A method based on impedance spectroscopy to determine transport properties of polymer electrolytes

A. K. Arof,* S. Amirudin, S. Z. Yusof and I. M. Noor

In this work, we introduce a method based on impedance spectroscopy and the equations developed to evaluate, with a good degree of accuracy, the number density, mobility and diffusion coefficient of mobile ions. Nyquist plots of electrolytes based on poly(acrylonitrile) or PAN and methyl cellulose (MC) incorporated with lithium bis(oxalato)borate have been established from impedance measurements. Equivalent circuits based on a resistor and “leaky capacitor(s)” have been determined and the relevant impedance equations derived. The values of the parameters required in the equation are obtained from the Nyquist plots and the parameters that cannot be obtained from the respective plots have been obtained by trial and error in order to fit the Nyquist plots. The transport parameters are calculated using the developed equations and the results have been compared with those obtained from the broadband dielectric response (BDR) method. Finally, Fourier transform infrared (FTIR) spectroscopy has been used to verify the results obtained from the two approaches at room and elevated temperatures.

1. Introduction

Electrochemical impedance spectroscopy (EIS) is a non-destructive and powerful technique to study ionic conductors. These include liquid electrolytes, fused salts and ionically conducting polymers and glasses. EIS is also useful for the study of fuel cells, rechargeable batteries, electrochemical double layer capacitors and corrosion. EIS can be used to study characteristics of the devices and transport studies in ionic conductors.

Transport studies have been carried out on lithiated transition metal oxides for the Li$_x$V$_2$O$_5$ (ref. 6) and Li$_2$O–TiO$_2$–V$_2$O$_5$ inorganic glassy solid electrolytes. The transport properties of such materials are important in order to assess the performance and also to suggest ways for improvement. By using impedance spectroscopy and the Rice and Roth model, these authors have been able to calculate the diffusion constant ($D$), mobility ($\mu$) and charge carrier concentration ($n$) of these materials. However, the Rice and Roth model is only relevant if the conductivity–temperature relationship obeys an Arrhenius-type of behavior, since the Rice and Roth equation is basically an Arrhenius equation.

A more direct method to calculate the parameters mentioned above has been developed by Bandara and Mellander. They have tested the method on an aqueous KI electrolyte as well as on a PEO-based iodide ion conducting polymer electrolyte. We have also developed another method with the necessary equations to evaluate the number, mobility and diffusion coefficient of mobile ions, which is also based on impedance spectroscopy. In this work, we will compare the results obtained from the broadband dielectric response (BDR) method developed by Bandara and Mellander. Finally, to verify the two approaches, the three parameters are also derived from Fourier transform infrared (FTIR) spectroscopy results. Petrowsky and Frech have used FTIR to determine number density and mobility of mobile ions in liquid electrolytes while Ericson et al. have used it for a gel polymer electrolyte.

2. Theory

The fundamental property of a polymer electrolyte is conductivity ($\sigma$). Conductivity in principle is the product of the number density ($n$), the mobility ($\mu$) of charge carriers and the elementary charge ($e$). It will be useful if $n$ and $\mu$ can be determined quantitatively and Bandara and Mellander have shown that the number density and mobility of charge carriers can be evaluated from impedance measurements.

According to these authors, the real and imaginary impedance of a polymer electrolyte sandwiched between two blocking
electrodes for impedance measurements can be represented by the following equations:

\[ Z_t = \frac{R}{1 + (\omega RC)^2} \]  

(1)

and

\[ Z_i = \frac{\omega R^2 C}{1 + (\omega RC)^2} + \frac{2}{\omega C_e} \]  

(2)

\[ Z_t \] and \[ Z_i \] are the real and imaginary impedance, respectively. \( \omega \) is the angular frequency. \( C_e \) is the electrical double layer (EDL) capacitance. \( C \) is the bulk geometrical capacitance and \( R \) is the bulk resistance of the polymer electrolyte. The form of eqn (1) and (2) implies that the Nyquist plot consists of a perfect semicircle with its center on the real impedance axis and a vertical spike. The spike is represented by the second term on the right hand side (RHS) of eqn (2) and implies a perfect capacitor. The factor 2 on the RHS of eqn (2) takes into account the two EDL layers formed on both sides of the electrolyte, which are in contact with the electrodes. The EDL is formed when ions accumulate at the electrode/electrolyte interfaces. These parameters are given by:

\[ C_e = \frac{\varepsilon_0 \varepsilon A}{\lambda} \]  

(3)

\[ C = \frac{\varepsilon_0 \varepsilon A}{2d} \]  

(4)

\[ R = \frac{2d}{\sigma A} \]  

(5)

Here, \( \varepsilon \) is the dielectric constant of the electrolyte, \( \varepsilon_0 \) is the vacuum permittivity \( (8.85 \times 10^{-14} \, \text{F cm}^{-1}) \), \( \lambda \) is the thickness of the electrical double layer, \( d \) is the half thickness of the polymer electrolyte and \( A \) is the electrode/electrolyte contact area. The dissipative loss curve following the BDR or Bandara–Mellander (B-M) approach is given by

\[ \tan(\phi) = \frac{\omega \tau_2 \sqrt{\delta}}{1 + (\omega \tau_2)^2} \]  

(6)

Bandara and Mellander\textsuperscript{9,10} have shown that the peak of the dissipative loss curve is given by

\[ (\tan(\phi))_{\text{max}} = \frac{\sqrt{\delta}}{2} \]  

(7)

Here, \( \omega \) is the angular frequency and \( \tau_2 \) is a time constant corresponding to the maximum dissipative loss curve, \( \delta = d/\lambda \). The B-M approach defines the diffusion coefficient \( (D) \), mobility \( (\mu) \) and number density \( (n) \) of the mobile ion by the following equations:

\[ D = \frac{d^2}{\tau_2 \delta} \]  

(8)

\[ \mu = \frac{ed^2}{kT \tau_2 \delta} \]  

(9)

\[ n = \frac{\kappa T \tau_2 \delta^2}{e^2 d^2} \]  

(10)

The values of \( D, \mu \) and \( n \) in eqn (8)–(10) are dependent on the EDL layer. The number density, \( n \), of the mobile ions in eqn (10) is actually the sum of the number density of cations, \( n_+ \), and anions, \( n_- \). The ionic mobility calculated here is the mean mobility of cations and anions \( (\mu = (n_- \mu_+ + n_+ \mu_-)/n) \). Knowing the transference number of the anions and cations, \( n_+ \), \( n_- \), \( \mu_+ \), \( \mu_- \), \( D_+ \) and \( D_- \) can be evaluated. Impedance measurements normally generate Nyquist plots that can consist of (i) a depressed semicircle, (ii) a tilted spike or (iii) a depressed semicircle with a tilted spike. This is in contrast to the Nyquist plot adopted by Bandara and Mellander\textsuperscript{9} in developing eqn (8)–(10), which assumes that the ions have a single relaxation time. An equivalent circuit comprising a constant phase element and a resistor connected in parallel can represent the Nyquist plot that takes the shape of a depressed semicircle. The constant phase element (CPE) is a “leaky capacitor”. A resistor in series with a CPE can represent the plot that takes the shape of a spike. The Nyquist plot that consists of a depressed semicircle with a tilted spike can be represented by a parallel combination of a resistor and CPE that are connected in series with another CPE.\textsuperscript{1,13} The depressed semicircle represents the bulk material while the tilted spike represents the electrical double layer.

The real and negative imaginary part of the complex impedance of the “leaky capacitor” is given by the equations:

\[ Z_t = \frac{\cos(\frac{\pi p}{2})}{k^{-1} \omega p} \]  

(11)

and

\[ Z_i = \frac{\sin(\frac{\pi p}{2})}{k^{-1} \omega p} \]  

(12)

Hence, the real and negative imaginary parts of a Nyquist plot consisting of a depressed semicircle and tilted spike are given by the equations:

\[ Z_t = \frac{R + R_k^{-1} \omega p \cos(\frac{\pi p_1}{2})}{1 + 2 R_k^{-1} \omega p \cos(\frac{\pi p_1}{2}) + R_k^{-2} \omega^2 p_1} + \frac{\cos(\frac{\pi p_2}{2})}{k^{-2} \omega p_2} \]  

(13)

and

\[ Z_i = \frac{2 R_k^{-1} \omega p \sin(\frac{\pi p_1}{2})}{1 + 2 R_k^{-1} \omega p \cos(\frac{\pi p_1}{2}) + R_k^{-2} \omega^2 p_1} + \frac{\sin(\frac{\pi p_2}{2})}{k^{-2} \omega p_2} \]  

(14)

According to Linford,\textsuperscript{13} the inverse of \( k \), i.e. \( k^{-1} \), in the complex impedance equation of the “leaky capacitor” corresponds to the capacitance. Thus, in eqn (13) and (14), \( k^{-1} \) is the bulk geometrical capacitance of the polymer electrolyte and \( k^{-1} \) is the capacitance due to the EDL formed at the electrode/electrolyte interface during the impedance measurement, which is equivalent to the capacitance, \( C_t \), in the impedance equation used by Bandara and Mellander.\textsuperscript{9} \( R \) is the bulk resistance of the electrolyte. \( p_1 \) is the ratio of the angle between the diameter of the depressed semicircle and the \( Z_i \) axis to the right angle subtended by the real and imaginary impedance axes. \( p_2 \) is the skew parameter that controls the degree of...
the inclination of the tilted spike from the \( Z \) axis. The values of the \( p_1 \) and \( p_2 \) parameters lie between 0 and 1, as shown in Fig. 1.

If the Nyquist plot consists of a depressed semicircle and a tilted spike, eqn (13) and (14) should be used to fit the graph. The values of \( R \), \( p_1 \) and \( p_2 \) can be determined from the Nyquist plot, as shown in Fig. 1. The values of \( k_1^{-1} \) and \( k_2^{-1} \) can be obtained by trial and error until the experimental plot is fitted. The values of \( k_1^{-1} \) and \( k_2^{-1} \) can also be obtained using nonlinear least squares software.

From Bandara and Mellander,\textsuperscript{9,10} the diffusion coefficient \( (D) \) of charge carriers in the electrolyte is given by:

\[
D = \frac{\lambda^2}{\tau_2} \tag{15}
\]

where \( \tau_2 = \frac{1}{\omega_2} \) with \( \omega_2 \) being the angular frequency corresponding to the minimum in the imaginary impedance, \( Z_i \) (Fig. 1). Since capacitance \( c_2 \) is equivalent to capacitance \( C_e \), eqn (3) can be written as:

\[
k_2^{-1} = \frac{e_0 A}{\lambda} \tag{16}
\]

Hence,

\[
\lambda = k_2 e_0 A \tag{17}
\]

The diffusion coefficient \( (D) \) in eqn (15) can be substituted using eqn (17) to obtain:

\[
D = \frac{(k_2 e_0 A)^2}{\tau_2} \tag{18}
\]

The mobility \((\mu)\) of the charge carriers can be determined from the Nernst–Einstein relation,

\[
\mu = \frac{eD}{k_b T} \tag{19}
\]

where \( k_b \) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ J K}^{-1})\), \( T \) is the absolute temperature in Kelvin and \( e \) is the electron charge \((1.602 \times 10^{-19} \text{ C})\). Eqn (18) can be substituted into eqn (19) to obtain:

\[
\mu = \frac{e(k_2 e_0 A)^2}{k_b T \tau_2} \tag{20}
\]

Since conductivity \((\sigma)\) is given by

\[
\sigma = n e \mu \tag{21}
\]
Fig. 3 Nyquist plots (○) and their corresponding fitted points (●) for PAN with (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50 wt% LiBOB concentration.

Fig. 4 Plot of the real part of the complex permittivity, $\varepsilon_r$, as function of frequency for the PAN–LiBOB electrolyte system. The inset figure shows $\varepsilon_r$ in the frequency range between $\log f = 4.5$ and $\log f = 5$. 

The number density of charge carriers ($n$) can be obtaining using equation:

$$n = \frac{\sigma k_B T \tau_2}{(\varepsilon k_2 e_0 A)^2} \quad (22)$$

Thus, using eqn (18), (20) and (22) the value of each parameter can be obtained from the fitted Nyquist plot, and the diffusion coefficient ($D$), mobility ($\mu$) and number density ($n$) of charge carriers in the electrolyte can be determined. These equations are not dependent on the value of $\delta$ and although the equations depend on the value of $\varepsilon_r$, transforming the impedance data into the permittivity formalism and plotting log $\varepsilon_r$ versus frequency will enable the value to be obtained.

3. Experimental

3.1. Materials and sample preparation

Polyacrylonitrile (PAN) with MW = 150 000 g mol$^{-1}$ was obtained from Aldrich and used as received. Lithium bis(oxalato)borate (LiBOB) with MW = 193.79 g mol$^{-1}$ was purchased from Chemetall. PAN–LiBOB polymer electrolytes were prepared by a solution casting technique. The desired amounts of the polymer and salt, as shown in Table 1, were dissolved in

Table 3  The values of $k_2$, $\varepsilon_r$, $\tau_2$, $D$, $\mu$ and $n$ for the PAN–LiBOB electrolyte system obtained using the proposed method

<table>
<thead>
<tr>
<th>LiBOB content (wt%)</th>
<th>$k_2$ (F$^{-1}$)</th>
<th>$\varepsilon_r$ (at 100 kHz)</th>
<th>$\tau_2$ ($\times 10^{-4}$ s$^{-1}$)</th>
<th>$D$ ($\times 10^{-10}$ cm$^2$ s$^{-1}$)</th>
<th>$\mu$ ($\times 10^{-8}$ cm$^2$ V$^{-1}$ s)</th>
<th>$n$ ($\times 10^{19}$ cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>150 000 ± 14 142</td>
<td>5.77 ± 2.08</td>
<td>1.84 ± 1.48</td>
<td>3.67 ± 1.31</td>
<td>1.43 ± 0.51</td>
<td>7.78 ± 0.26</td>
</tr>
<tr>
<td>20</td>
<td>118 333 ± 12 583</td>
<td>13.13 ± 4.03</td>
<td>3.04 ± 1.32</td>
<td>6.09 ± 0.33</td>
<td>2.37 ± 0.13</td>
<td>8.77 ± 0.57</td>
</tr>
<tr>
<td>30</td>
<td>35 575 ± 1786</td>
<td>34.7 ± 2.01</td>
<td>0.80 ± 0.00</td>
<td>14.92 ± 2.54</td>
<td>5.81 ± 0.99</td>
<td>17.30 ± 3.94</td>
</tr>
<tr>
<td>40</td>
<td>15 500 ± 804</td>
<td>83.53 ± 3.62</td>
<td>0.32 ± 0.00</td>
<td>40.73 ± 3.69</td>
<td>15.86 ± 1.44</td>
<td>25.85 ± 3.17</td>
</tr>
<tr>
<td>50</td>
<td>83 833 ± 1669</td>
<td>208.58 ± 30.47</td>
<td>0.77 ± 0.15</td>
<td>94.85 ± 20.07</td>
<td>36.93 ± 7.81</td>
<td>32.27 ± 3.50</td>
</tr>
</tbody>
</table>

Fig. 5  FTIR deconvolution of PAN with (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50 wt% LiBOB concentration at the band between 1750 and 1850 cm$^{-1}$. 
30 mL of N,N-dimethylformamide procured from Riendemann Schmidt. The mixtures were stirred continuously at room temperature to obtain homogeneous solutions. All the preparations were carried out in a dry box due to the hygroscopic nature of the LiBOB salt. The solutions were cast into glass petri dish and dried at 60 °C under vacuum for 24 hours to remove further traces of the solvent and even water.

Electrolytes based on methyl cellulose (MC) were also prepared by the solution casting technique using dimethyl sulfoxide (DMSO) as a solvent. MC was procured from Aldrich. Table 2 lists the composition of the MC–LiBOB electrolyte system. The desired amounts of MC and LiBOB were dissolved in 30 mL DMSO. The mixtures were stirred continuously at room temperature and the homogeneous solutions obtained were then poured into several glass petri dish. The solutions were left to evaporate under vacuum at 60 °C until films formed. The films were then kept in a desiccator to remove further traces of the solvent and water.

3.2. Sample characterization

3.2.1. Electrochemical impedance spectroscopy (EIS). In EIS, a small sinusoidal potential is applied across the sample and the current through the sample is measured. From these, the impedance was obtained for every operating frequency. The applied voltage was set small (10 mV) in order to minimize possible charge carrier concentration changes and the time average of the changes during the measurements. In this work, a HIOKI 3520 LCR Hi-Tester was used to carry out impedance measurements in the frequency range from 50 Hz to 100 kHz at room and elevated temperatures. Two stainless steel disc electrodes 2 cm in diameter were used to sandwich the polymer electrolyte films, which were cut into small discs with diameters of 2.2 cm.

3.2.2. Fourier transform infrared (FTIR) spectroscopy. A Thermo Scientific model Nicolet iS10 spectrometer has been used to obtain the IR spectrum of the samples. The spectrum was recorded in the transmittance mode between 4000 and 650 cm⁻¹ at a 4 cm⁻¹ resolution at room and elevated temperatures. Based on the report by Holomb et al.,¹⁴ the band from BOB⁻ anions can be observed at 1804 cm⁻¹ while contact ions appear at 1812, 1817 and 1828 cm⁻¹. Hence, the wavenumbers between 1850 and 1750 cm⁻¹ are of interest since the bands representing the free and contact ions are within this region. Before deconvoluting the band between 1850 and 1750 cm⁻¹, the spectrum for all the electrolytes was converted into the absorbance mode. The deconvolution was based on the Gaussian–Lorentz function using the non-linear least squares (NLLS) fitting software. In the deconvolution process, peaks due to LiBOB were selected and the sum of the intensity of all the deconvoluted peaks was ensured to fit the original spectrum. The peak close to 1804 cm⁻¹ was assigned to free ions and the peaks close to 1812, 1817 and 1828 cm⁻¹ were assigned to contact ions. The area under the peak was determined and the percentage of free ions was calculated using the equation below:

\[
\text{Percentage of free ions (\%)} = \frac{A_f}{A_f + A_c} \times 100\% \tag{23}
\]

Here, \(A_f\) is the area under the peak representing the free ions region and \(A_c\) is the total area under the peak representing the contact ions.

4. Results and discussion

4.1. PAN–LiBOB electrolyte system

Fig. 2 shows the room temperature (25 °C) conductivity of the PAN–LiBOB electrolytes as a function of LiBOB concentration.
Eqn (5) was used to calculate the conductivity of the electrolyte system after the bulk resistance was determined from the Nyquist plot. It is observed that the addition of 10 wt% LiBOB salt into the polymer host resulted in a polymer electrolyte with a conductivity of $1.79 \times 10^{-7}$ S cm$^{-1}$. The conductivity is observed to increase with an increase in the LiBOB salt content.

**Fig. 7** Dielectric loss tangents, tan(φ), (O) and their corresponding fitted lines (——) as a function of frequency for PAN with (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50 wt% LiBOB concentration.

**Table 5** The values of $2d$, $\tau_2$, $\delta$, $n$, $\mu$ and $D$ obtained using the B–M method

<table>
<thead>
<tr>
<th>LiBOB content (wt%)</th>
<th>$2d$ ($\times 10^{-2}$ cm)</th>
<th>$\tau_2$ ($\times 10^{-4}$ s$^{-1}$)</th>
<th>$\delta$</th>
<th>$n$ ($\times 10^{17}$ cm$^{-3}$)</th>
<th>$\mu$ ($\times 10^{-5}$ cm$^2$ V$^{-1}$ s)</th>
<th>$D$ ($\times 10^{-7}$ cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.50 ± 0.21</td>
<td>2.12 ± 1.50</td>
<td>360.43 ± 61.64</td>
<td>1.27 ± 0.30</td>
<td>0.88 ± 0.14</td>
<td>2.27 ± 0.35</td>
</tr>
<tr>
<td>20</td>
<td>0.99 ± 0.31</td>
<td>5.75 ± 3.96</td>
<td>416.95 ± 321.02</td>
<td>2.19 ± 1.71</td>
<td>0.95 ± 0.56</td>
<td>2.45 ± 1.43</td>
</tr>
<tr>
<td>30</td>
<td>0.58 ± 0.03</td>
<td>1.17 ± 0.34</td>
<td>337.71 ± 41.45</td>
<td>4.00 ± 0.88</td>
<td>2.45 ± 0.45</td>
<td>6.30 ± 1.15</td>
</tr>
<tr>
<td>40</td>
<td>1.00 ± 0.00</td>
<td>0.44 ± 0.02</td>
<td>238.71 ± 3.10</td>
<td>1.05 ± 0.01</td>
<td>38.84 ± 1.11</td>
<td>99.71 ± 2.85</td>
</tr>
<tr>
<td>50</td>
<td>1.20 ± 0.17</td>
<td>0.34 ± 0.14</td>
<td>235.60 ± 67.55</td>
<td>1.63 ± 0.27</td>
<td>74.31 ± 35.26</td>
<td>190.75 ± 90.56</td>
</tr>
</tbody>
</table>
in the PAN polymer. The conductivity increases until $1.94 \times 10^{-5}$ S cm$^{-1}$ at 50 wt% LiBOB. The increase in conductivity with salt concentration could be attributed to either an increase of mobility and/or number density of charge carriers. The mobile ions could also reduce in number due to recombination–ion association processes. This is where there is a need to evaluate

Fig. 8  Plot of charge carrier number density, $n$, against the LiBOB concentration obtained from the proposed method, FTIR and B–M method for the PAN–LiBOB electrolyte system.

Fig. 9  Charge carrier mobility, $\mu$, against the LiBOB concentration obtained from the proposed method, FTIR and B–M method for the PAN–LiBOB electrolyte system.

Fig. 10  Diffusion coefficient, $D$, against the LiBOB concentration obtained from the proposed method, FTIR and B–M method for the PAN–LiBOB electrolyte system.
the number density of mobile ions and their mobility. Although ion association can be determined through the FTIR technique and mobility can be determined by the nuclear magnetic resonance (NMR) technique or transient ionic current (TIC) technique, NMR is expensive and TIC has problems with reproducibility. The proposed method can be a way to determine these transport properties. Hence, the method proposed in this work was used to determine the diffusion coefficient \( D \), ion mobility \( \mu \) and the number density of charge carriers \( n \) in the polymer electrolyte.

From the Nyquist plot obtained by the impedance measurement, eqn (13) and (14) were used to fit the plot. The values of \( R \), \( p_1 \) and \( p_2 \) were determined by the concept shown in Fig. 1. The parameters \( k_1^{-1} \) and \( k_2^{-1} \) were determined by trial and error until the fitted points quite accurately approximate the Nyquist plot at the corresponding frequencies. Fig. 3 shows the Nyquist plots and their corresponding fitted points for the PAN–LiBOB electrolyte system. All the fitted points are observed to fit the plot and the average error percentage for \( Z_1 \) and \( Z_1 \) for all the samples is less than 5%.

It is to be noted that in the method proposed, the actual Nyquist plot representing the sample has been used in the analysis. From the impedance data, the dielectric constant, \( \varepsilon_r \), for each sample can be obtained by a plot of the real part of the complex permittivity, \( \varepsilon_r \), versus frequency, \( f \). The impedance data were substituted in the equation below:

\[
\varepsilon_r = \frac{Z_1}{(Z_1^2 + Z_2^2)} \left( \frac{d}{\omega \varepsilon_0 A} \right) \tag{24}
\]

Fig. 4 shows the plot of log \( \varepsilon_r \) versus log \( f \) for the PAN–LiBOB electrolyte system. The inset figure shows the enlarged real part of the complex permittivity, \( \varepsilon_r \), between log \( f = 4.5 \) and log \( f = 5 \). It is observed that all the samples show a constant value between log \( f = 4.5 \) and log \( f = 5 \). Hence, the value of the dielectric constant, \( \varepsilon_r \), for all the samples was taken at 100 kHz.

Using eqn (18), (20) and (22), the values of the diffusion coefficient \( D \), mobility \( \mu \) and number density \( n \) of the charge carriers of the PAN–LiBOB electrolyte system can be calculated if the values of \( k_2 \), \( \varepsilon_r \) and \( \tau_2 \) are known. From the fitting of the Nyquist plot (Fig. 3), the value of \( k_2 \) can be obtained. The value of \( \tau_2 \) was taken at the frequency corresponding to a minimum in the imaginary parts of the impedance, \( Z_i \), i.e. at \( Z_i \to 0 \). The value of \( \varepsilon_r \) was taken in the high frequency range and in this work at 100 kHz (Fig. 4). Table 3 lists the values of \( k_2 \), \( \varepsilon_r \), \( \tau_2 \), \( D \), \( \mu \) and \( n \) for the PAN–LiBOB electrolyte system obtained using the proposed method.

In order to validate the values of the diffusion coefficient \( D \), mobility \( \mu \) and number density \( n \) of the charge carriers of the PAN–LiBOB electrolyte system, FTIR spectroscopy was carried out on all the samples. Fig. 5 represents the FTIR band in the absorbance mode from 1850 to 1750 cm\(^{-1}\). The free ion peak is located at 1801–1802 cm\(^{-1}\) and the contact ions are observed at 1812–1813 and 1826 cm\(^{-1}\). The percentage area of the free ion and contact ion bands were determined by the software used and the areas are plotted as a function of LiBOB content in Fig. 6.
The area of the free ions is observed to increase as the LiBOB content increases, in contradiction to the behaviour of the contact ions which decreases with an increase in the LiBOB content. The number density, mobility and diffusion coefficient of the mobile ions were calculated following eqn (25)–(27):

\[ n = \frac{M \times N_A}{V_{\text{Total}}} \times \text{free ions (\%)} \]  

In eqn (25), \( M \) is the number of moles of salt used in each electrolyte, \( N_A \) is Avogadro's number \((6.02 \times 10^{23} \text{ mol}^{-1})\), \( V_{\text{Total}} \) is the volume of the total solution, and \( M_{\text{Total}} \) is the molar mass of the salt.

\[ \mu = \frac{\sigma}{ne} \]  

\[ D = \frac{\mu kT}{e} \]

In eqn (26), \( \mu \) is the mobility, \( \sigma \) is the electrical conductivity, \( n \) is the number density, \( e \) is the elementary charge, \( k \) is the Boltzmann constant, and \( T \) is the temperature.

In eqn (27), \( D \) is the diffusion coefficient.

Fig. 11  Plot of (a) the charge carrier number density, (b) mobility and (c) diffusion coefficient against the LiBOB concentration obtained using proposed method, FTIR and B–M method for the MC–LiBOB electrolyte system.
is the total volume of the solid polymer electrolyte and \( \sigma \) is dc conductivity. In eqn (26), \( e \) is the electric charge \( (1.602 \times 10^{-19} \) C), \( k \) is the Boltzmann constant \( (1.38 \times 10^{-23} \) J K\(^{-1}\)) and \( T \) is the absolute temperature in eqn (27). Table 4 lists the values of \( V_{\text{total}} \) the free ions (%), \( n \), \( \mu \) and \( D \) obtained from the FTIR method.

For comparison purposes, we now analyze the impedance data based on the BDR or B–M approach. The impedance data obtained from the experiment can be transformed into the loss tangent formalism, \( \tan(\phi) \), using the equation below.

\[
\tan(\phi) = \frac{Z_f}{Z_i}
\]

(28)

The plot derived from eqn (28) was fitted with the equation:

\[
\tan(\phi) = \frac{\omega \tau_2 \sqrt{\delta}}{1 + (\omega \tau_2)^2}
\]

(29)

Here, \( \tau_2 \) is the reciprocal of the frequency when \( \tan(\phi) \) is a maximum. The dissipative loss curves obtained using the impedance data and the fitting data (solid line) are shown in Fig. 7. Eqn (10), (14) and (16) were used to calculate the values of \( D \), \( \mu \) and \( n \). Table 5 lists the values for the number density \( (n) \), mobility \( (\mu) \) and diffusion coefficient \( (D) \) of the mobile ions determined by the B–M method.

It can be observed that the fitting of the dissipative loss curve is not that reliable on the low frequency side. This could be due to the type of Nyquist plot used to develop the B–M method. In this method, no parameter can be adjusted since \( \delta \) used in the equation is from a \( \tan(\phi) \) versus frequency curve based on experimental impedance data.

Fig. 8 compares the variation in the charge carriers or the number density of mobile ions \( (n) \) obtained using the method proposed, the broadband dielectric response (BDR) or the B–M method and is verified with the results from the FTIR spectroscopy. The results obtained from the proposed method and from the FTIR spectroscopy are quite close compared to the results from the BDR approach. The trend in the variation of \( n \) exhibited by the results from the proposed method and from FTIR results are also quite similar compared to the results from the BDR method, which shows a dip in \( n \) at a 40 wt% LiBOB concentration.

Fig. 9 and 10 show the variations in the ionic mobility and diffusion coefficient with LiBOB concentration. Again, the calculations show that the results from the proposed method show a closer agreement to the vibrational spectroscopy results compared to the results from the BDR method.

### 4.2. MC–LiBOB electrolyte system

In an effort to realize the versatility of the proposed method, it was tested on another polymer electrolyte system. The values of \( n \), \( \mu \) and \( D \) and other parameters vital for their calculation and their variation with the LiBOB content are shown in Table 6 and Fig. 11 respectively.

To provide further evidence of the versatility of this method, \( n \), \( \mu \) and \( D \) variation with temperature was analysed for the 91 wt% MC–9 wt% LiBOB sample. The results are listed in Table 7.
It can be observed that the results from the proposed method are much closer to the FTIR results compared to the results obtained from the B–M method in the temperature range from 35 to 100 °C for n, μ and D.

5. Conclusions

We have developed the equations required to calculate the number density, mobility and diffusion coefficient of mobile ions that are not dependent on the EDL layer and solely from impedance spectroscopy. Two types of polymer electrolyte systems, i.e. PAN–LiBOB and MC–LiBOB systems, were considered to test the method developed. The results from the present method are in better agreement with the results from FTIR spectroscopy compared to the results from the broadband dielectric response approach. The present method is also independent of any conductivity–temperature relationship and on the EDL layer.

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References

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