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Palm-based polyurethane-ionic liquid gel polymer electrolyte for quasi-solid state dye sensitized solar cell

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ABSTRACT

In this study, the effect of palm-based polyurethane (PU) gel polymer electrolytes with the addition of *1*-methyl-*3*-propylimidazolium iodide (MPII) on quasi-solid state dye sensitized solar cell (DSSC) was investigated. The PU was synthesized prior via pre-polymerization technique under nitrogen atmosphere. Different weight percentage of MPII ranging from 10 to 30 wt.% were added in PU solution to form a gel-polymer electrolyte. The chemical interactions of electrolytes were examined using Fourier transform infra-red spectroscopy (FTIR), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Meanwhile, the ionic conductivities of electrolytes and photovoltaic characteristics of quasi-solid state DSSC were investigated by electrochemical impedance spectroscopy (EIS) and current-voltage (IV) measurements. FTIR spectrum proved there were interactions between PU and MPII at N−H stretching, N−H bending and C=O stretching. The highest ionic conductivity values achieved were 9.07×10^{-4} S cm^{-1} for PU–25 wt.% MPII system. These results were supported by the decrement of the glass transition temperature (T_g) upon the addition of MPII which has also been proven by DSC results. The thermal stability measured by TGA also indicated that there were interactions which occurred between PU and MPII, correlated with the increment of ionic conductivities. The current-voltage characteristics of fabricated quasi-solid state DSSC (FTO/TiO_2-dye/PU-MPII-I_2/Pt at 25 wt.% MPII) demonstrated highest power conversion efficiency of 1.00% under a standard AM 1.5G illumination. These promising results could be a first step toward a new generation of low-cost and effective quasi-solid state DSSC from bio-based polymer electrolytes.

1. Introduction

Exploration on renewable materials in replacing depleted petrochemical-based feedstock is become a global challenge nowadays. Due to this concern, most of current research conducted focused on the usage of renewable and green materials such water and biopolymers which lead to sustainability and reduction of environmental toxicity (Bella et al., 2017a; Law et al., 2010). In parallel with that, the development of efficient, low cost and sustainable dye sensitized solar cell (DSSC) gained serious attention and the research related to the improvement of its performances in all aspects including dye (Zhou et al., 2011; Mathew et al., 2014), electrode (Galliano et al., 2017; Lee et al., 2008; Sahito et al., 2015), electrolyte (Singh et al., 2013; Tao et al., 2015) as well as the computational perspective (Obotowo et al., 2016) are aggressively expanded. As bio-based polymer are renewable materials and considered to be safe in terms of health and environmental, it has become an option to be used as host matrices in producing electrolytes for electrochemical devices. The variety of bio-based polymer such as cellulose (Bella et al., 2017b; Nair et al., 2016; Salvador et al., 2014), carrageenan (Mobarak et al., 2015; Jumaah et al., 2015; Rudhziah et al., 2015), chitosan (Buraidah and Arof, 2011; Yusuf et al., 2016), modified natural rubber (Glasse et al., 2002; Idris et al., 2001; Ali et al., 2013) and palm kernel oil (Su'ait et al., 2014) have been used and also widely explored.

In Malaysia, palm oil industry is one of the main agro-based industries which contribute to more than 86% of the world's total palm oil production and export, (Ofori-Boateng and Lee, 2013). Today, 4.49 million hectares of land in Malaysia is under oil palm cultivation; producing 17.73 million tonnes of palm oil and 2.13 tonnes of palm kernel oil. Being the most efficient oilseed crop in the world up to eight tonnes of oil per hectare annually, the production of palm oil and palm kernel oil (PKO) today occupied 11% of global oils and fats as well as 27% of export trade

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of oils & fats ("The Oil Palm Tree", 2013). Palm kernel oil is mainly composed of 91.85% saturated fatty acid contributed by 59.83% lauric acid, 14.92% myristic acid, 5.38% palmitic acid, 5.14% caprylic acid, 4.82% of capric acid, 1.52% of stearic acid and 0.24% caproic acid. The other 8.15% is by unsaturated fatty acid, including 6.87% oleic acid and 1.28% linoleic acid (Benjapornkulaphong et al., 2009). Palm kernel oil is commonly used in various applications such as personal care and cosmetics, food processing as well as fuel and biodiesel industries. Due to the abundance of palm kernel oil in Malaysia, this research is carried out to utilize the natural sources to be used as one of the components in electrochemical devices which lead to the production of green and clean energy. The palm kernel oil-based monoester polyol (PKO-p), which is the derivative of palm kernel oil had been used to prepare polyurethane (PU) which then would be used as electrolyte in dye sensitized solar cell (DSSC) (Su'ait et al., 2014).

The PU was synthesized via pre-polymerization technique by reaction with methylene diphenyl diisocyanate (MDI). The existence of polyols and isocyanates, which are soft and hard segments in PU backbone contributed to the multiphase structures. The soft segment of the PU can act as a polymeric solvent to solvate the cations, meanwhile the hard segment can be functionalized to maintain a wide electrochemical stability to allow for the fabrication of the polymer electrolytes in electrochemical devices (Wang and Min, 2010; Su'ait et al., 2014). Moreover, PU has strong adhesive properties which ensure that the electrode interfaces stick together during DSSC fabrication. The DSSC has been acknowledged as an electrochemical device that can convert solar energy into electrical energy (Grätzel, 2001). This has been described as the photovoltaic cell, created from low-to medium-purity materials through low-cost processes, which exhibit commercially realistic energy-conversion efficiency. The overall light-to-electric energy conversion yield is 7.1–7.9% in simulated solar light and 12% in diffuse daylight as firstly published by O'Regan and Grätzel, (1991). DSSC is commonly constructed by dye-coated nanoporous TiO_2 photoelectrode, a platinum-coated counter electrode and a thin layer of electrolyte sandwiched between these electrodes.

The common type of electrolyte used practically is liquid electrolyte, since it can provide high power conversion efficiency. However, the usage of liquid electrolyte has its drawbacks such as leakages, evaporation, photodegradation of the dye, corrosion of the platinum counter electrode and inefficient sealing of cells, which resulting the changing of using the liquid electrolyte into solid and gel electrolytes. Other than that, due to the problem of low dissociation of salts and the tendency of agglomeration while using inorganic salts (LiI, NaI and NH_4I) as electrolyte, the usage of ionic liquid served as charge carriers are in trend as they have special properties such as having highly thermal stability, non-volatility and high in ionic conductivity in room temperature which is desired as an electrolyte. On the other hand, ionic liquid can also act as a plasticizer which can help in polymeric backbone movement, leading to ionic conductivity increment. As ionic liquids have bulky cations, they would enhance the ionic conductivity through better ion dissociation (Dissanayake et al., 2014). Among the ionic liquid electrolytes used in DSSC, a lot of attention has been drawn to the ionic liquid with *1,3*-dialkylimidazolium cations, especially *1*-methyl-*3*-propylimidazolium iodide (MPII) because they can provide excellent efficiency and good stability in DSSCs (Ng et al., 2015).

In this present work, the performance of palm kernel oil-based PU with the addition of MPII in DSSC efficiency is investigated. It is expected that by incorporating MPII ionic liquid in PU electrolytes, it would provide high ionic conductivity and photovoltaic response under illumination. The novelty of this study is motivated by the synthesis of bio-based polyurethane polymer electrolytes and *in-situ* dissolution of MPII without the presence of organic solvents. The synthesis was carried out at room temperature without the presence of a catalyst, surfactants, additives, crosslinkers or chain extender. The presence of amine functional group in PKO-p provided an alternative route for catalysed PU polymerization. Therefore, production cost and chemical contact can be minimized.

2. Materials and method

2.1. Materials

PKO-p from palm kernel oil was synthesized by polyesterification in UKM in a laboratory using an established method by (Badri et al., 2000). Methylene diphenyl diisocyanate (MDI) was commercially obtained from Cosmopolyurethane (Malaysia) Sdn. Bhd., *1*-methyl-*3*-propylimidazolium iodide (MPII) (98%) by Sigma Aldrich, ethylene carbonate (EC), acetone and ethanol 99.9% were supplied by SYSTERM ChemAR (Kielce, Poland). DSSC components: iodine (I_2) (99.8%, solid) and titanium dioxide (TiO_2) were supplied by Sigma Aldrich (St. Louis, Mo, USA), di-tetrabutyl ammonium cis-bis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium (II) dye (N-719), platinum (Pt) paste under the commercial name Platisol T. Conventional electrolyte consists of lithium iodide salt in ionic liquid and pyridine derivatives with 50 mM of tri-iodide in acetonitrile (Iodolyte AN-50). 3 mm thick fluorine-doped tin oxide (FTO) with 8 and 15 Ω/cm^{-2} was used as transparent conductive oxide and were purchased by Solaronix (Aubonne, Switzerland). All materials were used without further purification.

2.2. Methods

Bio-based polyurethane (PU) films were synthesized by using palm kernel oil-based monoester-OH (PKO-p) and MDI. The PU was incorporated with MPII from 10 to 30 wt.% in order to prepare gel polymer electrolytes for DSSC by *in-situ* polymerization reaction. PKO-p was mixed together in 2,4′ MDI in acetone according to the 1:2 wt ratio (NCO:OH) at ambient room temperature and under nitrogen gas atmosphere. EC was added to the mixture as plasticizer at 20 wt.%. It was dissolved in separate acetone together with MPII at varying amounts of 10–30 wt.%. The mixture was stirred for an hour prior and further mixed. The solution then was cast into a teflon mould and let to be evaporated at room temperature for an hour.

2.3. Characterization

All samples were characterized using Fourier transform-infrared (FT-IR) spectroscopy to observe functional groups and chemical interactions in the system. FTIR was recorded by Perkin Elmer Spectrum 2000 equipped with attenuated total reflection (ATR) accessory in the range from 4000 to 650 cm^{-1} with the scanning resolution 2 cm^{-1} at room temperature (Full spectrum are given in supplementary data: **Fig. S1**). The T_g of the samples were observed using Mettler-Toledo DSC model 822 from 20 to 250 °C at a scanning rate of 10 °C/min under nitrogen atmosphere. Approximately, 2 mg of the electrolyte sample were used for each DSC measurement. The T_g of electrolyte was taken at mid-point of the endothermic peak and evaluated using STARe software. The thermal stability of the electrolyte was evaluated using thermogravimetric analysis (TGA) (model LabsysEvo, Setaram Instrument). The thermal stability was measured from 20 to 600 °C at heating rate of 10 °C min^{-1} under nitrogen atmosphere with 20 mL min^{-1} flow rate. The polymer decomposition temperature was determined from the derivative of TGA curves (DTG) as the peak maximum. The ionic conductivity measurements of the electrolytes were carried out by electrochemical impedance spectroscopy model Autolab potentiostat with frequency response analyzer (FRA) using NOVA software over a frequency range of 0.1 Hz–1 MHz at 100 mV amplitude. In this measurement, dip cell probe consisting of two platinum wires sheathed in a hollow cylinder glass designed by (Noor et al., 2015) was used to determine the conductance. Prior the measurement of every sample, the cell constant was determined with a solution of 0.01 M KCl at 25 °C which later been used for the calculation