

Effect of Additives in the Electrolyte on the Quasi Fermi Level of TiO₂ Films in Dye-Sensitized Solar Cells

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Introduction

Dye-sensitized solar cells (DSCs) fabricated inexpensively from environmentally friendly materials are among the most promising photovoltaic devices.^{1,2} A typical DSC consists of a dye-adsorbed nanocrystalline TiO₂ electrode based on a transparent conducting oxide substrate, a platinum counter electrode, and an electrolyte solution containing an I₃⁻/I⁻ redox couple between the electrodes. Under light irradiation, excited electrons in the dye are injected into the conduction band of TiO₂, and transport to the transparent conducting substrate. The oxidized dye is reduced by the iodide of the I₃⁻/I⁻ redox couple, then the iodide is regenerated at the counter electrode by reduction of triiodide, the circuit being completed through the external load. The open-circuit voltage (V_{OC}) and short-circuit photocurrent (J_{SC}) are critical parameters determining the energy conversion efficiency of a DSC. In a DSC, V_{OC} is related to the QFL of TiO₂ at open circuit and J_{SC} is affected by the QFL of TiO₂ at short circuit. Therefore, it is necessary to distinguish the QFL at the two different conditions and find out the correlation between them. On the other hand, studies have shown that the QFL of the TiO₂ films is sensitive to the contacted electrolyte in DSCs.³ For example, 4-*tert*-Butylpyridine (TBP) can shift the QFL toward more negative potentials and Li⁺ in the electrolyte can give a positive shift of the QFL.^{4,5} To investigate additives effect on the QFL, we focus on study the correlation between the QFLs of TiO₂ film at open circuit and short circuit. We employed TBP as additive and two different cations Li⁺ and TBA⁺ in the electrolyte. A three-electrode DSC was employed to measure the QFL shifts affected by additives in the electrolyte.^{6,7}

Experimental

In the three-electrode DSC (Fig.1), the thickness of the nanoporous TiO₂ film was about 6 μm. The TiO₂ film was sensitized by 0.3 mM N719 dye solution. The electrolyte consisted of 0.05 M I₂, 0.1 M LiI or 0.1 M TBAI, and 0.6 M 1,2-dimethyl-3-propylimidazolium iodide in acetonitrile; and TBP was added to the electrolyte at a concentration of 0.1–0.5 M. The active area of each DSC was 0.5 cm × 0.5 cm. The J - V characteristics were measured under air mass (AM) 1.5 simulated solar illumination at 100 mW·cm⁻². The QFL of the electrolyte side of the TiO₂ film is monitored during J - V testing. All the QFLs were measured with respect to the redox potential of the electrolyte. The QFL of the electrolyte side of TiO₂ film is referred as E_{QFL} and the values of QFL at short circuit and open circuit are referred as $E_{QFL,SC}$ and $E_{QFL,OC}$, respectively.

Results and Discussion

The variations of the E_{QFL} values of the TiO₂ films in DSCs were strongly influenced by the type of cation in both the presence and the absence of TBP (Fig. 2). In the cell containing 0.1 M Li⁺, the $E_{QFL,SC}$ and $E_{QFL,OC}$ values were much lower than those in the cell containing 0.1 M TBA⁺ (the differences were 0.2 and 0.12 V, respectively). This result implies that Li⁺ ions shifted the QFL of the TiO₂ film to lower potential much more than did the less-adsorptive TBA⁺ ions and that the influences of the two kinds of cations differed under short- and

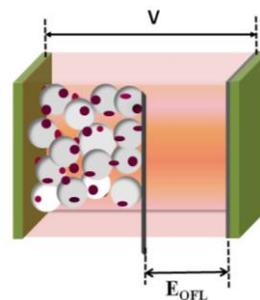


Figure 1. Schematic of the three-electrode dye-sensitized solar cell.

open-circuit conditions. For cells containing 0.1 M Li⁺, the $E_{QFL,SC}$ and $E_{QFL,OC}$ increases were almost the same based on two quite different initial values, which suggests that the adsorption of TBP was unaffected by the presence of Li⁺ ions on the surface of TiO₂ film. In the cell containing TBA⁺, $E_{QFL,SC}$ increased by 0.13 V after the addition of 0.3 M TBP, whereas $E_{QFL,OC}$ increased by only 0.08 V. This difference implies that TBA⁺ ions can adsorb on the surface of the TiO₂ film at open circuit, that the adsorbed TBA⁺ partially blocked the further adsorption of TBP, and that the blockage resulted in a lower increase in $E_{QFL,OC}$.

The concentration of TBP were varied from 0.1 M to 0.5 M in a fixed concentration of the cations to further investigate the correlation between the QFL shifts at open circuit and short circuit. In cells containing 0.1 M Li⁺, the values of corresponding $E_{QFL,OC}$ and $E_{QFL,SC}$ were different while the shifts in $E_{QFL,OC}$ and $E_{QFL,SC}$ of a same cell were almost same. The variation in the dependence of $E_{QFL,OC}$ on $E_{QFL,SC}$ with TBP concentration in cells containing 0.1 M Li⁺ has a linear relationship: $E_{QFL,OC} = 0.25 + 1.02 E_{QFL,SC}$, the slope was very close to 1, suggesting that the increases in $E_{QFL,SC}$ and $E_{QFL,OC}$ were same and that the QFL increases were the same at short circuit and open circuit. For the cells containing 0.1 M TBA⁺, the shifts in $E_{QFL,OC}$ were lower than those of the corresponding $E_{QFL,SC}$. There is also a linear relationship between the changes of $E_{QFL,OC}$ and $E_{QFL,SC}$: $E_{QFL,OC} = 0.38 + 0.62 E_{QFL,SC}$. The slope was 0.62, implying that the QFL increase was larger at short circuit than at open circuit, which in agreement with the relatively smaller increase of V_{OC} and larger decrease in J_{SC} . In this work, we found that the QFL of TiO₂ at short circuit and open circuit has different values and the shifts of $E_{QFL,OC}$ and $E_{QFL,SC}$ induced by additives may different.

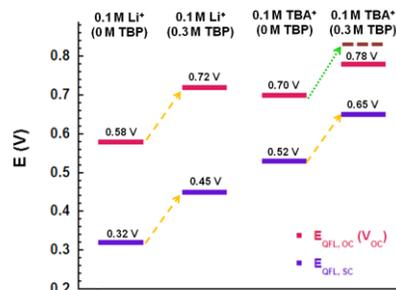


Figure 2. $E_{QFL,OC}$ and $E_{QFL,SC}$ values of cells containing Li⁺ and TBA⁺ in the absence of TBP and in the presence of 0.3 M TBP.

Conclusions

In summary, we investigated the correlation between the QFL shifts at open circuit and short circuit by directly measuring the effects of additives on the QFLs of TiO₂ films during *J-V* testing of DSCs. We found for the first time that the relationships between the TBP-induced QFL shifts at short circuit and open circuit were linear and that the slopes of the lines were influenced by the nature of cations in the electrolyte. Different QFL shifts at short circuit and open circuit were observed in the presence of TBA⁺. These quantitative results will provide valuable information for controlling the Fermi level of TiO₂ films for further optimization of the efficiency of DSCs.

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References

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