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A Novel Biopolymer Gel Electrolyte System for DSSC Applications

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Abstract: A novel biopolymer gel-electrolyte system was prepared using κ-carrageenan as polymer host incorporated with I^-/I_3^- redox couple dissolved in an environmentally benign solvent dimethylsulfoxide (DMSO). When the κ-carrageenan concentration is at 2% w/v, it forms a gel at room temperature. The gel-polymer electrolyte system was used in dye-sensitized solar cell (DSSC) applications with the configuration TiO_2/dye/κ-carrageenan gel electrolyte/Pt sandwiched in between two FTO conducting glass substrates. The assembled DSSC was characterized using EIS technique to describe the charge-transfer processes occurring in its interfaces and IV-measurements under AM 1.5 illumination to determine the overall solar cell efficiency. Comparison with DSSC without κ-carrageenan revealed better efficiency due to less charge recombination process occurring in the TiO_2/dye/electrolyte interface.

Key Words: Dye-sensitized solar cell, κ-carrageenan, benign solvent

1. INTRODUCTION

A dye-sensitized solar cell (DSSC) is a photovoltaic device that converts solar energy into electrical energy (Sumathy, Gong, Liang, 2012). A typical DSSC is composed of dye-coated mesoporous TiO2 thin film layer which absorbs light, a liquid electrolyte system composed of I^-/I_3^- redox couple and a platinum catalyst, in which all composed are sandwiched between two FTO or ITO conducting glass substrates (Narayan, 2012). However, the use of liquid electrolytes hinders the long-term stability as well as commercialization of DSSC due to leakage and evaporation of solvent (De Paoli, Nogueira, & Longo, 2004). One of the possible solutions to this problem is the incorporation of a gel-polymer electrolyte system capable of trapping the solvent in its polymer matrix.

Some naturally occurring polymers, particularly polysaccharides, are capable of forming gels and were studied for DSSC applications. To name a few – agarose (Guo, Wang, Yang, Cui, Yi, & Zheng, 2014), chitosan (Rhee, Singh, Bhattacharya, Nagarale, & Kim, 2010) and carrageenan (Kaneko, Hoshi, Kaburagi, & Ueno, 2004) were some of the few polysaccharides used as polymer electrolytes in DSSC applications with efficiencies reaching as high 7%. κ-Carrageenan is a linear sulfated polysaccharide extracted from specific red seaweeds (Carvalho, Campo, Kawano, da Silva, 2009). This polysaccharide forms stable gel at room temperature due to the formation of double helical structures and consequent cation-specific aggregation (Paulson, Nickerson, & Hallett, 2004; San Biagio, Mangione, Giacommazza, Bulone, Martorana, & Cavallaro, 2005).

In this paper, a novel gel biopolymer electrolyte using κ-carrageenan in DMSO, an environmentally benign solvent, containing a typical I-/I3- redox couple was used for DSSC applications.

2. METHODOLOGY

A κ-carrageenan (Mioka Biosystems, Inc.) electrolyte system was prepared by dissolving the polysaccharide in dimethylsulfoxide at 70˚C. A stable gel-state electrolyte system was attained when the concentration is at 2% (w/v). Electrolytes were prepared containing 0%, 1% and 2% (w/v) κ-carrageenan with 0.5 M tetrabutylammonium iodide (Aldrich, reagent grade, 98%), 0.05 M iodine (Aldrich >99.99% metal basis) and 0.1 M lithium iodide.

The photoanode was prepared by spreading titania paste in 0.25 cm^2 active area using doctor blade method. The prepared TiO_2 thin film was sintered at 450˚C for 30 mins and cooled slowly up to 80˚C. The photoanode was soaked in an ethanolic dye solution containing Ruthenizer 535-bisTBA (N719) (Solaronix) for 24 hours. The counterelectrode was prepared by brushing an alcoholic solution of H_2PtCl_6 in 2-propanol at 450˚C for 30 mins.

A DSSC was fabricated by sandwiching the electrodes with a 25μm thick hot-melt material. The hot κ-carrageenan electrolyte was inserted in between through pre-drilled holes in the counter-electrode. The DSSCs were characterized using IV-measurements and impedance spectroscopy both under AM 1.5 illumination using μAutolab III FRA.

3. RESULTS AND DISCUSSION

The IV-measurements and results of the photovoltaic performance of κ-carrageenan electrolytes in DSSC are shown in figure 1 and table 1, respectively.

Table 1: Photovoltaic parameters of DSSCs

Solar Cell	Short-circuit current, mA/cm²	Open-circuit voltage, V	Fill factor	Efficiency
Control (without κ-carrageenan)	0.690	0.781	0.410	0.221
Liquid-state PE, 1% w/v κ-carrageenan	0.960	0.763	0.483	0.354
Gel-state PE, 2% w/v κ-carrageenan	0.983	0.751	0.488	0.360

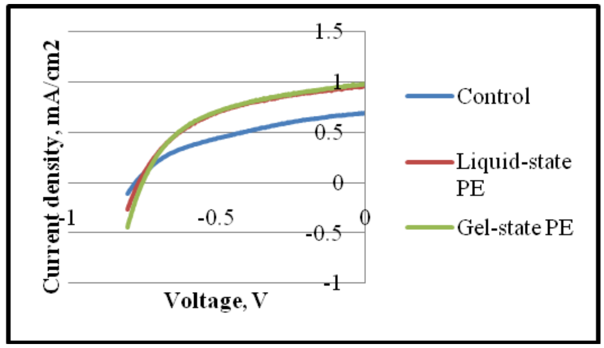

Figure 1: IV-measurements of DSSC under AM 1.5 illumination

Based on table 3, the addition of κ-carrageenan has increased the short-circuit current and decreased the open-circuit voltage of the fabricated DSSCs. The increase in overall efficiency of the κ-carrageenan polymer electrolyte-based DSSCs could be attributed to the imcrease in the short-circuit current.

FRA impedance analysis was employed to further explain the charge-transfer kinetics in the DSSC. Figure 2 shows the Nyquist plot and equivalent circuit model of each fabricated DSSCs. The equivalent circuit model is composed of R1 (solution resistance), R2 (charge-transfer resistance in the TiO_2/dye/electrolyte interface and CPE (constant phase element).

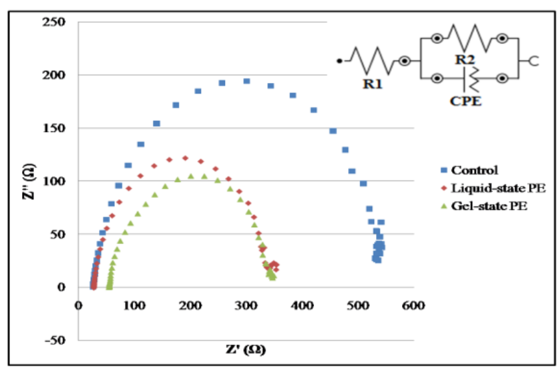

Figure 2: Electrochemical impedance spectroscopy spectrum of the fabricated DSSCs.

The Nyquist plot shows a single semi-circle arc which is an indication of R2, which is the charge-transfer resistance in the TiO_2/dye/electrolyte interface. The charge-transfer resistances obtained based on the the equivalent circuit model for 0% (w/v), 1% (w/v) and 2% (w/v) κ-carrageenan in DMSO containing the iodide/tri-iodide redox electrolyte are 515.19 Ω, 317.88 Ω and 292.86 Ω, respectively. A higher R2 (or a charge-transfer resistance in the dye/TiO_2/electrolyte interface) indicates a lower charge recombination between the photoanode conduction band electrons and I_3^- ions (Wang, Guo, Yi, Yang, Cui, Xiao, 2013). A lower charge recombination resistance leads to higher open-circuit voltages; thus, it is consistent with the photovoltaic parameters results.

4. CONCLUSIONS

A novel biopolymer gel-electrolyte system composed of κ-carrageenan and I^-/I_3^- redox couple in dimethylsulfoxide was developed. Addition of κ-carrageenan has increased the short-circuit current of the DSSCs but decreased the open-circuit voltage due to increase electron recombination. An efficiency of 0.360% was attained.

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