The potential of polyurethane bio-based solid polymer electrolyte for photoelectrochemical cell application

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A B S T R A C T

A photoelectrochemical cell was developed from bio-based polyurethane (PU), solid polymer electrolyte with lithium iodide as conducting material. At the initial stage, PU prepolymer was prepared via prepolymerization technique by reacting palm kernel oil-based monoester-OH (PKO-p) and 2,4'-methylene diphenyl diisocyanate (2,4'-MDI). The polyurethane electrolyte film was then prepared by inclusion of varying amount of lithium iodide (LiI) via solution casting technique. The formation of urethane linkages (NHCO backbone) and the chemical interaction between segmented polyurethane and lithium ion from LiI salts were confirmed by ATR-FTIR technique. Thermal studies carried out by TGA have proven the occurrence of polymer-salt complexation. Structural analysis by XRD has revealed that polyurethane electrolytes with 25 wt.% LiI reduced the semi-crystalline characteristics of plasticized polyurethane. The SEM morphological observation on the fractured film indicated the absence of phase separation. The ionic conductivity increased with the addition of 25 wt.% LiI resulted in the highest conductivity of $7.6 \times 10^{-4}$ S cm$^{-1}$. The temperature dependence conductivity of the electrolytes obeyed the Arrhenius law with the pre-exponential factor, $\sigma_0$ of $2.4 \times 10^{-3}$ S cm$^{-1}$ and activation energy, $E_a$ of 0.11 eV. A dye-sensitized solar cell of FTO/TiO$_2$-dye/PU-LiI-I$_2$/Pt give a response under light intensity of 100 mW cm$^{-2}$ indicated the photovoltaic effect with the $J_{sc}$ of 0.06 mA cm$^{-2}$ and $V_{oc}$ of 0.14 V respectively. These properties exhibited promising potentials for photo-electrochemical cell giving the focus on bio-based polymer electrolyte.

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1. Introduction

Nowadays, the world is facing a major crisis in regards to sustainable, safe and environmental friendly energy resources. The finding of ionic conductivity in polymer material complex with salt gives a breakthrough to the development of solid-state electrochemical devices for energy storage such as rechargeable batteries, photoelectrochemical cell, supercapacitor and electrochromic windows [1]. A photoelectrochemical solar cell (PEC) is an electrochemical device that can generate electrical and electrochemical energy upon absorption of light by one or more of the electrodes. It is generally composed of a photoactive semiconductor electrode (either n- or p-type) and metal counter electrode, which are immersed in the suitable redox electrolytes [2,3]. Recently, Grätzel cell or commonly known as dye-sensitized solar cell (DSSC), which is an extended of PEC devices developed by O’Regan & Grätzel [4] received more attention due to its high power conversion efficiency under cloudy and artificial light conditions, sustainable and low-cost starting materials and also simple fabrication technology. They are based on a molecular absorber based on that emits photoelectrons from an excited state upon illumination into photoactive semiconductor and receives ground-state electrons from a liquid redox carrier [4–6]. Ruthenium based complexes as photosensitizers have been dominant in DSSC application due to their favorable photoelectrochemical properties and high stability in the oxidized state, making practical applications feasible [7]. At present, DSSCs based on ruthenium(II)-polypyridyl complexes have overall power conversion efficiencies over 11% under standard air mass (AM) 1.5 illumination (light intensity of 100 mW cm$^{-2}$) [8]. The high efficiencies of the ruthenium(II)-poly(pyridyl) based DSSCs can be attributed to their wide absorption range from the visible to the near-infrared region. In addition, the carbonyl groups attached to the bipyridyl moiety lower the energy of the ligand π* orbital [9]. Thus, this article utilized the standard dye sensitizer. From dye-loading data reported by Sacco et al. [10], it’s easy to calculate that 1 g of N719 can sensitize 1.68 m$^2$ of TiO$_2$, that costs 158 EUR per gram by Solaronix company, whereas it affects the charge distribution at the semiconductor/electrolyte interface, and thereby also the potential distribution [21]. To overcome the problem, polymer electrolyte membranes provided alternative materials to be utilized in DSSC. There are various families of classic polymer electrolytes such as gel, plasticized, ionomer rubber polymer electrolytes and ion conducting polyelectrolytes. In addition, there are another two main families of hybrid inorganic-organic polymer electrolytes which is mono-phase and multi-phase polymer electrolytes as reported by Di Noto et al. [22]. Extensive studies have been conducted elsewhere in order to improve quasi-solid-state/solid-state PEC efficiency by replacing liquid electrolytes with gel/quasi-solid polymer electrolytes [23–28], hole-transport materials [29], p-type semiconductor [30,31] and ionogels based liquid or solid [32]. Recent study by Bella et al. [25] shows solar energy conversion efficiency of quasi-solid-state DSSC at 5.41% using (35:65) BEMA:PEGMA polymer membrane swelling in liquid electrolyte NaI/I$_2$ in acetonitrile. Joseph et al. [26] reported the quasi-solid-state DSSC containing the hybrid TEOS-poly(ethylene glycol) (PEG) gel electrolyte with an overall solar energy conversion efficiency of 4.1%. In addition, Kim et al. [27] discovered power efficiency of 4.2% by using poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) quasi-solid-state polymer electrolytes using the same LiI/I$_2$ redox-electrolytes solution.

Recently, polyurethane (PU) has attracted attention as promising polymer electrolytes candidate in the future [23,24,33–36]. PU has a unique multiphase structure formed from soft and hard segment of the polymeric chain contributed by the polyols and isocyanates respectively. The soft segment of the PU can act as a polymeric solvent to solvate the cations and the hard segment can be functionalized to maintain a wide electrochemical stability to permit the fabrication of the polymer electrolytes in electrochemical devices [24]. Moreover, the strong adhesions properties of PU allow the electrode interfaces to stick together during the PEC assemble [37]. PU is synthesized by polymerization reactions between polyester polyols and diisocyanate. Conventional polyester polyols are synthesized by direct polyesterification of high-purity diacids and glycols from virgin raw materials. They are distinguished by the choice of monomers, molecular weight, and degree of branching. Whereas, bio-based polyester polyols are derived from vegetable oils that provide better elastomeric properties, flexible and easy to mould. It offers physical properties that cannot be obtained by petrochemical-based polyester polyls such as PEG, including superior solvent, abrasion, and low resistance [38]. Research on bio-based PU synthesis from palm kernel oil-based monoester-OH (PKO-p) has been studied extensively by Badri and co-workers [37,39,40]. However, there is no report related to the potential of palm based PU bio-polymer electrolytes for solid-state electrochemical devices application. On the other hand, diisocyanate with two or more functional groups are required for the formation of polyurethane. The aliphatic isocyanate group is less reactive than the aromatic. Aliphatic isocyanates are used only if special properties such as light stable coatings and elastomeric properties are required for the final product. Even within the same class of isocyanates, there is a significant difference in reactivity of the functional groups based on steric hindrance. In the case of 2,4'-methylene diphenyl diisocyanate (MDI), the isocyanate group in the para
position to the methyl group is much more reactive than the isocyanate group in the ortho position. From the view of solid-state ionic perspective, oxygen and nitrogen atoms in the PU structure have electron pairs that are hard to be polarized, which is considered as hard bases; small cations without easily polarized or removed valence electron such as alkaline earth cations are considered as hard acid. Based on the hard/soft acid base principle, the strong interaction will occur by matching hard acids with hard bases or vice versa [41]. This will increase the ion dissociation between cations and anions from metal salts. Ionic mobility is expected to be increased, therefore in-situ chain extender. The presence of amine functional group in the PU synthesis was carried out at room temperature without any catalyst, surfactants, additives, crosslinkers or chain extender. The presence of amine functional group in PKO-p provides an alternative route for catalyzed PU polymerization. Therefore, production cost and chemical contact can be minimized.

2. Materials and methods

2.1. Materials

2,4'-Methylene diphenyl diisocyanate (MDI) was commercially obtained from Cosmopolyurethane (Malaysia) Sdn. Bhd. PKO-p from palm kernel oil were synthesized by polyesterification reaction in UKM laboratory using established method by Badri et al. [37]. Lithium iodide (LiI), ethylene carbonate (EC), iodine (I₂) and titanium dioxide (TiO₂) were supplied by Sigma-Aldrich (St. Louis, Mo, USA). DSSC component, di-tetrabutyl ammonium cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-di carboxylato) ruthenium (II) dye (N-719), platinum (Pt) paste under commercial name Platisol T, conventional electrolyte consist of lithium iodide salt in ionic liquid and pyridine derivated based electrolyte with 50 mM of tri-iodide in acetonitrile (iodolyte AN-50) and 3 mm tick fluoride-doped tin oxide (FTO) with ~15 Ω/cm² as transparent conductive oxide were purchased by Solaronix (Aubonne, Switzerland). Acetone and ethanol 99.9% were supplied by SYSTERM ChemAR (Kielce, Poland). All materials were used without further purification.

2.2. Synthesis of polyurethane solid polymer electrolytes and characterization

PKO-p was mixed together with 2,4'-MDI in 5 mL acetone at 1:2 ratio (NCO:OH) at ambient temperature under nitrogen gas atmosphere. These solutions were stirred to a homogenous solution for 5 min. EC was added in the mixture as the plasticizer at a fix amount of 20% (w/w). It was dissolved in acetone together with LiI at varying amount of 10–30% (w/w). This mixture was stirred for an hour prior to inclusion to PU prepolymer, and further mixed for another 5 min. The solution prepared will then be casted into Teflon mould and allowed to evaporate at room temperature for an hour. Fig. 1 shows scheme of polyurethane polymerization between diisocyanate and monoester polyols PKO-p. The reaction involved in this polymeric synthesis was additional polymerization via nucleophilic substitution reactions. The preliminary studies on the bio-based PU film have been reported in previous work [40,45]. The (1:2) NCO:OH ratio of PU composition is being considered for polymer electrolytes host due to their higher thermal stability and higher polydispersity index (PDI) values, with moderate weight average molecular mass (M_w) ~1230 x 10^6 g mol⁻¹, glass transition temperature (T_g) value (54 °C) and degree of crosslinking (47%). In addition to the physical properties, chemical analysis confirmed that urethane linkages is formed by the disappearance of v(N=C=O) peaks at ~2241 cm⁻¹ and the appearances of (N–H) peaks at ~3300 cm⁻¹, carbonyl v(C=O) at ~1713 cm⁻¹, carbamate (C–N) at ~1600 cm⁻¹, ether (C–O–C) at ~1065 cm⁻¹, v(O–C=O) ester functional groups at ~1217 cm⁻¹ and ~1309 cm⁻¹ after the polymerization [45].

The produced film was characterized using attenuated total reflection Fourier transform infrared (ATR-FTIR) to observe the functional group and chemical interaction in the system. FTIR spectra were recorded by computer interfaced with Spectrum 400 Perkin Elmer GX Spectrometer. The electrolyte film was placed onto ATR crystal and was analyzed in the frequency range of 4000 cm⁻¹ to 650 cm⁻¹ with a scanning resolution of 2 cm⁻¹ at room temperature. The weight average molecular mass (M_w), number average molecular mass (M_n), and polydispersity index (PDI) were derived from gel permeation chromatography (GPC) analysis. Thermal studies of the PU films were done using differential scanning calorimetry analysis (DSC) and thermogravimetric analysis (TGA). The T_g
of the samples were observed using Mettler-Toledo DSC model 822 from 20 °C to 250 °C at a scanning rate of 10 °C/min under nitrogen atmosphere. Approximately, 4 mg of the polyurethane films were used for each DSC measurement. The T_g of the polyurethane films were taken at mid-point of the endothermic peak and evaluated using STARe software.

The thermogravimetric analysis was carried out using a Mettler-Toledo TGA/SDTA 851 instrument under nitrogen atmosphere from room temperature to 600 °C at a heating rate of 10 °C/min. A sample size of ~5 mg in the form of fine powder was used to determine the weight loss of polymers. X-ray diffractometer (XRD) model D-5000 Siemen (Cu-Kα; λ = 1.5418 Å) was used to determine the crystallinity of the electrolyte samples. The data were collected in the range of diffraction angle 2θ from 5° to 80° at a scanning rate 0.04° s⁻¹.

The surface morphology of the sample was observed using SEM model ZEISS, SUPRA 55VP with 1000× magnification at 15 kV electron beam. The sample was fractured in liquid nitrogen and coated with gold sputtered-coated machine before the analysis. The ionic conductivity measurements were carried out by electrochemical impedance spectroscopy (EIS) using a high frequency resonance analyzer (HFRA) model 1255 with applied frequency from 1 MHz to 0.1 Hz at 1000 mV amplitude. The conductivity measurements were conducted at room temperature and temperature ranged from 303 K to 373 K. The 16 mm in diameter disc-shaped sample was sandwiched between two stainless steel block electrodes. The ionic conductivity (σ) was calculated from the bulk resistance (R_b), which was obtained from the intercept on the real impedance axis (Z' axis) and the film thickness (l) and contact area of the thin film (A = 2.01 cm²), in accordance with the equation σ = [l/(A.R_b)]. The analysis was carried out at room temperature.

### 2.3. Photoelectrochemical cell fabrication and characterization

The standard cell fabrication procedures were followed based on the instructions from Solaronix Company. TiO₂ paste was spread on the FTO using doctor-blade technique with the support of adhesive tapes on both sides. The TiO₂ paste was sintered at 450 °C for 20 min to activate quasi transparent platinum layer and was sensitized in 5 mM solution of N719 dye solution at room temperature for 12 h. Platinized FTO counter electrode was prepared by brush-painting technique, firing at 450 °C for 10 min. The TiO₂ photoanode electrode was then assembled with a platinum counter electrode and filled with iodide based electrolyte with 50 mM of tri-iodide in acetonitrile. The PU-Li/I₂ based electrolytes were fabricated by the same procedures. Fig. 2 showed the assembling procedure of FTO/TiO₂-Dye/PU-Li/I₂/Pt dye-sensitized solar cell. The current-voltage (I–V) measurement of the device in dark and under illumination was recorded using a Keithley high voltage source model 237 with tungsten light source under air mass (AM) 1.5 illumination (light intensity of 100 mW cm⁻²) controlled by radiometer. The illuminated cell area was set to 1 cm². All of the analysis was done at room temperature. The photoelectric performances (i.e. fill factor ff and light-to-electricity energy conversion efficiency, η) were calculated using the following equations:

$$ ff = \frac{V_{\text{max}} \times J_{\text{max}}}{V_{\text{oc}} \times J_{\text{sc}}} $$

(1)

$$ \eta = \frac{V_{\text{oc}} \times J_{\text{sc}} \times ff \times 100}{P_{\text{in}}} $$

(2)

where $V_{\text{oc}}$ is the open-circuit voltage (V), $J_{\text{sc}}$ is the short-circuit current density (mA cm⁻²), $P_{\text{in}}$ is the incident light power.
density (mW cm\(^{-2}\)); \(V_{\text{max}}\) (V) and \(J_{\text{max}}\) (mA cm\(^{-2}\)) are the voltage and the current density in the \(J-V\) curves, respectively, at the point of maximum power output [46].

### 3. Results and discussion

#### 3.1. FT-IR analysis

Fig. 3 shows FTIR spectrum of various functional groups which are responsible for polymer-salt complexes. The occurrence of stretching mode of hydrogen bonded (N–H) with oxygen (ether) appeared at 3297 cm\(^{-1}\) after PU polymerization proved the presence of secondary amides (–NHCO–) in the PU polymeric structure [40,47]. The secondary amides mainly existed in the trans conformation due to the free NH stretching. With inclusion of EC, this peak remains unchanged. The peaks were shifted to the higher wavenumbers with the addition of lithium salts between the regions of 3450 cm\(^{-1}\) to 3600 cm\(^{-1}\) which belongs to –OH functional groups caused by hygroscopic nature of lithium salt. Whereas, the tertiary amides in PKO-p will not show any absorption band in this region [48].

Fig. 4 shows the vibration regions of carbonyl, ether, ester and amine functional groups in polyurethane-LiI solid polymer electrolytes. The foremost interests are shown on the oxygen atoms of the carbonyl (C=O) (1750 cm\(^{-1}\)–1730 cm\(^{-1}\)) and ether and ester group (C–O–C) (1300 cm\(^{-1}\)–1000 cm\(^{-1}\)) and amine functional groups (C–N & N–H) (1650 cm\(^{-1}\)–1500 cm\(^{-1}\)) [49]. Additionally, Table 1 expresses the wavenumbers for the respective functional groups.

According to literature, the existence of the intense and broad peak at \(\sim 1740\) cm\(^{-1}\) is referred to non hydrogen bonded urethane stretching where the peak around \(\sim 1700\) cm\(^{-1}\) is always referred to the existence of an intermolecular interaction due to the lower frequencies of carbonyl (C=O) absorption [40,47,50]. We believed that the carbonyl (C=O) functional group of PU-EC at 1730 cm\(^{-1}\) in Fig. 4(a) is not affected by the intermolecular interaction, specifically hydrogen bonded urethane stretching. After the addition of lithium iodide salt, the functional group of carbonyl (C=O) group for PU was shifted to lower wavenumbers, which is at 1713 cm\(^{-1}\). This shifting indicates the existence of strong intermolecular interaction. We assume the strong intermolecular interaction is between lithium ion from doping salts and oxygen atoms resulting in polymer-salt complexes. The oxygen atoms from carbonyl functional group in the PU structure is expected to act as electron donor atoms and subsequently forming a coordinate bond with lithium ion from doping salts. Meanwhile, (C–O–C) peak of PU and PU-EC in Fig. 4(b) at 1065 cm\(^{-1}\) and 1072 cm\(^{-1}\), respectively were found to be slightly shifted to 1075 cm\(^{-1}\). The appearance of
two strong peaks for \((O-C=O)\) ester at \(~1310\,\text{cm}^{-1}\) and \(~1219\,\text{cm}^{-1}\) in Fig. 4(c) and (d) proved that the urethane linkages \((\text{NHCOO})\) are formed after polymerization. However, no peak shifting is observed. Nevertheless, the intensity of \(1181\,\text{cm}^{-1}\) peak’s shoulder disappeared after the amount of lithium salts increased.

Fig. 4(e) and (f) shows the vibration region for \((C-N)\) and \((N-H)\) functional groups in polyurethane polymer electrolytes.
The resonance structures of amide functional groups were found at 1602 cm⁻¹, which corresponds to carbamates (C–N). In secondary amides, the (C–N) stretching vibration was observed to have similar frequency to N–H bending mode. Interaction (coupling) of these two vibrations in the component (C–N–H) gives rise to N–H bending at a higher frequency (1550–1510 cm⁻¹). The intensity of N–H bending was found at 1515 cm⁻¹ and shifted to 1511 cm⁻¹ and disappeared at higher salt concentration. Whereas, the intensity of neighboring peaks at 1533 cm⁻¹ increased and shifted to 1531 cm⁻¹. However, stretching mode of –CH₂ and –CH₃ peaks for all samples remain to be unchanged at ~2922 cm⁻¹ and ~2853 cm⁻¹.

### 3.2 Weight average molecular mass (Mₐ), number average molecular mass (Mₙ) and polydispersity index (PDI)

Table 2 shows weight average molecular mass (Mₐ), number average molecular mass (Mₙ), and polydispersity index (PDI) derived from gel permeation chromatography (GPC) analysis. The weight average molecular mass (Mₐ) describing the average number of molecular mass in each component and the number average molecular mass (Mₙ) is average molecular weights of all individual macromolecules. Molecular weight of pristine PU is found to be around ~170,000 g mol⁻¹. This value decreased to ~163,000 g mol⁻¹ and ~104,000 g mol⁻¹ with the addition of EC and lithium iodide salt, respectively. The addition of EC and LiI does not break the main polymeric chains of polyurethane (both backbone/segmental chains). However, this phenomenon is related to the breaking of the intermolecular interaction (hydrogen bonds) between the main chains of polyurethane linkages as observed in FTIR [51].

### 3.3 Thermal analysis

Fig. 5 shows TGA thermogram and differential thermogravimetric (DTG) curves of PU solid polymer electrolytes at various loading percentage of LiI. The weight loss percentage of PU solid polymer electrolytes are summarized in Table 3. Lithium iodide is a hygroscopic material. Upon heating, it will evaporate some moisture. Thus, at a temperature region of 20–100 °C a vaporization of water state was observed. Excess of acetone might also be possible to contribute in the endothermic peak.

The thermal decomposition stage (Tₐ) of pristine PU and PU containing EC was observed at a temperature region of 150–220 °C, 240–370 °C and 370–520 °C for Tₐ₁, Tₐ₂ and Tₐ₃, respectively. The first decomposition stage (Tₐ₁) at the region of 100–160 °C was observed with the addition of EC representing the temperature of the initial degradation stage for thermal weight loss of EC. Tₐ₄ for PU-EC as the polymer host was located in the region of 125 °C to ~137 °C. Tₐ₄ of the PU block co-polymer referred to the degradation of the hard segmented block of the urethane linkages, while, Tₐ₃ is attributed to liberation of free isocyanate. Furthermore, Tₐ₄

![Figure 5](https://example.com/figure5.png)

**Table 1 – The wavenumbers of carbonyl, ether, ester and amine functional groups in polyurethane solid polymer electrolytes varying loading percentage of LiI.**

<table>
<thead>
<tr>
<th>Functional groups</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PU</td>
</tr>
<tr>
<td>C–O</td>
<td>1713</td>
</tr>
<tr>
<td>C–N</td>
<td>1601</td>
</tr>
<tr>
<td>N–H</td>
<td>1533,1515</td>
</tr>
<tr>
<td>O–C–O</td>
<td>1309,1217</td>
</tr>
<tr>
<td>C–O–C</td>
<td>1065</td>
</tr>
</tbody>
</table>

![Table 2 – Weight average molecular mass (Mₐ), number average molecular mass (Mₙ) and polydispersity index (PDI) of PU-LiI solid polymer electrolytes.](https://example.com/table2.png)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Molecular weight (Mₐ), g mol⁻¹</th>
<th>Molecular number (Mₙ), g mol⁻¹</th>
<th>Polydispersity index (Mₐ/Mₙ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PU</td>
<td>170,775</td>
<td>64,998</td>
<td>2.63</td>
</tr>
<tr>
<td>PU + 30% EC</td>
<td>163,286</td>
<td>68,243</td>
<td>2.39</td>
</tr>
<tr>
<td>PU + 20% LiI</td>
<td>104,582</td>
<td>45,485</td>
<td>2.30</td>
</tr>
</tbody>
</table>

![Fig. 5 – TGA thermogram and differential thermogravimetric (DTG) curves of PU-LiI solid polymer electrolytes at varying loading percentage of LiI.](https://example.com/figure5.png)
was contributed by the rupture of ester linkages [52]. The scheme of thermal degradation of PU polymeric chain is illustrated in Fig. 6.

DTG peak of $T_{d2}$ region increased from 160 °C to 300 °C with the presence of LiI salts. During $T_{d2}$ disruption of urethane bonds resulted in decomposition of hard segments. It has been proposed that three decomposition mechanisms for urethane bonds might occur simultaneously that were (i) degradation of urethane to isocyanate and alcohol, (ii) formation of primary amine and carbon dioxide and (iii) formation of secondary amine and carbon dioxide [53–58].

DTG peak of $T_{d3}$ region was also increased from 340 °C to ~410 °C in the presence of LiI salts. This region corresponded to the liberation of free isocyanate which led to the formation of thermally stable carbodiimide derivatives or compounds with isocyanurate rings as a result of a trimerization reaction [59].

DTG peak of $T_{d4}$ increased from 446 °C to 474 °C as LiI salts increases. It shows thermal decomposition of soft segments of PU (ester groups), which was seldom affected by the chemical composition and the 3 dimensional arrangement of polyurethane structure [52,53,57–61]. The amount of residue after 600 °C increased in accordance to the increase in the amount of LiI salts associated to polymer-salt complexes.

The increase in $T_{max}$ of PU upon loading of lithium salt indicated higher thermal stability of PU polymer electrolytes. Lithium salt in ionic forms have the capability to disrupt PU chain resulting in randomize arrangement. More heat is required to break PU polymeric bond due to the existences of strong intermolecular interaction between lithium ion and PU polymeric chain as supported by FTIR analysis. This phenomenon resulted in higher degradation temperature of PU polymer electrolytes as demonstrated in the TGA thermogram.

DSC analysis demonstrated a slight significant increased in the $T_g$ value of the PU electrolytes along with increasing amount of LiI. Nevertheless, there were only slight increases of the $T_g$ values and considered as insignificant. FT-IR spectrum indicated neither formation of new peak nor disappearance of the existing peaks. The $T_g$ of PU is observed at 68 °C and varying around 70 °C, 73 °C, 68 °C, 72 °C, 62 °C with loading percentage of LiI.

<table>
<thead>
<tr>
<th>Sample (wt.%)</th>
<th>% Weight loss (wt.)</th>
<th>Residue after 600 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{d1}$, 100–160 °C</td>
<td>$T_{d3}$, 150–220 °C</td>
</tr>
<tr>
<td>PU</td>
<td>–</td>
<td>11</td>
</tr>
<tr>
<td>PU-EC</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>$T_{d1}$, 100–160 °C</td>
<td>$T_{d3}$, 160–300 °C</td>
<td>$T_{d4}$, 300–430 °C</td>
</tr>
<tr>
<td>10</td>
<td>8</td>
<td>27</td>
</tr>
<tr>
<td>15</td>
<td>9</td>
<td>25</td>
</tr>
<tr>
<td>20</td>
<td>7</td>
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<td>30</td>
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3.4. Structural studies

The XRD analysis was used to determine the structure and crystallization of the polymer-salt complexes. Fig. 7 shows the XRD pattern of PU-LiI solid polymer electrolytes. From Fig. 7, pure LiI salt gave highly intense peaks at 20.8°, 25.7°, 29.7°, 42.1° and 50.3°. Meanwhile, PU gave a hump and highly intense peaks at 29.5°. Interestingly, the introduction of lithium salts to the PU polymer host was found to decrease the semi-crystalline phase of PU hard segments in the region between 10° and 30° by reducing the hump. An identical peak for PU hard segments at the angle of 29.5° was also found to decrease with the addition of LiI salt. This observation is supported by the reduction in degree of crystallinity of PU-LiI solid polymer electrolytes with addition of wt.% LiI as shown in Table 4. This finding is similar to those reported elsewhere, in which the high ionic conductivity still occurred due to the reduction of the crystalline region [36,62–65].

3.5. Morphology studies

The effects of lithium salt loading on the surface morphologies of fractured PU-LiI polymer electrolytes were investigated by SEM. Fig. 8 exhibited morphological appearance of cross-sectional cut of PU film at (a) 0 wt.%, (b) 20 wt.%, (c) 25 wt.% and (d) 30 wt.% LiI salts. The SEM micrograph in Fig. 8(a) shows a homogenous surface of PU prepared by additional polymerization via step-growth polymerization reaction using solution casting technique. There is no phase separation observed either by physical or SEM observation in both PU blank and PU-LiI. This observation signifies the existence of an intermolecular interaction between the polymeric chains as proved by FT-IR analysis [66]. The flexibility and elasticity properties of the PU films were attributed by the PU soft segments, while the hard segment gives strength to support the urethane linkages [24].

Formation of micro-pores on the films at higher dosage of LiI was observed in Fig. 8(c) and (d), possibly due to the usage of low boiling point solvent (acetone). The formation of micro-spheres in Fig. 8(d) is due to the trap air in the PU film. There is a probability of trap CO₂ gases produced during polymerization if diisocyanate reacts with moisture from hygroscopic LiI. Water could act as a blowing agent and conventionally used to produce PU foams and composites [67,68].

3.6. Ionic conductivity

The highest ionic conductivity found at room temperature for 25% LiI is 7.6 x 10⁻⁴ S cm⁻¹ in comparison to PU blank, 6.2 x 10⁻⁹ S cm⁻¹. The presence of 10–20 wt.% LiI increased the conductivity up to three magnitudes in comparison to pristine PU and achieved the optimum at 25 wt.% of LiI due to the contributions of ionic dissociation. However, the ionic conductivity decreased down at 30 wt.% LiI to two magnitudes lower from the optimum value might because of the formation of micro-spheres as discussed in SEM analysis. This process disturbed the conducting process in the electrolyte systems and provided a low conductivity in the systems.

Fig. 9 shows the conductivity, s dependence on temperature, T given by the Arrhenius plot for the PU with 25 wt.% LiI. It was observed that the conductivity increased with the temperature from 303 K to 373 K. The bulk resistance of the electrolyte was immeasurable after 373 K since the sample was unstable at temperatures higher than 373 K. The relationship between conductivity and temperature for PU-LiI was found to be linear with the regression line of 0.995. This indicates that the electrolyte system exhibited an Arrhenius-like behavior given by the Arrhenius equation, s = σ₀ e⁻Ea/kT where σ₀, Ea and k are pre-exponential factor, activation energy and Boltzmann constant (8.6 x 10⁻⁵ eV K⁻¹), respectively. Whereas, −Ea/kT is represented by the graph slope, m. Value for σ₀ and Ea can be calculated from y-axis and plot intercept between log s versus 1000/T [69–71]. From the Arrhenius plot, Ea value is 0.11 eV and the pre exponential factor σ₀ is 2.40 x 10⁻⁴ S cm⁻¹. The activation energy is related to the segmental motion of polymeric chain below Tg. The flexibility of polymer electrolyte leads to the increase in the dissociation rate of Li⁺. Thus, enhances the transport of ions in the polymeric chain and improving the mobility of the charge carrier. As a result, the ionic conductivity increases along with temperature [69–71].

3.7. Photoelectrochemical cell characterization

3.7.1. I–V measurement

The current–voltage characteristic in dark and under illumination at room temperature was performed to observe the photovoltaic response in the FTO/TiO₂-dye/PU-LiI-Pt devices.
Fig. 10 illustrated the I–V plot of DSSC with conventional liquid electrolyte and solid polymer electrolyte PU-LiI under illumination and in dark atmosphere. The photovoltaic parameters such as short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF) and power conversion efficiency (%) were obtained from the intersection axis of current and voltage from the current–voltage curve under illumination, respectively [72]. A DSSC consists of FTO/TiO$_2$-dye/PU-LiI-I$_2$/Pt indicated the photovoltaic response with the $J_{sc}$ of 0.06 mA cm$^{-2}$, $V_{oc}$ of 0.14 V, FF of 0.26 and power conversion efficiency of 0.003% respectively, under light intensity of 100 mW cm$^{-2}$. Whereas, a standard photovoltaic prepared in our lab give a response with the $J_{sc}$ of 3.35 mA cm$^{-2}$, $V_{oc}$ of 0.72 V, FF of 0.48 and power conversation efficiency of 1.15% respectively, under the same light intensity. Solid-state electrolytes based DSSC have lower power conversion efficiencies than conventional liquid-state electrolytes based DSSC due to lower ionic mobilities. This is because the ionic conductivity in liquid state is much higher than that in the solid state electrolytes. Generally, the power conversion efficiency obtained from these devices will be very low [73].

4. Conclusions

Bio-based polyurethane electrolyte from palm kernel oil with the inclusion of lithium iodide salts, LiI has been successfully prepared by solution casting technique and has been tested in dye-sensitized solar cell. The highest conductivity achieved was around $\sim 10^{-4}$ S cm$^{-1}$ at 25 wt.% of LiI. Infra-red and thermal analysis proved the occurrence of chemical interaction between segmented polyurethane and lithium ion to form a coordinate bond and subsequently forming polymer–salt complexes. The salt affects the overall ionic conductivity through the formation of complexes, the intramolecular cross-linking of the polymer chains and the degree of salt dissociation-number of charge carriers. A dye-sensitized solar cell of FTO/TiO$_2$-dye/PU-LiI-I$_2$/Pt gives the photovoltaic effect with the $J_{sc}$ of 0.06 mA cm$^{-2}$ and $V_{oc}$ of 0.14 V respectively.
respectively, under light intensity of 100 mW cm$^{-2}$. These properties exhibited promising potentials for photo-electrochemical cell giving the focus on bio-based polymer electrolyte and its conductivity.

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