Photoelectrochemical effects of hyperbranched polyglycerol in gel electrolytes on the performance of dye-sensitized solar cells

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1. Introduction

Dye-sensitized solar cells (DSSCs) based on visible dye sensitizers adsorbed onto nanoporous TiO2 electrodes are have attracted widespread scientific and technological interest because of their low manufacturing costs and relatively high energy conversion efficiencies compared with inorganic photovoltaic devices [1–6]. DSSCs contain a dye absorbed onto a TiO2 electrode, a platinum-coated counter electrode, and an electrolyte containing I3−/I− redox ions, which mediate electron flow between the photoelectrode and the counter electrode. Electrons generated from excited dye molecules upon irradiation with visible light are injected into the conduction band of the TiO2 electrode. Oxidized dye molecules are regenerated by I− ions in the electrolyte, and I− ions are oxidized to I3−. I3− ions are reduced to I− ions by accepting electrons at the counter electrode, and the process repeats [7,8]. The charge carrier transfer properties of an electrolyte play an important role in the regeneration of oxidized dye molecules, which significantly affects the performance of DSSCs. Since DSSCs were first invented by Grätzel and co-workers, energy conversion efficiencies in excess of 11% have been obtained using DSSC photovoltaic devices containing a liquid electrolyte, that exhibits a high ion conductivity [9,10]. However, a major shortcoming of liquid electrolyte-based DSSCs is their poor long-term stability due to solvent evaporation and leakage of the liquid electrolyte [11–13]. To improve the long-term stability of DSSCs, considerable investigative efforts have been applied toward developing durable electrolytes [14–17].

Gel electrolytes, which show good stability and can be prepared via gelation of a liquid electrolyte, are good candidates for replacing liquid electrolytes [8,18]. Inorganic gelators, such as silica nanoparticles, are promising materials because the resulting gel electrolytes provide better ion transfer properties due to ion exchange than that of gel electrolytes result from other materials [19–23]. Gel electrolytes are difficult to use in practical applications because the ion transfer rates are lower than in liquid electrolytes. Research efforts have focused on improving ion transfer properties in gel electrolytes, to enhance the performance of DSSCs. Some approaches have attempted to enlarge the ion transfer channels in gel electrolytes. For example, TiO2 nanoparticles were added as nanofillers to gel electrolytes composed of poly(ethylene oxide) (PEO) or poly(vinylidenefluoride-co-hexa-fluoropropylene) (PVDF-HFP), and the particles increased the ion conductivity by decreasing the crystallinity of the polymer and introducing carrier transfer channels in the gel electrolyte [21,24,25].

Hyperbranched-network polymers have been used as gel electrolytes to increase ion transfer by increasing the free volume within the gel electrolyte. Hyperbranched network-based gel polymer electrolytes consisting of modified bismaleimide oligomers (MBMI) as a free volume additive and poly(ethylene glycol) diacylate (PEGDA) as a crosslinking network were synthesized for...
use in lithium ion batteries, and their ion conductivities increased due to an increase in the free volume space [26]. Another route to improving ion transfer involved accelerating ion dissociation within the gel electrolyte. DSSCs with gel polymeric electrolytes based on a polymer matrix, such as poly(ethylene glycol) (PEG) have been reported by Kumar et al. Because PEG is a polar polymer, salts in the electrolyte dissociate easily and increases the concentration of charge carrier owing to the cation binding ability of PEG chain [27]. These studies prompted our interest in incorporating hyperbranched polyglycerol (HPG) into gel electrolytes for improvement in ion transfer property. HPG is a hyperbranched polymer which comprising a highly branched structure with many ether groups within the polymer chain [28]. In our previous work, it had been proven that the molecular mobility of hyperbranched polymer is higher than that of linear polymer due to its highly branched structure [29,30]. Thus, we expect that incorporating HPG may potentially promote carrier ion transfer in the gel electrolyte attributed to its high molecular mobility. Additionally, the polarity of the ether groups in HPG can improve ion dissociation within the gel electrolyte, to enhance carrier ion transport. Scheme 1 is a schematic drawing of the effects of HPG in the gel electrolyte proposed here. To the best of our knowledge, no reports have described gel electrolyte-based DSSCs using hyperbranched polymers as an ion transport enhancer.

In this study, a gel electrolyte containing HPG was prepared for use in DSSC applications. HPG was added as an ion transport enhancer into liquid electrolytes and silica nanoparticles were subsequently introduced as a gelator into liquid electrolytes/HPG mixture to form gel electrolytes. The effects of HPG on the charge transfer properties and the performance of DSSCs were investigated. Incorporation of HPG into the gel electrolytes proved to be an efficient method for enhancing the energy conversion efficiency of DSSCs.

2. Experimental

2.1. Materials

Glycidol, potassium methoxide, guanidine thiocyanate, silica (7 nm, fumed), and 4-tert-butylpyridine were purchased from Sigma–Aldrich. Iodine (99.99+%), and 3-methoxypropionitrile (99%) were acquired from Alfa Aesar, 1,1,1-Tris(hydroxymethyl)propane (TMP) and 1-butyl-3-methylimidazolium iodide (BMIII) were obtained from TCI and C-TRI, respectively. All chemicals were used as received without further purification.

2.2. Polymerization of hyperbranched polyglycerol (HPG)

A potassium methylate solution (3.7 M) was prepared by dissolving 0.285 g (4 mmol) potassium methoxide in methanol. TMP (1.818 g) was partially deprotonated (10%) with 3.7 M potassium methylate, and the by-product methanol was distilled off at 50 °C until no further bubbles appeared. Glycidol (13.43 mL) was slowly added dropwise using a syringe pump over 24 h to a flask maintained at 100 °C. Polymerization was terminated by dissolving the product in methanol. The methanol solution was then neutralized by filtration over a cation-exchange resin. The product was twice precipitated from methanol in acetone and subsequently dried for 15 h at 80 °C in a vacuum oven. Finally, the highly viscous HPG product was obtained.

2.3. Preparation of HPG-incorporated gel electrolytes

The liquid electrolyte was composed of 0.06 M iodine, 1.4 M 1-butyl-3-methylimidazolium iodide (BMIII), 0.2 M guanidine thiocyanate, and 0.2 M 4-tert-butylpyridine in 3-methoxypropionitrile. Several ratios of HPG (0.3 wt%, 0.5 wt%, 1 wt%, 1.5 wt% and 3.0 wt%) were dissolved in the liquid electrolyte by vigorous shaking (300 rpm) for 12 h. Silica nanoparticles (6 wt%) were mixed by magnetic stirring with the liquid electrolyte/HPG mixture to form the gel electrolyte. The resulting gel electrolytes were denoted H-0, H-0.5, H-1.0, H-1.5, and H-3.0 for of HPG composition ratios of 0, 0.3, 0.5, 1.0, 1.5 and 3.0 wt%, respectively.

2.4. Assembly of dye-sensitized solar cells (DSSCs)

A TiO2 nanoparticle paste (Ti-Nanoxide D, Solaronix) was spread onto a fluorine-doped SnO2 (FTO) conducting glass substrate (TEC-15, Pilkington) by the doctor-blade technique followed by sintering at 500 °C for 30 min to form a TiO2 nanocrystalline film. Nanocrystalline TiO2 electrodes 12 μm in thickness were immersed in an ethanolic solution containing 3 × 10^{-4} M ruthenium sensitizer dye, cis-dioctyldiisocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis (tetrabutylammonium) (DT719) for 12 h. The active areas of cells were from 0.310 to 0.340 cm². The platinized counter electrode was placed on top of the dye-coated TiO2 electrode sealed with a Surlyn polymer film.
(25 μm thick, DuPont), and the gel electrolyte was injected through a hole in the counter electrode. The holes were sealed with a Surlin film and glass cover slip. In this study, DH-x denotes a DSSC prepared with H-x.

2.5. Characterization

The structural properties of the hyperbranched polyglycerol (HPG) were qualitatively characterized by 1H nuclear magnetic resonance spectroscopy (1H NMR) employing a 600 MHz high-resolution Bruker AVANCE 600 spectrometer with tetramethylsilane (TMS) as the internal standard in methanol-d4 (CD4OD). Fourier-transform infrared (FT-IR) spectra were used to monitor the polymerization reaction using a PerkinElmer GX Fourier-transformed infrared spectrophotometer with a spectral resolution of 4 cm⁻¹ in the range of 4000–400 cm⁻¹. All samples were prepared by compression-molding, and potassium bromide (KBr) powder was used as both a sample matrix and a reference material. KBr pellets containing 2 mass% materials were analyzed.

The hyperbranched structure of HPG was examined via distoionless enhancement by polarization transfer (DEPT) 13C NMR and inverse gated (13C) 13C NMR (600 MHz high-resolution NMR spectrometer, Bruker AVANCE 600) with tetramethylsilane (TMS) as the internal standard in methanol-d4 (CD4OD). Different HPG structural types were characterized qualitatively and quantitatively according to 13C NMR spectral analysis. The degree of branching (DB), number average degree of polymerization, DPn, and number average molecular weight, Mn, were calculated based on equations reported in the literature [31]. The absolute molecular weight of HPG was estimated by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry employing a Voyager-DE™ STR Biospectrometry Workstation (Applied Biosystems Inc.).

The radius of gyration, Rg, of HPG was determined from small angle X-ray scattering (SAXS) experiments to determine the penetration of HPG into the TiO2 electrode pores. The SAXS intensity distribution, I(q), was measured using an X-ray generator (Bruker GADDS) operated at 40 kV and 45 mA. The X-ray source was monochromatized CuKα radiation (λ = 1.5406 Å), and the scattering angle ranges between 0° and 9° (2θ). The value of Rg was obtained by curve fitting of reciprocal plots of I(q) as a function of q using the Zimm scattering function. The pore size distributions in the TiO2 films were determined according to the Barrett–Joyner–Halenda method (BJH, Sorptomatic 1990) method using the nitrogen desorption branches of the isotherms to confirm whether the pore size in the TiO2 electrodes was sufficiently large to allow infiltration of HPG.

The ion conductivities of the gel electrolytes were measured using an impedance analyzer (Solatron 1260), with a frequency range of 0.1–105 Hz. The magnitude of the alternative signal was 10 mV. The experiments were performed with the gel electrolytes sandwiched between platinum-coated electrodes. The impedance parameters were determined by fitting of the impedance spectra using the Z-plot software.

Photovoltaic measurements of the DSSCs were conducted by illuminating the samples such that light from a 450 W Xe lamp was directed through an AM 1.5 solar simulator. The intensity of the simulated light was calibrated using a Si reference solar cell equipped with a BK7 filter to approximate AM 1.5, 100 mW cm⁻² global radiation. The photovoltaic characteristics of the DSSCs were obtained by applying an external potential bias to the cells and measuring the generated photocurrent using a Keithley 2400 source meter.

The charge transfer properties of the DSSCs were measured using an impedance analyzer (Solatron 1260), with a frequency range of 0.1–105 Hz and an AM 1.5 solar simulator, as described above. The impedance parameters were determined by fitting the impedance spectra using the Z-plot software.

The energy conversion efficiencies of DSSCs were measured over 30 days using solar simulator to evaluate the long-term stability. For comparison, gel electrolytes without HPG or liquid electrolyte were also investigated using the same method. DSSCs were maintained under normal atmospheric conditions and room temperature, and the experiments were conducted under at the identical conditions. All obtained values listed in tables are from the average data of five cells.

3. Results and discussion

3.1. Polymerization of HPG

Fig. 1 shows the FT-IR spectra of the glycidol and HPG. The spectrum of glycidol showed absorption bands due to the epoxy group. C–H stretches over the range 1280–1230 cm⁻¹ were attributed to ring C–H moieties with ring deformation. The C–H and C–H₂ peaks at 960–940 cm⁻¹ attributed to vibrations of the ring C–H wagging and ring C–H₂ twisting modes. Peaks related to ring stretching peaks at 930–910 cm⁻¹ and 890–820 cm⁻¹ were attributed to ring breathing modes and ring asymmetric deformations, respectively [32]. These peaks, which were related to the epoxy ring at the glycidol, disappeared in the HPG spectrum. These results showed that glycidol polymerized to form HPG via a ring-opening polymerization mechanism. The polymerization of HPG with latent AB₂ glycidol monomers was shown qualitatively. Fig. 2 shows the 500 MHz 1H nuclear magnetic resonance (1H NMR) spectrum of HPG. The peaks at 0.9 and 1.4 ppm corresponded to the methyl and methylene groups, respectively, of the TMP initiator. The methanol solvents signal at 3.2 ppm appeared as a sharp peak. The broad resonance between 3.4 and 4.0 ppm was assigned to the four methylene and one methine protons of polyglycerol. A strong peak at 4.8 ppm was attributed to the hydroxyl protons at the terminal HPG group and the methanol solvent. The 1H NMR spectrum of HPG could not be used to quantify HPG structural information because overlap among the methyl and methylene signals confounded the calculation of peak rations or peak integration. Incorporation of the TMP initiator as a core unit of HPG, however, was clearly confirmed.

13C nuclear magnetic resonance (13C NMR) analysis was conducted to confirm the branched structure of HPG. The various structural units of HPG: the linear unit (L), terminal unit (T), and dendritic unit (D) were revealed within the distortionless enhancement by polarization transfer (DEPT) spectrum, and the

![Fig. 1. FT-IR spectra of glycidol and HPG.](image-url)
relative abundance of each structural unit in HPG was calculated by integration of the signals obtained from the inverse gated (IG) \textsuperscript{13}C NMR spectrum of HPG, as shown in Fig. 3(a) and (b), respectively. The relative abundance of each structural unit was used to calculate the DB of an HPG, 0.57, according to the equation provided below.

\[
DB = \frac{D + T}{D + T + L}
\]

In the equation, D, T, and L indicate the fractions of dendritic, terminal, and linear units in HPG obtained from \textsuperscript{13}C NMR analysis. The values of \(DP_n\) and \(M_n\) were found to be 8.51 and 760.74 g mol\textsuperscript{-1}, respectively.

3.2. Interfacial contact between HPG and TiO\textsubscript{2} layer

It is crucial for improving overall efficiency of DSSC to increase interfacial contact between electrolytes and nanoporous electrodes. Kang et al. has reported that low molecular PEODME has good interfacial contact to TiO\textsubscript{2} mesopores since the radius of gyration, \(R_g\) of PEODME is smaller than the pore size of TiO\textsubscript{2} semiconductor layer [18]. Thus, we measured the radius of gyration, \(R_g\) of HPG and the pore size of semiconductor layer whether there is good interfacial contact between HPG and TiO\textsubscript{2} layer. Small angle X-ray scattering (SAXS) can be used to study the size and structural features of colloids. SAXS results provide a scattering function that may be fit to a scattering intensity \(I(q)\) as a function of scattering vector \(q\), according to the size and shape of the polymer. \(R_g\) may be calculated from the scattering data using a most common graphical techniques, the Zimm plot method, in which a plot of \(1/I(q)\) vs. \(q^2\) is fit to a fitting function [33]. The Zimm plots of the HPG SAXS curves are shown in Fig. 4. \(R_g\) was calculated from the slope of the from Zimm plot and the particle scattering function, \(P_{Zimm}(q)\), given by

\[
P_{Zimm}(R_g, q) = \frac{1}{1 + (qR_g^2/3)}
\]

The curve fit provided an \(R_g\) for HPG of 0.67 nm.

The pore diameter distribution of the TiO\textsubscript{2} electrode shown in Fig. 5 was estimated from BJH measurements to figure out pore size of TiO\textsubscript{2} layer. The average pore diameter of the TiO\textsubscript{2} was approximately 12 nm from the N\textsubscript{2} desorption isotherm. The BJH results, found that the average TiO\textsubscript{2} electrode pore diameter was larger than \(R_g\) of HPG. Therefore, it can be concluded that there are good interfacial contact between HPG and TiO\textsubscript{2} layer.

3.3. Ion conductivity of HPG contained gel electrolytes

The ion conductivity of a gel electrolyte depended on the HPG composition, as listed in Table 1. H-0.5 showed the highest ion conductivity, 2.98 × 10\textsuperscript{-4} S cm\textsuperscript{-1}, whereas a value of 1.96 × 10\textsuperscript{-4} S cm\textsuperscript{-1} was obtained using H-0. The high ion conductivity of the gel electrolytes H-0.3, H-0.5, and H-1.0 were thought to arise from an enlarged ion transfer channel due to the high molecular mobility of HPG. Larger channels promoted carrier ion transfer in the gel electrolyte due to increased solvation of salt by HPG with numerous ether groups in the polymer chains [34,35]. The decrease in ion conductivity at higher HPG content could be explained in terms of a higher concentration of hydrogen bonds in the gel electrolyte as a result of additional hydroxyl groups on the ends of the HPG [35]. Fig. 8 shows the FT-IR spectra of gel electrolytes with different HPG content, (a) H-0, (b) H-1.5, and (c) H-3. As the HPG concentration in the gel electrolytes increased, the O–H stretch (3650–3200 cm\textsuperscript{-1}) corresponding to hydrogen bonds broadened. Thus, the hydrogen bonds appeared to become more numerous in the gel electrolyte due to the presence of hydroxyl groups at the ends of the HPG, which depended on the HPG concentration in the gel electrolyte. Hydrogen bonds in a gel electrolyte have been shown to disturb ion transport, therefore, excessive HPG concentrations in the gel electrolyte were assumed to be responsible for the lower ion conductivity.
3.4. Photovoltaic performances of the DSSCs

Fig. 6 shows the photocurrent density–voltage (J–V) properties of DSSCs containing gel electrolytes as a function of the HPG composition in comparison with a DSSC containing a liquid electrolyte. DSSCs containing a liquid electrolyte or H-0 showed energy conversion efficiencies of 6.75% and 6.14%, respectively. The energy conversion efficiencies obtained from DH-0.3, DH-0.5, and DH-1.0 were higher than that of DH-0 as shown in Table 2. DH-0.5 yielded the highest energy conversion efficiency, 6.78%. The energy conversion efficiencies obtained were lower than those of DSSCs, described in the literature. It should be noted that the purpose of our study was to characterize the photoelectrochemical performance of DSSCs containing HPG in gel electrolytes. From this perspective, it is noteworthy that the energy conversion efficiencies of DSSCs containing HPG in gel electrolyte were similar to those of DSSCs containing liquid electrolyte. In general, DSSC performance depends on the dye molecule, the presence of a porous TiO2 layer, an FTO substrate, a Pt counter electrode, and an electrolyte. To enhance DSSC performance using an HPG comprised gel electrolyte, efforts are underway to optimize the dye and electrode, and a detailed report is forthcoming. DH–1.5 and DH–3.0 showed lower energy conversion efficiencies compared to DH-0. A comparison of the performances of DH-0 and DH-0.5 demonstrated that addition of an appropriate amount of HPG improved $J_{SC}$ and $V_{OC}$. These results indicated that incorporation of HPG into the gel electrolyte improved the DSSC’s performance.

3.5. Effects of HPG on the open circuit voltage

The open circuit voltage, $V_{OC}$, of the DSSCs increased in proportion to the HPG content in the gel electrolyte, as shown in Fig. 7. The lowest $V_{OC}$ was 0.73 V for DH-0, and the highest $V_{OC}$ was 0.77 V for DH-3.0. The increase in $V_{OC}$ appeared to arise from a shift in the TiO2 conduction band [36]. This can be interpreted that the presence of HPG in the gel electrolyte disrupted the adsorption of cations due to the polarity of HPG while cations in the gel electrolyte lacking HPG were easily adsorbed at the surface of the TiO2 electrode which shifted the potential of the TiO2 conduction band positively. The cations bound to the lone pair electrons of the HPG ether groups, which decreased the quantity of cations adsorbed to the TiO2 electrode surface. As a result, the TiO2 conduction band shifted negatively in the presence of HPG. Because $V_{OC}$ is determined by the potential difference between the Fermi level of the TiO2 electrode and the redox potential of the electrolyte, a shift in the TiO2 conduction band would manifest as a change in $V_{OC}$. Therefore, a positive shift in the potential of the TiO2 conduction band would decrease $V_{OC}$, and vice versa [37]. Hence, cation binding by HPG shifted the potential of the TiO2 conduction band in the negative direction, which increased $V_{OC}$.
3.6. Effects of HPG on the short-circuit current

The value of $J_{sc}$, which indicated the ion conductivity, also depended on HPG content, shown in Fig. 7, although the dependent was not monotonic. DH-0.5 displayed the highest $J_{sc}$, 14.90 mA cm$^{-2}$, for DH-0.5 whereas DH-0 displayed a value of 13.59 mA cm$^{-2}$. $J_{sc}$ decreased beyond a certain HPG content (0.5 wt%) in the gel electrolyte. The sensitivity of $J_{sc}$ to HPG content depended on several factors. The high molecular mobility of HPG, due to its hyperbranched molecular structure, expanded the ion transfer channels within the gel electrolyte upon incorporation of HPG and promoted the carrier ion transfer [34]. Moreover, the HPG ether groups facilitated ion transfer in the gel electrolyte. It has been reported that the lone pair electrons of the ether groups bound cations, which promoted dissociation of the salts in the electrolyte, and salt aggregation, which inhibited ion transfer, was reduced [35]. Thus, we expect that HPG may promote the carrier ion transfer in the gel electrolyte due to its polarity. These effects (that is, the expanded carrier transport channels and the accelerated salts dissociation in the gel electrolyte) increased the ion conductivity and the rate of reduction of oxidized dye molecules adsorbed onto the TiO$_2$ electrodes. Consequently a higher rate of dye reduction facilitated electrons injection into the TiO$_2$ electrodes, which increased $J_{sc}$. The decrease of $J_{sc}$ at higher HPG content could be explained in terms of a reduction in the ion conductivity due to a higher concentration of hydrogen bonds in the gel electrolyte. The reduction of oxidized dye molecules on the TiO$_2$ electrode was delayed beyond a certain HPG concentration due to a decrease in the ion conductivity. The lower rate of reduction of oxidized dye molecules slowed the injection of electrons into the TiO$_2$ electrode, which decreased $J_{sc}$. In conclusion, $J_{sc}$ increased with HPG up to a concentration of 0.5 wt% HPG and subsequently decreased at HPG concentrations beyond 0.5 wt% due to poorer ion transfer properties and a higher number of hydrogen bonds in the gel electrolyte (Fig. 8).

3.7. Effects of HPG on the charge transfer properties

Electrochemical impedance spectroscopy (EIS) analysis provided information about the electrochemical reactions within DSSCs. The EIS measurements revealed the charge transfer behavior in DSSCs containing an HPG in gel electrolytes. The Nyquist plots of the EIS spectra for the DH-0 and DH-0.5 are shown in Fig. 9. The real parts of each semicircle expressed in the spectra could be assigned to the internal resistances at the Pt counter electrode ($R_1$), the TiO$_2$/dye/electrolyte interface ($R_2$), and the diffusion of the redox couple at the Pt/electrolyte interface ($R_3$). The HPG compositions of the gel electrolytes did not affect the electrochemical reaction at the Pt counter electrode, and $R_1$ was not observed to change. The resistance of the electrochemical reaction at the TiO$_2$/electrolyte interface in DH-0.5 showed a higher $R_2$ than was observed in DH-0. DH-0.5 showed a higher $R_2$ value because recombination of excited electrons at the dye-absorbed TiO$_2$ electrodes with the gel electrolyte was less favorable. The lower rate of electron recombination at the TiO$_2$ electrode/electrolyte interface upon incorporation of HPG into the gel electrolyte resulted from the enhanced ion transfer properties of the gel electrolyte. An electrolyte with a high ion transfer rate, the I$_3^-$ ions formed by oxidation of I$^-$ ions as a result of reduction of oxidized dye molecules, may rapidly diffuse far from the TiO$_2$/electrolyte interface. Hence, the rate of recombination between electrons injected at the TiO$_2$ electrode and I$_3^-$ ions in the

Table 3

<table>
<thead>
<tr>
<th>DSSCs</th>
<th>$R_0$ ($\Omega$)</th>
<th>$R_1$ ($\Omega$)</th>
<th>$R_2$ ($\Omega$)</th>
<th>$R_3$ ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DH-0</td>
<td>16.7 ± 0.3</td>
<td>11.9 ± 0.6</td>
<td>34.4 ± 0.7</td>
<td>20.4 ± 0.5</td>
</tr>
<tr>
<td>DH-0.5</td>
<td>16.8 ± 0.2</td>
<td>11.0 ± 0.8</td>
<td>39.7 ± 0.4</td>
<td>6.5 ± 0.7</td>
</tr>
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Fig. 10. Long-term stability of the DSSCs based on the liquid electrolyte and the gel electrolyte with or without HPG.
electrolyte decreases, which increased $R_2$, $R_3$, which is connected to the transport of charge carriers in the gel electrolyte, decreased in DH-0.5 relative to DH-0. The smaller value of $R_2$ for DH-0.5 was attributed to the higher ion conductivity in H-0.5 than in H-0.

3.8. Long-term stability

Long-term stability tests were conducted by measuring the energy conversion efficiency of each DSSC using a solar simulator with operation over 30 days. The tests were executed for DSSC containing a liquid electrolyte, DH-0.5, and DH-0, as shown in Fig. 10. The energy conversion efficiency of DSSC containing the liquid electrolyte decreased significantly, from 6.75% to 4.91%, after 30 days operation. In contrast, the energy conversion efficiencies of DH-0.5 and DH-0 decreased only slightly, from 6.78% and 6.14% to 6.31% and 5.52%, respectively. In other words, the DSSC containing a liquid electrolyte displayed 73% of their initial energy conversion efficiencies after 30 days, whereas DH-0.5 and DH-0 maintained 93% and 90% of their initial energy conversion efficiencies, respectively. The low stability of the liquid electrolyte originated from the volatility and leakage, which dramatically decreased the energy conversion efficiencies after 30 days. The slight decrease in the energy conversion efficiencies of DH-0 and DH-0.5 demonstrated that DSSCs containing a gel electrolyte are advantage in terms of long-term stability, most likely due to reduced volatility and leakage. Incorporation of HPG into the gel electrolyte did not affect the long-term stability of the DSSCs.

4. Conclusions

Gel electrolytes containing various concentrations of HPG were prepared for use in DSSCs. HPG is predicted to penetrate the mesopores of TiO$_2$ electrodes because $R_g$ measured for HPG is smaller than the TiO$_2$ electrode pore diameter. EIS analysis of the gel electrolytes showed that incorporation of appropriate quantities of HPG into the gel electrolyte increased the ion conductivity. In particular, DH-0.5 based on the H-0.5 gel electrolyte yielded the highest energy conversion efficiency, of 6.78%, under 100 mW cm$^{-2}$. $V_{oc}$ improved as the HPG content in the gel electrolyte increased. An increase in $V_{oc}$ originated from a negative shift in the TiO$_2$ conduction band due to cation binding of the HPG ether groups, which interrupted the adsorption of cations to the TiO$_2$ electrodes. The $J_{sc}$ values measured for the various DSSCs indicated that $J_{sc}$ was sensitive to the ion conductivity. Higher ion conductivities were attributed to larger carrier transfer channels and rapid salt dissociation in the gel electrolyte upon addition of HPG. The rate of reduction of oxidized dye molecules increased, which increased $J_{sc}$. However, incorporation of HPG concentrations beyond a threshold increased the degree of hydrogen bonding within the gel electrolyte and decreased the ion conductivity. Consequently, the rate of reduction of the oxidized dye molecules decreased, along with $J_{sc}$. EIS measurements of the DSSCs showed that addition of HPG to the gel electrolytes improved the internal charge transfer properties of the DSSCs by increasing charge carrier transfer in the electrolyte and decreasing interfacial recombination at the TiO$_2$ electrode. Long-term stability tests indicated that DH-0.5 maintained 93% of its initial energy conversion efficiency over a period of 30 days. Overall, the hyperbranched polymer comprised gel electrolyte provided a new DSSC electrolyte composition that improved the properties of DSSCs.

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