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Non-linear Electron Transport Kinetics in Nanocrystalline TiO₂-Based Solar Cells

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ABSTRACT

An analytical model describing electron transport in dye-sensitized nanocrystalline TiO₂ solar cells is shown to account for the non-linear dependence of the electron transport rate on the electron concentration. Equations relating the influence of an exponential distribution of surface states to electron transport are derived and verified by intensity-modulated photocurrent spectroscopy measurements. A slope of 69 meV is inferred for the surface-state distribution curve.

1. Introduction

Injected electrons from optically excited dye can either traverse the TiO₂ particle network and be collected at the transparent conducting glass back-contact or can recombine with redox species (e.g., I₃⁻) or dye molecules at the particle/electrolyte interface. Because the collection of electrons competes with recombination, slow electron transport (with respect to recombination) leads to a low charge-collection efficiency, and hence, to a low conversion efficiency [1,2].

Recently, we introduced a statistical model relating the time constants for recombination and charge collection to the charge-collection efficiency (η_{cc}) and the incident photocurrent conversion efficiency (IPCE) over a wide range of applied biases [2]. Electrical impedance spectroscopy and intensity-modulated photocurrent spectroscopy (IMPS) were used to measure the time constants for the recombination and collection of photoinjected electrons. As the applied bias is varied from

short-circuit to open-circuit conditions at one-sun illumination, recombination becomes faster, the collection of electrons becomes slower, and the IPCE strongly decreases. The drop-off of IPCE was shown to correlate with the decline of the charge-collection efficiency as calculated from the model. Although the strength of the statistical model is its predictive value, it does not provide detailed information on the mechanism of charge transport.

In this paper, we introduce an analytical model [3] to understand quantitatively the mechanism of charge transport. It is assumed that electrons undergo multiple trapping-detrapping events, involving an exponential distribution of surface states, during their transit through the film. The predictions of this model are compared with experimental results obtained by IMPS.

2. Results and discussion

The conduction-band electron concentration profile $n_{cb}(x)$ can be calculated by solving the continuity equation:

$$\frac{dn_{cb}(x)}{dt} = \alpha\eta_{inj}I(x) + \frac{1}{q} \frac{dJ_n(x)}{dx} - U_i(x) + U_e(x) \quad (1)$$

The concentration of electrons in surface states, however, depends on the energy distribution of traps. A single exponential describes the energy distribution of the density of surface states ($N_{SS}(E) = N_{SS0} e^{\frac{E-E_{E0}}{m_c}}$) in nanocrystalline TiO₂ films [4]. From this equation, one can calculate the concentration profile for trapped electrons $n_t(x)$:

$$n_t(x) = m_c N_{SS0} \left[e^{\frac{E_F(x) - E_{F0}}{m_c}} - 1 \right] = m_c N_{SS0} \left[\left(\frac{n_{cb}(x)}{n_{cb}(0)} \right)^{\frac{kT}{m_c}} - 1 \right] \quad (2)$$

Because the density of trapped electrons is much larger than that of free electrons [1], the electron concentration $n(x) = n_{cb}(x) + n_t(x)$ in the film is essentially equal to $n_t(x)$ (Eq 2). Thus, $n_{cb}(x)$ is related to $n(x)$ by the expression $n_{cb}(x) \propto n(x)^{m_c/kT}$. Validation of the power-law dependence of n_{cb} on n has been obtained by IMPS measurements [1].

The total number of electrons in the film Q can be obtained by integrating Eq. 2 with respect to x :

$$Q = m_c N_{SS0} n_{cb}(0)^{\frac{m_c}{kT}} \left(\frac{\eta_{\text{inj}} I(0)}{\alpha D_n} \right)^{\frac{kT}{m_c}} \int_0^d \left[1 - \alpha x e^{-\alpha d} - e^{-\alpha x} \right]^{\frac{kT}{m_c}} dx \quad (3)$$

Q is, therefore, related to the incident light intensity by the relation $Q \propto I(0)^{kT/m_c}$. Alternatively, because the short-circuit current density J_{sc} depends linearly on the light intensity, one can obtain the expression:

$$J_{sc} \propto Q^{\frac{m_c}{kT}} \quad (4)$$

Figure 1 shows the relationship between J_{sc} and Q , measured by IMPS, for a typical dye-sensitized nanocrystalline TiO₂ solar cell.

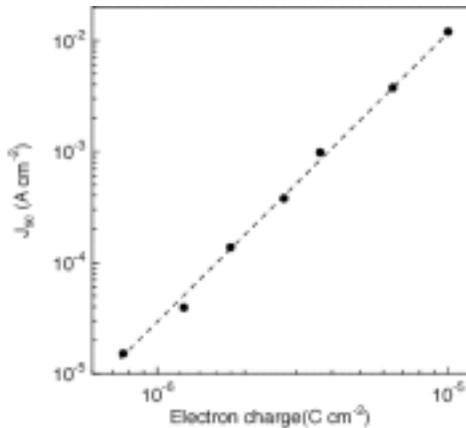


Fig.1 The relation between the short-circuit photocurrent density and electronic charge for a typical dye-sensitized cell. The dashed line is a fit to Equation (4).

Equation (4) describes well the experimental data in Figure 1. From the fit of the data, the slope of the surface-

state distribution curve is obtained as $m_c = 69$ meV, which is in good agreement with values determined from time-of-flight [5] and electrical impedance spectroscopy [2] in the light intensity range (<1-sun) used in the present study.

3. Conclusions

Expressions that relate an exponential distribution of surface states to electron transport are derived and verified by intensity-modulated photocurrent spectroscopy measurements. A slope of 69 meV is inferred for the surface-state distribution curve.

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