

An advanced model for determining charge recombination kinetic parameters in dye-sensitized solar cells

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ABSTRACT

Charge recombination between dye-sensitized TiO₂ electrodes and I₃⁻ in the electrolytes governs the performance of dye-sensitized solar cells. The present work features a theoretical model constructed to explore the discrepancy of the recombination kinetics in light and dark. This study yielded two modified equations describing recombination behaviors in light and dark. These two equations simulated the photocurrent–voltage characteristics of a cell under illumination and the open-circuit voltage decay behavior with illumination interrupted, rendering the recombination parameters (including the back reaction rate constant, k_{et} , and electron concentration in the conduction band). We found that while the value of k_{et} in light does not vary with changes in voltage, in the dark it decreases exponentially with voltage decay. These results are consistent with the recombination kinetics in dark being strongly dependent upon the trapping/detrapping process. This developed model was applied to cells with and without the presence of 4-tert-butylpyridine, which significantly improved their open-circuit voltage (from 0.49 to 0.69 V). This increase in the open-circuit voltage is ascribed to the TiO₂ conduction band edge's movement into negative potentials. This study developed a simple method for quantifying recombination parameters to explain the details of the back reaction suppression.

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1. Introduction

Dye-sensitized solar cells (DSSCs) based on porous nanocrystalline TiO₂ films have achieved a light-to-electric energy conversion efficiency of up to 10% (Barbé *et al.*, 1997; Nazeeruddin *et al.*, 1993; O'regan and Grätzel, 1991). The photo-electrochemical reactions of the cells mainly occur in a two-phase medium consisting of the porous TiO₂ matrix interpenetrated by an I⁻/I₃⁻ redox electrolyte. There is an increasing interest in the interfacial charge transfer kinetics of dye-sensitized nanocrystalline semiconductors (Duffy *et al.*, 2000; Fabregat-Santiago *et al.*, 2005; Huang *et al.*, 1997; Katoh *et al.*, 2004; Li and Teng, 2010; Schlichthörl *et al.*, 1997). Scientists agree that interfacial charge transfers govern the energy conversion efficiency of DSSCs (Fisher *et al.*, 2000; Hsiao *et al.*, 2010; Kopidakis *et al.*, 2003; Oekermann *et al.*, 2004; Schlichthörl *et al.*, 1999; Wu *et al.*, 2009). The present work aims to provide a kinetic model that gives a complete picture of charge transfer in DSSCs.

Fig. 1 shows the electron transfer process in a dye-sensitized TiO₂ film. The visible light is absorbed by a monolayer of adsorbed dye to form the photoexcited dye (D^{*}), from which electrons are

injected into the conduction band of TiO₂. The oxidized dye molecules (D⁺) are reduced by I⁻ ions to form the original dye molecules (D⁰). In general, the photo-induced electrons must diffuse through the interconnecting network of TiO₂ nanoparticles to produce photocurrent. However, during diffusion the electrons may be exhausted through two possible routes, leading to energy loss (Haque *et al.*, 2000; Montanari *et al.*, 2002). In one of the routes, the electrons recombine with the oxidized dye before the dye is regenerated by I⁻ ions. Energy loss due to this recombination route is negligible in a Ru-complexes dye-sensitized cell containing the standard I₃⁻/I⁻ redox couple as an electrolyte (Gragg *et al.*, 2001; Kopidakis *et al.*, 2003). The other route is the recombination of photo-induced electrons with the oxidized redox species of the electrolyte. Several studies have provided the rate kinetics and mechanism of this recombination type (Bisquert *et al.*, 2002, 2004; Motonari *et al.*, 2006). These studies explored electron recombination kinetics at open-circuit conditions. However, the difference between the recombination kinetics at open-circuit and connected circuit conditions requires further exploration (Wang *et al.*, 2006).

This work aims to study recombination kinetics in a Ru-complexes dye-coated nanocrystalline TiO₂ electrode surrounded by the I⁻/I₃⁻ redox couple electrolyte. We developed a technique to quantify important parameters in the recombination kinetics based on unsophisticated DSSC measurements. This technique yields a complete kinetic model by incorporating the parameters

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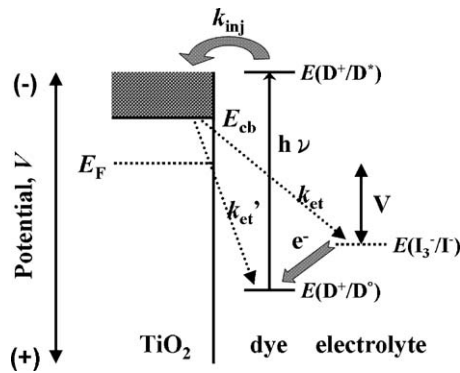


Fig. 1. Schematic representation of the electron transfer processes in a dye-sensitized solar cell. A potential is determined by the difference between E_F and $E(I^-/I_3^-)$. The redox energy of the ground state $E(D^+/D)$ rises to the excited state $E(D^*/D^*)$ by illumination. Optical excitation of the sensitizer dye causes injections of electrons into semiconductor conduction band (E_{cb}), which is described by k_{inj} ; k_{et} and k_{et}' are respective rate constants for back electron transfer to oxidized redox species and oxidized dye molecules at the semiconductor/electrolyte interface. Usually, the recombination is dominated by interaction between conduction band electrons and oxidized redox species in the electrolyte.

obtained from open-circuit pseudo-equilibration in the light with those obtained from open-circuit voltage decay measurements in the dark. The pyridine compound 4-tert-butylpyridine (TBP) provides suppression of back electron transfer in TiO_2 , enabling examination of the derived kinetic model.

2. Experimental

An anatase TiO_2 colloid derived from a titanate was used to fabricate the mesoporous film. To obtain the titanate, 3 g of a commercially-available TiO_2 powder (P25, Degussa AG) was hydrothermally treated with 10 mL of 10 N NaOH in an autoclave at 130 °C for 20 h, followed by repeated washing with 0.1 N HNO_3 to reach a pH value of ca. 1.5. The anatase TiO_2 colloid was obtained by autoclaving the titanate at 240 °C for 12 h (Chen *et al.*, 2009; Hsiao *et al.*, 2007; Lee *et al.*, 2009; Tsai and Teng, 2004, 2006). The solution of the colloid was concentrated to a TiO_2 concentration of 14 wt% via evaporation under reduced pressure, and then mixed with polyethylene glycol (PEG; Fluka, 20,000 in molecular weight) to form a viscous TiO_2 dispersion at a PEG/ TiO_2 weight ratio of 0.4 (Liau *et al.*, 2008). The viscous dispersion was coated on a conducting glass substrate (F-doped SnO_2 overlayer TCO glass; TEC8, Hartford Glass Co.). The area of the film was 0.5 cm × 0.5 cm. The TiO_2 -coated substrate was calcined at 450 °C for 30 min to form a mesoporous electrode. The film thickness was measured with a profilometer (Alpha-step 200, Tencor instruments).

A ruthenium complex dye, N3 (cis-di(thiocyanate)bis(2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II); ruthenium 535, Solaronix), was used as the sensitizer for DSSCs. The dye-sensitized TiO_2 electrode and a Pt-coated conducting glass were assembled to form a cell by sandwiching a redox (I^-/I_3^-) electrolyte solution, which was composed of 0.1 M LiI, 0.05 M I_2 , 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPII), and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile. The addition of TBP in the electrolyte is optional. In the cell performance test, an Oriel 300-W Xe lamp served as a light source in conjunction with an IR filter (Oriel 59044). The AM 1.5 Globe filter (Oriel 81094) was placed in the light beam to simulate the AM 1.5-type solar emission with the intensity ranging between 60 and 220 $mW\ cm^{-2}$.

For the open-circuit photovoltage (V_{oc}) decay measurements, the cell was illuminated to a steady voltage at a constant intensity before the illumination was interrupted. The variation of V_{oc} with time after the illumination interruption was recorded at an interval

of 10 ms. We have omitted the final region of decay at voltages <50 mV, in which the data were poorly resolved (Quintana *et al.*, 2007; Zaban *et al.*, 2003).

3. Theoretical basis

3.1. Voltage scan under illumination

A potential difference V is defined as difference between the quasi-Fermi level of electrons in TiO_2 in the light (E_F) and the Fermi level in the dark (E_F^0) (Frank *et al.*, 2004; Huang *et al.*, 1997):

$$V = E_F - E_F^0 \quad (1)$$

In the dark, the electrochemical potential of the electrons in the TiO_2 is the same as that in the electrolyte, i.e. E_F^0 . Illumination promotes the electrochemical potential of the electrons in the TiO_2 because the number of the electrons in the TiO_2 increases through electron injection from the photoexcited dye. At the same time, the electrochemical potential in the electrolyte is still situated at the same value E_F^0 because of the high concentration of the redox species (I^-/I_3^- here) (Frank *et al.*, 2004). Hence, photovoltage originates from an elevated quasi-Fermi level in the TiO_2 with regard to the electrolyte redox level. The electron population in TiO_2 is exponentially related to the photovoltage, which is demonstrated by the equation (Huang *et al.*, 1997):

$$n = n_0 \exp\left(\frac{qV_{ph}}{kT}\right) \quad (2)$$

where q is the electronic charge (1.602×10^{-19} C), k is the Boltzmann constant (1.38×10^{-23} J/K), and T is the absolute temperature (298 K here), and n and n_0 are the electron concentrations (in units of cm^{-3}) in the conduction band of the TiO_2 in the light and dark, respectively.

As stated above, the degree of electron recombination with the oxidized electrolyte governs the performance of DSSCs. The recombination current density (J_r) can be obtained by subtracting photocurrent density (J_{ph}) from the current density of the electron injection from the photoexcited dye (J_{inj}). The recombination rate depends on the rate constant for back electron transfer k_{et} , the concentration of the oxidized half of the redox couple C_{ox} (in unit of cm^{-3}), and the difference between the electron concentrations in the conduction band of TiO_2 in the light and dark (Huang *et al.*, 1997; Schlichthörl *et al.*, 1997) i.e.:

$$J_r = \frac{q}{A} k_{et} C_{ox}^m (n^{u\alpha} - n_0^{u\alpha}) \quad (3)$$

where m is the reaction order with respect to the oxidized species, u is the order with respect to electron concentration, α is the electron transfer coefficient, and A is the cross-area of the TiO_2 films (Huang *et al.*, 1997).

At open-circuit, V is equal to V_{oc} , and J_r is equal to J_{inj} ($= q\sigma I_o$, where σ is the ratio of absorbed photon flux to light intensity, I_o). For the general case of $\sigma I_o \gg n_0^{u\alpha} k_{et} C_{ox}^m$, combining Eqs. (2) and (3) gives the relationship between V_{oc} and I_o , i.e.:

$$V_{oc} = \frac{kT}{qu\alpha} \ln\left(\frac{\sigma I_o}{n_0^{u\alpha} k_{et} C_{ox}^m}\right) \quad (4)$$

Eq. (4) shows that we can obtain the value of $u\alpha$ from the linear relationship of V_{oc} vs. $\ln I_o$ at a constant C_{ox} . Alternatively, the linear relationship of V_{oc} vs. $\ln C_{ox}$, gives the value of m at a constant light intensity.

With the circuit connected, combining Eqs. (2) and (3) gives the relationship between J_r and V_{ph} under illumination, where V_{ph} is

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