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Influence of nitrogen-containing heterocyclic additives in I^-/I_3^- redox electrolytic solution on the performance of Ru-dye-sensitized nanocrystalline TiO_2 solar cell

Hitoshi Kusama[a,*], Mitsuhiko Kurashige[a], Hironori Arakawa[b]

[a] *Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology (AIST), AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan*

[b] *Faculty of Engineering, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan*

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Abstract

The influence of nitrogen-containing heterocyclic additives on the performance of a bis(tetrabutylammonium)*cis*-bis(thiocyanato)bis(2,2′-bipyridine-4-carboxylic acid, 4′-carboxylate)ruthenium(II) (N719) dye-sensitized nanocrystalline TiO_2 solar cell with an I^-/I_3^- redox electrolyte in acetonitrile was studied. The current–voltage characteristics were measured under AM 1.5 (100 mW/cm^2) for 10 different five- and six-membered nitrogen-containing heterocyclic compounds. The heterocyclic additives tested had varying effects on the cell performance. Most of the additives enhanced the open-circuit photovoltage (V_{oc}), fill factor (ff), and the solar energy conversion efficiency (η), but reduced the short circuit photocurrent density (J_{sc}). The physical and chemical properties of the nitrogen-containing heterocycles such as the partial charge, dipole moment, and ionization energy were computationally calculated in order to elucidate the reasons for the additive effects on the cell performance. The greater the lowest partial charge of the nitrogen atoms in the heterocyclic ring, the larger the $V_{oc,}$ but the smaller the J_{sc} values. The dark current at the bare TiO_2 electrode without a dye coating decreased as the lowest partial charge of the nitrogen atoms increased. The V_{oc} of the cell also increased as the ionization energy of the nitrogen-containing heterocyclic molecules decreased. These results suggest that the electron donicity of the nitrogen-containing heterocyclic additives influenced the interaction with the nanocrystalline TiO_2 photoelectrode and the I^-/I_3^- electrolyte, which altered the Ru-dye-sensitized solar cell performance.

Keywords: Dye-sensitized solar cell; Electrolytic solution; Nitrogen-containing heterocycles; Additive

1. Introduction

Heterocyclic compounds contain a ring structure similar to benzene and aromatic hydrocarbons, but the ring contains atoms other than carbon such as sulfur, oxygen, or nitrogen. Nitrogen-containing heterocycles are important in various fields. Recently, heterocyclic compounds such as imidazole and pyridine have been used in dye-sensitized solar cells [1]. A typical solar cell consists of nanostructured TiO_2 film electrodes covered with a monolayer of a sensitizing dye such as Ru(II) complex (N719), a redox electrolyte like I^-/I_3^-, and a counter electrode such as Pt. Usually, an imidazolium halide like dimethyl hexyl imidazolium iodide is the electrolyte [2–4]. On the other hand, pyridine derivatives such as 4-*t*-butylpyridine (TBP) are used as additives in the electrolyte solution to enhance the open-circuit photovoltage (V_{oc}) and the solar energy conversion efficiency (η) [5–7]. The donating properties of the nitrogen lone pair in TBP are responsible for the enhanced V_{oc} and η [8].

Pyridines such as TBP have one nitrogen atom in their structure, but heterocycles such as triazole and pyridazine have more than two nitrogens and each nitrogen can donate lone pair electrons. Although various five- and six-membered

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[*] Corresponding author. Tel.: +81 29 861 4867; fax: +81 29 861 6771.
E-mail address: h.kusama@aist.go.jp (H. Kusama).

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nitrogen-containing heterocycles are known, only TBP has been reported as an additive in an electrolytic solution for dye-sensitized solar cells. It should be possible to determine if other nitrogen-containing heterocycles additives improve solar cell performance. This paper presents the effects of 10 different five- and six-membered nitrogen-containing heterocycles including imidazole and pyridine in an I^-/I_3^- electrolyte and an acetonitrile electrolytic solution on solar cell performance. To elucidate the influence of the additives on the dye-sensitized solar cell performance, the chemical and physical properties of the heterocyclic compounds such as the partial charge, dipole moment, and ionization energy were evaluated using molecular orbital calculations.

2. Experimental

2.1. TiO_2 electrode preparation and dye coating

The nanocrystalline TiO_2 photoelectrode (thickness, 15 μm) was prepared as previously described [9,10]. The dye was adsorbed on the TiO_2 surface by soaking the TiO_2 photoelectrode in a *t*-butanol/acetonitrile (1:1) solution of the N719 dye (Solaronix S.A.; concentration, 3×10^{-4} mol/dm^3) for 100 h at 293 K. The photoelectrode was washed, dried, and immediately used to measure solar cell performance.

2.2. Photovoltaic characterization

A sandwich-type electrochemical cell, which was composed of a dye-adsorbed TiO_2 electrode, a 25 μm thick Lumirror spacer film, and a counter electrode, was used for the photocurrent measurements. The counter electrode was a Pt sputtered FTO conducting glass. The electrolytic solution was injected into the space between the two electrodes using a microsyringe. The electrolytic solution was composed of 0.5 mol/dm^3 of a nitrogen-containing heterocyclic additive, 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide, 0.1 mol/dm^3 LiI, 0.05 mol/dm^3 I_2, and acetonitrile (Tomiyama Pure Chemical Industries Ltd.) as the solvent.

The dye coated semiconductor film was illuminated through a conducting glass support. The solar-to-electric energy conversion efficiency was measured under simulated solar light (Wacom Co., WXS-80C-3, AM 1.5, 100 mW/cm^2). The photocurrent, photovoltage, and *I–V* curves were measured using a Keithley Model 2400 digital source meter and a data acquisition system (Eiko Seiki Co.). The apparent cell area of TiO_2 photoelectrode was 0.25 cm^2 (0.5 cm × 0.5 cm).

2.3. Computational details

The computational chemical calculations were performed using the CAChe WorkSystem Version 5.04 from Fujitsu Limited (Tokyo) implemented on a Windows XP system. The geometries of the nitrogen-containing heterocycles were optimized by a MOPAC (Molecular Orbital Package, Parametric Model 5, PM5) application. The chemical and physical properties such as partial charge, dipole moment, and ionization energy were evaluated from optimized geometry using a ProjectLeader application [11].

3. Results

3.1. Solar cell performance using nitrogen-containing heterocycles as additives

I–V measurements were performed on the electrolyte with various nitrogen-containing heterocyclic additives. Fig. 1 illustrates the structures of the five- and six-membered compounds used in this work. Fig. 2 shows the open-circuit photovoltage (V_{oc}) and short circuit photocurrent density (J_{sc}) results when illuminating with 100 mW/cm^2 and an additive concentration of 0.5 mol/dm^3. Typically, the V_{oc} values for cells containing nitrogen-containing heterocycles were greater than the cell without an additive, but adding 1,2,3-triazole, tetrazole, and pyridazine slightly reduced the V_{oc}. When comparing isomers, the V_{oc} with imidazole was higher

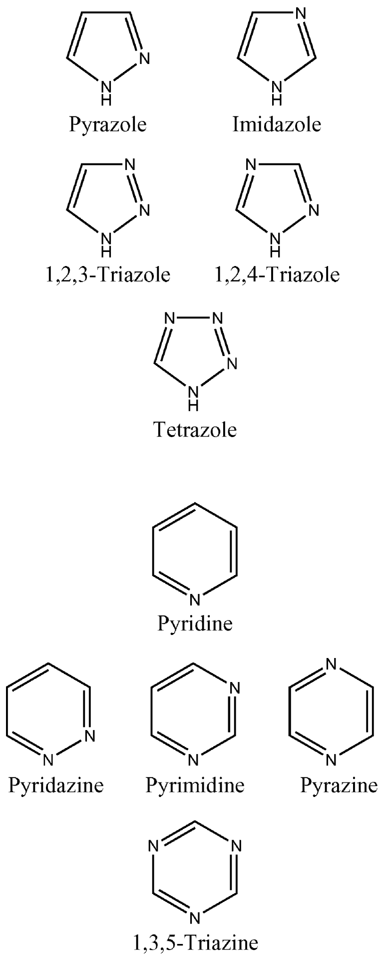

Fig. 1. The structures of the nitrogen-containing heterocyclic additives tested in this study.

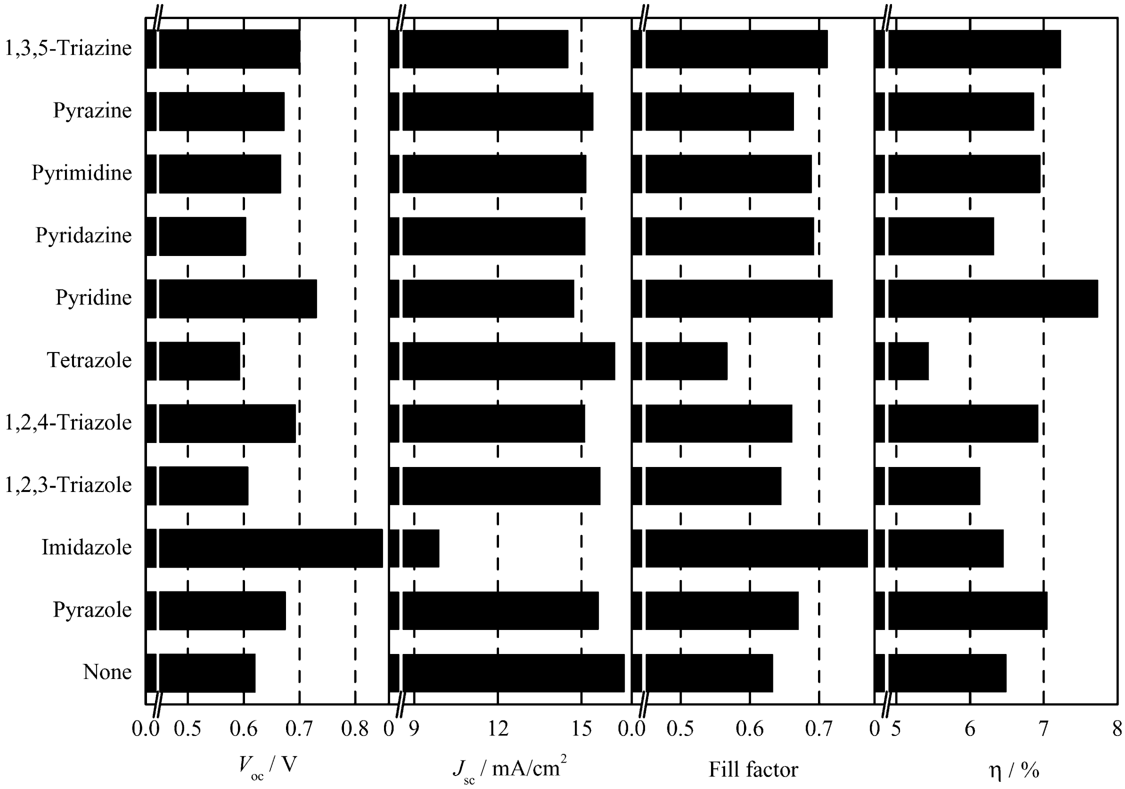

Fig. 2. The influence of the nitrogen-containing heterocycles in the electrolytic solution on the solar cell performance for a N719 dye-sensitized TiO_2 solar cell. Conditions: electrolyte, 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I_2 + 0.5 mol/dm^3 additive in acetonitrile; light intensity, 100 mW/cm^2, AM 1.5.

than pyrazole. 1,2,4-Triazole showed larger V_{oc} value than 1,2,3-triazole. For six-membered isomers, the value of V_{oc} increased in the following order: pyridazine < pyrimidine < pyrazine. The J_{sc} values for the cells with nitrogen-containing heterocycles were less than the cell without an additive. Imidazole drastically reduced the J_{sc} value. Among the tested nitrogen-containing heterocycles, imidazole displayed the lowest J_{sc}, but the largest V_{oc}, 0.85 V.

Fig. 2 also represents the influences of the nitrogen-containing heterocyclic additives in the electrolytic solution on the fill factor (ff) and solar energy conversion efficiency (η) of the cell. In general, nitrogen-containing heterocycles enhanced the ff of the solar cell. The highest and lowest ff values were observed when imidazole and tetrazole were the additive, respectively. The η value was remarkably enhanced when nitrogen-containing heterocycles such as pyrazole, 1,2,4-triazole, pyridine, pyrimidine, pyrazine, and 1,3,5-triazine were used, but tetrazole decreased the η value. Among the tested nitrogen-containing heterocycles, pyridine resulted in the highest η.

3.2. Computational calculations

As mentioned in Section 3.1, the tested nitrogen-containing heterocyclic additives affected the dye-sensitized solar cell performance. Dye desorption was not observed after the photovoltaic measurements from the TiO_2 electrode to the electrolytic solution when nitrogen-containing heterocycles were present. Thus, it was determined that the varying effects on the solar cell performance were due to the properties of the nitrogen-containing heterocycles and not variations in the amount of adsorbed N719 dye on the TiO_2 electrode. Therefore, the physical and chemical properties of the nitrogen-containing heterocycles such as the partial charge, dipole moment, and ionization energy were computationally calculated to investigate the reasons for the observed effects of the heterocyclic additives. Various correlations between the properties of the additives and solar cell performance such as V_{oc} and J_{sc} were found.

It has been reported that the surface of a nanocrystalline TiO_2 photoelectrode is positively charged since Ti^{4+} is a Lewis acid [5,12–16]. Accordingly, the atoms with the lowest partial charge in the compounds could be preferential points for their adsorption on TiO_2 surface [16–18]. The partial charges of the atoms in the heterocycles were calculated at the PM5 level using the MOPAC system available in the CAChe package to estimate their ability to adsorb on TiO_2 surface. Due to the lone pair electrons, the nitrogen atoms were lower than the other atoms such as carbon and hydrogen. Fig. 3 depicts the correlation between the V_{oc} and the lowest partial charge of the N atoms in the heterocyclic rings in acetonitrile. The larger the lowest partial charge, the more the V_{oc} was enhanced regardless of the lone pair location in the heterocyclic ring. Fig. 4 shows the correlation between the

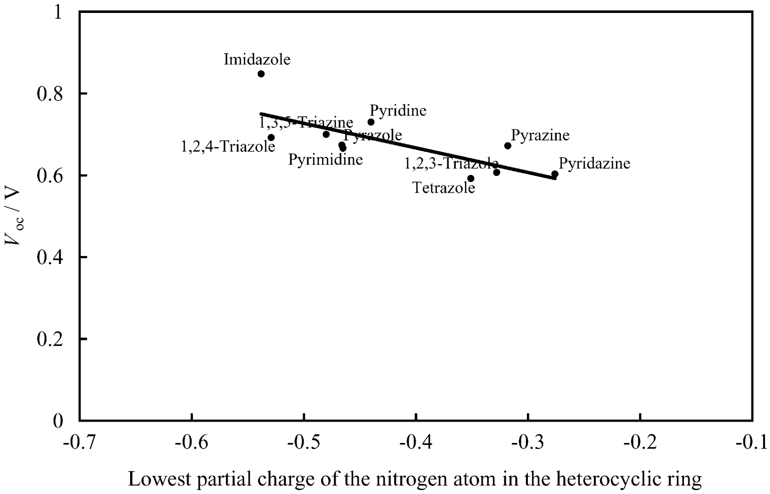

Fig. 3. The correlation between the V_{oc} of the cell and the lowest partial charge of the nitrogen atom in the heterocyclic ring in acetonitrile.

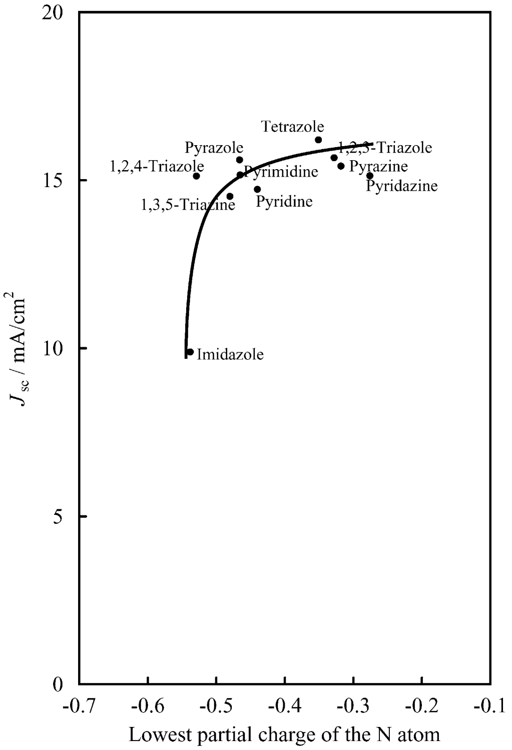

Fig. 4. The correlation between the J_{sc} of the cell and the lowest partial charge of the nitrogen atom in the heterocyclic ring in acetonitrile.

J_{sc} of the cell and the lowest partial charge of the N atoms in the heterocyclic rings in acetonitrile. Unlike the V_{oc} trend, the greater the lowest partial charge, the more the J_{sc} value was reduced. To further clarify the donating effects of the additives, the dark current at the bare TiO_2 electrode without dye coating was measured using the same electrolytic solution as in Section 3.1. Fig. 5 illustrates the correlation between the dark current of the bare TiO_2 electrode without dye coating at 0.7 V when illuminating with 100 mW/cm^2 and the lowest partial charge of the nitrogen atom in the heterocyclic ring in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package. Similar to the V_{oc} trend in Fig. 3, the dark current decreased as the lowest partial charge of nitrogen atom in the heterocyclic ring increased.

The dipole moment and ionization energy of the nitrogen-containing heterocyclic derivatives were calculated at the PM5 level using the MOPAC system available in the CAChe package. Fig. 6 represents the correlation between the V_{oc} of the cell and the dipole moment of the nitrogen-containing heterocycles. The results indicate that as the dipole moment of the nitrogen-containing heterocycles increased, the V_{oc} of the cell increased except for 1,2,3-triazole, tetrazole, and pyridazine. Fig. 7 illustrates the correlation between the J_{sc} of the cell and the dipole moment of the nitrogen-containing heterocycles. The J_{sc} value increased the greater the absolute difference in the dipole moments of the nitrogen-containing heterocycles and acetonitrile, which was 3.4 D (dashed line).

Fig. 8 depicts the correlation between the V_{oc} of the cell and the ionization energy of the nitrogen-containing heterocycles in acetonitrile. The results indicate that as the ionization energy of the nitrogen-containing heterocycles decreased, the V_{oc} of the cell increased.

4. Discussion

The nitrogen-containing heterocyclic additives in the I^-/I_3^- electrolytic solution influence Ru-dye-sensitized nanocrystalline TiO_2 solar cell performance and in particular, the V_{oc} and J_{sc} values are drastically altered, as represented in Fig. 2. Typically, cells with nitrogen-containing heterocycles display higher V_{oc} values, but show lower J_{sc} values compared to a cell without an additive. Computational calculations investigated the reasons why the nitrogen-containing heterocyclic additives influence on the cell performance. The calculated partial charges of the N atoms in the heterocyclic ring estimate the donating ability of the N lone pairs and

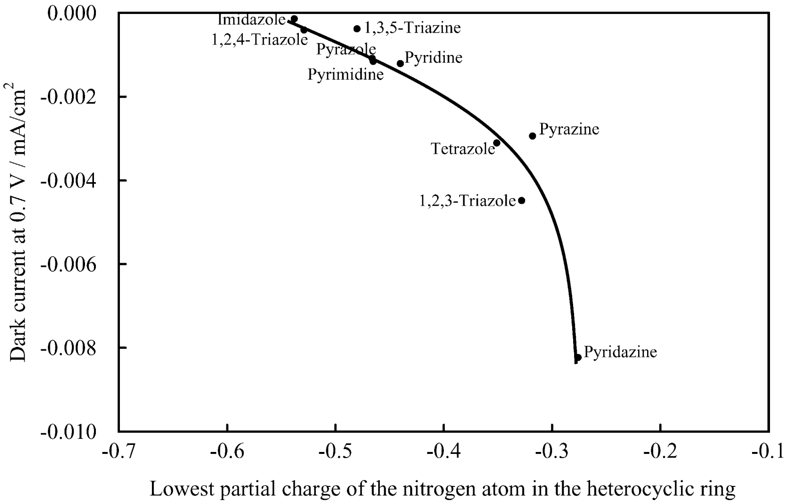

Fig. 5. The correlation between the dark current of the bare TiO_2 electrode without dye coating at 0.7 V and the lowest partial charge of the nitrogen atom in the heterocyclic ring in acetonitrile.

these calculations are compared to the experimental results of the solar cell performance. It is determined that as the lowest partial charge of the N atoms increases, the V_{oc} increases (Fig. 3), but the J_{sc} decreases (Fig. 4). These results suggest that the molecules of nitrogen-containing heterocycles adsorb on the free areas of the TiO_2 electrode, which would increase the V_{oc}, but decrease the J_{sc} values. Grätzel and his co-workers hypothesized that the adsorption of the additive onto the free area of the TiO_2 photoelectrode exposed to I^-/I_3^- redox electrolyte suppressed the dark current arising from the I_3^- reduction by the conduction band electrons at the semiconductor electrolyte junction [5,19] (Eq. (1)).

$$2e_{cb}^-(TiO_2) + I_3^- \xrightarrow{k_{et}[I_3^-]} 3I^- \tag{1}$$

For regenerative photoelectrochemical systems, Eq. (2) holds [6]:

$$V_{oc} = \left(\frac{kT}{e}\right) \ln\left(\frac{I_{inj}}{n_{cb}k_{et}[I_3^-]}\right) \tag{2}$$

where k and T are the Boltzmann constant and the absolute temperature, respectively. I_{inj} is the charge flux that results from the sensitizing dye injecting an electron and n_{cb} is the concentration of electrons at the TiO_2 surface, while k_{et} is the rate constant for the reduction of I_3^- by the conduction band electrons. The V_{oc} increases as the k_{et} decreases [5,6,20]. In fact, as depicted in Fig. 5, the dark current decreases as the lowest partial charge of nitrogen atom in the heterocyclic ring increases. As mentioned in Section 3.2, it was reported that the surface of nanocrystalline TiO_2 photoelectrode is positively charged since Ti^{4+} is a Lewis acid [5,12–16]. Accordingly, atoms bearing the lowest partial charge in the compounds could be preferential points for their adsorption on TiO_2 surface [16–18]. The greater the lowest partial charge

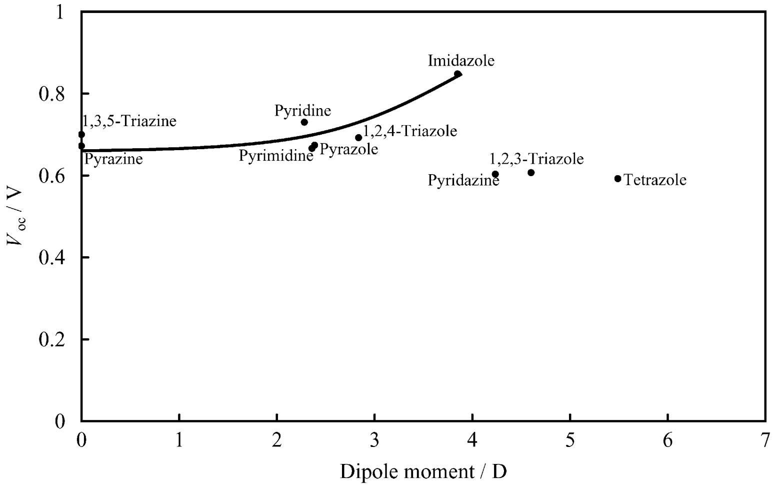

Fig. 6. The correlation between the V_{oc} of the cell and the dipole moment of the nitrogen-containing heterocycles.

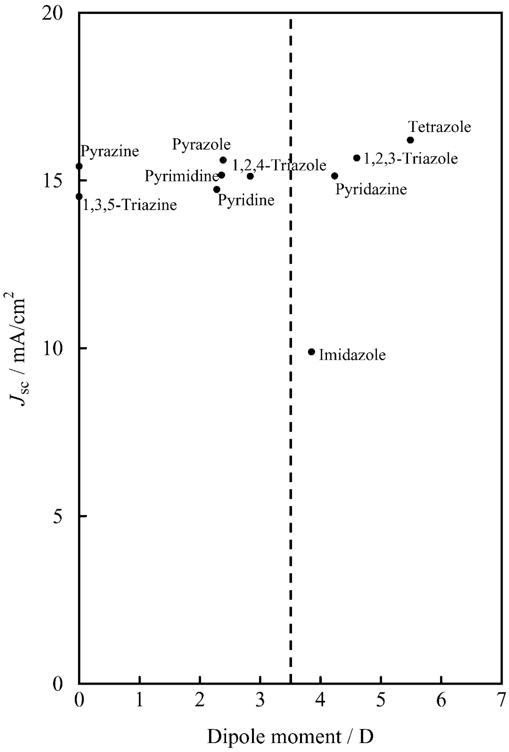

Fig. 7. The correlation between the J_{sc} of the cell and the dipole moment of the nitrogen-containing heterocycles.

of the N atom in the heterocyclic ring, the easier and more often the nitrogen-containing heterocycles can adsorb on the free area of the TiO_2 surface [17,18,21–23], which more efficiently suppresses the dark current.

More recently, Kim and his co-workers proposed that the influence of the additives on V_{oc} and J_{sc} is due to raise the flatband potential (V_{FB}) of the TiO_2 photoelectrode [3]. Absorbing additives in the electrolytic solution onto the TiO_2 surface may raise the flatband potential (V_{FB}) of the TiO_2 electrode [24,25]. Under Fermi level pinning, these two parameters are linked by Eq. (3),

$$V_{oc} = |V_{FB} - V_{red}| \tag{3}$$

where V_{red} is the standard reduction potential of a redox coupling. According to the literature [26], the change in V_{red} is negligible when pyridines are added in acetonitrile. Consequently, if V_{red} remains constant when nitrogen-containing heterocycles are added, then increasing the V_{FB} by adsorbing nitrogen-containing heterocycles on the TiO_2 surface should increase $V_{oc.}$ Raising V_{FB} would also cause a negative shift in the conduction band edge of TiO_2, which would decrease the electron injection rate from the exiting dye and explain the reduced J_{sc} upon adding nitrogen-containing heterocyclic derivatives. The greater the lowest partial charge of the N atom in the heterocyclic ring, the easier and more often the nitrogen-containing heterocycles can adsorb on the Lewis acid sites of the TiO_2 surface, which would increase the V_{oc} and decrease the J_{sc}.

The other results support these hypotheses. As depicted in Fig. 6, except for 1,2,3-triazole, tetrazole, and pyridazine, the V_{oc} of the cell increases as the dipole moment of the nitrogen-containing heterocycles increases. This finding also suggests that the additives adsorb onto the free areas of the TiO_2 photoelectrode. The larger the dipole, the easier and more often the nitrogen-containing heterocycles can adsorb onto TiO_2 surface since the adsorption energy become more negative [27–29], which leads to a higher V_{oc} of the cell. Moreover, as described in Section 3.1, the V_{oc}, except for 1,2,3-triazole and pyridazine, is lower than those isomers since in the former two N atoms (1,2 or 2,3-position) can interact with the TiO_2 surface, but the latter cannot (1,3 or 2,4 or 1,4-position). Therefore, the amount of former molecules such as 1,2,3-triazole and pyridazine that adsorb onto the free area of the TiO_2 may be half of the latter such as 1,2,4-triazole, pyrimidine, and pyrazine, which results in a lower V_{oc} value. In fact, typically as the additive concentration increases, the V_{oc} increases, but the J_{sc} decreases [30]. Tetrazole may interact

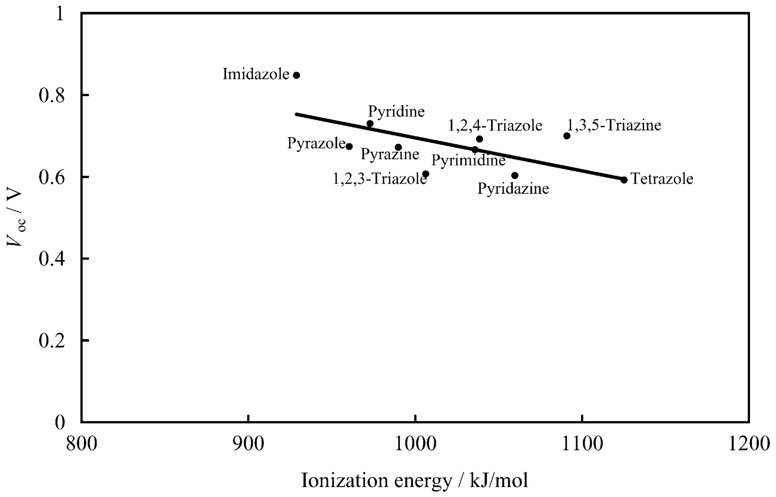

Fig. 8. The correlation between the V_{oc} of the cell and the ionization energy of the nitrogen-containing heterocycles in acetonitrile.

with the TiO_2 surface using three N atoms in positions 2,3,4, but did not enhance the value of V_{oc}.

The other effect on the V_{oc} is explained by the electron donicity of the nitrogen-containing heterocycles. As represented in Fig. 8, the V_{oc} increases as the calculated ionization energy of the heterocycles decreases. Nitrogen-containing heterocycles react with iodine in the solvent to form charge-transfer complexes between the N of the heterocyclic ring and I atoms [31–36]. The chemical reactions are written as reaction (4).

$$\text{Heterocycles} + I_3^- \rightleftarrows \text{Heterocycles}\, I_2 + I^- \qquad (4)$$

This reaction decreases the I_3^- concentration, but increases the I^- concentration, which improves the hole collection by I^- [37,38] and increases the V_{oc} of the cell. Decreasing the I_3^- concentration may also reduce the reaction between the injected electrons and I_3^- (Eq. (1)), which would increase the electron concentration in the TiO_2 film and improve the V_{oc} (Eq. (2)) [6,8,20]. The theory of intermolecular charge-transfer complexes is explained by the interaction between the HOMO of the donors (nitrogen-containing heterocycles) with the LUMO of the acceptors (iodine). The greater the overlap and/or the smaller energy difference of the HOMO of donors and the LUMO of acceptors, the greater the stabilization energy, Δ, and the greater the extent of mixing, which causes a greater charge transfer from the donor to the acceptor. Therefore, it is easier to form a charge-transfer complex when the ionization energy of the donor is small and the electron affinity of acceptor is large [39]. Thus, the lower the ionization energy of the nitrogen-containing heterocyclic derivatives, the more efficiently the holes are collected and/or the electron concentration in the TiO_2 film is increased, which results in a higher V_{oc}.

Molecular orbital calculations also explain the other effects on the $J_{sc.}$ The J_{sc} value increases with the greater the absolute difference of the calculated dipole moment of the nitrogen-containing heterocycles from acetonitrile, which is 3.4 D (Fig. 7). This correlation is consistent with the idea previously proposed. The dielectric constant of an electrolytic solution decreases as the difference in dipole moments of the additive and solvent increases since the additive screens more of the solvent dipoles and lowers the dielectric constant [40–43]. Thus, the J_{sc} value is smaller in the cell [44,45].

Therefore, it is concluded that the electron donating properties of the nitrogen-containing heterocycles to the I^-/I_3^- electrolyte solution significantly influence the Ru-dye-sensitized nanocrystalline TiO_2 solar cell performance.

5. Conclusion

The influence of 10 different nitrogen-containing heterocyclic additives on the performance of a Ru-complex (N719) dye-sensitized nanocrystalline TiO_2 solar cell was investigated for an I^-/I_3^- redox electrolyte in acetonitrile. Typically, adding nitrogen-containing heterocycles reduced the J_{sc} of the solar cell, but enhanced the V_{oc}, ff, and η. As the lowest partial charge of the nitrogen atoms in the heterocyclic ring increased, V_{oc} was enhanced, but the J_{sc} value was reduced. The dark current at the bare TiO_2 electrode without dye coating decreased as the lowest partial charge of the nitrogen atoms in the heterocyclic ring increased. The V_{oc} also increased as the ionization energy of the nitrogen-containing heterocycles decreased. These correlations suggest that the electron donicity of nitrogen-containing heterocycles influenced the interaction with the TiO_2 electrode and the I^-/I_3^- electrolyte and caused the changes in solar cell performance.

Acknowledgments

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