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Characterization of Electron Trapping in Dye-Sensitized Solar Cells by Near-IR Transmittance Measurements

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In situ near-IR transmittance measurements have been used to characterize the density of trapped electrons in dye-sensitized solar cells (DSCs). Measurements have been made under a range experimental conditions including during open-circuit photovoltage decay and during recording of the IV characteristic. The optical cross section of electrons at 940 nm was determined by relating the IR absorbance to the density of trapped electrons measured by charge extraction. The value, $\sigma_n = 5.4 \times 10^{-18} \text{ cm}^2$, was used to compare the trapped electron densities in illuminated DSCs at open and short circuit in order to quantify the difference in the quasi Fermi level, $\Delta_n E_F$ under the two conditions. It was found that $\Delta_n E_F$ for the cells studied was 250 meV over wide range of illumination intensities. IR transmittance measurements have also been used to quantify shifts in conduction band energy associated with dye adsorption.

Introduction

Dye-sensitized nanocrystalline solar cells^{1–4} (DSCs) continue to attract attention as potential low-cost alternatives to inorganic photovoltaic devices. The light-harvesting element in the DSC is a sensitizer dye such as *cis*-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) bis(tetrabutylammonium) (N719) that is adsorbed on the high internal surface of a thin mesoporous titania film spread on a conducting glass substrate. Photoexcitation of the dye results in electron injection into the conduction band of the TiO₂ film, and electrons are then transported to the conducting substrate. The dye is regenerated from its oxidized state by a I^-/I_3^- redox electrolyte that permeates the mesoporous film. The I_3^- ions formed during the regeneration step diffuse to a platinized conducting glass cathode, which forms the second half of the thin sandwich cell. The passage of electrons through the external circuit to the cathode completes the cycle.

It has become clear that the large majority of electrons in the DSC are trapped^{5–9} and that the current is carried by a much lower density of mobile electrons in the conduction band. The density of trapped electrons can be measured as a function of trap occupancy by electrical techniques such as impedance¹⁰ and charge extraction.^{8,11} The latter technique involves shorting the DSC and integrating the resulting current spike in order to obtain the charge passed as electrons exit the cell. Here we show that in situ measurements based on the near-infrared absorbance of electrons in the mesoporous oxide film provide a simple and reliable way to characterize the trapped electron density under a variety of experimental conditions. Steady-state IR transmittance measurements are well established as a way of following electron accumulation in mesoporous oxides.^{12–15} Transient IR absorption measurements on colloidal TiO₂ and on DSCs have been widely used to follow electron injection and trapping on a subpicosecond time scale^{16,17} as well as on longer time scales,¹⁸ and frequency-resolved IR measurements were developed in this laboratory some time ago as a tool for following the dynamic behavior of electrons in the DSC.¹⁹ The present

study used near-IR transmittance to follow changes in the density of trapped electrons under different conditions. Comparison of electron density data obtained by IR transmittance and by charge extraction indicates that the IR method may be more reliable under conditions where the transit of electrons to the anode in the charge extraction measurements is very slow.

Improvements in DSC performance associated with changes in electrolyte composition or electrode morphology are frequently attributed to enhanced diffusion of electrons or to slower back reaction of electrons with a redox mediator. However, the conclusions drawn from transient photocurrent or photovoltage measurements may not be valid unless care is taken to establish conditions where comparison of DSC fabricated with different components is possible. Measurements carried out at the same trap occupancy seem to be the most reliable way of accounting for shifts in the conduction band brought about by the use of additives and different electrolytes.² The IR method is a convenient way of establishing trap occupancy and deserves more widespread use. This paper explores several applications of the method for characterization of DSCs.

Theory

The performance of a DSC depends on a range of processes including light harvesting, electron injection, electron transport, and loss of electrons during transit to the anode by back reaction with I_3^- . It has become clear that both electron transport and back reaction in the DSC are strongly influenced by electron trapping/detrapping. The density of the electron traps appears to fall exponentially with energy below the conduction band, fitting a distribution of the form^{8,20–23}

$$g(E_t) = \frac{N_{t0}}{k_B T_0} \exp\left(-\frac{E_c - E_t}{k_B T_0}\right) \quad (1)$$

Here N_{t0} is the total trap density, $E_c - E_t$ is the trap depth below the conduction band, and T_0 is a characteristic temperature that is usually in the range 600–1200 K.

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The density of trapped electrons is determined by the integrals

$$\Delta n_t = \int_{-\infty}^{\infty} f_{FD}^{\text{light}}(E)g(E) dE - \int_{-\infty}^{\infty} f_{FD}^{\text{dark}}(E)g(E) dE \quad (2)$$

where f_{FD}^{light} and f_{FD}^{dark} are the Fermi–Dirac functions

$$f_{FD}^{\text{dark}} = \frac{1}{1 + \exp\left[\frac{E_c - E_{F,\text{redox}}}{k_B T}\right]} \quad \text{and} \quad f_{FD}^{\text{light}} = \frac{1}{1 + \exp\left[\frac{E_c - n E_F}{k_B T}\right]} \quad (3)$$

$E_{F,\text{redox}}$ is the Fermi level of the I_3^-/I^- couple. As an approximation (the “zero Kelvin approximation”), the two Fermi–Dirac functions can be replaced by step functions at $E_{F,\text{redox}}$ and $n E_F$, respectively, to give the simpler expression

$$\Delta n_t \approx \int_{E_{F,\text{redox}}}^{E_{F,\text{redox}} + q U_{\text{photo}}} g(E) dE \quad (4)$$

The density of trapped electrons under steady-state conditions can be predicted theoretically using the following approach. The starting point is the continuity equation, which describes the injection, transport, and back reaction of conduction band electrons in the DSC. For illumination from the substrate side

$$\frac{\partial n_c}{\partial t} = \alpha I_0 \exp(-\alpha x) + D_0 \frac{\partial^2 n_c}{\partial x^2} - \frac{(n_c - n_{\text{eq}})}{\tau_0} = 0 \quad (5)$$

Here α is the absorption coefficient (determined by the dye), D_0 is the diffusion coefficient of conduction band electrons, and τ_0 is the lifetime of conduction band electrons (determined by kinetics of electron transfer to I_3^-). Solution of the continuity equation with appropriate boundary conditions gives the profiles of conduction band electrons through the device. The quasi-Fermi level (QFL) relative to the conduction band can then be obtained from the relationship

$$n_c = N_c \exp\left(-\frac{E_c - n E_F}{k_B T}\right) \quad (6)$$

where N_c is the conduction band density of states.

Once the QFL profile is known, the local total trapped electron density can be obtained from eq 3 or eq 4. Figure 1 illustrates the profiles of conduction band and trapped electrons calculated in this way for short-circuit conditions.

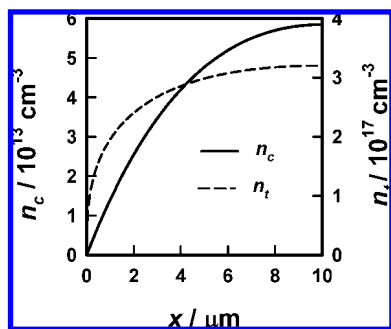


Figure 1. Profiles of conduction band and trapped electrons in a DSC calculated for short-circuit conditions from eq 5. Integration of the n_t profile across the DSC gives the trapped electron density determined by charge extraction and IR transmittance. Illumination from substrate side. $D_0 = 0.5 \text{ cm}^2 \text{ s}^{-1}$, $\tau_0 = 10^{-4} \text{ s}$, $\alpha = 1500 \text{ cm}^{-1}$, $I_0 = 10^{17} \text{ cm}^{-2} \text{ s}^{-1}$, $N_c = 10^{21} \text{ cm}^{-3}$, $N_{t,0} = 10^{20} \text{ cm}^{-3}$, $T_0 = 850 \text{ K}$.

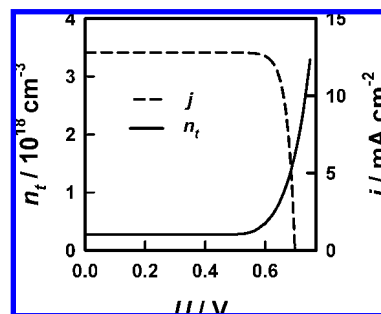


Figure 2. Changes in the concentration of trapped electrons predicted from the solution of the steady-state continuity equation. Parameter values are the same as those used to calculate the plots shown in Figure 1.

The concentration of trapped electrons in a DSC will increase as the forward bias voltage is increased. Figure 2 illustrates the results of a calculation carried out using typical values of the trap density and characteristic temperature.

For small changes in transmittance, the normalized change in IR transmittance, $\Delta T/T$, associated with the increase in concentration of excess trapped electrons in the films is given by

$$\frac{\Delta T}{T} = -\Delta n_t \sigma_n(\lambda) d \quad (7)$$

where $\sigma_n(\lambda)$ is the optical cross section of electrons at the IR wavelength used and d is the thickness of the mesoporous film. It is assumed in eq 7 that $\sigma_n(\lambda)$ is independent of the trap depth from which electrons are excited to the conduction band. Since the IR photon energy is 1.3 eV, this seems a reasonable assumption, but it was tested by measuring the dependence of the transmittance on trapped electron density using the charge extraction method. Absorption by conduction band electrons is neglected in the analysis since their concentration is much lower (cf. Figure 1).

The dynamic exchange of electrons between traps and the conduction band effectively “buffers” the transient behavior of conduction band electrons, increasing the response time to external perturbation of the system. It has been shown by Bisquert and co-workers²³ that the relaxation times associated with electron transfer to I_3^- and with electron transport to the anode can be defined in terms of effective values of the electron lifetime τ_n and electron diffusion coefficient D_n , which are related to the corresponding values τ_0 and D_0 in the absence of trapping/detrapping effects by the expressions

$$\tau_n = \frac{\partial n_t}{\partial n_c} \tau_0 \quad (8)$$

$$D_n = \frac{\partial n_c}{\partial n_t} D_0 \quad (9)$$

where n_t and n_c are number of trapped electrons and free electrons, respectively. The $\partial n_t / \partial n_c$ term and its inverse can be obtained from eqs 1 and 6. If $N_{t,0}$ and N_c are similar in magnitude and T_0 is greater than ambient temperature, $\partial n_t / \partial n_c$ decreases as the QFL moves toward the conduction and $\partial n_c / \partial n_t$ increases. This explains why the effective electron lifetime decreases with light intensity, whereas the effective diffusion coefficient increases. It can also be seen that the electron diffusion length, defined as

$$L_n = (D_0 \tau_0)^{1/2} = (D_n \tau_n)^{1/2} \quad (10)$$

is constant (note that D_n and τ_n must be measured at the same value of the QFL). L_n is an important figure of merit for a

DSC—for efficient electron collection it needs to be substantially greater than the thickness of the mesoporous layer. In the present study, the IR transmittance method was used to relate the trap occupancies and hence the nE_F values under open-circuit and short-circuit conditions.

Experimental Section

A thin blocking layer of titanium dioxide was deposited onto cleaned fluorine-doped tin oxide conducting glass (TEC 15, Pilkington, UK) from 0.2 M titanium diisopropoxide bis(acetylacetonate) isopropanol solution (Aldrich) by spray pyrolysis at 400 °C. Then a layer of colloidal titanium dioxide paste (Solaronix T or Dyesol, DSL-18NR-T) was deposited on the top of the compact layer by doctor-blading. The film was dried at 100 °C for 15 min and then sintered at 500 °C for 30 min to form a mesoporous structure. The thicknesses of the films (11–13 μm) were determined by profilometry. The freshly annealed TiO_2 film was immersed into a dye bath of N-719 (Dyesol) with the concentration of 2.5×10^{-4} M in acetonitrile/*tert*-butanol (1:1, v/v) for 16 h before use and then washed with acetonitrile (HPLC grade) to remove excess dye. A thermally platinized cathode was sealed onto the anode using Surlyn (25 μm , Solaronix). Two electrolytes were used. Electrolyte “Li” was 0.5 M LiI + 0.05 M I_2 + 0.5 M *tert*-butylpyridine in methoxypropionitrile, and it was used for cells fabricated with Solaronix T paste. Electrolyte “Na” was 0.6 M 1-propyl-3-methylimidazolium iodide + 0.2 M NaI + 0.06 M I_2 + 0.1 M guanidinium thiocyanate + 0.5 M *tert*-butylpyridine in 3-methoxypropionitrile. It was used in cells made with Dyesol DSL paste. The electrolytes were introduced into the space between the two electrodes through a hole drilled in the counter electrode. The hole was then sealed with a microscope slip using Surlyn. The contact areas of the cell were coated with silver paint to reduce the series resistance. Dye-free cells were fabricated by the same procedures using Solaronix T paste.

A high-intensity light-emitting diode (LED, 530 nm) was employed to illuminate the DSCs. The intensity and illumination period of the LED were controlled by a waveform generator PPR1 via an LED driver. A Kodenshi GaAlAs IR LED (OPE5594, 940 nm) provided the probing IR illumination, and a Si photodiode detector (Sharp, PD481PI) was used to monitor the transmission variation of the cell. The IR LED was modulated at 30 kHz and the signal from the photodiode was detected by a lock-in amplifier (SR850, Stanford Research Systems) via a fast current amplifier. A GaAs filter was employed to eliminate stray light from the green LED. The output signal from the lock-in amplifier was fed to an auxiliary input of an Autolab PG12 potentiostat which simultaneously recorded the voltage or current from the DSC. The IR transmission of the DSC was measured during open-circuit voltage decay and along with the current–voltage characteristic at a scan rate of 1 mV s^{-1} . For infrared transmittance measurements in the dark, an external bias in the range of 0–0.8 V was applied to the cell by the Autolab Potentiostat.

The setup for dark charge extraction measurements during photovoltage decay has been described elsewhere.^{8,11} In the dark charge extraction technique,²⁴ the Fermi level of the DSC was first set to a predetermined level by applying an external voltage via the potentiostat. Then the voltage was switched to zero and the current pulse due to extraction of the accumulated electrons was integrated for 300 s.

Results and Discussion

The IR method can be applied to monitor changes in trapped electron density during a range of different perturbations of the

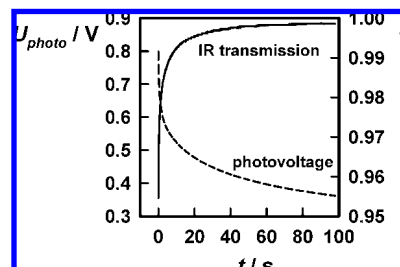


Figure 3. Variation of the IR transmission measured during the open-circuit voltage decay of a dye-sensitized solar cell (“Li” electrolyte).

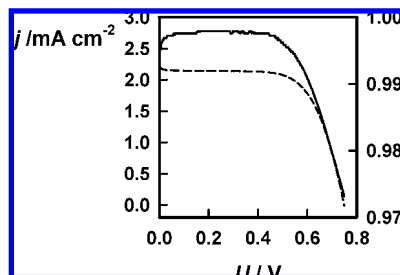


Figure 4. Variation of IR transmittance (940 nm) of a DSC recorded during a slow scan of the I – V characteristic (broken line) under illumination at 530 nm. “Li” electrolyte. Compare with Figure 2.

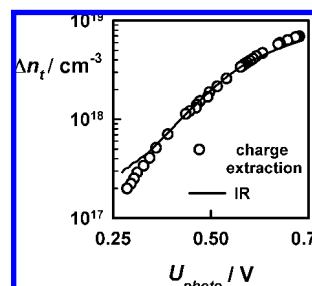


Figure 5. Plot of extracted charge density as a function of photovoltage. The IR transmittance data were also used to calculate the trapped charge density, and the optical cross section $\sigma_n(\lambda)$ was chosen to give the best fit. The fit shown gives $\sigma_n(940 \text{ nm}) = 5.4 \times 10^{-18} \text{ cm}^2$.

DSC. For example, Figure 3 shows the change in IR transmittance measured during open-circuit voltage decay of the DSC following a period of illumination. The transmission has been normalized to the transmission measured when the DSC was kept in dark for an hour to allow all excess electrons to exit the mesoporous film. It can be seen that the transmission increases as electrons are removed from the oxide film by transfer to I_3^- . The simultaneous recording of the photovoltage and the IR transmission allows the trapped electron density to be derived as a function of quasi Fermi level.

A second example of the application of the IR method is shown in Figure 4. Here the increase in electron concentration in an illuminated DSC under forward bias was detected optically as the voltage of the DSC was scanned slowly from short circuit to open circuit. It can be seen that the decrease in transmittance follows closely the behavior predicted from the solution of the steady-state continuity equation and shown in Figure 2. A similar measurement can be performed in the dark (data not shown).

Quantitative interpretation of IR transmittance data requires the value of optical absorption cross section $\sigma_n(\lambda)$ to be determined. This was done by using the dark extraction technique to measure the trapped electronic charge as a function of bias voltage. The semilogarithmic plot in Figure 5 shows the electron density determined from the extracted charge. The

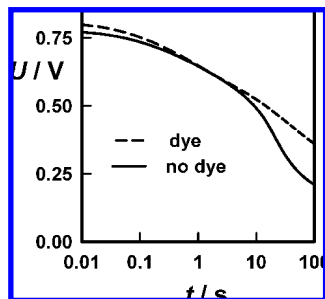


Figure 6. Open-circuit voltage decay plots for a DSC (“Li” electrolyte) compared with the decay measured for an identical cell without N719 dye.

corresponding charge density values obtained from the IR transmittance data were fitted to the extracted charge by variation of the optical cross section of electrons. The best fit between the charge and transmittance measurement gave $\sigma_n = 5.4 \times 10^{-18} \text{ cm}^2$ at 940 nm, which is consistent with previously reported values for similar wavelengths.^{19,25} The good overlap between the two data sets over most of the voltage range indicates that the assumption that $\sigma_n(\lambda)$ is independent of trap depth is valid. The deviation between the two plots at low voltages can be attributed to the fact that the charge extraction technique does not measure all of the trapped electrons at low photovoltages since the maximum integration time is limited to 300 s by drift. As shown elsewhere,⁸ the transit time for electrons to reach the anode becomes prohibitively long at low photovoltages, and below 0.3 V, not all trapped electrons will be extracted.

Once σ_n has been obtained, it is possible to use the IR transmittance directly to obtain values of the trapped charge density. An example of the application of this approach is a comparison of the behavior of dyed and undyed mesoporous titania films. The rate of open-circuit decay of a DSC provides a useful measure of the rate of the back reaction of electrons with I_3^- in solution. In principle the adsorbed N719 dye could inhibit or promote electron transfer, or it may have little direct influence. However, the dye may indirectly influence interfacial electron transfer by affecting the conduction band energy of the TiO_2 . In order to measure the open-circuit decay of a cell in which the TiO_2 layer is free of dye, it is necessary to use a potentiostat to poise the cell voltage at a suitable initial value. The cell is then switched to open circuit to measure the voltage decay. Figure 6 contrasts the decay measured in this way with the photovoltage decay of an identical cell in which the TiO_2 layer had been dyed with N719. It can be seen that the early part of the decay is similar in both cases, although the voltage of the dye-free cell falls more rapidly at longer times, probably due to imperfections in the blocking layer. The results suggest the dye has little influence of the back transfer of electrons from the TiO_2 .

The IR transmittance of the cells with and without dye was recorded during the voltage decay transients, and the results were analyzed to obtain the trapped electron density as a function of voltage. The results presented in Figure 7 show that, although the trap distribution seems not to be affected to any large extent by the presence of the dye, the trapped electron density at any given voltage is higher for the dyed film. The two charge plots are shifted relative to each other by around 60–70 mV, and this can be interpreted as evidence that the conduction band of the TiO_2 is lower in the presence of the dye. This may be a consequence of the fact that adsorption of the N719 dye releases two protons per adsorbed molecule. The

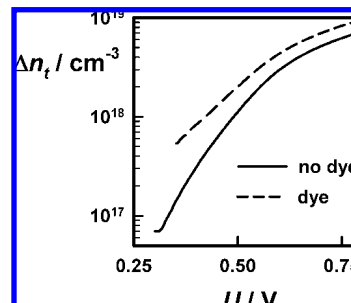


Figure 7. Comparison of the trapped electron density as a function of voltage corresponding to the photovoltage decay plots in Figure 6. The shift between the two plots is attributed to a lowering of the conduction band of the TiO_2 due to adsorption of protons released from N719.

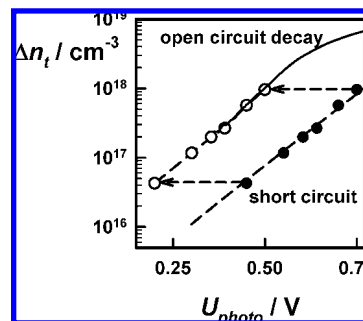


Figure 8. Electron density measured by IR transmittance during open-circuit decay (line) and under short-circuit conditions (filled circles). DSC with “Li” electrolyte. Note that the short circuit data points are plotted against the photovoltage measured for the same intensity values. Displacement of these data points by $\Delta_n E_F = 250 \text{ meV}$ brings them into coincidence with the plot obtained during open-circuit voltage decay.

resulting protonation of the TiO_2 surface will change the surface dipole potential, moving the conduction band energy down relative to the redox Fermi level.

In order to interpret the values of τ_n and D_n determined by techniques such as intensity modulated photovoltage and photocurrent spectroscopy (IMPS and IMPS), it is important to know the relative positions of the quasi Fermi level under open-circuit and short-circuit conditions. This issue has been addressed in a number of ways, including using an addition probe electrode to sense the quasi Fermi level,^{26–28} comparison of charge extracted at short circuit and open circuit²⁴ and measuring the so-called “short-circuit voltage”, V_{sc} .²⁹ In the present study, the IR transmittance was measured during the photovoltage decay and then a series of open-circuit and short-circuit experiments was performed over a wide range of illumination intensities. In each case the photovoltage at open circuit was measured followed by an IR transmission measurement of the trapped electron density under short-circuit conditions. In order to allow comparison with the Δn_t plot derived from the IR transmittance measured during the photovoltage decay, the Δn_t data for the short-circuit measurements have been plotted in Figure 8 as a function of the open-circuit photovoltage. It can be seen that the short-circuit data points lie to the right of the open-circuit plot, which is expected since modeling shows that the QFL under short-circuit conditions should be lower than under open-circuit conditions. Horizontal translation of the short-circuit data by 250 mV to take this into account brings the two plots into coincidence, indicating that the difference in QFL between open and short circuit is $\Delta_n E_F = 250 \text{ meV}$. This is in excellent agreement with values derived by other methods.^{26,30} Details on the derivation of the diffusion length from IMPS

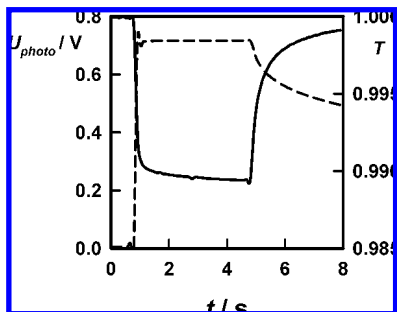


Figure 9. Response of IR transmittance and photovoltage of dye-sensitized solar cell to a square wave illumination pulse (DSC with “Na” electrolyte). The light is switched on after ~ 1 s and off after 5 s.

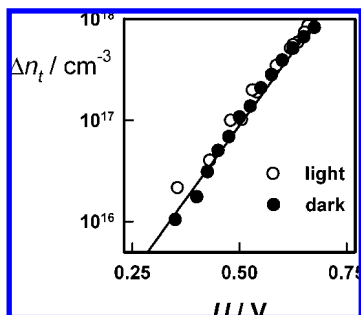


Figure 10. Variation of electron density in a DSC with external potential (DSC with “Na” electrolyte). The QFL was varied either using illumination at open circuit or by controlling the external voltage in the dark. The line shows the fit to eq 3. $N_{t,0} = 7 \times 10^{19} \text{ cm}^{-3}$, $T_0 = 860 \text{ K}$, $E_c - E_{F,\text{redox}} = 1.0 \text{ eV}$.

and IMVS taking this shift into account have been presented recently elsewhere.^{24,30}

One of the problems with recording the IR transmittance during the open-circuit photovoltage decay of a DSC is that cells with blocking layers show exceptionally slow decays. This can lead to drift problems in the IR transmittance measurements. A more convenient way of obtaining Δn_t as a function of photovoltage is illustrated in Figure 9. Here, a square light pulse is used to generate a photovoltage, and the change in IR transmittance is measured simultaneously. By varying the light intensity, the Δn_t vs photovoltage relationship can be explored over a wide range. If necessary, a number of transients can be averaged to improve the signal noise ratio and to minimize drift effects.

An alternative approach is to record the change in IR transmittance for a DSC in the dark as a function of forward bias voltage. In this case, a square voltage pulse is used starting from zero. Figure 10 compares plots of Δn_t vs potential obtained by illumination and by external voltage control. It can be seen that the two methods give consistent results, and the fit shown gives $N_{t,0} = 7 \times 10^{19} \text{ cm}^{-3}$ and $T_0 = 860 \text{ K}$.

The Δn_t values shown in Figure 10 for the “Na” electrolyte are substantially lower than those shown in Figure 5 for the “Li” electrolyte. This indicates that the conduction band of the TiO_2 is higher in the “Na” electrolyte. This is consistent with the generally accepted view that adsorption of Li^+ ions lowers the conduction band of TiO_2 in the DSC.

Conclusions

The use of infrared transmission to characterize dye-sensitized solar cells has been explored. It has shown that the trapped electron density in DSCs can be obtained conveniently by light-induced IR transmittance or by voltage-induced IR transmittance in dark. The optical absorption cross section of electrons $\sigma_n(940 \text{ nm})$ in the DSC was obtained by comparing data obtained by the charge extraction technique and by IR transmittance. The IR method is a useful as a diagnostic method to relate the effects of electrolyte composition and additives to shifts in the conduction band.

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