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Exploring the effect of novel *N*-butyl-6-methylquinolinium bis(trifluoromethylsulfonyl)imide ionic liquid addition to poly(methyl methacrylate-co-methacrylic) acid electrolyte system as employed in gel-state dye sensitized solar cells

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ABSTRACT

With the aim of replacing liquid electrolytes in dye sensitized solar cells (DSSCs) due to the evident issues the system has, we have prepared and optimized gel polymer electrolytes (GPEs) consisting of poly (methyl methacrylate-co-methacrylic) acid, P(MMA-co-MAA), sodium iodide (NaI), iodine (I_2), ethylene carbonate (EC), propylene carbonate (PC) with a novel lab-made ionic liquid *N*-butyl-6-methylquinolinium bis(trifluoromethylsulfonyl)imide [C_4mquin][NTf_2]. Synthesized via metathesis following an alkylation, the quinolinium based ionic liquid has a yield of 87%. The highest ionic conductivity obtained for this system is 2.26×10^{-3} S cm^{-1} at room temperature for the GPE at 25 wt.% of [C_4mquin][NTf_2]. XRD and FTIR studies have been done to confirm the formation of complexes of the materials. With a standard DSSC arrangement of glass/FTO/TiO_2/N719dye/electrolyte/Pt/FTO/glass, the co-polymer based conducting electrolyte displayed power conversion efficiency of 5.67% with a maximum short circuit current density (J_{sc}) of 15.32 mA cm^{-2}, open circuit voltage (V_{oc}) of 0.62 V and fill factor of 59% at 25 wt.% of [C_4mquin][NTf_2] under AM 1.5 (100 mW cm^{-2}) illumination. The Nyquist plot and Bode plot studies have been done in order to understand the electrochemical properties of the GPE based DSSCs.

1. Introduction

One definition of dye sensitized solar cell would be a tiny device that functions alike plants by harvesting sunlight but converts them to electrical energy instead. Resembling a sandwich, the original cell consists of a top dye-dipped nanoporous TiO_2 layer and a bottom platinum coat both on a transparent conducting surface, filled by a thin layer of I_3^-/I^- redox electrolyte in the middle. The very first report of this technology was by O'Reagan and Gratzel in 1991 and research over the years has led to a substantial achievement ~ 15% efficienc.[1–3]. As the solar market grows substantively every year, meeting a greener energy demand, DSSCs have become more important considering their low production cost, simple assembly, ecological nature, good to high efficiency values and performance even in low-light conditions [4–6].

Some notable growth following 20 years of research on this solar harvesters include, photoanodes consisting of semiconductors like TiO_2, ZnO and SnO_2 that are now not only coated but also grown on the conductive surface, the use of myriad sensitizers ranging from the most used ruthenium based dyes (e.g. N719 & N3) to organic dyes and even quantum dots like CdS, CdSe and PbS to generate photo-excited electrons, alternative redox mediator namely Co^{2+}/Co^{3+} couple and the exploration for cheaper counter electrode containing carbon materials [7,8]. The fact that this discovery has not reached its pinnacle and every constituent of the cell still needs working on, continuous studies are done addressing the problems associated, in which one of is the replacement of liquid electrolytes with gel polymer counterparts. Despite having high photovoltaic efficiency, DSSCs carrying liquid electrolyte fallback on practical usage due to common complications like evaporation, leakage, desorption, photodegradation of the dye,

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corrosion of the platinum secondary electrode, flammability issues and ineffective sealing of cells [9–11].

Thus, came the shift in research attention towards gel polymer electrolytes (GPEs) containing a polymer network swollen with a solvent. One common method of gelation would be by the means of incorporating polymer matrices to organic solvents containing redox mediator, additives or ionic liquids. Polymeric gels are extensively developed as they are highly available with a low cost, barely undergo phase separation over time and yield good sunlight to electricity conversion efficiency [12–14]. Being a hybrid, GPEs retain the cohesive nature of solids electrolytes as well as being diffusive as liquid electrolytes producing reasonable ionic conductivity, low vapour pressure, good thermal stability and flexibility which creates good contact between components within the DSSCs [15–18]. GPEs prove to be suitable substitutes of their liquid counterparts as they make DSSCs more stable without considerable loss in efficiency.

In recent years, a correlation between the ionic conductivity and DSSC performance is established whereby, a hike in ionic conductivity is shown to enhance cell performance provided the ion conduction is the rate determining step among other transport processes irrespective of liquid, solid or gel- state DSSCs utilizing polymer electrolytes [19]. Evidently, it can be somehow concluded that the moderate energy conversion efficiency in DSSCs utilising GPE is significantly controlled by the ionic conductivity of the electrolytes. Besides, there are also postulations claiming that the possible performance reduction in gel-state DSSC maybe be due to restricted charge transport caused by the gel network inside the polymer matrix which commonly results in a photocurrent decrease when compared to those liquid equivalents. In contrast, it is also common to observe a photovoltage increase in DSSC containing GPEs due to the decrease in recombination process at the interface between the redox electrolyte and dye-adsorbed semiconductor electrode in the presence of new polymer barriers. Despite a usual increase in photovoltage, lower regeneration phenomena means a reduction in overall cell performance as well [20,21]. Another probability would be the gelators may have reacted with other components in the electrolyte [22].

As most GPE systems respond, we believe by adding ionic liquids to GPE systems which are primarily made of polymer and salt will have a progressive effect on photovoltaic performance of these GPE-based DSSCs. Generally, an organic cation and inorganic anion make up the ionic liquid [23]. By far, this combination functions better than most organic solvents with additional properties like high chemical and thermal stability, low vapour pressure, non-flammability, and few are known to have high electrochemical stability and hydrophobicity [24]. The use of ionic liquids namely with imidazolium, ammonium, pyridinium and sulfonium cation in not uncommon in the field of electrolyte research. However, these ionic liquids with high viscosities result in lower conversion efficiency owing to mass-transport limitation [25]. Thus, new cation-anion combinations to make up ionic liquids are vigorously explored. As we are aware of, only Huang et al. have successfully tested the implementation of a quinolinium based ionic liquid with a conversion efficiency of 4.04% [26].

In this work, GPE systems consisting of P(MMA-co-MAA) were prepared using NaI salt, EC/PC as solvent cum plasticizers with varied addition of [C_4mquin][NTf_2] ionic liquid to further examine the correlation between ionic conductivity and cell performance by conducting electrochemical impedance study. The copolymer content in the resulting GPE ranges from 18% to 26% by mass. We used a generic DSSC configuration of FTO-coated-glass/TiO_2 sensitized with N719 dye/electrolyte/Pt/FTO-coated-glass. Along with this, temperature dependence study on the GPEs and sample characterisations were also done.

2. Experimental

2.1. Synthesis of novel N-butyl-6-methylquinolinium bis (trifluorosulfonylmethyl)imide

The Centre of Research in Ionic Liquids (CORIL), Universiti Teknologi PETRONAS (UTP), conducted the synthesis of this ionic liquid. It was done via a metathesis reaction following an alkylation.

Firstly, 6-methylquinoline (50.02 g, 0.35 mol) of was dissolved in 50 ml of acetonitrile. 1-bromobutane (56.51 g, 0.41 mol) was added drop-wise to the reaction mixture using a dropping funnel. The mixture was then stirred vigorously at 75 °C at 500 rpm under continuous nitrogen supply. Next, the mixture was washed with ethyl acetate (5 × 50 ml). Subsequently, the sample was dried under vacuum. The resulting mixture was recrystallized using a 1:1 ratio of acetonitrile and ethyl acetate forming light pink crystals of *N*-butyl-6-methylquinolinium bromide [C_4mquin][Br].

The initial product, [C_4mquin][Br] (10.00 g, 0.035 mol) was then dissolved in distilled water. The mixture was heated at 50 °C followed by the addition of equimolar lithium bis(triflouromethylsulfonyl) imide (10.05 g, 0.035 mol). The solution was allowed to mix for 3 h and the ionic liquid was separated from water through decanting. The product was washed with cold distilled water (5 × 20 ml). The resulting solution was dried under vacuum forming light red crystals of *N*-buytl-6-methylquinolinium bis (trifluoromethylsulfonyl) imide [C_4mquin][NTf_2]. The ^{1}H, ^{13}C and ^{19}F NMR spectra confirmed the structure of [C_4mquin][NTf_2], which showed the following chemical shift: ^{1}H NMR δ 0.90–0.93 (t, 3H), 1.35–1.43 (m, 2H), 1.90–1.97 (m, 2H), 2.61 (s, 3H), 5.04–5.07 (t, 2H), 8.12–8.16 (m, 2H), 8.26 (s, 1H), 8.54–8.56 (d, 1H), 9.18–9.19 (d, 1H), 9.52–9.54 (d, 1H); ^{13}C NMR δ 13.91, 19.59, 21.28, 33.02, 57.52, 119.21, 122.59, 129.62, 130.35, 136.40, 138.08, 140.72, 146.96, 149.00; ^{19}F NMR δ −78.73. The presence of halide impurities was quantified using Metrohm 850 Professional Ion Chromatography and MetrosepASupp 4 column based on a technique described by

Table 1
Composition of P(MMA-co MAA) GPEs with varying [C_4mquin][NTf_2] wt % content.

Samples	[C_4mquin][NTf_2] (wt. %)	Polymer (g)	NaI (g)	I_2 (g)	[C_4mquin][NTf_2] (g)	EC/PC (g)
Q0	0	1.300	1.0	0.2	0	2.5
Q5	5	1.235	0.95	0.19	0.125	2.5
Q10	10	1.170	0.90	0.18	0.250	2.5
Q15	15	1.105	0.85	0.17	0.375	2.5
Q20	20	1.040	0.80	0.16	0.500	2.5
Q25	25	0.975	0.75	0.15	0.625	2.5
Q30	30	0.910	0.70	0.14	0.750	2.5