peak is not affected by conductivity, the plot of $\tan \delta$ vs frequency allows to obtain information of the parameters M , τ_{EP} , τ , ϵ_s , $\Delta\epsilon_{EP}$ and ϵ_{EP} , and then calculate the mobility, diffusivity, and the charge carrier density. According to Klein et al.,³ the equation of $\tan \delta$ can be modeled by Eq. 2:

$$\tan \delta = \frac{\omega\tau_{EP}}{1 + \frac{(\omega\tau_{EP})^2}{M}} \quad [2]$$

where the maximum in $\tan \delta$ satisfies Eq. 3:

$$\omega_{\max}^{\tan \delta} = \frac{M^{\frac{1}{2}}}{\tau_{EP}} = \frac{1}{(\tau \cdot \tau_{EP})^{1/2}} \quad [3]$$

In this article, we propose the use of the distribution of the relaxation times given by a more complex Debye length model (L_D), which allows the calculation of parameters such as mobility, diffusivity, and charge density as a function of L_D in a more concise approach.

Results

A transparent film made of a supported ionic-liquid-like phase (SILLP) doped with the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM][NTf₂]) was prepared by polymerization of 60 wt% of 1-vinyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide ([VBIm][NTf₂]), 40 wt% of trimethylolpropane trimethacrylate (TMPTMA) and 1 wt% of azobisisobutyronitrile (AIBN) as initiator (see Supporting Information for further details).²² The film was sandwiched between two gold circular electrodes coupled to the impedance spectrometer by compressing film in a sandwich cell configuration. The assembly membrane-electrode was annealed in the Novocontrol setup under an inert dry nitrogen atmosphere before starting the measurement. The temperature was gradually raised from 0 °C to 130 °C in steps of 10 °C, recording the dielectric spectra in each step. During the conductivity measurements, the temperature was kept constant at each measuring step controlled by a nitrogen jet with a temperature error of 0.1 °C during every single sweep in frequency. Figure 1a shows the $\tan \delta$ as a function of the frequency for the SILLP sample containing 60 wt% VBIm][NTf₂] and 40 wt% of TMPTMA in all the

^zE-mail: vicommo@ter.upv.es

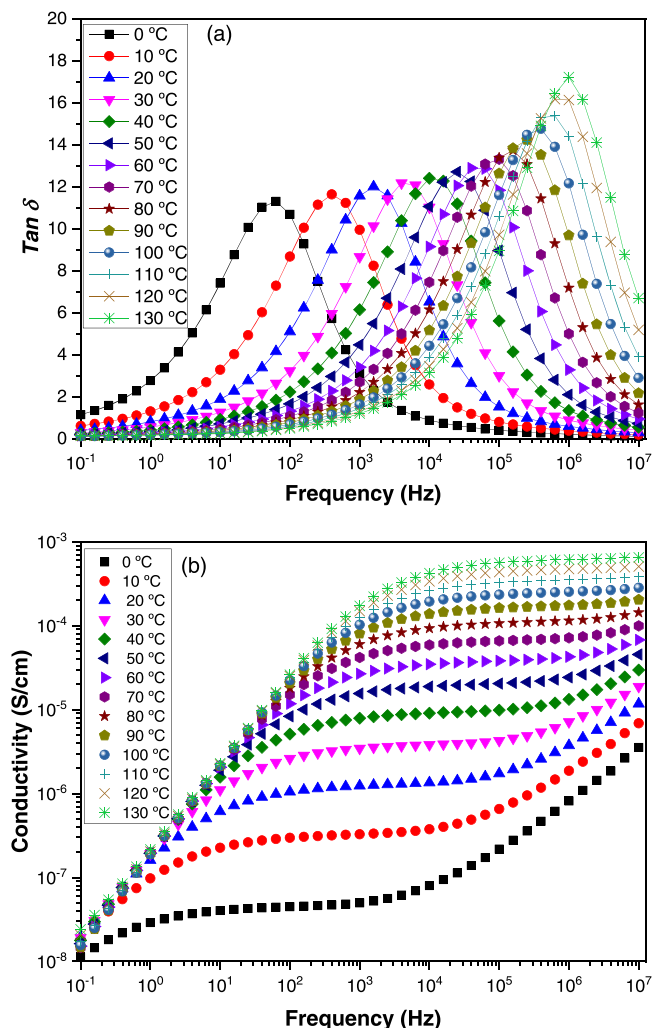


Figure 1. (a) $\tan \delta$ vs frequency for the SILLP sample containing 60 wt% of [VBIm][NTf₂] and 40 wt% of TMPTMA in the range of 0 to 130 °C. (b) Bode diagram for the sample in the same range of temperatures.

range of temperatures. As shown a maximum in all curves at each temperature is observed. This peak is associated to the plateau of the real part of the conductivity observed in the Bode diagram of Fig. 1b.

Figure 2 shows the variation of $\tan \delta$ vs frequency at 80 °C for a sample composed of a supported ionic-liquid-like phase (SILLP). Black points correspond to the experimental data obtained by electrochemical impedance spectroscopy measurements and the blue line corresponds to the fitting data using a single Debye relaxation by means of Eq. 2. From this fit, the parameters M and τ_{EP} were obtained, being $M = 780$ and $\tau_{EP} = 3.06 \times 10^{-5}$ s. However, a closer inspection at Fig. 2, shows that the maximum of the peak in $\tan \delta$ represented by a single Debye relaxation time does not correctly fit with the experimental data. In order to improve the data fitting, it is necessary to consider a model that broadens the function that describes the peak in $\tan \delta$, with a more appropriate amplitude. For the complete range of temperatures studied we can see the fits to experimental data in Supplementary Information, Fig. S11 (available online at stacks.iop.org/JES/169/013506/mmedia).

Accordingly, the peak in $\tan \delta$, should be modeled differently as predicted by a single relaxation time according to a Debye model. The classic approach to encircle this problem is the use of a slightly more sophisticated model such as the Cole–Cole model, where the dependence of the complex permittivity on frequency is represented by Eq. 4.

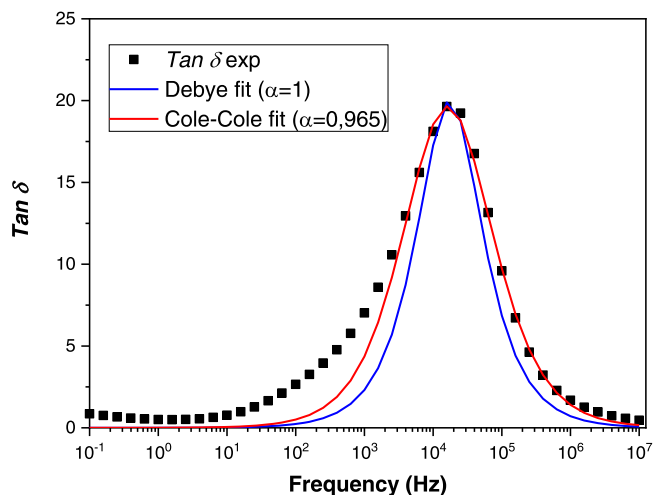


Figure 2. $\tan \delta$ vs frequency at 80 °C for a sample of a supported ionic-liquid-like phase (SILLP). Points correspond to experimental data; the blue line is the fitting using a single Debye relaxation (Eq. 2) and the fitting using a Cole–Cole relaxation (Eq. 4) is shown in red. The calculated values for the parameters are $M = 780$ and $\tau_{EP} = 3.06 \times 10^{-5}$ s, for a Debye single relaxation and $M = 6600$, $\tau_{EP} = 11 \times 10^{-5}$ s and $\alpha = 0,965$ for a Cole–Cole model.

$$\epsilon^* = \epsilon_s + \frac{\Delta\epsilon_{EP}}{1 + (j\omega\tau_{EP})^\alpha} \quad [4]$$

This model involves the introduction of an alpha exponent (α) to Debye's equation, whose physical meaning is to induce to a distribution of relaxation times.²³ In Eq. 4, the alpha exponent ($0 \leq \alpha \leq 1$) is the blockage coefficient of the electrode, assuming the same value for the two electrodes where the sample is sandwiched.²⁴ This exponent is an indication of accumulative process in the sample because of the interactions among the charge carriers.^{8–10} A comparison of Eqs. 1 and 4 shows the main difference between the Cole–Cole and Debye descriptions is essentially, the alpha exponent (α), which describes the manifestation of cumulative processes in the system that are related to interactions among charge carriers, when this exponent is $\alpha < 1$ the process displays a sub-diffusion. When $\alpha \ll 1$ these interactions are strong, and in contrast, when $\alpha \lesssim 1$ the interactions do not dominate the transport process. Therefore, a process with high conductivity will be associated to values of $\alpha \lesssim 1$.

The distribution time has been a matter of discussion along the past decades because different researchers have suggested that this should be explained in terms of a distribution of molecular surroundings of charges instead of a time relaxation distribution.²⁵ However, it is generally admitted that the existence of this distribution time has a physical meaning, and therefore, the substitution of distribution of times of relaxation instead of a single relaxation time could be appropriate for some systems and, particularly, for the system under study.^{26,27}

Following a typical Cole–Cole relaxation, the $\tan \delta$ can be expressed, assuming that the contribution of the conductivity at low frequencies can be generally omitted, and, when the Maxwell–Wagner–Sillars (MWS) conditions are accomplished (i.e., when the bulk conductivity dominates as for a pure ohmic conduction at high frequencies),²⁸ then $\epsilon'(\omega, T) = \sigma_{dc}(\omega, T)/\epsilon_0\omega$, and the loss tangent, $\tan \delta = \epsilon''/\epsilon'$,^{11,18} can be expressed in terms of Eq. 5:

$$\tan \delta = \frac{(\omega\tau_{EP})^\alpha \sin\left(\frac{\pi}{2}\alpha\right)}{1 + (\omega\tau_{EP})^\alpha \cos\left(\frac{\pi}{2}\alpha\right) + \frac{(\omega\tau_{EP})^{2\alpha}}{M}} \quad [5]$$

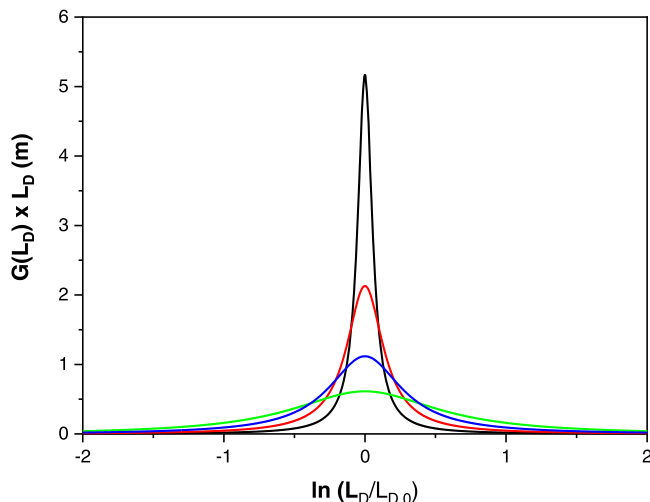


Figure 3. The distribution function $G(L_D)$ associated with the Cole–Cole distribution relaxation Debye length for different values of α . Black ($\alpha = 0.99$), red ($\alpha = 0.95$), blue ($\alpha = 0.90$) and green ($\alpha = 0.80$) and $L_{D,0} = 1.5 \times 10^{-8}$ m.

whose maximum satisfies Eq. 6:

$$\omega_{\max}^{\tan \delta} = \frac{M^{1/\alpha}}{\tau_{EP}} = \frac{1}{(\tau \cdot \tau_{EP})^{1/2}} \quad [6]$$

Therefore, using a Cole–Cole distribution to fitting the experimental values of $\tan \delta$ vs frequency at 80 °C (see Supplementary Information, Fig. IS2, for the other temperature,) gives a more realistic fit as displayed in Fig. 2 (curve in red color). From this plot, it can be concluded that the Cole–Cole distribution is more appropriate for these systems, where the interaction between the charge carriers is associated to the distribution of molecular surroundings charges in the system that display a continuous interaction among charge carriers and cross-linked charges with the polymeric matrix. On the other hand, the use of a Cole–Cole model allows a more appropriate estimation of the values of mobility, diffusivity, and charge density. The error χ^2 , calculated as the difference between the experimental and theoretical values, obtained for Debye fit is higher than the obtained by Cole–Cole, (175 vs 29). Further investigations carried out using the Debye model, with the aim to study the influence of ion mobility and mobile ion concentration of single-ion polymer electrolytes, have provided more precise results for these parameters. However, there are several systems, such as mixed salts based on CsH_2PO_4 , ionic liquids composite membranes or hexacyanocobaltates with divalent transition metals, where the Debye model shows some inconsistencies.¹⁰ Under these circumstances, other models such as Cole–Cole have shown that the calculated transport properties are more consistent with the measured values for conductivity, mobility, and diffusivity.^{9–11}

From the peak in $\tan \delta$, the time at which the onset of EP is produced into the system can be defined and represented by the expression $\tau_m = \frac{1}{\omega_{\max}^{\tan \delta}} = \frac{1}{2\pi f_{\max}}$. This onset represents a time constant and is characteristic for each system at a constant temperature, which is related with the electrode polarization time relaxation τ_{EP} and the sample relaxation time τ , defined by $\tau = \frac{\epsilon}{\sigma_{dc}}$, at the same temperature by means of Refs. 3, 9, 18

$$\tau_m^2 = \tau \cdot \tau_{EP} \quad [7]$$

The combination Eqs. 3 and 6 with Eq. 7, allows to obtain Eq. 8 for the M parameter:

$$M = \frac{\tau_{EP}}{\tau} = \left(\frac{\tau_{EP}}{\tau_m} \right)^2 = \frac{L}{2L_D} \quad [8]$$

where for the case of a single Debye model, and using the Cole–Cole model, it can be expressed as given by Eq. 9:

$$M^{1/\alpha} = \frac{\tau_{EP}}{\tau} = \left(\frac{\tau_{EP}}{\tau_m} \right)^2 = \left[\frac{L}{2L_D} \right]^{1/\alpha} \quad [9]$$

The electrode polarization model in case of charged polymers with fixed cations along the polymeric matrix chains and anions as mobile counterions, can be considered as a polymeric sample charged of thickness $L = 150 \mu\text{m}$ sandwiched between two electrodes, where in the steady state, the system is practically considered as a macroscopic dipole, and the relaxation time is directly related to the diffusion time of the charge carriers that contribute to the macroscopic polarization. Therefore, it should be related to the thickness of the sample, where the Debye length can be associated to the average distance that the ion travels through hopping in the sample with a relaxation time given by $\tau = \frac{L_D^2}{D}$, being D the diffusion coefficient. Consequently, all the above commented allows us to assume that the distance between molecules in molecular surroundings must be of the order of magnitude than Debye length, L_D . Then, considering the relationship between the thickness of the sample, L , the relaxation times τ_{EP} and τ , respectively, together with the Debye length, L_D , the use of a Debye length distribution can be used instead of a time relaxation distribution. Under this approximation, the differences observed between the experimental values and the theoretical fit in Fig. 2 can be understood. Moreover, in the case of lower values for the α -parameter (below 0.8), the differences in the treatment of the experimental data could be even more striking.

It is well known that the Cole–Cole equation for a distribution of relaxation times is a similar function to that of Debye, being also flared and symmetrical respect to a central frequency or relaxation time. Therefore, considering the above-mentioned treatment, the substitution of the distribution of the relaxation times by a distribution of L_D is proposed according to Eq. 10, see Appendix for its derivative^{29–31}

$$G(L_D) = \frac{1}{2 \cdot \pi \cdot \alpha \cdot L_D} \frac{\sin((1 - \alpha) \cdot \pi)}{\cosh \left[\ln \left(\frac{L_D}{L_{D,0}} \right) \right] - \cos((1 - \alpha) \cdot \pi)} \quad [10]$$

Figure 3 shows the distribution function for Debye length associated with the Cole–Cole relaxation model calculated for the same sample of supported ionic-liquid-like phase (SILLP) containing ([VBIm][NTf₂]) with a thickness of 150 μm . The parameters obtained for this sample by fitting $\tan \delta$ with the Cole–Cole relaxation model are $M = 6600$, $\tau_{EP} = 11 \times 10^{-5}$ s and $\alpha = 0.965$. As can be seen that Debye length distribution function of a Cole–Cole equation displays the same behavior that a single Debye relaxation, being also flared and symmetrical respect to a central frequency or relaxation time, in accordance with the electrode polarization model proposed by Coelho where the EP is characterized with a single Debye relaxation. These results show that the thickness of the Debye length (L_D) can be a good alternative to describe the behavior of a sample when analyzed from the electrode polarization using a Cole–Cole relaxation model and can be of interest in mobility, diffusivity, and charge carrier density, such as we can see in advance.

In general, in polyelectrolytes considered as binary systems, both cations and anions participate in the conduction process and then the conductivity is the sum of the contributions of all the constituent charge carriers, i.e., $\sigma = \sigma^+ + \sigma^-$, considering that both cations and anions have the same valence. However, in case of composite membranes such as PBI@BMIM-X ($X = \text{Cl}^-$, NTf_2^- , BF_4^-) the

highest possible contribution to the total conductivity are the anions, and therefore the anion conductivity can be estimated supposing that anion transference number is practically equal to one. In this approximation, the cations are practically immobile due to the reduced mobility that BMIM cation because of its size in comparison with the other counterpart. Therefore, the cation mobility is negligible and then, the dominated mobility will be mainly restrictive to the anion contribution. In these cases, the ionic conductivity, σ , corresponding to the anion can be described as

$$\sigma_{dc} = nq\mu \quad [11]$$

Where n is the equilibrium number density of free negative charges, μ is the mobility of the anion and q the charge of anion. Then, the effective ionic diffusivity, D , can be calculated considering the Nernst-Einstein relationship

$$\mu = \frac{qD}{k_B T} \quad [12]$$

where, k_B is the Boltzmann constant and T the absolute temperature. From Eqs. 11 and 12

$$D = \frac{\sigma_{dc} k_B T}{n q^2} \quad [13]$$

Considering that the Debye length is defined as $L_D = \sqrt{\frac{\varepsilon_s \varepsilon_0 k T}{n q^2}}$ and $\tau = \frac{\varepsilon_s \varepsilon_0}{\sigma_{dc}}$ then we also can determine the diffusivity as

$$D(L_D) = \frac{\sigma_{dc} L_D^2}{\varepsilon_s \varepsilon_0} = \frac{L_D^2}{\tau} \quad [14]$$

Being τ the relaxation time of the ionic conduction in the sample.

The anion mobility (μ) can be obtained from the diffusivity as

$$\mu(L_D) = \frac{q}{k_B T} \frac{L_D^2}{\tau} \quad [15]$$

Finally, the free charge carrier density by

$$n(L_D) = \frac{\sigma_{dc} k_B T}{q^2} \frac{\tau}{L_D^2} \quad [16]$$

Equation shows the relationship between the parameter M , the electrode polarization relaxation time τ_{EP} and the relaxation time of ionic conduction, τ , when the fit of $\tan \delta$ have been modeled using the single Debye model, then

$$M = \frac{\tau_{EP}}{\tau} = \frac{L}{2L_D} \quad [17]$$

where L is the sample thickness sandwiched between the two electrodes. From Eq. 17, the Debye length can be expressed as

$$L_D = \frac{L}{2M} \quad [18]$$

And in terms of the function of electrode polarization relaxation time as

$$L_D = \frac{L\tau}{2\tau_{EP}} \quad [19]$$

Considering the Cole–Cole relaxation model, then the M parameter can be expressed as

$$M^{1/\alpha} = \left[\frac{L}{2L_D} \right]^{1/\alpha} = \frac{\tau_{EP}}{\tau} \quad [20]$$

And the Debye length as

$$L_D = \frac{L}{2} \left(\frac{\tau}{\tau_{EP}} \right)^\alpha \quad [21]$$

Where τ_{EP} and τ are determined from experimental results. τ_{EP} from the fitting curves in $\tan \delta$ vs frequency or also directly from the peak of ε'' ($\log \varepsilon''$ vs $\log f$) when these peaks are present in the plot of ε'' vs $\log f$. Finally, τ can be obtained from the frequency at the peak in $\tan \delta$.

As can be seen from Eqs. 19 and 20, the value taken by the alpha parameter will mark the difference between the values of L_D and therefore the differences found in the mobility, diffusivity, and free charge density, according to Eqs. 12–14. When $\alpha = 1$, both Eqs. 20 and 21 are the same, while if $\alpha < 1$ then the Debye thickness will be different, being more different for values of α smaller than the unity.

Discussion

The calculated results obtained in terms of the parameters M , τ_{EP} , τ and α , for the film composed of supported ionic-liquid-like phase, using the Debye relaxation model and the Cole–Cole relaxation model as a function of the temperature from the fits in $\tan \delta$ are shown in Table I.

Figure 4 shows the variations with the temperature of the different parameters namely τ , τ_{EP} and Debye length (L_D) calculated

Table I. Calculated values for M , τ_{EP} , τ and α using the Eqs. 2 and 3 for Debye relaxation model and Eqs. 5 and 6 for Cole–ole relaxation model.

T (°C)	Debye model				Cole–Cole model			
	M	$\tau_{EP} \times 10^3$ (s)	$\tau \times 10^5$ (s)	α	M	$\tau_{EP} \times 10^3$ (s)	$\tau \times 10^5$ (s)	α
10	570	9.86	1.730	1	4500	30.8	0.50	0.962
20	604	2.53	0.419	1	4700	8.6	0.14	0.966
30	626	0.55	0.088	1	5000	3.0	0.0445	0.966
40	645	0.36	0.056	1	5500	1.3	0.0175	0.966
50	666	0.157	0.024	1	5800	0.67	0.0085	0.966
60	696	0.085	0.012	1	6100	0.32	0.0039	0.966
70	730	0.046	0.0063	1	6300	0.19	0.0022	0.967
80	780	0.0306	0.004	1	6600	0.11	0.0012	0.965
90	830	0.0196	0.0024	1	6800	0.065	0.00073	0.970
100	890	0.0140	0.0016	1	7100	0.043	0.00047	0.970
110	970	0.0096	0.00098	1	7300	0.030	0.00032	0.970
120	1100	0.0070	0.00064	1	7500	0.022	0.00023	0.970
130	1230	0.0055	0.00045	1	7600	0.015	0.00016	0.970

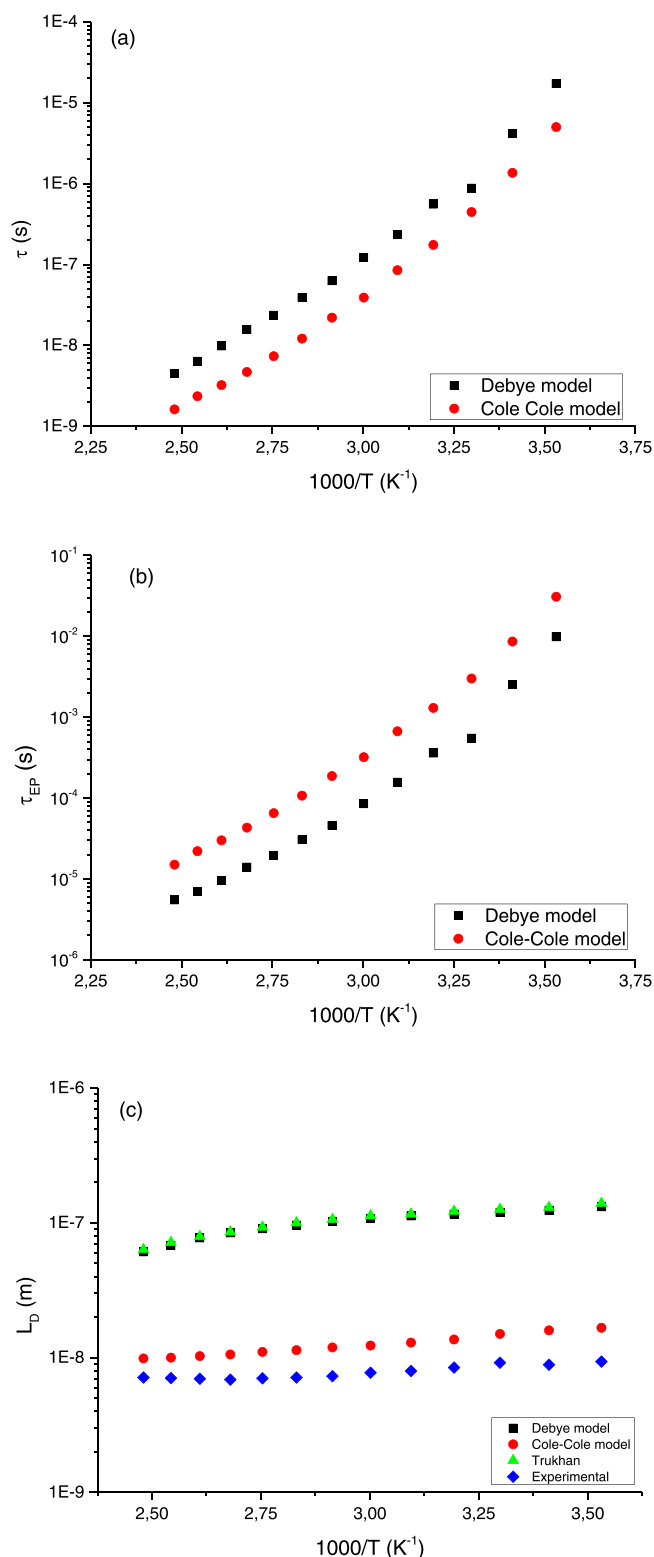


Figure 4. Values of (a) τ , and (b) τ_{EP} obtained for the sample of supported ionic-liquid-like phase (SILLP) following a Debye model (black) a Cole-Cole relaxation model (red). (c) Values of Debye length calculated from Eq. 19, using the Debye model (black) and Eq. 21 for Cole-Cole model (red). For comparison the values of Debye length obtained following the Trukhan model (green) and from experimental values of ε_s and ionic charge density, n , as $L_D = \sqrt{\frac{k_B T \varepsilon_0 \varepsilon_\infty}{nq^2}}$ are also given (blue).

from the values obtained in the fits for τ , τ_{EP} and M , considering Eqs. 19 and 20, respectively. A closer inspection at Fig. 4 allows the observation that experimental data fit using a single Debye to

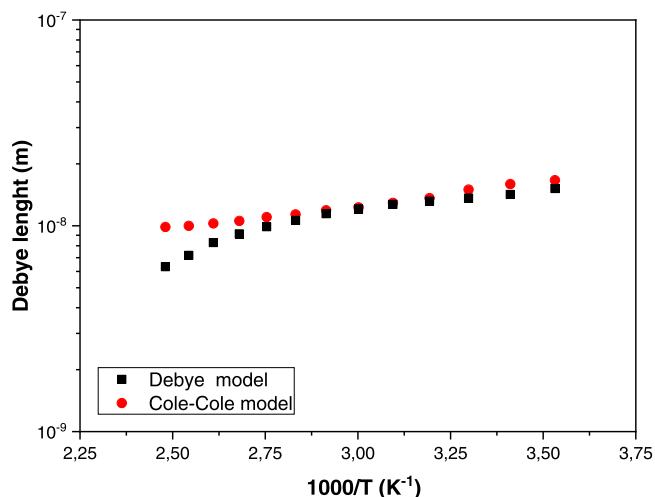


Figure 5. Correlation between the Debye length calculated from Debye model and Cole-Cole model using the value of parameter α determined from experimental fits.

electrode polarization model to analyze the conductivity results from the fits in loss tangent gives an underestimation of the electrode polarization relaxation time respect to the value obtained following the Cole-Cole model. This underestimation is observed for all the temperatures under study with a similar behavior. This has produced a similar increase in the Debye length for all temperatures, this increase being an order of magnitude higher for all of them. This is a consequence of the relaxation time associated with the conduction process obtained from the adjustments in $\tan \delta$. Notice that Eqs. 8 and 9 are different for $\alpha \neq 1$ and therefore the values of τ and τ_{EP} obtained in each fit, Debye and Cole-Cole, are different. Considering Eqs. 19 and 21, the Debye length from the values obtained in the fit of $\tan \delta$, for τ_{EP} , M and τ can be calculated and the obtained values are plotted in Fig. 4c. In this figure, we can observe that the Debye length obtained by Cole-Cole model are around ten times smaller than those obtained using the Debye model and quite similar to the values obtained following the experimental values calculated from $L_D = \sqrt{\frac{k_B T \varepsilon_0 \varepsilon_\infty}{nq^2}}$, where k_B is the Boltzmann constant, T the temperature, ε_0 the vacuum permittivity, ε_∞ the static permittivity, q the is the charge quantity of the ion and n the ionic charge density imbedded into the polymeric matrix of the sample. The differences agree with the value of the parameter α used in the fit of $\tan \delta$ to experimental data by means of the Cole-Cole model.

As displayed in Fig. 5, the results from both models are similar for several temperatures when correlating the two values of the Debye length and considering the value of $\alpha = 0.965$ for the film of supported ionic-liquid-like phase. In this figure the value of Debye length raised to $1/\alpha$ (i.e. $L_D^{1/\alpha}$) and is practically identical to the Debye length determined from the Cole-Cole model to the same experimental data, despite small differences can be appreciated at high temperatures.

From the calculated values of the parameters plotted in Fig. 4 we have calculate the mobility, diffusivity, free charge density and Debye length, following the equations discussed above (Eqs. 14–16) and the results are shown in Fig. 6.

A comparison between Debye and Cole-Cole models with other reported models based on the generalization of the theory of Trukhan³² following the Nernst-Planck electrodiffusion equations linearized for the dielectric dispersion caused by the electrodiffusion of ions in a polymeric membrane charged and confined between two electrodes^{33–37} has been done. The Trukhan model has recently used to estimate ion transport parameters in solid polymer electrolytes.^{38,39} In these studies, the diffusion coefficient of the ionic charge, the mobility, the ionic charge density and the Debye

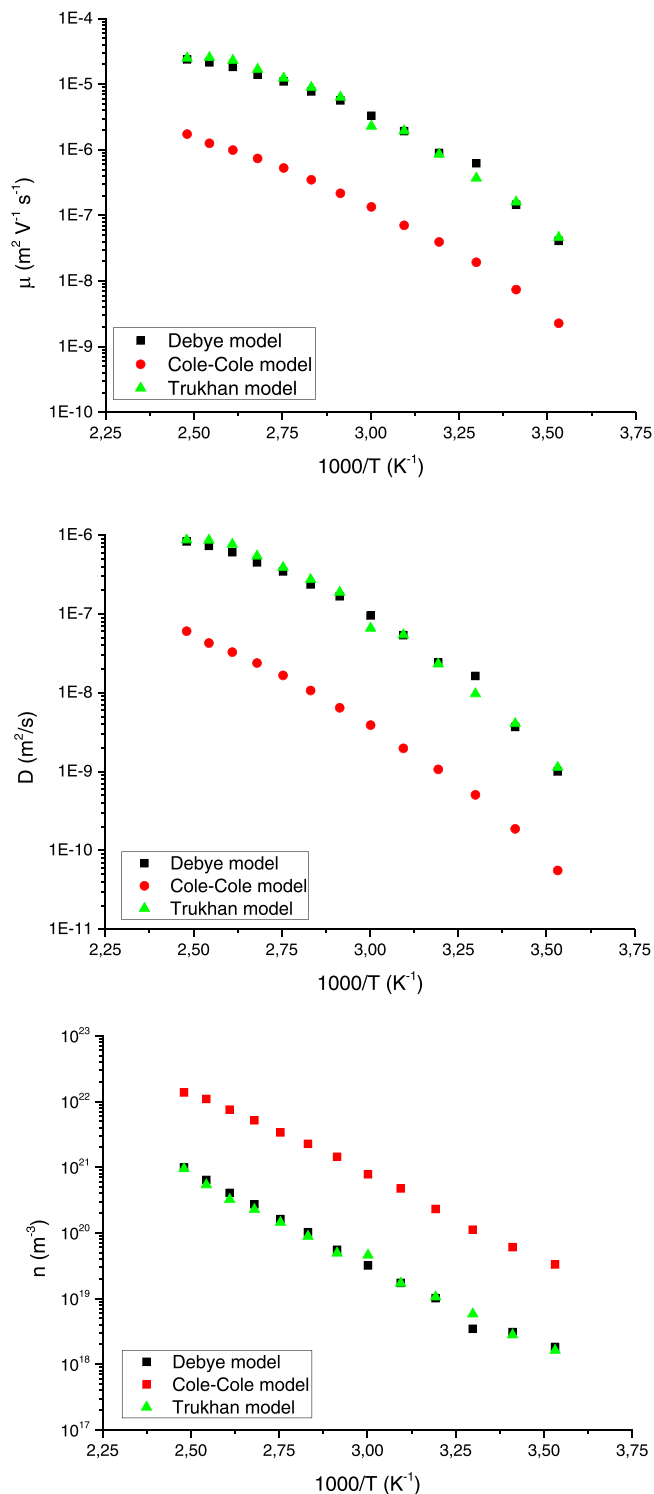


Figure 6. Values of the mobility, diffusion coefficient and free charge density obtained for the sample of supported ionic-liquid-like phase (SILLP) following a Debye model (black), a Cole–Cole relaxation model (red) and Trukhan model (green).

length L_D can be estimated in samples where the peak in loss tangent is clearly observed. In this kind of analysis, the shape of loss tangent plots is correlated to both the capacitive and resistive component of the solid electrolytes. Furthermore, it is rationalized that the shifting of $\tan \delta$ peaks towards the high frequency side is associated with the thermally activated anions.^{6,40–43} Therefore, following the Trukhan model the diffusion coefficient of the charge mobile is given as

$$D = \frac{\omega_{\max}^{\tan \delta} \cdot L^2}{32(\tan^3 \delta)_{\max, \omega}} \quad [22]$$

where $\omega_{\max}^{\tan \delta}$ is the angular frequency corresponding to the peak in loss tangent and $(\tan \delta)_{\max, \omega}$ its value at this frequency, and L the sample thickness. From values of D , it is easy to calculate the mobility by means of Eq. 12 and the carrier charge density from Eq. 11 considering the conductivity values obtained from Bode diagram displayed in Fig. 1b. On the other hand, the Debye length can be estimated from the maximum in loss tangent $\tan \delta_{\max}$ ^{33,34} as

$$L_D = \frac{8 \cdot (\tan \delta_{\max})^2}{L} \quad [23]$$

Then, from the experimental values where the detection of the maximum in $\tan \delta$ is given at moderate or high frequencies, as observed in the sample under study, we have obtained the Debye length, L_D , and the results are plotted in Fig. 6, and compared with the values calculated from Debye and Cole–Cole models.

From these plots, it can be concluded that mobility and diffusivity have the same behavior (Figs. 6a and 6b), as both parameters increase with temperature being higher in the case of the Debye single model, where both parameters decrease one order of magnitude for each temperature if we apply the Cole–Cole model instead of Debye or Trukhan. For the free charge density (Fig. 6c), an increase of the charge density can be observed when using the Cole–Cole model, as expected according to Eq. 16, being the free charge density for each temperature higher when applying the Cole–Cole model instead of the Debye model or Trukhan model. The values shown in Fig. 6c were obtained using the τ_{EP} , M and τ parameters obtained for each one of the two models, i.e. Debye and Cole–Cole, fitting the experimental values in $\tan \delta$ and calculating the Debye length for each model and substituting these values together with the conductivities obtained from Bode diagram for each temperature in agreement with Fig. 1b in Eq. 16.

In summary, the analysis of experimental data using electrochemical impedance spectroscopy under an applied electric field in terms of Coelho model analyzed EP by a Debye relaxation or by a Cole–Cole relaxation model leads to the obtention of different values for the parameters related to mobility, diffusivity, and charge carrier density. Such determination comes from the determination of the other parameters such as τ , τ_{EP} , M and α from fitting the experimental results in $\tan \delta$. Therefore, considering the above-mentioned treatment, the substitution of the distribution of the relaxation times by a distribution of L_D can be very useful when using the Cole–Cole model to better fit experimental data, as shown in the case of high alpha values ($0.9 < \alpha < 1$). However, in cases where the values of α may be minor than 0.9 the differences would still be more pronounced. As can be seen, there is an overestimation in obtaining the diffusivity and consequently an underestimation of the mobile carrier density when using the single Debye model respect, the Cole–Cole relaxation model.

Conclusions

In conclusion, we propose the substitution of the distribution of the relaxation time given by a distribution of L_D which allows to calculate the parameters mobility, diffusivity and carriers charge density as a function of the Debye length. From the electrode polarization analysis used to analyze the ionic transport from experimental measurements of electrochemical impedance spectroscopy, we have shown a correlation between the Debye length with the diffusivity, mobility, and charge carriers' density. This approach allowed us to obtain these parameters with a closer approximation than using the single Debye model. With our approach based on the use of a Cole–Cole relaxation model, the fitting curves of $\tan \delta$ are more precise than these obtained by the single Debye model and the

values of the obtained parameters will allow the obtention of more realistic values of the transport parameters than those obtained following the Debye model.

As can be seen, there is an overestimation in obtaining the diffusivity and consequently an underestimation of the mobile carrier density when using the single Debye model respect, the Cole–Cole relaxation model. All of them are correlated with the Debye length calculated from both models. Our study allows to analyze in detail the charge transport mechanism at the ion-metal interfaces from the Debye length variations. The difference found between the use of a single Debye instead of a Cole–Cole model is attributed with the value of the α parameter, as shown by means of Eqs. 19 and 21.

Appendix

Taking into account Eq. 9, the expression for τ can be obtained

$$\frac{\tau}{\tau_{EP}} = \left[\frac{2L_D}{L} \right]^{1/\alpha} \Rightarrow \tau = \tau_{EP} \left[\frac{2L_D}{L} \right]^{1/\alpha} \quad [\text{A}\cdot 1]$$

whose derivative is given by

$$d\tau = \tau_{EP} \frac{1}{\alpha} \frac{2}{L} \left[\frac{2L_D}{L} \right]^{\frac{1}{\alpha}-1} dL_D \quad [\text{A}\cdot 2]$$

substituting the distribution function for the time constant¹⁶

$$G(\tau) = \frac{1}{2 \cdot \pi \cdot \tau} \frac{\sin(\alpha \cdot \pi)}{\left[\cosh(1 - \alpha) \cdot \log\left(\frac{\tau}{\tau_{EP}}\right) \right] - \cos(\alpha \cdot \pi)} \quad [\text{A}\cdot 3]$$

we have for a distribution of L_D

$$G(L_D) = \frac{1}{2 \cdot \pi \cdot \alpha \cdot L_D} \frac{\sin((1 - \alpha) \cdot \pi)}{\cosh\left[\ln\left(\frac{L_D}{L_{D,0}}\right)\right] - \cos((1 - \alpha) \cdot \pi)} \quad [\text{A}\cdot 4]$$

ORCID

Vicente Compañ  <https://orcid.org/0000-0001-8233-7472>
 Ricardo Diaz-Calleja  <https://orcid.org/0000-0002-0746-3804>
 Joaquín Diaz-Boils  <https://orcid.org/0000-0001-6756-0991>
 Jorge Escorihuela  <https://orcid.org/0000-0001-6756-0991>

References

1. K. D. Kreuer, S. J. Paddison, E. Spohr, and M. Schuster, *Chem. Rev.*, **104**, 4637 (2004).
2. K. D. Fong, J. Self, B. D. McCloskey, and K. A. Persson, *Macromolecules*, **54**, 2575 (2021).
3. R. J. Klein, S. H. Zhang, S. Dou, B. H. Jones, R. H. Colby, and J. Runt, *J. Chem. Phys.*, **124**, 144903 (2006).
4. H. J. Shütt, *Solid State Ionics*, **70**, 505 (1994).
5. T. S. Sorensen, V. Compañ, and R. Diaz-Calleja, *J. Chem. Soc. Faraday Trans.*, **91**, 4235 (1996).
6. T. M. W. J. Bandara, M. A. K. L. Dissanayake, I. Albinsson, and B.-E. Mellander, *Solid State Ionics*, **189**, 63 (2011).
7. F. Tian and Y. Ohki, *J. Phys. D: Applied Phys.*, **47**, 045311 (2014).
8. Y. Wang, C.-N. Sun, F. Fan, J. R. Sangoro, M. B. Berman, S. G. Greenbaum, T. A. Zawodzinski, and A. P. Sokolov, *Phys. Rev.*, **87**, 042308 (2013).
9. D. Valverde, A. García-Bernabé, A. Andrio, E. García-Verdugo, S. V. Luis, and V. Compañ, *Phys. Chem. Chem. Phys.*, **21**, 17923 (2019).
10. A. Andrio, S. I. Hernández, C. García-Alcantara, L. F. del Castillo, V. Compañ, and I. Santamaria-Holek, *Phys. Chem. Chem. Phys.*, **21**, 12948 (2019).
11. V. Compañ, J. Escorihuela, J. Olvera, A. García-Bernabé, and A. Andrio, *Electrochim. Acta*, **354**, 136666 (2020).
12. A. Barjola, J. Escorihuela, A. Andrio, E. Giménez, and V. Compañ, *Nanomaterials*, **8**, 1042 (2018).
13. J. L. Reyes-Rodriguez, J. Escorihuela, A. García-Bernabé, E. Giménez, O. Solorza-Feria, and V. Compañ, *RSC Adv.*, **7**, 53481 (2017).
14. I. Fuentes, A. Andrio, A. García-Bernabé, J. Escorihuela, C. Viñas, F. Teixidor, and V. Compañ, *Phys. Chem. Chem. Phys.*, **20**, 10173 (2018).
15. J. Escorihuela, A. García-Bernabé, A. Montero, A. Andrio, Ó. Sahuquillo, E. Giménez, and V. Compañ, *Polymers*, **11**, 1182 (2019).
16. J. Olvera-Mancilla, J. Escorihuela, L. Alexandrova, A. Andrio, A. García-Bernabé, L. F. del Castillo, and V. Compañ, *Soft Matter*, **16**, 7624 (2020).
17. J. Escorihuela, A. García-Bernabé, and V. Compañ, *Polymers*, **12**, 1374 (2020).
18. R. Coelho, *J. Non-Cryst. Solids*, **131**, 1136 (1991).
19. R. Coelho, *Rev. Phys. Appl.*, **18**, 137 (1983).
20. J. R. MacDonald, *Phys. Rev.*, **92**, 4 (1953).
21. J. R. MacDonald, *J. Chem. Phys.*, **61**, 3977 (1974).
22. B. Altava, V. Compañ, A. Andrio, L. F. del Castillo, S. Molla, M. I. Burguete, E. García-Verdugo, and S. V. Luis, *Polymer*, **72**, 69 (2015).
23. S. Diahm and M. L. Locatelli, *J. Appl. Phys.*, **112**, 13710 (2012).
24. J. Perez, *Acta Metall.*, **32**, 2163 (1984).
25. G. A. Cohen, D. Gelman, and Y. Tsur, *J. Phys. Chem. C*, **125**, 11867 (2021).
26. G. P. Johari and M. J. Goldstein, *J. Chem. Phys.*, **53**, 2372 (1970).
27. G. P. Johari and M. J. Goldstein, *J. Chem. Phys.*, **55**, 4245 (1971).
28. G. P. Johari, *Ann. N.Y. Acad. Sci.*, **279**, 117 (1976).
29. M. Samet, V. Levchenko, G. Boiteux, G. Seytre, A. Kallel, and A. Serghei, *J. Chem. Phys.*, **142**, 194703 (2015).
30. J. R. MacDonald and W. B. Johnson, "Fundamentals of impedance spectroscopy.", ed. E. Barsoukov and J. R. MacDonald *Impedance Spectroscopy: Theory, Experiment, and Applications* (John Wiley & Sons Inc., Hoboken, New Jersey, NJ) 3rd ed. (2018).
31. E. Riande and R. Diaz-Calleja, *Electrical Properties of Polymers*. (Marcel Dekker, Inc, New York, NY) 186 (2004).
32. E. M. Trukhan, *Sov. Phys. Solid State*, **4**, 2560 (1963).
33. T. S. Sorensen, V. Compañ, and R. Diaz-Calleja, *J. Chem. Soc. Faraday Trans.*, **92**, 1947 (1996).
34. V. Compañ, T. S. Sorensen, R. Diaz-Calleja, and E. R. Riande, *J. Appl. Phys.*, **79**, 403 (1996).
35. R. J. Klein, S. Zhang, S. Duo, B. H. Jones, R. H. Colby, and J. Runt, *J. Chem. Phys.*, **124**, 144903 (2006).
36. M. Watanabe, S. Nagano, K. Sanui, and N. Ogata, *Solid State Ionics*, **28–30**, 911 (1988).
37. H. J. Schütt, *Solid State Ionics*, **70**, 505 (1994).
38. H. J. Schütt and E. Gerdes., *J. Non-Crystalline Solids*, **144**, 1 (1992).
39. R. Coelho, *Physics of Dielectrics* (Elsevier Scientific Publishing Company, New York, NY) 97 (1979).
40. S. B. Aziz, W. O. Karim, M. A. Brza, R. T. Abdulwahid, S. R. Saeed, S. Al-Zangana, and M. F. Z. Kadir, *Int. J. Mol. Sci.*, **20**, 5265 (2019).
41. S. B. Aziz, R. B. Marif, M. A. Brza, M. H. Hamsan, and M. F. Z. Kadir, *Polymers*, **11**, 1694 (2019).
42. C. Krause, J. R. Sangoro, C. Iacob, and F. Krmer, *J. Phys. Chem. B*, **114**, 382 (2010).
43. T. M. W. J. Bandara, M. A. K. L. Dissanayake, O. A. Ieperuma, K. Varaprathan, K. Vignarooban, and B.-E. Mellander., *J. Solid State Electrochem.*, **12**, 913 (2008).