Angewandte
International Edition Chemie

DOI: 10.1002/anie.201205036

Electrochemistry

Nitroxide Radicals as Highly Reactive Redox Mediators in Dye-Sensitized Solar Cells**

*Fumiaki Kato, Akitomo Kikuchi, Takumi Okuyama, Kenichi Oyaizu, and Hiroyuki Nishide**

The organic radical 2-azaadamantan-*N*-oxyl (AZA) used as a stable and highly reactive redox mediator in a dye-sensitized solar cell (DSSC) is reported. AZA exhibits both an appropriate redox potential and significantly high values for the diffusivity, heterogeneous electron-transfer rate, and electron self-exchange reaction rate. These properties give rise to an enhanced electron-transfer mediation which leads to a high fill factor or low cell resistance and thus excellent photovoltaic performance to achieve a conversion efficiency of 8.6 %.

Organic radicals are usually highly reactive and have been considered unstable and intractable. However, some of these radicals have been converted to stable compounds through chemical modification to provide steric protection around the unpaired electrons and/or resonance structures involving the unpaired electrons.[1] 2,2,6,6-Tetramethylpiperidin-*N*-oxyl (TEMPO) is a typical example of a stable radical, in which the oxygen-centered unpaired electron is sterically protected by the surrounding tetramethyl groups and is stabilized by the resonance structure of the N−O group.[2] Stable radicals have been studied in the field of organic magnetism and as catalytic reagents based on their unpaired electron spin and their electron-releasing and electron-accepting character in redox reactions.[3] For example, TEMPO was applied as an organic, metal-free oxidizing catalyst of primary alcohols.[4] To enhance the catalytic activity, 2-azaadamantan-*N*-oxyl was also employed, which exhibits a much higher reactivity because of the reduced steric hindrance around its radical center compared to that of TEMPO.[5]

Recently, we successfully used radical polymers bearing redox-active TEMPO moieties in their repeating units as a cathode-active organic material and demonstrated an amazingly high power rate capability in an organic secondary battery.[6] The high charging and discharging rates were analyzed and ascribed to fast charge propagation and transport through the TEMPO moieties derived from their reversible and rapid redox reactivity and their efficient electron self-exchange reaction.[7] The reactivity and redox potential of the redox reagents were tunable by the molecular structure of the nitroxide derivatives.[8]

DSSCs have recently received much attention because of their ease in wet-chemical fabrication and their still improvable conversion efficiency.[9] In DSSCs, photoexcitation of the dye sensitizer molecule is followed by electron injection into the conduction band of titanium oxide (TiO_2) on which the dye is adsorbed. The dye molecule is then regenerated or reduced by a redox mediator in the electrolyte solution. The most widely used mediator is the iodide/triiodide (I^-/I_3^-) redox couple, which is regenerated at the counter electrode. The redox mediator acts as a shuttle transporting the electrons (hole charges) through diffusion in the solution. The charge separation at the interface between TiO_2/dye solid phase and the mediator solution and the charge transport in the solution play important roles in the current generation in DSSCs. Recently, attention has focused on the redox mediator of DSSCs, because the open-circuit voltage (V_{oc}) of DSSCs is dominated by the energy difference between the Fermi level of TiO_2 and the redox potential of the mediator. One drawback of the iodide mediator is the mismatch of its redox potential (about 0.4 V vs. Ag/AgCl), that is, it has an excess driving force or energy loss of 0.6 V for the dye regeneration process, resulting in a limited V_{oc} value (up to 0.9 V as previously reported).[10] Undesirable corrosion of the electrode metals and the strong visible absorption of the iodide mediator are also problematic.

Many redox couples have been explored as alternatives to the iodide redox mediator in the past decade. For example, Spiccia and co-workers used the ferrocene/ferrocenium redox couple and demonstrated 7.5 % conversion efficiency by optimizing the additives and the composition of the electrolyte and by synthesizing carbazole derivatives as new dye sensitizers.[11] Redox couples of metal complexes, such as Co^{II}/Co^{III}, Cu^{I}/Cu^{II}, and Ni^{I}/Ni^{II}, have also been widely investigated.[12] Recently, Grätzel and co-workers achieved the highest record for the conversion efficiency (12.3 %) in DSSCs by incorporating cobalt tris(bipyridyl) complexes as redox couple and appropriately designed porphyrin derivatives as organic dye sensitizers.[13]

TEMPO has also been applied as a redox mediator in a DSSC by Grätzel et al.[14] To search for an appropriate redox potential of the mediator for dye regeneration, we examined a series of TEMPO derivatives and succeeded in improving the V_{oc} by modifying the molecular structure of TEMPO with various 4-substituents.[15] Nitroxide derivatives were further studied as DSSC mediators by other groups.[16] However, the V_{oc} was enhanced at the expense of the short-circuit current

---

[*] Dr. F. Kato, A. Kikuchi, T. Okuyama, Prof. K. Oyaizu, Prof. H. Nishide
Department of Applied Chemistry, Waseda University
Tokyo 169-8555 (Japan)
E-mail: nishide@waseda.jp

[**] This work was partially supported by the FIRST Program on "Development of Organic Photovoltaics toward a Low-Carbon Society" from JSPS (Japan) and by Grants-in-Aid for Scientific Research (grant numbers 19105003, 24225003, and 24108739) from MEXT (Japan). We appreciate Prof. H. Segawa (The University of Tokyo) for his productive comments. We are grateful to T. Sekiguchi, M. Suzuka, and N. Hayashi (Advanced Technologies Development Laboratory of Panasonic Co.) for technical discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201205036.

density (J_{sc}) of the cell, as V_{oc} and J_{sc} are inversely proportional; a narrow dye–mediator potential gap leads to a reduced forward electron-transfer rate at the dye interface.

In contrast to the redox potential or the energy level of the mediator, little attention has been paid to the reactivities or kinetic features of the redox mediators during dye regeneration, electron self-exchange reaction among mediator molecules, or the reduction of the mediator at the counter electrode. These reactivities should be determined by electrochemical and spectroscopic analyses and are potentially tuned by modifying the chemical structures of the mediator molecules, especially in the case of organic mediators. We focused on the significantly high and tunable reactivity of nitroxide radical molecules to enhance the overall photovoltaic performance.

The redox reaction of a nitroxide radical, exemplified by TEMPO, is based on a simple one-electron transfer without any chemical bond formation, recombination, or cleavage (Figure 1 a; the dot is an unpaired electron).[17] AZA is a stable nitroxide radical because its rigid and symmetric adamantane framework inhibits elimination of the α-substituted protons.[18] We isolated both the TEMPO and AZA radicals and their oxidized oxoammonium species (the right-hand species in Figure 1 a) as crystals and determined their molecular structures. In other words, not only the radicals but also the corresponding oxoammonium species are chemically stable for application as redox mediators.

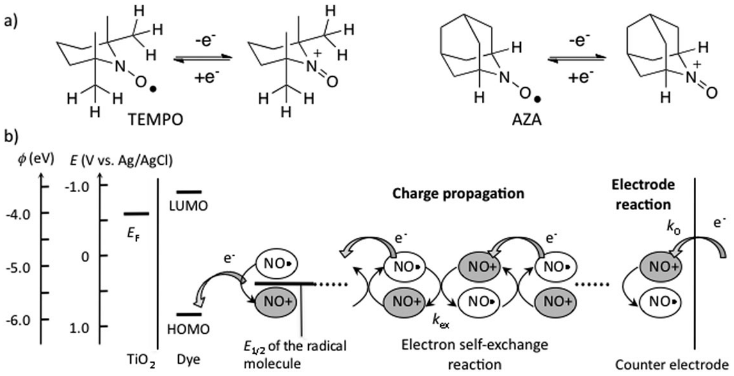

Figure 1. a) Chemical structures and redox reaction of nitroxide radicals and b) scheme for the mediation process with the nitroxide radical redox couple in a DSSC (ϕ = energy, E = redox potential, and E_F = Fermi energy).

AZA and TEMPO produced electrochemically reversible responses with redox potentials at 0.64 and 0.67 V versus Ag/AgCl, respectively (Figure S1 in the Supporting Information). These values were appropriate for regenerating or reducing the oxidized dye molecules in DSSCs. These redox potentials are also suitable for DSSCs because they yield an appropriate V_{oc} as their potentials are about 0.3 V deeper than that of the iodide redox couple (0.34 V vs. Ag/AgCl).

The heterogeneous electron-transfer rate constant (k_0) indicates how fast the regeneration reaction of the mediator cation is on the counter electrode of the DSSC (the reaction is shown at the right edge in Figure 1 b and the rate constant is given in Table 1). The k_0 values for the nitroxide radical mediators were 10^0 to 10^{-1} cm s^{-1} and were 100 times higher than that of the iodide redox couple (10^{-3} cm s^{-1}, also given in Table 1). The significantly high k_0 of the nitroxide radicals, especially AZA, is expected to reduce the electrode-reaction resistance and improve the photovoltaic performance of the resulting DSSC.

Table 1: Electrochemical and photochemical properties for the mediator molecules.[a]

Mediator	$E_{1/2}$ [V] vs. Ag/AgCl	k_0 [$\times 10^{-1}$ cm s^{-1}]	D_0 [$\times 10^{-5}$ cm^2 s^{-1}]	k_{ex} [$\times 10^7$ M^{-1} s^{-1}]
AZA	0.63	16	12	33
TEMPO	0.69	2.9	7.5	2.9
iodide	0.34	0.053	5.8	–

[a] See the Supporting Information for details.

The diffusion coefficient (D_0) of the mediator is also an important parameter determining the cell resistance of the DSSC (the diffusion process is shown in the center of Figure 1 b). The D_0 value is dominated by both the redox-gradient-driven charge propagation through electron self-exchange, which mainly tunes the reaction of the mediator, and the physical diffusion of the mediator. The D_0 values for AZA and TEMPO were larger than that for iodide: It is significant that bulky organic radicals have larger D_0 values than the compact sized inorganic iodide mediator.

The reactivity of the nitroxide radical mediator was analyzed by electron spin resonance (ESR) spectroscopy. The electron self-exchange reaction rate constant (k_{ex}) of the nitroxide mediators was evaluated and is given in Table 1. The k_{ex} of AZA was about 10^8 M^{-1} s^{-1}, which is 10 times higher than that of TEMPO. The fast self-exchange reaction is the most important feature of AZA as a redox mediator. This is reflected in the tremendously high diffusivity of the AZA mediator and may help to reduce the resistance or enhance J_{sc} and/or the fill factor (FF) in the DSSC.

The solutions of the nitroxide radicals, AZA, and TEMPO, and their corresponding N-oxoammonium cations were almost colorless and transparent in the UV/Vis region (molar extinction coefficient < 10 M^{-1} cm^{-1}, see Figure S2). Thus, the radical mediators avoided energy loss by light absorption of the electrolyte in the DSSCs.

Next, DSSC cells were fabricated with a TiO_2 layer of a thickness fixed at 1.5 μm. The nitroxide radicals were used as redox mediator, and the composition of the electrolyte in an acetonitrile solution, including additives, was optimized by taking into account the electrochemical properties and the kinetic reactivity described above.

The current density–voltage characteristics and the photovoltaic parameters of the DSSC cells using the AZA- and TEMPO-based electrolytes are given in Figure 2 and Table 2 along with those of the reference cell using the conventional iodide electrolyte. By using a radical mediator with a more positive redox potential (in Table 1) in comparison with that of the iodide mediator, we succeeded in obtaining a larger V_{oc} of 0.85 V.

Table 2: Photovoltaic parameters of the cells composed of the nitroxide radical mediator electrolytes and the indoline dye sensitized under 100 mW cm^{-2} full sunlight irradiation.

Entry	Mediator	Sensitizer	Electrolyte[a]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	*FF*	η [%]
1	AZA	D205	A	12.3	0.84	0.76	7.8
2	AZA	D205	B	12.9	0.82	0.76	8.1
3	AZA	D205/D131	B	13.3	0.85	0.75	8.6
4	TEMPO	D205	A	9.88	0.88	0.75	6.5
5	TEMPO	D205/D131	B	13.5	0.78	0.66	7.0
6	iodide	D205	C	13.9	0.56	0.50	3.9
7	iodide	D205/D131	C	14.7	0.54	0.48	3.8

[a] The optimized electrolyte A consisted of 1.0 M nitroxide radical mediator, 0.1 M of the corresponding *N*-oxoammonium tetrafluoroborate salt, and 0.1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in acetonitrile as solvent. In electrolyte B, 0.1 M chenodeoxycholic acid (CDCA) was added to electrolyte A. Electrolyte C was the reference solution using the iodide mediator, composed of 0.6 M 1-methyl-3-propylimidazolium iodine, 0.06 M I_2, 0.1 M LiI, and 0.5 M 4-*tert*-butylpyridine.

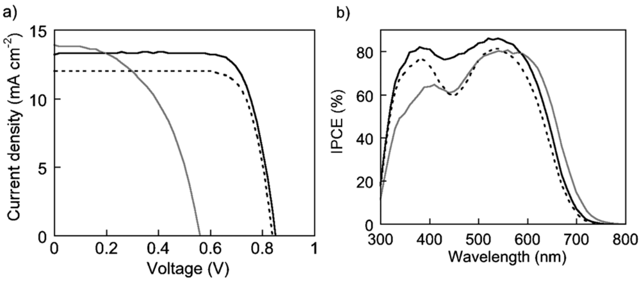

Figure 2. a) Current density–voltage characteristics and b) IPCE spectra of the cells composed of the AZA-based electrolyte with the D205/D131 co-sensitizer (black line) and with the D205 sensitizer (dashed line) and composed of the iodide-based electrolyte (gray line) with D205 as the reference. Current density–voltage characteristics were measured under 100 mW cm^{-2} full sunlight irradiation.

The AZA mediator cell achieved 8.6 % conversion efficiency (η) when the electrolyte additives and the indoline dye sensitizers (D205 and D131) were optimized.[19] The improvement in η was caused by combination of the high J_{sc}, V_{oc}, and *FF*. The incident photon-to-electron conversion efficiency (IPCE) spectra in Figure 2b showed IPCE values of almost 80 % in the visible region, which were attained by employing two indoline dyes, D205 and D131, as sensitizers. The D205 dye exhibited high molar absorption efficiency but was not effective at 400–500 nm, while the D205/D131 co-sensitized cell provided an excellent panchromatic photocurrent response. The significantly high *FF* (above 0.75) of the AZA mediator cell was ascribed to the low cell resistance resulting from the highly effective charge propagation and regeneration of the mediator. Electrochemical impedance analysis on the cell performance (see Figure S9 in the Supporting Information) also indicated low resistance characteristics of the cells using the radical mediators, especially for AZA. These results strongly support the conclusion that the highly reactive AZA mediator contributed to effective dye regeneration and charge transport, which enhanced the values of J_{sc}, *FF*, and η.

The high reactivity and yet reversible redox behavior of the nitroxide radicals dramatically enhanced the charge diffusivity, the electrode reaction rate, and the photovoltaic performance. The conversion efficiency reached 8.6 % for the AZA-based cell. We have reported that nitroxide radical-bearing polymers also provided effective charge transport through rapid electron self-exchange reactions among the neighboring radical moieties along the polymer chain.[6,8] Now, we are testing these polymers as polymer mediator electrolyte in a quasi-solid-state DSSC.

Received: June 27, 2012

Keywords: charge transfer · dye-sensitized solar cells · electrochemistry · phase transitions · radicals

---

[1] a) R. G. Hicks, *Stable Radicals*, Wiley, Chichester, **2010**; b) C. Chatgilialougu, S. Armodo, *Encyclopedia of Radicals in Chemistry, Biology and Materials*, Wiley, Chichester, **2012**.

[2] a) E. Breuer, G. H. Aurich, A. Nielsen, *Nitroenes, Nitronates and Nitroxides*, Wiley, New York, **1989**; b) L. B. Volodarsky, A. V. Reznikov, *Synthetic Chemistry of Stable Nitroxides*, CRC, Boca Raton, FL, **1993**.

[3] a) P. M. Lahti, *Magnetic Properties of Organic Materials*, Marcel Dekker, New York, **1999**; b) A. Rajca, J. Wongsriratanakul, S. Rajca, *Science* **2001**, *294*, 1503–1504; c) H. Nishide, T. Ozawa, M. Miyasaka, E. Tsuchida, *J. Am. Chem. Soc.* **2001**, *123*, 5942–5946; d) E. Fukuzaki, H. Nishide, *J. Am. Chem. Soc.* **2006**, *128*, 996–1001; e) "Application of Stable Radicals as Mediators in Living-Radical Polymerization": R. A. Szkurhan, J. Lukkarila, K. M. Georges, *Stable Radicals* (Ed.: R. G. Hicks), Wiley, Chichester, **2010**; f) L. Tebben, A. Studer, *Angew. Chem.* **2011**, *123*, 5138–5174; *Angew. Chem. Int. Ed.* **2011**, *50*, 5034–5068; g) "Nitroxide-Catlyzed Alcohol Oxidations in Organic Synthesis": C. Brückner, *Stable Radicals* (Ed.: R. G. Hicks), Wiley, Chichester, **2010**; h) "Nitroxides in Synthetic Radical Chemistry": C. Tansakul, R. Braslau, *Encyclopedia of Radicals in Chemistry, Biology and Materials* (Eds.: C. Chatgilialougu, S. Armodo), Wiley, Chichester, **2012**.

[4] a) R. A. Sheldon, I. W. C. E. Arends, *Adv. Synth. Catal.* **2004**, *346*, 1051–1071; b) T. Miyazawa, T. Endo, S. Shiihashi, M. Okawara, *J. Org. Chem.* **1985**, *50*, 1332–1334.

[5] M. Shibuya, Y. Osada, Y. Sasano, M. Tomizawa, Y. Iwabuchi, *J. Am. Chem. Soc.* **2011**, *133*, 6497–6500.

[6] a) H. Nishide, S. Iwasa, Y. J. Pu, T. Suga, K. Nakahara, M. Satoh, *Electrochim. Acta* **2004**, *50*, 827–831; b) H. Nishide, T. Suga, *Electrochem. Soc. Interface* **2005**, *14*, 32–36; c) T. Suga, H. Konishi, H. Nishide, *Chem. Commun.* **2007**, 1730–1732; d) H. Nishide, K. Oyaizu, *Science* **2008**, *319*, 737–738; e) T. Suga, H. Ohshiro, S. Sugita, K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 1627–1630; f) K. Nakahara, K. Oyaizu, H. Nishide, *Chem. Lett.* **2011**, *40*, 222–227.

[7] K. Oyaizu, Y. Ando, H. Konishi, H. Nishide, *J. Am. Chem. Soc.* **2008**, *130*, 14459 – 14461.

[8] a) T. Suga, Y. J. Pu, K. Oyaizu, H. Nishide, *Bull. Chem. Soc. Jpn.* **2004**, *77*, 2203 – 2204; b) T. Suga, Y. J. Pu, S. Kasatori, H. Nishide, *Macromolecules* **2007**, *40*, 3167 – 3173; c) K. Oyaizu, H. Nishide, *Adv. Mater.* **2009**, *21*, 2339 – 2344; d) M. Armand, S. Grugeon, H. Vezin, S. Laruelle, P. Ribière, P. Poizot, J.-M. Tarascon, *Nat. Mater.* **2009**, *8*, 120 – 125.

[9] a) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737 – 740; b) A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49 – 68; c) M. Grätzel, *Acc. Chem. Res.* **2009**, *42*, 1788 – 1798.

[10] G. Boschloo, A. Hagfeldt, *Acc. Chem. Res.* **2009**, *42*, 1819 – 1826.

[11] T. Daeneke, T. H. Kwon, A. B. Holmes, N. W. Duffy, U. Bach, L. Spiccia, *Nat. Chem.* **2011**, *3*, 211 – 215.

[12] a) S. Nakade, Y. Makimoto, W. Kubo, T. Kitamura, Y. Wada, S. Yanagida, *J. Phys. Chem. B* **2005**, *109*, 3488 – 3493; b) S. M. Feldt, E. A. Gibson, E. Gabrielsson, L. Sun, G. Boschloo, A. Hagfeldt, *J. Am. Chem. Soc.* **2010**, *132*, 16714 – 16724; c) T. C. Li, A. M. Spokoyny, C. She, O. K. Farha, C. A. Mirkin, T. J. Marks, T. J. Hupp, *J. Am. Chem. Soc.* **2010**, *132*, 4580 – 4582.

[13] A. Yella, H. W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* **2011**, *334*, 629 – 634.

[14] a) Z. Zhang, P. Chen, M. N. Murakami, M. S. Zakeeruddin, M. Grätzel, *Adv. Funct. Mater.* **2008**, *18*, 341 – 346.

[15] F. Kato, N. Hayashi, T. Murakami, C. Okumura, K. Oyaizu, H. Nishide, *Chem. Lett.* **2010**, *39*, 464 – 465.

[16] a) J. Lee, C. Lee, Y. Lee, K. Cho, J. Choi, J.-K. Park, *J. Solid State Electrochem.* **2012**, *16*, 657 – 663; b) Gryn'ova, J. M. Barakat, J. P. Blinco, S. E. Bottle, M. L. Coote, *Chem. Eur. J.* **2012**, *18*, 7582 – 7593.

[17] Y. Yonekuta, K. Oyaizu, H. Nishide, *Chem. Lett.* **2007**, *36*, 866 – 867.

[18] M. Shibuya, M. Tomizawa, Y. Sasano, Y. Iwabuchi, *J. Org. Chem.* **2009**, *74*, 4619 – 4622.

[19] a) S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, *Chem. Commun.* **2008**, 5194 – 5196; b) T. Horiuchi, H. Miura, S. Uchida, *Chem. Commun.* **2003**, 3036 – 3037.