

Redox Reaction Mechanisms with Non-Triiodide Mediators in Dye-Sensitized Solar Cells by Redox Potential Calculations

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INTRODUCTION

Dye-sensitized solar cells (DSSCs) are devices for renewable energy sources that have been extensively investigated from both experimental and theoretical points of view. To achieve practical use of DSSCs, many studies have focused on enhancing the light-to-electron conversion efficiency (η), which is defined by the following equation:

$$\eta = J_{SC} \cdot V_{OC} \cdot ff / P_{in}$$

where J_{SC} is the short-circuit current density, V_{OC} is the open circuit photovoltage, ff is the fill factor and P_{in} is the power density of the incident light. A straightforward way to improve η is to increase the values of J_{SC} and V_{OC} . There have been many studies of developing new dyes to increase J_{SC} , because J_{SC} largely depends on the photon absorbance ability of the dyes. On the other hand, studies on improving V_{OC} are in the minority.

In this work, we revisit the redox reaction mechanism of the iodide mediators in DSSCs for improving V_{OC} s. We also examined cobalt complex mediators as references to obtain the Fermi level of titanium oxide. We take the experimental value of this redox potential into account and discuss the relation between V_{OC} and the redox potential of the mediators, and possible redox reaction mechanism of the iodide mediators.

METHOD

The thermodynamic cycle method was used to calculate the redox potentials of the elementary processes in acetonitrile solution. The B3LYP density functional in the Gaussian09 software package was used with the DGDZVP basis set. The quartet states were used for calculations of reduced cobalt complexes. The normal hydrogen electrode $E(H^+/H_2)$ was set to 4.44 V. We dealt with only the complexes and iodides atomically and used a polarized continuum model using the IEFPCM for all the solvent molecules, assuming that the first solvation shell of acetonitrile is not as anisotropic as that of water.

RESULTS

We first calculated the redox potentials of three cobalt complexes with respect to the normal hydrogen electrode (NHE) as reference. According to the experimentally reported Fermi energy of TiO_2 , -0.2 V vs NHE, the maximum V_{OC} s of cobalt complex mediators are estimated and are consistent with the observed V_{OC} s. It shows the validity of the position of the Fermi energy of TiO_2 . Therefore, we use this Fermi energy of TiO_2 to estimate the V_{OC} of DSSCs.

We next examined all the relevant redox reactions among the I , I_2 and I_3 species. The calculated redox potentials of these half-reactions with respect to NHE are quite reasonable. Our calculation results give useful insights into the redox reaction at the counter-electrode. A metal (e.g., Pt) is usually used as the counter-electrode, and the Fermi energy of Pt coincides with the redox potential of the mediator at the electrode, as shown above. Because the Fermi energy of TiO_2 is located near -0.2 V vs NHE, as shown in the cobalt calculations, and the typical V_{OC} for DSSCs using N719 dye with iodide mediators is around 0.72 V, the Fermi energy and actual electronic active redox mediator should lie at 0.52 V vs NHE. However, the redox potential of $I_3^- / 3I^-$ in acetonitrile solution is 0.3–0.35 V, which is inconsistent with the observations. The redox potential of the $I_2 / 2I^-$ reaction is more suitable to explain the typical V_{OC} for DSSCs using N719 dyes. We have also calculated the redox potentials using HSE06, PBE0 and BHandHLYP functionals and *ab initio* MP2 method for checking the validity of B3LYP results. The upper limit of the redox potential of I_3^- / I^- reaction is +0.39 V vs NHE, leading to 0.59 V of V_{OC} . This V_{OC} is still much lower than the experimental value of 0.72 V. This indicates that our conclusion of inconsistency between the I_3^- / I^- redox couple and the observed redox potential is robust among typical functionals used here although the calculated redox potentials depend on functionals and differ about 0.2 eV from each other.

CONCLUSION

We propose a reaction mechanism for the redox mediators in DSSCs based on redox potential calculations, which is in better agreement with experimental V_{OC} observations. The maximum V_{OC} s for the mediators calculated in this work show that the $I_2^{\bullet-} / 2I^-$ and $I_2 / I_2^{\bullet-}$ as well as the net $I_2 / 2I^-$ redox couples are responsible for the regeneration at the photoanode and the redox reaction at the cathode.

REFERENCE

JONO, R., SUMITA, M., TATEYAMA, Y. and YAMASHITA, K. *J.Phys.Chem.Lett.* submitted.