

고체형 염료감응 태양전지용 초분자 전해질 개발

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Design of Supramolecular Electrolytes for Solid State Dye-sensitized Solar Cells

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Abstract : Solid-state dye-sensitized solar cells (DSSCs) have been constructed employing supramolecular electrolytes with multiple hydrogen bonding. A supramolecule was facilely synthesized by one-pot reaction between the amines of methylisocytosine (MIC) and the epoxy groups of poly(ethylene glycol diglycidyl ether) (PEGDGE) to produce quadruple hydrogen bonding units. Hydrogen bonding interactions and dissolution behavior of salt in supramolecular electrolytes are investigated. The ionic conductivity of the supramolecular electrolytes with ionic liquid, i.e. 1-methyl-3-propylimidazolium iodide (MPII) reaches 8.5×10^{-5} S/cm at room temperature, which is higher than that with metal salt (KI). A worm-like morphology is observed in the FE-SEM micrographs of TiO₂nanoporous layer, due to the connection of TiO₂ nanoparticles resulting from adequate coating by electrolytes. DSSCs employing the supramolecular electrolytes with MPII and KI exhibit an energy conversion efficiency of 2.5 % and 0.5 %, respectively, at 100 mW/cm², indicating the importance of the cation of salt. Solar cell performances were further improved up to 3.7 % upon introduction of poly(ethylene glycol dimethyl ether) (PEGDME) with 500 g/mol.

1. 서 론

Dye-sensitized solar cells (DSSCs) have become one of the major topics for next generation energy devices since highly efficient performances (~11%) together with low cost were reported by Grätzel' s group in 1991. Initial works were mostly based on liquid-state electrolytes, but this type of DSSC has unsolved critical problems such as leakage and evaporation of the liquid medium. Furthermore, solid-state or quasi solid-state DSSCs are advantageous over liquid based counterparts in terms of lightness, flexibility and long-term stability. Thus, there has been a great deal of research in the development of solid-state DSSC with higher efficiencies and long-term stability. However, the energy conversion efficiencies of

solid-state DSSCs are still lower than those of liquid-state DSSC. The basic reason is the lower ionic mobility of the redox species in

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the polymeric medium and poor interfacial contact between electrolytes and electrodes, which directly affects the cell performances. One of the most effective methods of improving the performances in the solid-state DSSC is the "oligomer approaches", proposed by Kang' s group. Here, similar concept was adopted to fabricate solid-state DSSC in terms of using supramolecular material with multiple hydrogen bonding units but the material was facilely synthesized by a single-step reaction between the amine of MIC and the epoxy group of poly(ethylene glycol diglycidyl ether) (PEGDGE). The resultant electrolytes are characterized in terms of ionic conductivity, thermal, structural and mechanical properties, as well as energy conversion efficiencies of DSSC.

2. 실험

2.1 Synthesis of Supramolecule, MIC-PEGDGE

A supramolecule with multiple hydrogen bonding units was synthesized according to the previously reported method. Briefly, 10 g of poly(ethylene glycol diglycidyl ether) (PEGDGE, $M_n=526$ g/mol, Polysciences, Inc.) were dissolved in 50 ml of ethyl acetate and then 9.6 g of methyl isocytosine (MIC, 2-amino-4-hydroxy-6-methylpyrimidine, Aldrich) was added to the solution. The mixture was refluxed at 120 °C for 18 hours. Then the solution was allowed to cool to room temperature, and some excess of THF was added. This mixture was separated into two layers, and top solution part was filtered by syringe. The solution was dried in a hood at room temperature for 24 hours, and dried in a drying oven at 60 °C for 24 hours. The resultant material was placed in a vacuum oven for 24 hours to remove the residual solvent. The resultant orange product was obtained in a yield of 95 %.

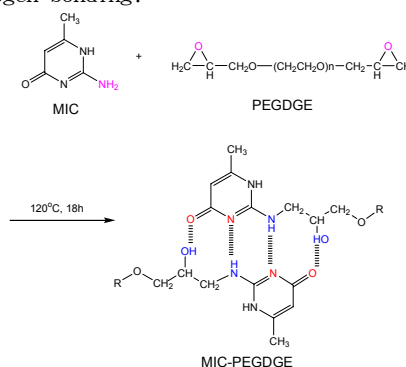
2.2 Preparation of Electrolytes

Depending on the concentrations of salt, predetermined amounts of MIC-PEGDGE supramolecule, salt and I_2 were dissolved in acetonitrile to make up 10 wt% of polymer solutions. Three kinds of salt, i.e. only metal salt (KI), only ionic liquid (1-methyl-3-propylimidazolium iodide, MPII) and salt mixture (KI+MPII at 50:50 wt%) were used to make polymer electrolytes. The solutions were then cast on a teflon-glass plate and dried in an N_2 environment at room temperature. The films were further dried in a

vacuum oven for two days at room temperature.

3. 결과 및 토론

The schematic drawing of the reaction for a supramolecule containing multiple hydrogen bonding units is presented in Scheme 1. The reaction involves one-pot synthesis between the primary amine (NH_2) of MIC and the epoxy group of PEGDGE to produce four functional groups of $-C=O$, $-N=$, $-NH$ and $-OH$, providing the appropriate units for multiple hydrogen bonding.



Scheme. 1 Schematic representation of one step reaction for multiple hydrogen bonded supramolecule

The resultant MIC-PEGDGE supramolecule was complexed with salt such as potassium iodide (KI) and ionic liquid (MPII) to produce supramolecular electrolytes. Pristine PEGDGE with low molecular weight ($M_n=526$ g/mol) is in the liquid state at room temperature and fluidic upon external force such as gravity. When multiple hydrogen bonding units such as $-C=O$, $-N=$, $-NH$ and $-OH$ were introduced, however, the supramolecule became non-fluidic at room temperature, indicating the improvement of mechanical properties, i.e. viscosity. Interestingly, the MIC-PEGDGE supramolecule became fluidic upon heating up to 70 °C and again non-fluidic upon removal of heat, representing that its property changes are reversible with respect to external forces such as temperature and solvent. When a metal salt such as KI was subsequently introduced, the supramolecule showed transparency and film-forming properties resulting from the further enhancement of mechanical properties. The supramolecule electrolytes containing I_2 still exhibited the flexible properties of film.

The ionic conductivities of supramolecular electrolytes were measured as a function of salt weight fraction and presented in Figure 1. All three electrolytes with MPII, KI and MPII+KI (50:50 wt%) exhibited the

similar behavior of ionic conductivity.

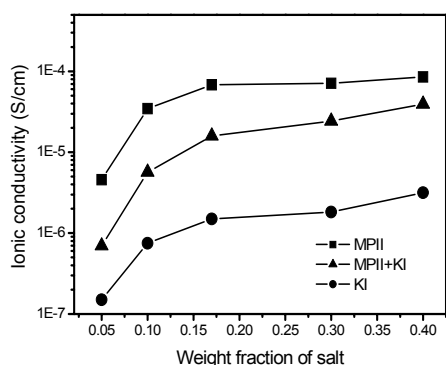


Figure. 1 Ionic conductivities of supramolecular electrolytes containing MPII, KI and MPII+KI (50:50 wt%) as a function of salt concentration

General behavior is that the ionic conductivity increases sharply at low salt concentrations (i.e. up to 0.17 of salt weight fraction) but does not vary significantly at high concentrations. It is well known that the initial increase of ionic conductivity is due to the increased number of charge carrier and the decrease results from the formation of ion pairs or higher order ionic aggregates in the polymer electrolytes. However, the ionic conductivity of our supramolecular electrolytes did not decrease significantly even at high salt concentrations up to 0.4 weight fraction of salt. This unusual behavior could be elucidated in terms of unusually high solubility of salt in polymer electrolytes. It was also found that the ionic conductivities of MPII electrolytes were always higher than those of KI electrolytes, demonstrating that ionic liquid is more effective in making polymer electrolytes flexible than metal salt. Maximum ionic conductivity was obtained for MPII electrolytes on 8.5×10^{-5} S/cm at room temperature.

DSSC employing supramolecular electrolytes were fabricated and the cell performances were measured using linear sweep voltammetry as presented in Figure 2. The total salt concentration was fixed at 0.17 since ionic conductivity was not significantly changed above 0.17 of salt weight fraction. The cell performance of DSSC employing MIC-PEGDGE/KI electrolyte was as low as 0.5 % at 100 mW/cm^2 , which seemingly results from low ionic conductivity due to high T_g of electrolytes. When more flexible salt, i.e. MPII was used as an ion carrier, the conversion efficiency of DSSC was increased up to 2.5 % at the same conditions. It was also found that DSSC employing mixed salts of KI

and MPII (50:50 wt%) exhibited intermediate cell performances between the two values of electrolytes containing KI and MPII only, representing the importance of the cation of salt. One of the "oligomer approaches" includes additional incorporation of low molecular weight oligomer, which improves ionic conductivity as well as interfacial contact between electrolytes and electrodes.

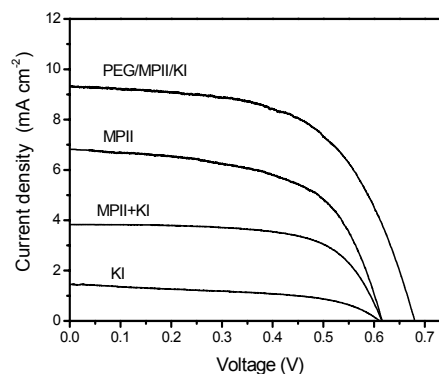


Figure. 2 J-V curves of DSSC employing MIC-PEGDGE/KI, MIC-PEGDGE/MPII, MIC-PEGDGE/KI+MPII and MIC-PEGDGE/KI+MPII+PEG electrolytes

In this work, thus, poly(ethylene glycol dimethyl ether) (PEGDME) oligomer with 500 g/mol was additionally introduced at 30 wt% to enhance the cell performances. As a result, the overall energy conversion efficiency of DSSC was further improved to 3.7 % with a short circuit current density (J_{sc}) of 9.3 mA/cm^2 , an open circuit voltage (V_{oc}) of 0.68 V and a fill factor (FF) of 59% at 100 mW/cm^2 .

4. 결론

A supramolecule containing multiple hydrogen bonding units has been designed for use as an electrolyte in DSSCs by single-step reaction between the amine of MIC and the epoxy group of PEGDGE. The ionic conductivity of the supramolecular electrolytes with ionic liquid (MPII) reached 8.5×10^{-5} S/cm at room temperature, which is always higher than that with metal salt (KI). The ionic conductivity of supramolecular electrolytes did not significantly decrease even at high salt concentration ranges, mostly due to the high solubility of metal salt in supramolecular matrix. When multiple hydrogen bonding units were dangled from PEGDGE supramolecule, the T_m disappeared completely and the T_g was increased significantly. T_g was further increased upon the incorporation of metal salt such as KI but marginally changed in the case of ionic liquid such as MPII, resulting from

the coordinative interactions between polymeric chains and salt. All the supramolecular materials were amorphous and the salts such as KI and MPIO were well dissolved in the PEGDGE matrix, as revealed by WAXS analysis. The mechanical properties of supramolecule were significantly enhanced upon introduction of multiple hydrogen bonding units and further increased upon the incorporation of metal salt. FE-SEM micrographs demonstrated that the good interfacial contact between nanocrystalline TiO₂ layer and electrolytes was achieved upon introduction of MIC-PEGDGE electrolytes. DSSCs employing the MIC-PEGDGE supramolecular electrolytes with MPIO, KI and MPIO+KI exhibited 2.5, 0.5 and 1.5 %, respectively, of overall energy conversion efficiency at one sun condition (100 mW/cm²). When PEGDME oligomer with 500 g/mol was additionally introduced, the overall energy conversion efficiency of DSSC was further improved to 3.7 % at the same conditions.

후기

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