Study FTIR and AC Conductivity of Nanocomposite Electrolytes

Elaaf Ali Swady*, Mohammed Kadhim Jawadb
Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq
bEmail: elaafalie@gmail.com, mohamedkadhom@yahoo.com
*Corresponding author: mohamedkadhom@yahoo.com

Abstract
In the present work polymer electrolytes were formulated using the solvent casting technique. Under special conditions, the electrolyte content was of fixed ratio of polyvinylpyrrolidone (PVP): polyacrylonitrile (PAN) (25:75), ethylene carbonate (EC) and propylene carbonate (PC) (1:1) with 10% of potassium iodide (KI) and iodine I2 = 10% by weight of KI. The conductivity was increased with the addition of ZnO nanoparticles. It is also increased with the temperature increase within the range (293 to 343 K). The conductivity reaches maximum value of about (0.0296 S.cm-1) with (0.25 g) ZnO. The results of FTIR for blend electrolytes indicated a significant degree of interaction between the polymer blend (PVP and PAN) and the KI salt. From the electrolyte observations of the nanocomposites, the broad peak became narrower after adding the ZnO nanoparticle to the KI salt. The dielectric reaction decreased with the increase of the frequency at room temperature. The high dielectric permittivity of the polymer at lower frequencies can be attributed to the dipoles having sufficient time to get aligned with the electric field, resulting in higher polarization.

Key words: Blend polymer, Conductivity, Iodide salts, Nanomaterial, Dielectric constant.

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1. Introduction
In the coming future, thanks to the full exploitation of nanotechnology, lithium batteries are expected to play a major role not only in powering small electronic equipment, but also in fueling more demanding sectors such as automobile storage and massive networks [1]. However, this paradigm change is hardly achievable. Research have been directed to the preparation and characterization of electrolytes that display higher ionic conductivity at room temperature[2]. The electrolyte is sandwiched between anode and cathode of a battery to complete the circuitry. Initially, the routine fluid electrolytes were supplanted by gel polymer electrolytes and afterward by composite strong polymer electrolytes [3]. With the utilization of polymer electrolyte of lithium batteries, tall particular vitality and particular control, secure operation, adaptability in bundling and fetched of creation can be anticipated [4]. The conductivity of strong polymer electrolyte can be upgraded by including a plasticizer to create a gel polymer electrolyte occurs [5-7]. The nanocomposite improves the mobility of cation, while drastically reduce the mobility of anion due to the intercalation of cations into the layered silicate where the bulky anions are not able to enter. Such a class of materials is termed polymer nanocomposites [8]. This featuring idea was put forward by Aranda and Ruiz-Hitzky and it was popularized by Vaia et al. [9]. Lately, a number of studies on polymer nanocomposites have been published [10, 11]. It is emphasized that the ionic transport takes place in the amorphous phase as compared to the crystalline phase [12-14]. The mean aim of this search is to study the effect of ZnO nanoparticle on the conductivity and dielectric properties of the polymer blend nanocomposites, in addition to the variation of the band and bond position.
2. Experimental work

2.1. Materials and method

PAN (Mw 150000), PVP (average Mw 40.000), KI, ZnO, I₂, (PC), and (EC) all with pureness more than 98%, were bought from Sigma Aldrich. The samples were prepared with a constant ratio of PAN (75%), PVP (25%), KI 50%, EC, and PC of (1:1) ratio as tabulated in Table 1. At first, sufficiency amount of EC, PC, and KI were blended in a glass tube with uninterrupted stirring for 2 h at 50 °C. PAN and PVP were added to the mixture with an additional stirring for 2 h at 40 °C. After that ZnO nanoparticles were added to the electrolyte with diverse weight percent with very slow stirring for half hour to prevents much as possible any aggregation and any agglomeration of ZnO nanoparticles. Finally, iodine I₂ (10% wt. of KI) was added to the mixture seen in Table 2 with uninterrupted stirring for 20 min until obtained gelation.

Table 1: The composition of (PVP&PAN) electrolytes Cs.

<table>
<thead>
<tr>
<th>Assignments</th>
<th>KI %</th>
<th>KI (g)</th>
<th>Nano-ZnO (g)</th>
<th>I₂ (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>50</td>
<td>0.4</td>
<td>0.05</td>
<td>0.0612</td>
</tr>
<tr>
<td>C2</td>
<td>50</td>
<td>0.4</td>
<td>0.1</td>
<td>0.0612</td>
</tr>
<tr>
<td>C3</td>
<td>50</td>
<td>0.4</td>
<td>0.15</td>
<td>0.0612</td>
</tr>
<tr>
<td>C4</td>
<td>50</td>
<td>0.4</td>
<td>0.2</td>
<td>0.0612</td>
</tr>
<tr>
<td>C5</td>
<td>50</td>
<td>0.4</td>
<td>0.25</td>
<td>0.0612</td>
</tr>
</tbody>
</table>

Table 2: FTIR bands for pure blend PVP: PAN and nanocomposites reinforced with different ZnO NPs concentrations.

<table>
<thead>
<tr>
<th>Band Type</th>
<th>Pure (Cm⁻¹)</th>
<th>F1 (Cm⁻¹)</th>
<th>F2 (Cm⁻¹)</th>
<th>F3 (Cm⁻¹)</th>
<th>F4 (Cm⁻¹)</th>
<th>F5 (Cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>3583.08</td>
<td>3563.41</td>
<td>3560.91</td>
<td>3563.41</td>
<td>3575.88</td>
<td>3563.41</td>
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<tr>
<td>CH2 symmetric</td>
<td>2988.52</td>
<td>2989.60</td>
<td>2989.60</td>
<td>2989.60</td>
<td>2987.11</td>
<td>2989.60</td>
</tr>
<tr>
<td>CH2 asymmetric</td>
<td>2928.70</td>
<td>2929.73</td>
<td>2929.73</td>
<td>2929.73</td>
<td>2929.73</td>
<td>2929.73</td>
</tr>
<tr>
<td>C≡N</td>
<td>2354.08</td>
<td>2353.43</td>
<td>2350.94</td>
<td>2350.94</td>
<td>2350.94</td>
<td>2350.94</td>
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<tr>
<td>C≡N</td>
<td>2323.26</td>
<td>2323.49</td>
<td>2321.00</td>
<td>2323.49</td>
<td>2318.50</td>
<td>2321.00</td>
</tr>
<tr>
<td>C=O stretching</td>
<td>1788.52</td>
<td>1787.11</td>
<td>1792.10</td>
<td>1789.60</td>
<td>1789.60</td>
<td>1787.11</td>
</tr>
<tr>
<td>C≡C aromatic</td>
<td>1683.38</td>
<td>1684.82</td>
<td>1679.83</td>
<td>1664.86</td>
<td>1677.34</td>
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<tr>
<td>C-H</td>
<td>1558.31</td>
<td>1555.09</td>
<td>1557.59</td>
<td>1555.09</td>
<td>1557.59</td>
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<tr>
<td>CH2 bending</td>
<td>1453.17</td>
<td>1452.81</td>
<td>1452.81</td>
<td>1452.81</td>
<td>1452.81</td>
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<tr>
<td>K-I</td>
<td>-</td>
<td>1390.44</td>
<td>1390.44</td>
<td>1390.44</td>
<td>1387.94</td>
<td>1390.44</td>
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<tr>
<td>C-O phenol</td>
<td>-</td>
<td>1353.01</td>
<td>1350.52</td>
<td>1353.01</td>
<td>1350.52</td>
<td>1353.01</td>
</tr>
<tr>
<td>C–O–C stretching</td>
<td>1174.02</td>
<td>1173.39</td>
<td>1175.88</td>
<td>1173.39</td>
<td>1173.39</td>
<td>1170.89</td>
</tr>
<tr>
<td>Alkaline mono substitution</td>
<td>1120.64</td>
<td>1121.00</td>
<td>1121.00</td>
<td>1118.50</td>
<td>1118.50</td>
<td>1118.50</td>
</tr>
<tr>
<td>Aromatic meta substitution</td>
<td>1072.51</td>
<td>1076.09</td>
<td>1073.60</td>
<td>1073.60</td>
<td>1071.10</td>
<td>1073.60</td>
</tr>
<tr>
<td>Zn-O</td>
<td>-</td>
<td>470.50</td>
<td>470.66</td>
<td>471.45</td>
<td>470.34</td>
<td>470.34</td>
</tr>
</tbody>
</table>
2.2. Characterization of materials

FTIR analysis using a Prestige-21 Spectrum over a range of 400-4000 cm\(^{-1}\) with a resolution of 4 spectra were acquired at room temperature. The resistance value was completed using LCR-8110G/8105G, impedance analyzer in the 50 Hz – 1 MHz frequency range for the samples. The specific ionic conductivity \(\sigma\) with the bulk resistance \(R_b\) can be shown in Eq. (1) [15]:

\[
\sigma = \frac{L}{(R_b \cdot A)}
\]  

where \(L\) (cm) represents the separation distance between the electrodes, and \(A\) (cm\(^2\)) is the area of the electrode. The temperature of the sample changed from 293-343 K. The real parts of dielectric constant \(\varepsilon_r\) values were obtained using the following Eq. (2).

\[
\varepsilon_r = \frac{Z_i}{\omega C_0 \left[Z_r^2 + Z_i^2\right]}
\]

where \(\omega\) is the angular frequency \((\omega = 2\pi f)\), \(C_o\) is vacuum capacitance and \(Z_r\) and \(Z_i\) are real and imaginary parts of resistance.

3. Results and discussion

3.1. FTIR

FTIR spectroscopy is a fundamental mechanism in studying the band structure of materials that varies relying on their formulations and it might display the complexity and the interaction between different components, such as polymer, ions, and cations [16]. Fig.1 displays a comparison between the pure blend PVP: PAN and the blend nanocomposites with fixed ratio (50%) KI salt at different concentration of ZnO NPs. Additional peaks appearance in the reinforced samples of the doublet band at \((1391.86\ \text{cm}^{-1},\ 1351.70\ \text{cm}^{-1})\) for the K-I bond and the broad band appeared around \(470\ \text{cm}^{-1}\) corresponding to the Zn-O bond as tabulated in Table 2[17]. The intensity of the C=O band at \(1788\ \text{cm}^{-1}\) was enhanced at low addition ratio and decreased with more ratio suggesting the incorporation of carbonyl groups in the conjugated structure. Also the intensities of nitrile peaks and C–H group peaks at \(1482\ \text{cm}^{-1}\) were decreased according to the dehydrogenation and cyclization reactions between the polymer chains [18].

3.2. Ionic conductivity

Fig.2 (a and b) show the conductivity of Cs electrolyte as the temperature rises from 293 K to 343 K. Salt and ZnO nanoparticles are dissolved in a solvent to form free ions, ion pairs, and ion groups in the electrolyte framework. As the concentration of nano-ZnO increases, the probability of the occurrence of aggregation increases, resulting in the observed initial rise in conductivity as seen in Fig.2 (a). It is obvious that increasing the weight ratio of ZnO NPs by 0.1 g increases the conductivity rather than decreasing it [19]. The electrolyte C5 showed the highest conductivity with a value of \((0.0296\ \text{S.cm}^{-1})\). Different forms of polymer electrolytes have also shown similar findings. The ionic conduction action of Cs electrolytes is depicted in Figure (2-b), it is clear that the ionic conductivity rises as the ZnO weight ratio rises.
Figure 1: FTIR spectra for pure blend PVP: PAN electrolyte and blend nanocomposites reinforced with different ZnO NPs concentrations.

The formulation of the ZnO ratio can aid in improving the synergistic effects of polymer blends. As a result, pre-determination of the ZnO mixture ratio is critical for improving the versatility and efficiency of the polymer electrolyte. The combination of KI and nano-ZnO helps to improve electrical conductivity [20].
3.3. Dielectric constant

In the materials that make up the polymer electrolytes, dipole relaxation occurs. A wide frequency spectrum was investigated [21]. When an electric field is first created, the dipoles are added to a substance, the material's propensity to orient itself is shown in the direction of the field of application. In reality, the dipole's mobilization is reliant on based on the materials properties the polymer dipoles delayed response dielectric relaxation occurs when an electrical field is exerted on it [22]. Figure 3 depicts that the dielectric constant values on adding the nanomaterial (ZnO) at low frequency is very high values are at room temperature. This is due to the polarization of the insulating material. Mobile ions cannot move into the external circuit as the electrode does blocking portable ions [23, 24].

As a result, the moving ions move around the polymer and the arrays will accumulate at the electrode, electrolyte interface. At a higher frequency fast average reflection occurs because mobile ions cannot simply point a direction applied field. Hence, the interface cannot be created because there is no time for that. Therefore, the dielectric loss decreases as the polarization decreases because of the accumulation of shipments. This phenomenon indicates a multiplicity relaxation mechanism [25, 26].
4. Conclusions

In this study, polymer blend electrolytes and polymer blend nanocomposite electrolytes systems were prepared and characterized. FTIR results for electrolytes F indicate a significant degree of interaction between (PVP) and PAN molecules. For electrolytes, C indicates that the interactions among polymer blends and KI are associated with changes in intensity, shape, and position of stretching modes. The results showed that the ionic conductivity values increased with increasing the weight of the ZnO nanoparticles. Conductivity was found to rise upon increasing the temperature. When temperature increases, the electrolytes are expands incrementally, which creates more freedom. Maximum conductivity was reached for the electrolyte C5 when 0.25gm ZnO nanomaterial was added i.e., as the nanoparticle increases the conductivity increases. It was observed that $\varepsilon_r$ decreases with increasing the frequency at the lower frequency region and stops leveling at the higher frequency domain.

Acknowledgements

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Conflict of interest

Authors declare that they have no conflict of interest.

References

دراسة تحويلات فورير للاشعة تحت الحمراء والتوصيلية المستمرة للالكتروليات النانوية المتراكبة

ايلاف علي سوادي، محمد كاظم جواد
قسم الفيزياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة

تم في هذا العمل تشكيل الالكتروليات البوليمر باستخدام تقنية صب المذيبات تحت ظروف معينة، تم تحليل محتوى الالكتروليت للبوليمرات بنسبة ثابتة (25:75) و (1:1) من الكرتونات (EC، PC) المزدوجتين مع 10% أيوديد البوتاسيوم (KI) و 10% من وزن أيوديد البوتاسيوم. ازدادت التوصيلية مع اضافة ذرات اوكسيد الزنك النانوية. وايضا ازدادت مع زيادة درجة الحرارة ضمن المدى (293 إلى 343) كلف. وصلت قيمة التوصيلية الى حوالي (0.0296) مع (0.25 غرام) اوكسيد الزنك (ZnO). اشارت نتائج تحويلات فورير للاشعة تحت الحمراء لخليط الالكتروليات المتراكبة النانوية، الى ان تشمل تجاوز تحويلات فورير للاشعة تحت الحمراء لخليط الالكتروليات الموجودة درجة كافية للتفاعل بين الخليط البوليمر وملح أيوديد البوتاسيوم. من ملاحظات الالكتروليات المتراكبة النانوية، أصبح انسجام القمة أقل مع اضافة اوكسيد الزنك النانوي إلى ملح أيوديد البوتاسيوم، بتناقص تفاعل العازل الكهربائي مع زيادة التردد في درجة حرارة الغرفة. يمكن ان تعزى السماحية الكهربائية العالية للبوليمير عند الترددات المنخفضة إلى توفر الوقت الكافي لثنائية الأقطاب لتكون بمحاذاة المجال الكهربائي، مما يؤدي إلى زيادة الاستقطاب.