Improvement of N-phthaloylchitosan based gel polymer electrolyte in dye-sensitized solar cells using a binary salt system

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ABSTRACT

A binary salt system utilizing lithium iodide (LiI) as the auxiliary component has been introduced to the N-phthaloylchitosan (PhCh) based gel polymer electrolyte consisting of ethylene carbonate (EC), dimethylformamide (DMF), tetrapropylammonium iodide (TPAI), and iodine (I2) in order to improve the performance of dye-sensitized solar cell (DSSC) with efficiency of 6.36%, photocurrent density, Jsc of 17.29 mA cm−2, open circuit voltage, Voc of 0.59 V and fill factor, FF of 0.62. This efficiency value is an improvement from the 5.00% performance obtained by the DSSC consisting of only TPAI single salt system. The presence of the LiI in addition to the TPAI improves the charge injection rates and increases the iodide contribution to the total conductivity and both factors contribute to the increase in efficiency of the DSSC. The interaction behavior between polymer–plasticizer–salt was thoroughly investigated using EIS, FTIR spectroscopy and XRD.

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1. Introduction

Dye-sensitized solar cells (DSSCs), the third generation solar cells, receive enormous attention among electrochemists due to their high efficiency obtained with simple, low cost fabrication technique. To date, the traditional liquid electrolyte solar cell comprising organic solutions has recorded a remarkable power conversion efficiency of 12% (Yella et al., 2011). Despite such high efficiency, the technology could not be implemented in large scale due to difficulty in assembly, leakage and evaporation of the organic liquid electrolytes. Thus, various attempts have been done to introduce a solid or quasi-solid electrolyte instead. Among these efforts, polymer based quasi-solid-state electrolytes have been attracting particular interest because of their effectiveness in overcoming the technical difficulties imposed by the liquid electrolyte system without compromising the power conversion efficiency (Grätzel, 2005; Nei de Freitas, Nogueira, & De Paoli, 2009).

An extensive study on a variety of synthetic polymers such as poly(aniline) (PAN), poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), poly(vinyl alcohol) (PVA) and poly(vinylidene fluoride) (PVdF) (Suait, Rahman, & Ahmad, 2015; Wu et al., 2015) has been covered in the recent literature. However, the current trend of green material motivations need to explore biopolymers as prospective polymer hosts in DSSCs. Although various polysaccharides including chitosan (Ma & Sahai, 2013), cellulose (Ahmad & Is, 2016) and agarose (Singh, JadHAV, Majumder, Bhattacharya, & Singh, 2013) have been employed as polymer electrolytes, the fabrication of these natural polymers as competent electrolytes is often inhibited by their crystallinity and inability to be dissolved in an organic medium. A promising candidate to address this problem would be chitosan as the presence of its functionally active amino group can easily be phthaloylated in order to improve its solubility in organic solvents such as DMF, DMSO, DMAc and pyridine (Kurita, Ikeda, Shimojoh, & Yang, 2007). The simple esterification process was proven to be very effective in modifying the natural polymer and has been successfully used as a host matrix in polymer electrolytes (Azzahari, Yusuf, Selvanathan, & Yahya, 2016; Yusuf et al., 2014).

In our previous study, a bulky quaternary ammonium iodide salt was employed since it was expected to reduce cationic conductivity while enhancing the iodide anionic conductivity in the electrolyte (Yusuf et al., 2016). However, recently it has been reported that by including small cations such as Li+, K+ or Mg2+ into the gel polymer electrolytes along with the bulky cations, the efficiency of solar cells can be significantly improved (Dissanayake et al., 2012;...
justifies the drop in $J_{SC}$ value from B3 to B6. In total, the two competing mechanisms imposed by the small and large cations, work synergistically in this binary iodide system to produce an optimum $J_{SC}$ and hence efficiency at B3.

A brief summary of some recent work in the literature for the parameters of mixed iodide salt studies in polymer electrolyte based DSSC is shown in Table 3. In all cases, it was observed that the mixed salt systems were always superior in performance compared against systems consisting of only single salts. To the best of our knowledge, GPE systems utilizing biopolymers are still scarce, and yet from the table, it is evident that this work has shown that the solar cell efficiency attained is comparable or in some cases, even better than synthetic polymer based DSSCs.

### 4. Conclusions

The novelty of this system is the chitosan-based component of the electrolyte. A gel polymer electrolyte was successfully prepared with N-phthaloylchitosan as the polymer host matrix, EC and DMF as the entrapped solvents, and a triiodide salt system consisting of mixtures of tetrapropylammonium iodide and lithium iodide which can dissociate into large and small cations respectively. In the context of the microstructure, FTIR analyses have shown that at high ratios of LiI, complexation of the salt with the polymer/plasticizer matrix leads to an increase in the amorphousness of the gel polymer electrolyte which is corroborated by XRD spectra. Apart from conductivity, the number density of mobile ions, $n$ and mobility of charge carriers, $\mu$ play an important role towards the characteristics of the GPE. The optimum performance was obtained for the sample B3 where PhCh:EC:DMF:TPAI:LiI in weight ratio (g) of 0.1:0.3:0.3:0.06:0.06:0.012 showed efficiency of 6.36%, with $J_{SC}$ of 17.29 mA cm$^{-2}$, $V_{OC}$ of 0.59 V and fill factor of 0.62. Where other previous literature has been focused on synthetic polymer electrolytes, this work has shown that the improvement by synergistic salt-matrix interactions properties of the binary salt system which is superior to that of either single salt system is also applicable to electrolytes based on natural polymers.

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### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2016.10.032.