

Dynamic Response of Charge Transfer and Recombination at Various Electrodes in Dye-sensitized Solar Cells Investigated Using Intensity Modulated Photocurrent and Photovoltage Spectroscopy

Gyeong-Ok Kim and Kwang-Sun Ryu*

Department of Chemistry, University of Ulsan, Ulsan 680-749, Korea. *E-mail: ryuks@ulsan.ac.kr
Received November 4, 2011, Accepted December 2, 2011

Intensity modulated photocurrent spectroscopy and intensity modulated photovoltage spectroscopy were investigated to measure the dynamic response of charge transfer and recombination in the standard, TiCl_4 -treated and the combined scattering layer electrode dye-sensitized solar cells (DSSCs). IMPS and IMVS provided transit time (τ_n), lifetime (τ_r), diffusion coefficient (D_n) and effective diffusion length (L_n). These expressions are derived that generation, collection, and recombination of electrons in a thin layer nano-crystalline DSSC under conditions of steady illumination and with a superimposed small amplitude modulation. In this experimental, IMPS/IMVS showed that the main effect of TiCl_4 treatment is to suppress the recombination of photogenerated electrons, thereby extending their lifetime. And the Diffusion coefficient of combined scattering layer electrode is 6.10×10^{-6} higher than that of the others, resulting in longer diffusion length.

Key Words : TiO_2 , TiCl_4 treatment, Scattering layer, IMPS, IMVS

Introduction

Dye-sensitized solar cells (DSSCs) are regarded as a potential low-cost alternative to conventional solar cells and have attracted considerable interest during the past decades. A typical DSSC consists of a dye-sensitized semiconductor electrode, redox electrolyte, and counter electrode. Under light irradiation, electrons generated by photo-excited dye molecules are injected into the conduction band of the TiO_2 and transported from the injection sites to the contact electrode. Finally, electrons are collected and pass through the external circuit. Meanwhile, the oxidized dye molecules are regenerated by the redox couple (iodide/tri-iodide) in the electrolyte. To achieve high energy conversion efficiency, many researchers studied several parameters such as morphology, pore volume, and the crystallinity of TiO_2 influenced the charge transport and recombination processes.¹

The transport and interfacial transfer of electrons in dye-sensitized solar cells have been investigated using intensity modulated photocurrent and photovoltage spectroscopy (IMPS and IMVS, respectively). IMPS measures the periodic photocurrent response of the cell to a small sinusoidal perturbation of the light intensity superimposed on a largely steady background level. IMVS uses the same intensity perturbation but measures the periodic modulation of the photovoltage, which is dictated by the difference in Fermi level in the dark and the quasi Fermi level under illumination. IMPS provides information about the dynamics of charge transport and back reaction under short circuit conditions, whereas the IMVS response is determined by the electron lifetime under open circuit conditions.²

In this paper, electron transit time, lifetime, diffusion

coefficient and diffusion length related to DSSC performance were investigated for different working electrode conditions by IMPS and IMVS.

Experimental

Dye-sensitized solar cells were prepared on SnO_2 :F-coated glass substrates ($8 \Omega/\text{square}$, 2 mm thickness, Pilkington). FTO glass plates were first cleaned in a detergent solution using an ultrasonic bath for 15 min and were then rinsed with water and ethanol. Three kinds of working electrodes were formed under different conditions. First, the FTO glass plates were coated with a layer of 20 nm TiO_2 paste (Solaronix) using a doctor blade technique. The 20 nm TiO_2 thin film coating on the FTO glass was then sintered at 450 °C for 30 min. Second, TiCl_4 treatment was conducted before and after TiO_2 deposition for some samples. Thereby, FTO glass plates were immersed in 40 mM TiCl_4 solution (99.99%, Aldrich at 70 °C for 30 min and were then washed with water and ethanol, followed by sintering at 500 °C for 30 min. Third, light-scattering TiO_2 films containing 400-nm-sized particles (CCIC) 2-5 μm in thickness were formed on 20 nm TiO_2 thin films, followed by sintering. After cooling to 80 °C, the TiO_2 electrodes were immersed into the N-719 dye solution (0.5 mM in ethanol) and were held at room temperature for 24 h. For the counter electrodes, the FTO plates were drilled and coated with a drop of 10 mM H_2PtCl_6 (99.99%, Aldrich) solution and were then heated at 400 °C for 15 min. Dye-coated TiO_2 films and Pt counter electrodes were assembled into sealed sandwich-type cells by heating with hot-melt films used as spacers. An electrolyte solution (AN 50, Solaronix) was injected into each of

the drilled holes in the counter electrodes. Finally, the holes were sealed using hot-melt and cover glasses (0.1 mm thickness).

Photovoltaic measurements of the DSSC employed an AM 1.5 solar simulator (100 mW cm⁻², IVIUM STAT). The power of the simulated light was calibrated using a reference Si photodiode. Electron transport time and electron lifetimes were measured by intensity modulated photocurrent spectroscopy (IMPS) and intensity modulated photovoltage spectroscopy (IMVS). A diode laser with variable power and modulation control (red LED source, 635 nm) was used as the light source for these studies. Illumination was always incident on the working electrode side of the solar cell. The intensity was measured using a calibrated Si-photodiode. The cell was illuminated with sinusoidally modulated light having a small AC component (10% of the DC component). IMPS and IMVS responses were measured at different bias-light intensities.

Results and Discussion

Figure 1 shows the J-V curves for three different samples, the 20 nm standard TiO₂ electrode, the TiO₂ electrode treated with TiCl₄ and the combined 400-nm-sized TiO₂ electrode scattering layer. Table 1 provides detailed information about current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and conversion efficiency (EF). Current densities of electrodes with TiCl₄ treatment and a scattering layer increase significantly compared to those of the standard electrode, resulting in higher efficiencies. To investigate this improved current density and performance, we employed IMPS and IMVS to study electron migration.

Figure 2 provides results for studies carried out over a range of illumination intensities of three orders of magnitude. A red LED (635 nm) was used as the modulated light source. Both photocurrent and photovoltage lag behind the illumination, leading to a response in the fourth quadrant (positive real, negative imaginary) of the complex plane. In

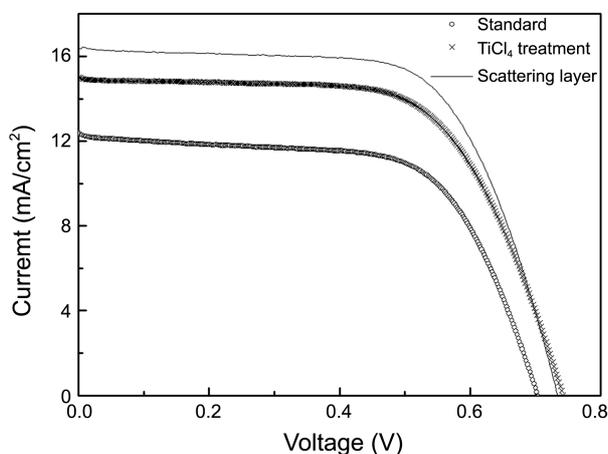


Figure 1. J-V curves of the standard, TiCl₄-treated, scattering layer electrodes under simulated AM 1.5 light. Sample thickness is 12 μm, 14 μm, 16 μm, respectively.

Table 1. Characteristics of DSSCs prepared from various TiO₂ electrodes

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	EF (%)
Standard	12.92	0.7040	63.63	5.79
TiCl ₄ -treated	15.02	0.7420	63.69	7.10
Scattering layer	16.36	0.7340	65.63	7.88

the absence of electron-hole recombination, the phase shift of the IMPS semicircle is a result of the time decay between the generation and collection of charge carriers. At low frequencies, the IMPS plots converge to a point on the real axis that corresponds to the steady-state photocurrent. At high frequencies, the modulated photocurrent tends to zero, indicating that the modulation frequency is faster than the relaxation of the charge carrier density by transport to the contacts and back reaction.²⁻⁴ In the case of the IMVS experiment, the response is semicircular, and the phase lag is due to relaxation of electrons by back reaction with cations in the electrolyte. The measurement frequencies that result in the lowest imaginary component in the IMPS and IMVS plots (f_{min}) are of special interest. In Figure 2, the points which best represent f_{min} in the plots are therefore marked with their corresponding frequencies. The frequency of the minima in both types of plots was observed to decrease with reduced light intensity. This variation in the minimum frequencies as a function of the short circuit photocurrent (I_{sc}) is based on the reference cell ($I = 0.609$ mA at 1 sun, Ashai).

Figure 3 indicates transit time (τ_n), lifetime (τ_r), diffusion coefficient (D_n) and diffusion length (L_n). Figure 3 (a, b) shows τ_n and τ_r calculated from $1/2\pi f_{min}$. With short current, transit time depends on the ratio of free-to-trapped electrons and on the diffusion coefficient of electrons in the conduction band. Thus, τ_n is influenced by the total number of surface states in the film, the position of the Fermi level, and the electrical connectivity of the TiO₂ network.⁵ Table 2 shows that the transit time is about 2.0 ms, 3.0 ms and 6.0 ms, respectively, when the average lifetime is 20.0 ms, 24.0 ms and 24.4 ms. Electron transfer and lifetime in the standard electrode are lower than the others. Because TiCl₄ treatment provides good electric connectivity within the TiO₂ network, this DSSC not only absorbed a large amount of dye, but also reduced recombination centers including surface or trap sites. Further, the combined scattering layer electrode has a light-harvesting effect, which generated more electrons. At short circuit and for homogeneously absorbed light, the electron diffusion coefficient can be estimated from the relation $D_n = d^2/2.35 \tau_n$, where d is the layer thickness of the TiO₂,⁴ and D_n increases with increasing light intensity, as shown in Figure 3(c). The dependence of D_n on light intensity arises from the change in trap occupancy with intensity. At low light intensity, electrons are exchanged between deep traps and the conduction band, and the transport rate is slower. At high light intensity, deep traps are filled, and electron trapping/detrapping involves shallower levels, so that the transport rate is faster. TiCl₄ treatment and

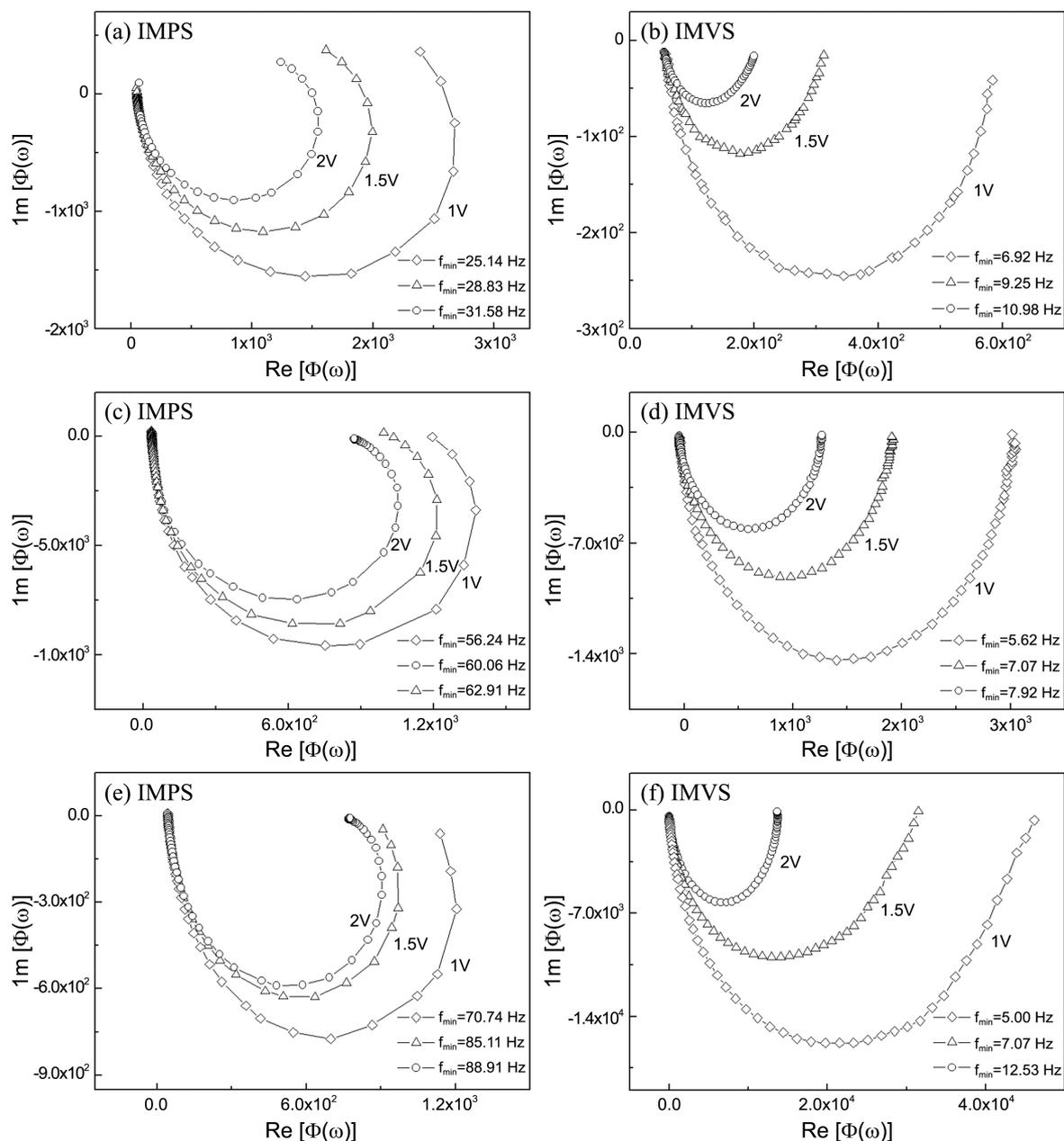


Figure 2. IMPS and IMVS plots (a, b) Standard (c, d) TiCl_4 -treated electrode and (e, f) scattering layer electrode.

addition of a scattering layer have higher diffusion coefficients than that of a standard electrode, along with shorter transit times. These two electrodes have a photon trapping effect and produce more electrons relative to the standard. Thus, many electrons transfer through the TiO_2 band and reach the back contact, thereby resulting in faster rates. Electron diffusion coefficient and electron lifetime values can be used to calculate the electron diffusion length, $L_n = (D_n \tau_n)^{1/2}$, which is determined by the competition between electron transport and back reaction.⁶ This length is an important factor in DSSCs, as L_n should be greater than the film thickness to enable an efficient collection of photo-generated electrons at the back contact. The thicknesses of all three electrodes studied herein are theoretically smaller

than the diffusion length. As a result, the performances of TiCl_4 -treated and scattering layer electrodes are higher than that of the standard electrode, which implies that dye absorption, electron transport in the TiO_2 network, and electron back-reaction with electrolyte all affect DSSC performance.

Conclusion

Highly efficient DSSCs were fabricated using TiCl_4 treatment and scattering layer electrode. Their charge transport and recombination properties were investigated and compared with those of typical standard TiO_2 electrode. At higher light intensity, deep traps are filled, and electron

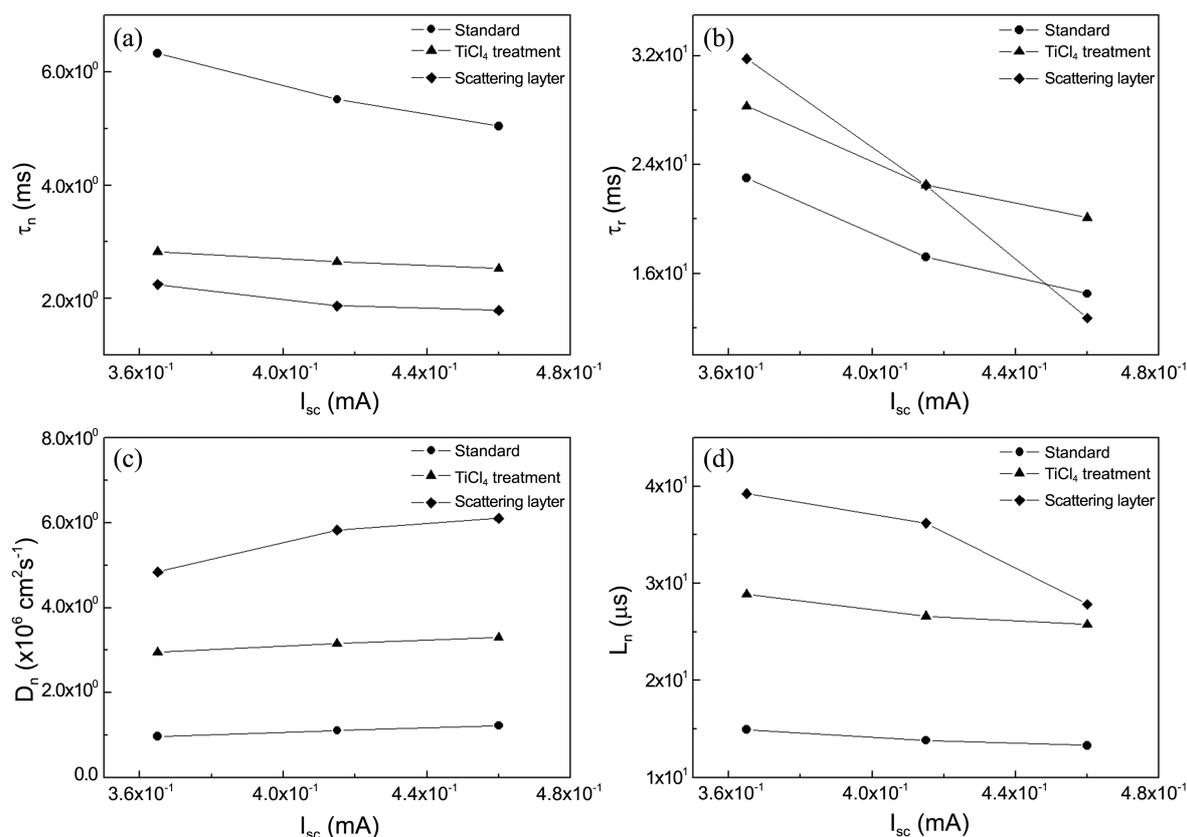


Figure 3. Transit times (τ_n); (a) lifetimes (τ_r); (b) electron diffusion coefficients (D_n) (c) and diffusion lengths (L_n) (d) of the standard, TiCl_4 -treated, and scattering layer electrodes.

Table 2. Characteristics of electron transit times, lifetimes, diffusion coefficients and diffusion lengths with standard, TiCl_4 -treated and scattering layer electrodes measured using IMPS and IMVS

	I (mA)	τ_n (ms)	τ_r (ms)	D_n (cm^2/s)	L_n (μm)
Standard	0.365	6.63	23.0	0.97×10^{-6}	14.9
	0.415	5.52	17.2	1.11×10^{-6}	13.8
	0.460	5.04	14.5	1.22×10^{-6}	13.3
TiCl_4 -treated	0.365	2.83	28.3	2.95×10^{-6}	28.9
	0.415	2.65	22.5	3.15×10^{-6}	26.6
	0.460	2.53	20.1	3.30×10^{-6}	25.8
Scattering layer	0.365	2.25	31.8	4.84×10^{-6}	39.2
	0.415	1.87	22.5	5.83×10^{-6}	36.2
	0.460	1.79	12.7	6.10×10^{-6}	27.8

trapping/detrapping involves shallower levels, so that the transport rate is faster. Electron transfer and lifetime in the standard electrode are lower than the others. TiCl_4 treatment and addition of a scattering layer have higher diffusion coefficients than that of a standard electrode, along with shorter transit times. Transit time and recombination time of this electrode are high 2.25 ms and 31.8 ms at current of 0.460 mA. The results of IMPS/IMVS suggest that TiCl_4 -treated electrode reduced recombination centers including surface or trap sites because of good electric connectivity

within the TiO_2 network. The combined scattering layer electrode has highly performance due to light-harvesting effect. Diffusion coefficient of this electrode is 6.10×10^{-6} higher than that of TiCl_4 -treated and standard electrode at a current of 0.460 mA, resulting in longer diffusion length. IMPS and IMVS is useful to investigate electron transfer and recombination kinetics.

Acknowledgments. This work was supported by the Priority Research Centers Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0093818).

References

- Liu, W.; Hu, L. H.; Dai, S. Y. *J. Electrochim. Acta* **2010**, *55*, 2338.
- Jessica, K.; Robert, P.; Petra, J. C.; Laurence, M. P. *J. Phys. Chem. B* **2003**, *107*, 7536.
- Lagemaat, J. V.; Frank, A. J. *J. Phys. Chem. B* **2000**, *104*, 2044-2047.
- Dloczik, L.; Ileperuma, O.; Uhlendorf, I. *J. Phys. Chem. B* **1997**, *101*, 10281.
- Park, N.-G.; Schlichthorl, G.; Frank, A. J. *J. Phys. Chem. B* **1999**, *103*, 3312.
- Bandic, Z. Z.; Bridger, P. M.; Piquette, E. C. *Appl. Phys. Lett.* **1998**, *73*, 3276.