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Exploitation of Ionic Liquid Electrolyte for Dye-Sensitized Solar Cells by Molecular Modification of Organic-Dye Sensitizers

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When an alkyl-functionalized metal-free organic dye (MK-2) was employed as a sensitizer, dye-sensitized TiO_2 solar cells (DSSCs) fabricated with an ionic liquid (IL) electrolyte showed an energy conversion efficiency of 7.6%, which was comparable to that with a volatile liquid electrolyte. This contrasts with the case of DSSCs employing conventional Ru complex sensitizer (N719), whose efficiency was decreased markedly when the electrolyte was replaced from the volatile to IL. As a result, with the IL electrolyte, the conversion efficiency with MK-2 was higher than that with N719. The result was mainly attributed to longer electron lifetime in the DSSCs with MK-2. The longer electron lifetime is remarkable because with conventional volatile electrolyte, the lifetimes with many organic dyes including MK-2 were shorter than that with N719. This high compatibility of MK-2 with the IL electrolyte shows that the molecular modification of organic dyes can overcome the both disadvantages of ILs and organic dyes, mostly originated from their high viscosity and from the short electron lifetime observed with volatile electrolyte, respectively. Long-term stability of the DSSCs with MK-2 and the ionic electrolyte was also investigated, showing the efficiency of more than 7% for 2000 h under 1 sun conditions.

Introduction

Dye-sensitized solar cells (DSSCs), employing nanoporous electrode developed by Grätzel and co-workers, have been attracting considerable attention in industrial and academic circles because of their potential of low cost and high efficiency.[1] High solar-to-electric power conversion efficiencies (η) more than 11% have been achieved with DSSCs using volatile solvent-based electrolyte.[2] However, the current stability of DSSCs using volatile electrolytes is not sufficient because of the difficulty of the sealing of the electrolytes, severely restricting their practical applications. To reduce the difficulty, solvents that have high boiling point and low vapor pressure or ionic liquids (ILs) have been examined for DSSCs.

IL-based electrolytes are attractive because of their almost zero vapor pressure, wide electrochemical window, and good thermal and photostability. Among the ILs, imidazolium iodides, such as 1-methyl-3-*n*-propylimidazolium iodide (MPImI) and 1-methyl-3-*n*-hexylimidazolium iodide (HMImI), have been examined widely because they can act both as a solvent and an iodide source in electrolyte. However, the η values for DSSCs based on Ru complex dyes and IL electrolytes using HMImI or MPImI are lower than those for DSSCs with volatile solvent-based electrolytes.[3] Because ILs have high viscosities relative to those for volatile solvents, their high viscosities suppress the diffusion of redox ions. To compensate the slow diffusion, higher I_3^- concentration is needed. However, since I_3^- ions absorb visible light and act as acceptors for injected electrons, the high I_3^- concentration increases light absorption and charge recombination rate significantly, decreasing short-circuit current and open-circuit voltage, respectively. In addition, facile absorption of water by ILs results in desorbing the Ru dye molecules in part from the TiO_2 surface, decreasing the long-term stability.[4] Therefore, achieving veritable long-term stability of IL based DSSCs with comparable efficiencies as those of DSSCs with volatile solvent-based electrolytes still remains a major challenge.

In view of sensitizers, besides Ru dyes, metal-free organic dyes are also attractive for DSSCs because of their high extinction coefficient and possible wide

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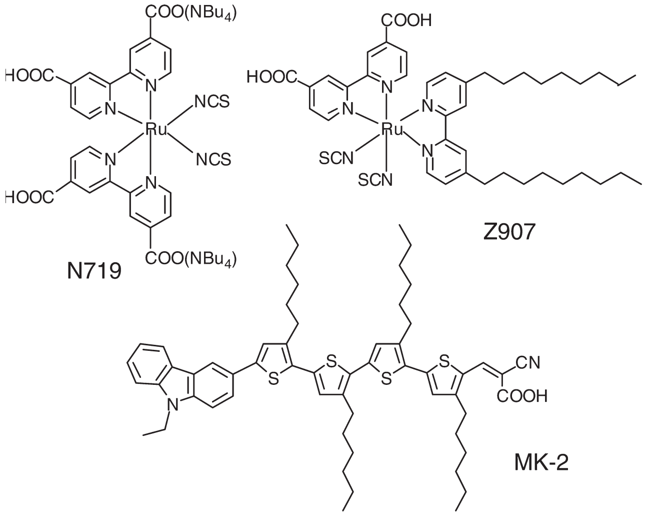

Figure 1. Molecular structures of N719, Z907, and MK-2.

absorption spectrum.[5] On the other hand, open-circuit voltage (V_{oc}) of the DSSCs using organic dyes is lower than those using Ru-complex sensitizers. The low V_{oc} was attributed to faster charge recombination.[6] In view of stability, organic dyes are generally considered to be unstable under light irradiation, whereas recent several papers reported relatively high stability of DSSCs using organic dyes.[7]

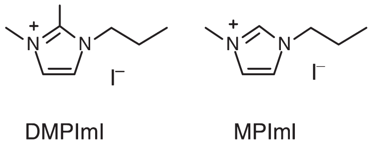

Figure 2. Molecular structures of imidazolium iodides (DMPImI and MPImI).

In our previous report, a carbazole dye with hexyl-substituted oligothiophene, MK-2 (Figure 1), is effective to improve electron lifetime and hence V_{oc}.[8] Later we found this kind of dyes can produce high efficiency even at a high content of I_3^- ions because of the blocking effect on the charge recombination by highly packed dye layer.[9] Therefore, MK-2 is expected to be suitable with IL electrolytes containing high concentration of I_3^-. Furthermore, hydrophobicity of MK-2 due to the alkyl chains would suppress desorption of the dye from the TiO_2 surface by water contained in IL electrolytes, resulting in higher stability. In this paper, we report high solar-cell performance and good long-term stability of DSSCs based on MK-2 and IL electrolytes. We show a concerted effect of MK-2 and IL in DSSCs and discuss the effect in view of molecular size, position of alkyl chain, and electrolyte viscosity.

Experimental Section

Materials and Reagents. Transparent conducting oxide (TCO, F-doped SnO_2, 10 Ω/square, Nippon Sheet Glass Co.) coated glass was used as the substrate for the TiO_2 thin film electrode after washing. Reagent grade of LiI, I_2, 4-*tert*-butylpyridine (TBP), 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI, Tomiyama Pure Chemical Industries Ltd.), acetonitrile (AN, Wako Pure Chemicals), toluene (Kanto Chenmicals, dehydrated) were used without further purification. N719 and Z907 were purchased from Solaronix SA and DYESOL, respectively, and were used without further purification. MPImI was prepared according to the literature method.[10] Synthesis procedure of MK-2 is available from our previous study.[8] Molecular structures of imidazolium iodides used in this work are shown in Figure 2.

Fabrication of DSSCs. Twelve micrometer TiO_2 films composed of 6 μm nanoparticle (20 nm) layer in direct contact with the TCO substrate and 6 μm light scattering particle (80% 20 nm TiO_2 + 20% 100 nm TiO_2) layer were fabricated with a screen-printing method and used in this study unless specified.[11] The films were sintered at 525 °C for 2 h to achieve good necking of neighboring TiO_2 particles. The film thickness was measured with a Tencor Alpha-Step 500 Surface Profiler. The sintered films were then treated with 0.05 M $TiCl_4$ aqueous solution at 70 °C for 30 min followed by calcinations at 450 °C for 30 min. When TiO_2 electrodes were cooled down at around 100 °C, the electrodes were dipped in dye solutions, which were 0.3 mM in toluene for MK-2 and 0.3 mM in *tert*-butanol/AN (1:1 in volume) for N719 and Z907, more than 12 h at room temperature for complete dye adsorption. The dipping at 100 °C was to accelerate the dye adsorption. The dye-loaded TiO_2 film as working electrode and the Pt-coated TCO as counter electrode were separated by a hot-melt Surlyn film (30 μm) and sealed together by pressing them under heat. The electrolyte was

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introduced into the interspace between the working and the counter electrodes from the two holes predrilled on the back of the counter electrode. Finally, the two holes were sealed with a Surlyn film covered with a thin glass slide under heat. Three different electrolytes, A: 0.6 M DMPImI + 0.1 M LiI + 0.05 M I_2 + 0.5 M TBP in AN; B: MPImI + 0.4 M I_2 + 0.1 M LiI + 0.5 M TBP and C: MPImI + 0.4 M I_2, were used in this work.

Photovoltaic Measurement. Incident photon-to-current conversion efficiency (IPCE) action spectra were recorded on a CEP-99W system (Bunkoh-Keiki Co., Ltd.) by illuminating DSSCs with direct current (DC) mode and high-intensity monochromatic light (e.g., 5 mW cm^{-2}) without bias white light. The current−voltage characteristics of DSSCs were measured on a computer-controlled Current−Voltage source meter (Advantest R6243) under illumination of simulated AM 1.5 G solar light from an AM 1.5 solar simulator (Wacom Co., Japan, WXS-80C-3 with a 300-W Xe lamp and an AM filter). The incident light intensity was calibrated by using a standard crystalline silicon solar cell, which was produced and calibrated by Japan Quality Assurance Organization, with an IR-cutoff filter (Schott, KG-5), giving the photoresponse range of amorphous silicon solar cell. The sealed DSSC devices at open-circuit equipped with a 420 nm cutoff filter were subjected to continuous light soaking (100 mW cm^{-2}, device surface temperature was ca. 50 °C), and the $I-V$ curves were measured regularly. To avoid the stray light penetrating into the active dye-loaded film, a black mask with an aperture area of 0.2354 cm^2, measured with an optical microscope, LEICA M420, equipped with a digital camera (Nikon DXM1200), was employed to test photovoltaic performance. Considering that the J_{sc} of DSSCs in this work at 100 mW cm^{-2} simulated AM 1.5 G light is ~5% lower than the integrated current density from the spectra of IPCE and AM 1.5 G solar emission, we believe the J_{sc} and η measured in this work are not overestimated.

Characterization. Electron lifetimes (τ) of the DSSCs were obtained by stepped light-induced transient measurements of photovoltage. Experimental procedures of the measurements are described in detail elsewhere.[12] In short, DSSCs were irradiated by a diode laser (Coherent, Lablaser, λ = 635 nm) and the decay of V_{oc}, caused by stepwise decrease of a small fraction of the laser intensity, was recorded. The measurement was repeated with various initial laser intensities, giving different electron densities in the DSSCs. The values of τ was obtained by fitting an exponential function, $\exp(-t/\tau)$, to the voltage decay. The electron density was estimated by the charge extraction method introduced by Peter and co-workers.[13] The DSSCs prepared for the measurements employed around 3 μm thick TiO_2 electrode. Electrochemical impedance spectroscopy (EIS) for fresh and light-soaking aged DSSCs under 100 mW cm^{-2} AM 1.5 G simulated solar light were measured with an Impedance/Gain-Phase Analyzer (Solartron SI 1260) connected with a potentiostat (Solartron SI 1286). The DSSCs were scanned in a frequency range of 10^{-1} × 10^5 Hz at room temperature with applied potential set at open circuit. The AC amplitude was set at 10 mV.

Results and Discussion

***I−V* Characteristics.** Table 1 summarizes the solar-cell performance parameters of DSSCs based on MK-2, N719, and Z907 using the electrolytes A, B, and C. With the volatile solvent-based electrolyte A, N719 and Z907 showed higher performance than MK-2 in terms of J_{sc}, V_{oc}, and η. On the other hand, with electrolyte B and C, MK-2 based DSSCs produced higher J_{sc}, V_{oc}, and η than the two Ru dye-based DSSCs. Between the electrolyte B and C, the V_{oc} values of the DSSCs with electrolyte B containing TBP were higher than those with electrolyte C. By optimization of TiO_2 electrode in terms of thickness and scattering particle ratio, we attained 7.6% (J_{sc} = 13.9 mA cm^{-2}, V_{oc} = 0.73 V, FF = 0.75, with an aperture mask, and without antireflection film) with a DSSC based on MK-2 and electrolyte B.

Table 1. Photovoltaic Performances of DSSCs Based on MK-2, N719, and Z907 with Three Electrolytes[a]

electrolyte	dye	J_{sc} (mA cm^{-2})	V_{oc}(V)	FF	η (%)
A	MK-2	14.5	0.76	0.69	7.6
	N719	15.9	0.78	0.74	9.2
	Z907	16.0	0.72	0.72	8.3
B	MK-2	14.2	0.72	0.72	7.4
	N719	10.2	0.67	0.75	5.1
	Z907	11.4	0.63	0.72	5.2
C	MK-2	13.6	0.68	0.73	6.8
	N719	10.1	0.58	0.72	4.2
	Z907	12.7	0.59	0.69	5.2

[a] Electrolyte A, 0.6 M DMPImI + 0.1 M LiI + 0.05 M I_2 + 0.5 M TBP in AN; electrolyte B, 0.4 M I_2 + 0.1 M LiI + 0.5 M TBP in MPImI; electrolyte C, 0.4 M I_2 in MPImI.

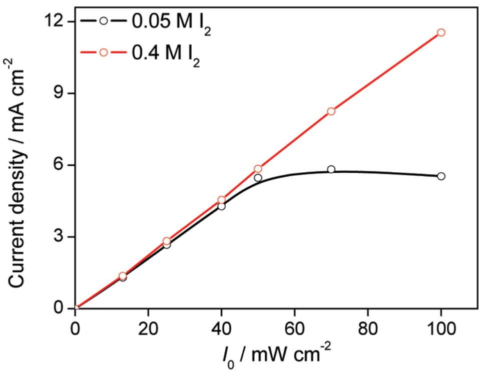

Figure 3. Relationship between J_{sc} and light intensity for DSSCs using MK-2 with 0.05 or 0.4 M I_2 in MPImI as solvent.

Figure 3 shows the dependence of J_{sc} on light intensity with two different I_3^- concentrations in MPImI as a solvent. When 0.05 M I_3^- was dissolved in the IL-based electrolyte just as the case of the volatile solvent based electrolyte A, J_{sc} increased linearly under low light intensities until 25 mW cm^{-2} and then increased slowly followed by a saturation above half sun. The slow diffusion of I_3^- in the IL electrolyte to the counter electrode slows down the reduction of I_3^- to I^- at the counter electrode, thus reducing J_{sc} at 1 sun conditions (ca. 100 mW cm^{-2}) much lower than expected by a proportional increase from the currents at low light intensity. For this reason, the η at 1 sun is much lower than that at low light intensities when 0.05−0.1 M iodine is dissolved in the IL based electrolyte. When the concentration of I_3^- was increased to 0.4 M, J_{sc} increased linearly with the increase in light intensity up to 1 sun

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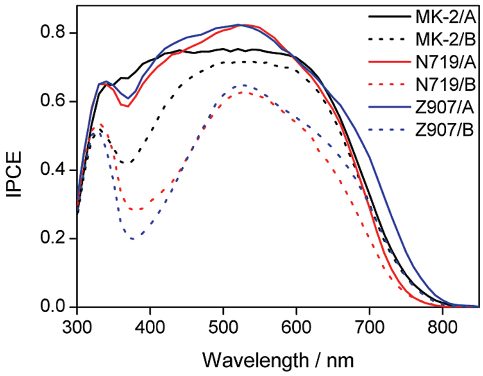

Figure 4. IPCE spectra for DSSCs using electrolyte A and B.

(Figure 3). This tendency was also observed for the DSSCs based on the two Ru dyes in this work and in the previously published work.[3] Although the increase in I_3^- concentration allows higher diffusion current, absorption loss due to the light absorption of I_3^- is also increased. By varying the iodine content up to 0.5 M, we found that 0.4 M iodine was the optimal condition for MPImI electrolyte with our TiO_2 electrodes. The optimal concentration was consistent with previously published results.[3] Note that the optimal concentration depends on the thickness and pore conditions of TiO_2 electrodes, where the optimized TiO_2 electrode conditions depend on the absorption coefficients and molecular size of sensitizers.

Influence of Electrolyte on Incident Photon-to-Current Conversion Efficiency. Between electrolyte A and B, DSSCs with MK-2 showed comparable J_{sc}, whereas those with N719 and Z907 resulted in large decrease of J_{sc}. Figure 4 compares the IPCE spectra of the DSSCs. When the electrolyte was changed from A to B, the IPCE below 500 nm decreased largely for the all dyes, but the effect was more significant for N719 and Z907. The decreases are mainly ascribed to the higher concentration of I_3^-, which absorbs strongly in this spectral region and thus filters the incident light below 500 nm. At 532 nm, where 0.4 M of I_3^- absorbs 7% of light in 4 μm, the IPCE decreased remarkably for the Ru dye-based DSSCs, upon electrolyte change from A to B, whereas the IPCE for MK-2-based DSSC decreased by the same order of the I_3^- absorption. The IPCE is associated with light harvesting efficiency (LHE), electron injection efficiency (CIE), and charge collection efficiency (CCE).[14] Since the around 20% decrease of IPCE at 532 nm for the case of N719 and Z907 cannot be explained by the absorption of the electrolyte, the change of IPCE (532 nm) is due to the decrease in the CIE and/or CCE. The CCE becomes unity when the electron diffusion length (L) in the TiO_2 is longer than the TiO_2 thickness. The estimated L from the values of electron diffusion coefficient (now shown) and lifetime (shown in the following section) was longer than 20 μm, suggesting the decreases in CIE for the case of Ru dyes with IL.

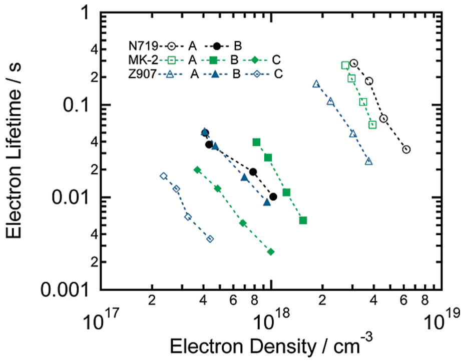

Figure 5. Electron lifetime in DSSCs with N719, MK-2, and Z907 with electrolyte A (acetonitrile base), B (MPImI base with TBP) and C (MPImI base) as a function of electron density in the DSSCs. Porosity was not taken into account to calculate the density.

Influence of Dye Molecular Structure on Open-Circuit Voltage. When electrolyte B or C were employed, DSSCs with MK-2 showed higher V_{oc} than with N719 and Z907. This result is remarkable because most of reported dyes were not able to achieve higher V_{oc} than N719. Lower V_{oc} of DSSCs observed with coumarin dyes, carbazole dyes including MK-2, indoline dyes, porphyrin dyes, and phthalocyanine dyes was attributed to faster recombination rate in comparison to with N719 dye.[6,15,16] The increased rate for recombination between the injected electrons and I_3^- in electrolytes was attributed to increased I_3^- concentrations by the adsorbed dyes.[6] The observed higher V_{oc} with MK-2 and IL electrolytes in Table 1 could be due to the retardation of the recombination and/or the positive shift of E_{CB}.

Figure 5 shows a double logarithmic plot of electron lifetime in the DSSCs examined here as a function of electron density in the electrodes. All DSSCs showed the decrease of τ with the increase of electron density. This has been partially modeled with transport-limited recombination, where the recombination rate is limited by the probability of electrons located at the interface of TiO_2 and electrolytes.[17,18] Among the electrolytes, volatile liquid electrolyte A showed the longest lifetime. This was due to the lowest I_3^- concentration in the electrolyte A. Among the dyes with electrolyte A, the order of lifetime was $\tau_{N719} > \tau_{MK\text{-}2} > \tau_{Z907}$, whose order was the same as for V_{oc}. Between N719 and MK-2, and N719 and Z907, the orders were consistent with previously published results.[6,19] Noteworthy is that the $\tau_{MK\text{-}2}$ was longer than τ_{Z907}. Among the examined dyes with electrolyte B, the order of lifetime was changed to $\tau_{MK\text{-}2} > \tau_{N719} > \tau_{Z907}$ as well as the order of V_{oc}. On the basis of the results with electrolyte A, it seems that the packing density of MK-2 layer on the TiO_2 surface was equivalent

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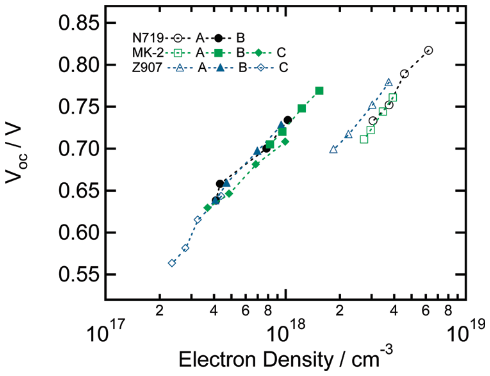

Figure 6. Open-circuit voltage of DSSCs examined in Figure 5 as a function of electron density in the DSSCs.

to or less sufficient than that of N719 to prevent I_3^- from approaching to the TiO_2 surface. However, the layer of MK-2 as a blocking layer became more effective with the IL electrolyte. Because in ionic liquid, the alky chains of the MPIm cations interact each other, a MPIm cation would not be separated from other MPIm cations, resulting in less penetration of the ionic liquid into the layer of MK-2. In contrast, single DMPIm cation in acetonitrile can exist through solvation, allowing the cation to penetrate into the dye layer. Because the TiO_2 in DSSCs is negatively charged under operating conditions, anions such as I_3^- hardly approach to the TiO_2 surface unless the surface is screened by cations.[20] Therefore, the distance between I_3^- and TiO_2 surface is limited by the accessibility of MPIm cations. The molecular size of MK-2 is about triple of that of N719. Even if the groups of MPIm caions can penetrate into the half length of the MK-2 layer but hardly penetrate into N719 layer, still, the distance between the TiO_2 surface and I_3^- is longer for the case of MK-2 than of N719.

Figure 6 shows the values of V_{oc} as a function of electron density. The V_{oc} measures the difference between the Fermi level of TiO_2 and redox potential of I^-/I_3^-. At the matched electron density, the Fermi level of TiO_2 respect to the conduction band edge is the same among the samples having different electrolytes and dyes but the same TiO_2 electrodes. Among the dyes with electrolyte B, the V_{oc} at the matched electron density are the same, showing that the high V_{oc} with MK-2 than those of N719 and Z907 under one sun conditions is solely due to the longer electron lifetime. Between electrolyte A and B, the V_{oc} values of DSSCs with electrolyte B were higher. Because the concentration ratio of I^- is higher for electrolyte B, the change of I^-/I_3^- redox potential cannot explain the increase of V_{oc}. Between electrolytes B and C, the V_{oc} were the same. Various papers reported that the addition of TBP negatively shifts, whereas Li^+ positively shifts the potential of the TiO_2 in DSSCs employing volatile liquid electrolyte. Little influence of these electrolytes in the electrolyte C might be due to the effects canceling each other.

Another possibility is that because TBP and Li^+ shift the potential of the TiO_2 electrode when they are adsorbed, little shift can be interpreted when the electrolytes are isolated from the TiO_2 surface by the adsorbed dye layer. With the results of increased lifetime for the case of MK-2, the isolation of electrolyte seems more likely the case. If so, an electric field existed in the dye layer, which would be related to the difference in the charge injection efficiency, although this should be substantiated further. In view of electron lifetime, the additions of Li^+ and TBP increased the electron lifetime, and consequently the V_{oc}. The effect of TBP on the lifetime has been examined but its mechanism has not yet been revealed completely.[20,21] At least, Figure 4 shows that it seems effective with ionic liquid of MPImI.

Concerted Effect of Sensitizer and Ionic Liquid Electrolyte. With AN based electrolyte, in comparison to N719, the structure of alky-functionalized MK-2 was not enough to impede the charge recombination. With N719, the V_{oc} of DSSCs with IL electrolytes was lower than with AN based electrolyte. With the combination of MK-2 and IL, the DSSCs showed higher performance than N719 with IL. This was achieved by the large molecular size of MK-2 for both lateral and normal directions from the TiO_2 surface, and by high viscosity of ionic liquid, which makes it difficult to penetrate into the layer of highly packed MK-2 molecules.

In view of alky chain, Z907 has two long alky chains. However, the electron lifetime was the shortest for the all electrolytes. This suggests that the alky chain itself does not have large effect on the lifetime but how much adsorbed molecules cover the TiO_2 surface is essential.[19] Note that the results of Z907 also imply that the long electron lifetime with N719 is not originated from the nature of Ru complex itself, but the position and composition of ligands. With electrolyte A, electron lifetimes in DSSCs with MK-3, which is similar to MK-2 but has no alky chains, were much shorter than those in DSSCs with MK-2.[6] These results suggest that alky-chains attached at normal direction of the semilong axis of dyes are effective to cover the TiO_2 surface.

In view of J_{sc}, the dyes like MK-2 having high absorption coefficients are also suitable with IL. This is because it reduces the loss of photons for sensitizer by light absorption by I_3^-. The thickness of TiO_2 can be also reduced for high absorption coefficients dyes, allowing further reduction of the loss by decreasing I_3^- concentrations in ionic liquid electrolytes.

In a previous report, with N719, HMImI showed the highest efficiency among the imidazolium cations up to 1-nonyl-3-methylimidazolium[10] It was attributed to the fact that higher a viscosity of HMImI increases the electron lifetime, and consequently the V_{oc}, but a further increase in viscosity requires more concentration of I_3^- and decreasing values of J_{sc} and FF.[3] This condition was derived because of the fast recombination when N719 was employed with MPImI. On the other hand, a drawback of the HMImI is its requirement for higher

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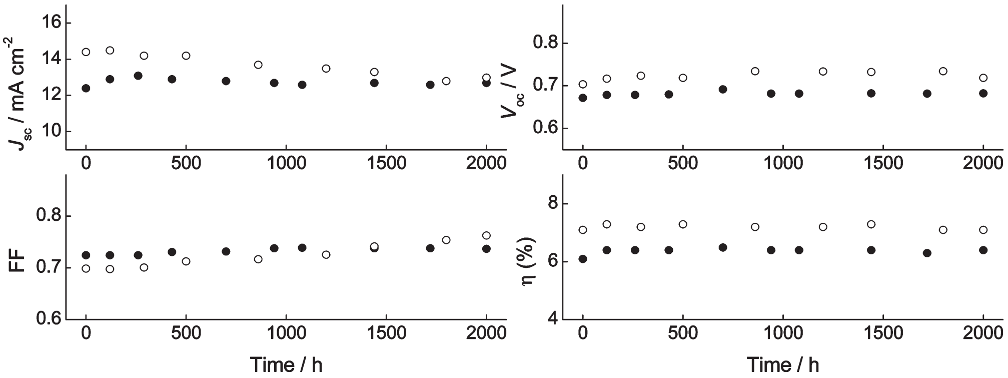

Figure 7. Photovoltaic performance parameter evolution under visible light soaking (100 mW cm^{-2}) for MK-2 based DSSCs with electrolyte B (open circle) and C (closed circle).

I_3^- concentration, which reduces J_{sc}. For the case of MK-2 with ionic liquid, the recombination rate is not as fast as with N719, and thus, MPImI with lower concentration I_3^- can be applied. This condition minimized the loss of J_{sc}.

Long-Term Stability. The stability data for a DSSC with electrolyte B and C is depicted in Figure 7. During visible light soaking up to 2000 h, J_{sc} decreased by ~9%, FF increased by ~9%, and V_{oc} remained almost constant, resulting in almost constant η (> 7%) in the entire course of light soaking. It was reported that the presence of Li^+ is unfavorable for long-term stability because of the lithium interaction into the TiO_2 lattice.[22] For this reason, relatively stable DSSCs based on Ru dyes were fabricated using electrolytes without Li^+ ions. However, we obtained stable DSSCs based on MK-2 and electrolyte B containing 0.1 M Li^+ (Figure 7). This is consistent with the interpretation above that the IL cannot penetrate into the MK-2 layer, and thus no intercalation and adsorption of caions occurred. Note that the long-term stability of DSSCs based on MK-2- and IL-based electrolytes with Li^+ is comparable to that of DSSCs based on Ru dyes and electrolytes without Li^+ ions and much better than the stability of Ru dye-based DSSCs with electrolytes containing Li^+ ions.

To reduce the total cost and the number of factors affecting the DSSC stability, we favored fewer components in the electrolyte. The stability data of MK-2 based DSSC using electrolyte C is also shown in Figure 7. This is quite a stable DSSC because all four parameters remained almost unchanged during visible light soaking after aging for a couple of days. In particular, MK-2 based DSSCs with electrolyte B and C did not undergo V_{oc} drops, sharply contrasting with the Ru dye-based and IL electrolyte-based DSSCs, which usually suffered from V_{oc} drops of ~100 mV.[23] It has been reported that Z907 showed improved long-term stability as compared to N719, suggesting the long alkyl chain plays a key role in achieving good stability.[4] However, Z907-based DSSC using electrolyte C experienced a decrease in η by 15−20% under light soaking for 2000 h, much bigger efficiency drop than MK-2 based DSSC. The above results indicate that not only the presence of alkyl chains but also the high coverage of TiO_2 surface by hydrophobic alky chains and/or dye molecules themselves is essential to achieving good long-term stability.

Another reason of low stability for DSSCs is the acceleration of charge recombination during light soaking.[23] This acceleration would be caused by the change of TiO_2/electrolyte interface conditions, e.g., change of local concentration of Li^+ and TBP.[24] However, again, the isolation of electrolyte and TiO_2 surface solve the problem. The existing water in IL-based electrolytes also impairs the long-term stability because water would loosen the binding of dye molecules to the TiO_2 surface and even detach some dye molecules into the electrolyte. The water contact angles of MK-2 and N719 loaded TiO_2 films were 137 and 19°, respectively, indicating that the former was hydrophobic and the latter was hydrophilic. Moreover, MK-2 cannot be dissolved in water and even in 0.1 M NaOH aqueous solution as well, sharply contrasting to the case for N719, which can be easily detached into basic solutions. The water-resistant feature of MK-2 in combination with its hydrophobic character is therefore beneficial to the long-term stability. Even if 10% water was added to the electrolyte, we found that the efficiency and stability was not influenced significantly for MK-2-based DSSCs using IL-based electrolytes.

To scrutinize the change of charge transfer and ionic transport processes in DSSCs after visible light soaking, we carried out electrochemical impedance spectroscopy measurements. Figure 8 shows the Nyquist and Bode plots of DSSCs with electrolyte C, respectively, for fresh and after 2000 h visible light soaking. The three semicircles from left to right were assigned to Pt/electrolyte interface, TiO_2/dye/electrolyte interface, and electrolyte diffusion, respectively.[25] Note that the middle semicircle may not be described as a simple parallel connection of a capacitor and a resistance.[26] However, experimentally,

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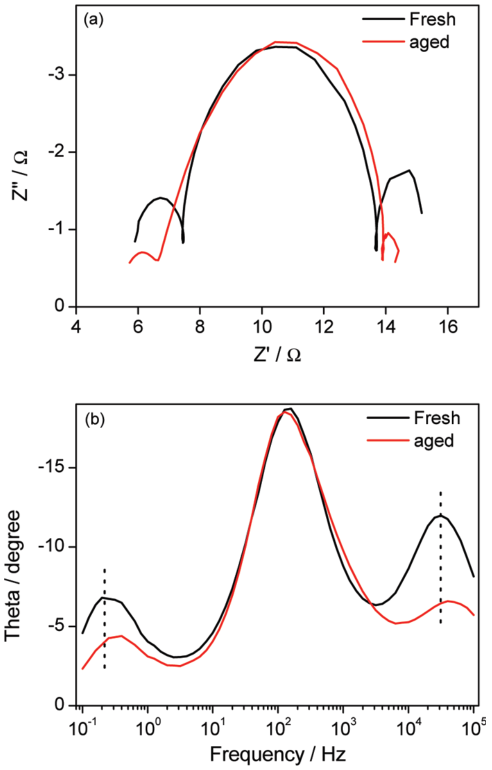

Figure 8. EIS Bode plots for fresh and aged DSSCs based on MK-2 and electrolyte C. Conditions: open-circuit, 100 mW cm^{-2} simulated solar light.

we observed that the frequency giving the top of middle semicircle is related with the electron lifetime measured by photovoltage transients. In Figure 8a, it is seen that the frequency for middle semicircle did not change significantly, showing little influence on the electron lifetime with time. The radii of the high-frequency (left) and the low-frequency semicircles (right) were decreased after 2000 h light soaking, suggesting that both the resistance for I_3^- reduction at the Pt electrode and the diffusion resistance of the electrolyte became smaller. The improved electrolyte diffusion and I_3^- reduction at the Pt surface account for the increase in FF and J_{sc} after light soaking.

Conclusions

A dilemma that long-term stable IL-based DSSCs usually have much lower η than their volatile solvent electrolyte-based counterpart was successfully overcome using a hydrophobic alkyl-substituted oligo-thiophene dye as the sensitizer. The present highest efficiency of a DSSC based on MK-2 and an IL electrolyte is 7.6% (J_{sc} = 13.9 mA cm^{-2}, V_{oc} = 0.73 V, FF = 0.75, with an aperture mask and without an antireflection film). We found that the dense dye layer of MK-2 with hydrophobic long alkyl chains along with MPImI based IL electrolyte favors electron lifetime, whereas the Ru dye-based DSSCs showed insufficient property. The excellent combination of MK-2 dye and IL electrolytes was realized by high coverage of TiO_2 surface by MK-2 and moderate viscosity of IL electrolytes. In addition, stability test showed that the DSSC based on MK-2 and IL electrolyte survived for 2000 h with almost constant efficiency greater than 7% under continuous visible light soaking (100 mW cm^{-2} AM 1.5 G simulated solar light) at temperatures of 50 °C.

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