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Electrochemical approach to enhance the open-circuit voltage (V_{oc}) of dye-sensitized solar cells (DSSCs)

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ABSTRACT

The net enhancement of open-circuit voltage (V_{oc}) of dye-sensitized solar cells (DSSCs) was achieved with the novel electrolyte composed of interhalogen based binary-redox couples without regard to the choice of sensitizers. The interhalogen ion, I_2Br^-, was formed in the conventional iodine-based electrolyte by both chemically and electrochemically and it was found to produce an extra redox pair, (I^-, Br^-)/I_2Br^-, with new energy state at a more positive potential than that of I^-/I_3^-. The Fermi level of the electrolyte shifted positively by the weighted-average of the two redox systems. It induced the increase of V_{oc} up to 30, 60, and 50 mV for *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N719), *cis*-dicyano-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II) (Ruthenizer 505 or Ru505), and 2′,4′,5′,7′-tetrabromofluorescein (eosin Y) dyes, respectively, without affecting the short circuit current much. It corresponded to the enhancement of the overall power conversion efficiency (η) up to 8, 14, and 13%, respectively. Moreover, the degree of enhancement of V_{oc} was controllable by varying [I_2Br^-] since the higher the contribution of [I_2Br^-] the more positive shift in the energy level of the binary redox couples.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been receiving considerable attention for last two decades, as they offer an inexpensive and promising alternative [1,2] to conventional solar cells. Photovoltaic parameters of DSSCs have been optimized to enhance the solar energy conversion efficiency (η) [3]. Open-circuit voltage (V_{oc}) is an important photovoltaic parameter that determines the η provided that the fill factor (*ff*) of the DSSC remains almost unchanged. The difference between the quasi-Fermi level of TiO_2 photoelectrode under illumination and the redox energy level of the electrolyte is considered as the theoretical maximum value of V_{oc}. The back reaction of photoelectrons in the TiO_2 film to the oxidized species in the electrolyte (*e.g.*, I_3^-) is considered as a major source of V_{oc} decay to result in the decrease of η. Even though, many strategies were suggested to minimize the V_{oc} decay of DSSCs by slowing down the back reaction of photoelectron, most of these approaches have inherent limitations due to the reduction of charge injection rate [4,5]. They include the adsorption of organic hydrophobic moiety [6,7] and deposition of thin layer of inorganic metal oxides [5,8] on the surface of TiO_2 nanoparticles as well as the direct addition of molecular adsorbents to the electrolyte [4,9–11].

Since, V_{oc} of DSSCs is highly dependent on the electrochemical potential of redox couple in the electrolyte, many redox mediators including bromine [12], pseudohalogens [13–15], organic redox couples [16–19], and cobalt-complex redox couples [20–23] have been studied to replace I^-/I_3^- couple for higher V_{oc}. Meanwhile, a redox couple of more positive potential is expected to offer a larger value of V_{oc}, none of them were successful in rivaling I^-/I_3^- in reaching a higher photovoltaic performance mostly due to the significant retardation of dye regeneration [13,14,24]. The elongated life time of the oxidized dyes by inefficient regeneration causes the significant enhancement of electron recombination, which essentially resulted in the decay of the V_{oc} of the cells. For efficient regeneration, the highest occupied molecular orbital (HOMO) of the dye should be at least *ca.* 100–200 mV more positive than the redox potential of the mediator [25,26]. Recently, the significant increase of photovoltage with Br^-/Br_3^- couple, of which the redox potential

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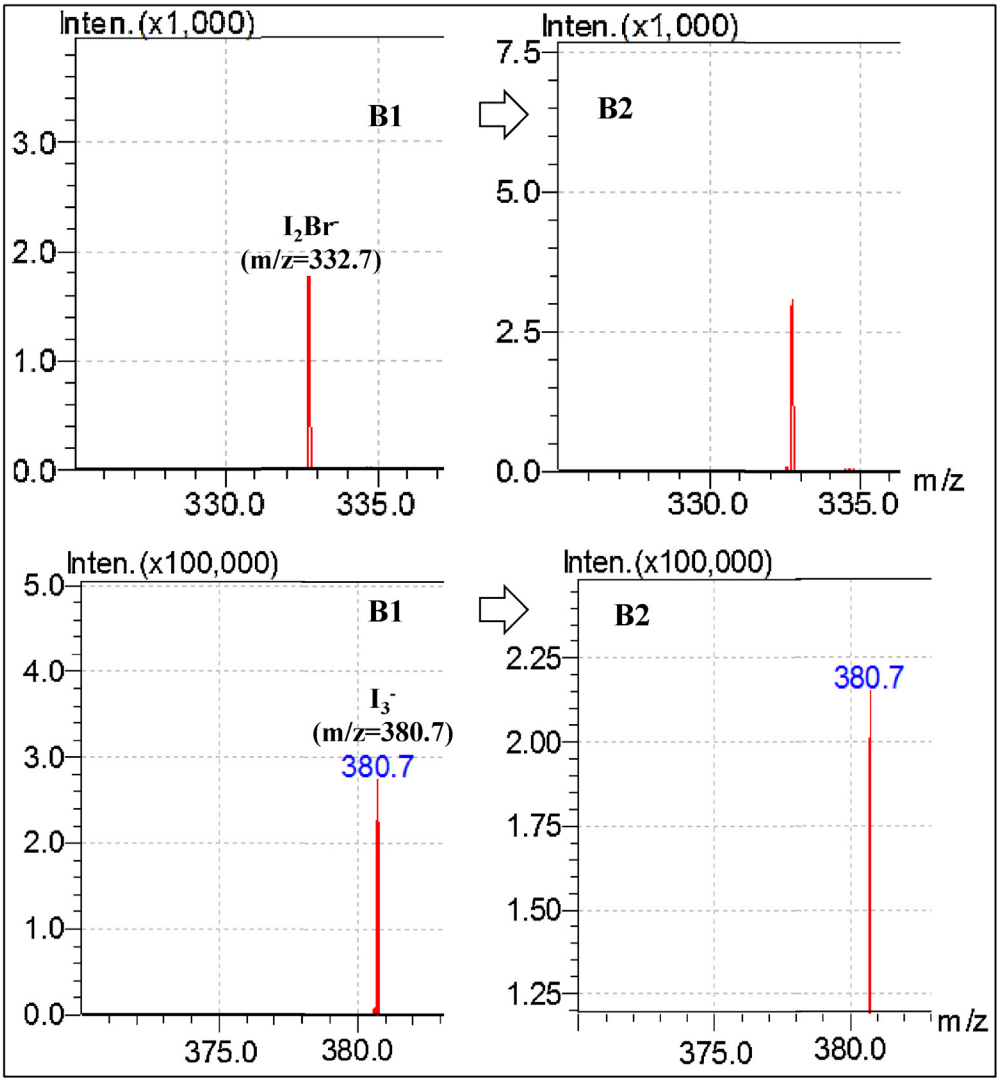

Fig. 1. ESI-MS of **B1** and **B2** electrolytes. All electrolytes were diluted by the factor of 20 before the measurement.

is *ca.* 0.4 V more positive than that of I^-/I_3^-, was reported. However, it was only with the dye having a HOMO level much more positive than that of the conventional and the most effective dyes, such as *cis*-bis(isothiocyanato)bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) (N3) and *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N719) [12]. It is very challenging to introduce a novel redox couple with more positive formal potential to boost up the V_{oc} of DSSCs without compromising the rate of regeneration of these dyes. In the present work, we prepared an electrolyte containing interhalogen-based binary redox couples denoted by $(I^-, Br^-)/(I_3^-, I_2Br^-)$, with which we can increase the open-circuit voltage (V_{oc}) of DSSCs.

2. Experimental

2.1. Materials

All reagents and solvents were purchased from Sigma–Aldrich unless otherwise mentioned. *cis*-diisothiocyanato-bis(2,2′-bipyridyl-4,4′-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (N719), and *cis*-dicyano-bis(2,2′-bipyridyl-4,4′-dicarboxylic acid) ruthenium(II) (Ruthenizer 505 or Ru505) were purchased from Solaronix.

2.2. Preparation of electrolytes

Conventional electrolytes with single halogen-based redox couple, X^-/X_3^- (X = I and Br, and denoted as **S1** and **S2**, respectively), were prepared as usual, by mixing 0.4 M LiX and 0.04 M X_2 in acetonitrile. The electrolyte with interhalogen based binary redox couples, denoted as **B1**, was prepared by mixing 0.4 M LiI and 0.04 M Br_2 in the same solvent. The electrolytes with higher concentration of I_2Br^- in the binary system, denoted as **B2** and **B3**, was obtained by addition of LiBr up to 0.05 and 0.1 M, respectively, to **B1**. The estimated concentrations of I_2Br^- for **B1**, **B2**, and **B3**, were 0.28, 0.42, and 0.58 mM, respectively.

2.3. Preparation of TiO_2 mesoporous film

TiO_2 paste was prepared from commercial TiO_2 nanoparticles (25–30 nm, P25; Degusa, Germany) mixing with 50% (w/w) hydroxypropyl cellulose (HPC) (Aldrich) after pretreatment with acetylacetone and Triton X [27,28]. Thin TiO_2 films, with active area of *ca.* 0.2 cm^2, were deposited on SnO_2: F (FTO) layered glass substrate (15 mm × 20 mm, 15 Ω/□, Pilkington Co. Ltd.) by doctor blade technique. Then, the films with *ca.* 10 μm thickness were sintered at 500 °C for 30 min in air [27]. After cooling down to 100 °C, the TiO_2 coated FTO glass substrates were dipped into the 0.3 mM solution