

## Comparison of Electrochemical Impedance Spectroscopy between Illumination and Dark Conditions

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Electrochemical impedance spectroscopy (EIS) is an excellent method to determine simultaneously many parameters concerning electron-transport processes in dye-sensitized solar cells under the same conditions as those for the cell in operation. A number of studies analyzed the electron-transport processes based on EIS measurements under dark conditions, although the photocurrent density–voltage ( $I$ – $V$ ) measurements were carried out under one-sun illumination conditions. The result of EIS measurement obtained under dark conditions, however, is quite different from that obtained under illumination. The EIS measurement should thus be carried out under the same illumination conditions as the  $I$ – $V$  measurement is performed to obtain properly analyzed results in regard to the electron-transport processes. The main factor contributing to such difference between dark and illumination conditions was elucidated to be the difference in the electron density in the steady-state cell performance between dark and illumination conditions.

Electrochemical impedance spectroscopy (EIS) is known to be an excellent method to obtain information concerning the electron-transport processes in dye-sensitized solar cells (DSSCs).<sup>1–5</sup> The EIS, in particular, can determine many parameters involved in the electron-transport processes in DSSCs simultaneously under the very conditions applied to the cell in operation.<sup>5,6</sup> A number of studies in the literature analyzed the electron-transport processes based on EIS measurements under dark conditions, while the photocurrent–voltage ( $I$ – $V$ ) measurements were carried out under one-sun illumination conditions.<sup>6,7</sup> Furthermore, 680-nm bias light, which is only weakly absorbed by the dye, was used to measure EIS in place of one-sun illumination to provide a constant and homogeneous electron injection throughout the film.<sup>8</sup> The spectrum obtained from the EIS measurement under dark conditions or utilizing only weakly absorbed light, however, is quite different from that obtained under illumination conditions by one-sun lighting. Thus, the EIS measurement should be carried out under the same illumination conditions as the  $I$ – $V$  measurement is performed to acquire properly analyzed results for the electron-transport processes.

Let us consider why the EIS measurement is extensively carried out under dark conditions. In the EIS measurement, the cell is irradiated steadily, indicating that the generation of electrons due to lighting occurs also in steady state. The time-dependent continuous equation with respect to electrons for obtaining an impedance equation thus does not include the

photogeneration term as given in eq 1, where  $\tilde{n}$  represents the time-dependent electron density,  $\Delta n$  stands for the amplitude of time-dependent electron-density oscillations with the frequency  $\omega$ ,  $D_{\text{eff}}$  represents the effective diffusivity of electron,  $k_{\text{eff}}$  stands for the effective rate constant of the recombination reactions,  $t$  is time, and  $x$  is the distance from the interface between the titania electrode and the transparent conducting glass electrode.

$$\frac{\partial \tilde{n}}{\partial t} = D_{\text{eff}} \frac{\partial^2 \tilde{n}}{\partial x^2} - k_{\text{eff}} \tilde{n}, \quad \tilde{n} = \Delta n \exp(i\omega t) \quad (1)$$

Each of the boundary conditions at the interface between the titania electrode and the transparent conducting glass electrode ( $x = 0$ ) and the interface between the titania electrode and the electrolyte ( $x = L$ ) is identical under both illumination and dark conditions. This is because the current  $\Delta J$  at  $x = 0$  is proportional to the diffusion rate at  $x = 0$ , where  $q$  represents the charge of electron, and electrons are assumed not to be able to cross the interface of  $x = L$ . That is,

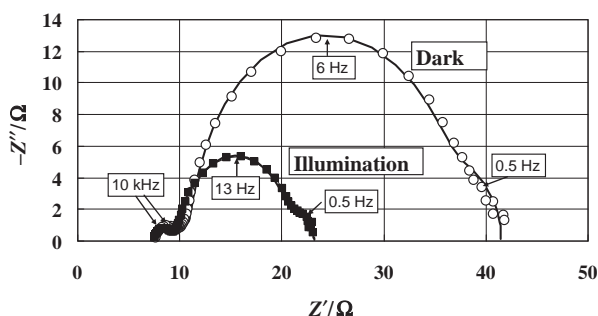
$$x = 0, \quad \Delta J = q D_{\text{eff}} \frac{\partial \Delta n(x)}{\partial x} \quad (2)$$

$$x = L, \quad \frac{\partial \Delta n(x)}{\partial x} = 0 \quad (3)$$

Thus, the solution of eq 1 to be obtained should be the same for both illumination and dark conditions, resulting in the same impedance equation for both the illumination and dark conditions. On the other hand, the equation for the steady-state distribution of electrons within the titania electrode, of course includes the photogeneration term under the illumination conditions; however, that for the dark conditions does not include the photogeneration term, leading to entirely different electron distributions to be attained. Different electron distributions cause different spectra of EIS as will be discussed later in detail.

Wang et al.<sup>4</sup> pointed out the noticeable difference in EIS spectrum under illumination conditions from that in the dark. Their explanation states that with illumination  $I_3^-$  is formed in situ by dye regeneration at the mesoporous  $\text{TiO}_2$ /electrolyte interface, whereas in the dark  $I_3^-$  is generated at the counter electrode and will penetrate the mesoporous  $\text{TiO}_2$  film by diffusion.

Figure 1 shows an example of comparison of the EIS measurement under illumination with that in the dark. The  $I$ – $V$  performance of the cell evaluated under AM 1.5 illumination includes  $J_{\text{sc}} = 15.3 \text{ mA cm}^{-2}$ ,  $V_{\text{oc}} = 0.755 \text{ V}$ , a fill factor of  $FF = 0.723$ , and a power conversion efficiency of  $\eta = 8.36\%$ . Note that while the  $I$ – $V$  measurement under illumination was



**Figure 1.** Comparison of EIS measurements under illumination condition with that under dark condition. Circles and squares represent experimental values, while solid lines designate calculated curves.

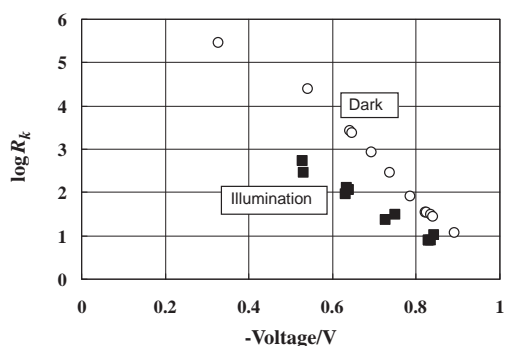
carried out in AM-1.5 open-circuit conditions, that in the dark was conducted with no light at the same bias voltage as in the illuminated open-circuit conditions, i.e., 0.755 V. Figure 1 signifies a drastic difference in the spectrum of EIS under illumination from that in the dark.

The arcs at a high frequency of 10 kHz correspond to the impedance of electron transport through the surface of a platinum electrode.<sup>4,6</sup> The arc obtained under illumination almost coincided with that in the dark, indicating that similar electrochemical properties were attainable for the platinum electrode under both conditions. The arcs at a low frequency of 0.5 Hz, corresponding to the impedance of  $I_3^-$  diffusion in the electrolyte,<sup>4,6</sup> did not differ so much, while the arc under illumination at an intermediate frequency of 13 Hz, corresponding to the impedance of charge transfer across the  $TiO_2$  electrode/dye/electrolyte interface,<sup>4,6</sup> differed significantly from that under dark conditions at a frequency of 6 Hz. The resistance corresponding to the intermediate arc is known to be the resistance for the recombination reactions,  $R_k$ , in the case of efficient dye-sensitized solar cells, i.e., with the power conversion efficiency exceeding, say, 7%.<sup>5,6,9</sup>

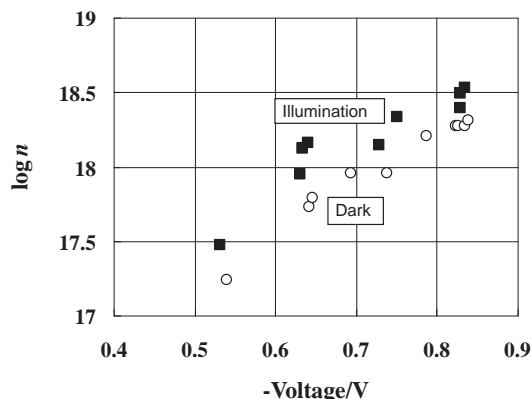
Network structure of titania nanowires (TNWs) were prepared as previously described.<sup>10,11</sup> We synthesized highly crystallized titania nanoparticles (TNPs) with diameter of 3–5 nm in addition to TNWs.<sup>12</sup> The cells were prepared as described previously.<sup>10,11</sup>

Electron-transport processes were measured by electrochemical impedance spectroscopy (EIS) (Solartron 1255B). When evaluated under illumination, the EIS measurements were carried out using the AM 1.5 solar simulator. In the case of dark evaluation, EIS measurements were carried out without light but with the same bias voltage as that under illumination. In order to change the irradiation area, masks were used to confine the area (Detailed experimental procedure is shown in Supporting Information; SI<sup>13</sup>).

In order to elucidate the main reason why the different EIS spectra were obtained under illumination and dark conditions, we obtained a series of EIS spectra measured at various bias voltages ranging from  $-0.3$  to  $-0.9$  V under both these conditions (Figure 2). The parameters concerning the electron-transport processes were determined from the EIS spectra by our analytical method proposed previously.<sup>5</sup> The  $I$ - $V$  performance of this cell resulted in  $J_{sc} = 14.8 \text{ mA cm}^{-2}$ ,  $V_{oc} = 0.821 \text{ V}$ ,  $FF =$



**Figure 2.** Relationship between bias voltage and resistance for recombination reactions ( $R_k$ ).

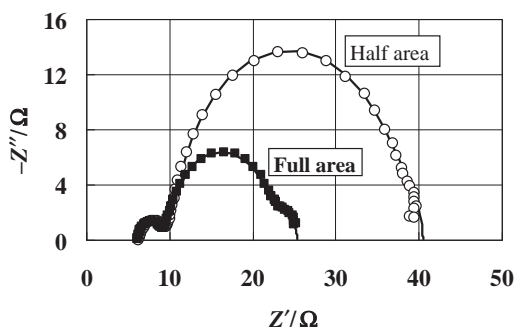


**Figure 3.** Relationship between bias voltage and electron density in titania electrode ( $n$ ).

0.719, and  $\eta = 8.71\%$ . When the absolute value of applied voltage was decreased,  $R_k$  values for both illumination and dark conditions increased significantly in contrast to the decrease in the electron density in the titania electrode as shown in Figure 3.

The trend that  $R_k$  values increased significantly with decreasing electron density needs to be envisaged mechanistically. Wang et al.<sup>4</sup> claimed that with illumination the  $R_k$  value became small because the concentration of  $I_3^-$  ions increased near the interface of  $TiO_2$  electrode/electrolyte due to the regeneration of dyes. In Figure 2, the  $R_k$  value under illumination at  $-0.5$  V was 2 orders of magnitude smaller than that in the dark, suggesting that the difference in  $R_k$  value of such an extent seems to be too large to be explained only in terms of the concentration difference in  $I_3^-$  ions. It is thus speculated that the concentration of  $I_3^-$  ions cannot be the main factor for the difference in  $R_k$  value between dark and illumination conditions.

Let us reassess the variation in the concentration of  $I_3^-$  ions with a decrease in the absolute voltage. In open-circuit conditions, photoelectrons generated by lighting should balance with electrons consumed by recombination reactions, signifying that the number of  $I_3^-$  ions consumed by the recombination reactions would be maximum in the open-circuit conditions. At absolute voltages lower than the open-circuit voltage, some of photogenerated electrons flow as the external current; the electrons consumed by the recombination reactions then decrease at lower absolute voltages, indicating that the concen-



**Figure 4.** Effect of irradiation area on electron-transport properties. Circles and squares represent experimental values, while solid lines designate calculated curves.

tration of  $I_3^-$  ions should increase with a decrease in the absolute voltage. Such a mechanistic argument—and Figure 2—suggest that the  $R_k$  value should increase significantly with increasing concentration of  $I_3^-$ . This outcome conflicts with the literature claim<sup>4</sup> which attributed smaller  $R_k$  values to an increase in the concentration of  $I_3^-$  ions near the titania electrode interface. In the present experiment, the  $R_k$  value was found to increase significantly with a decrease in electron density.

As an alternative method to change the electron density, we carried out EIS measurements under open-circuit conditions with different irradiation areas. Figure 4 shows the results with a full irradiation area ( $0.24 \text{ cm}^2$ ) and half the area ( $0.12 \text{ cm}^2$ ). The parameters determined for electron-transport processes by our analytical method<sup>5</sup> for both the areas are provided separately in Table S1 in the SI.<sup>13</sup> When the irradiation area was cut by half, the electron density was reduced by 20% in comparison to that for the full area—i.e., from  $2.14 \times 10^{18}$  (full) to  $1.71 \times 10^{18} \text{ cm}^{-3}$  (half); the resistance for recombination reactions  $R_k$ , on the other hand, increased by more than two times—i.e., from  $11.9 \text{ } \Omega$  (full) to  $26.4 \text{ } \Omega$  (half) (Table S1 in the SI<sup>13</sup>). It is thus confirmed that the  $R_k$  value did increase with decreasing electron density. Concurrently, the reduction in the irradiation area causes a decrease in the number of electrons consumed by the recombination reactions under open-circuit conditions, resulting in an increase in the concentration of  $I_3^-$  ions with decreasing irradiation area. The claim that smaller  $R_k$  values should be attributed to the increase in the concentration of  $I_3^-$  ions will not hold again.

Another interesting finding provided in Table S1 in the SI<sup>13</sup> covers the parameters evaluated for the platinum electrode ( $R_{\text{Pt}}$  and  $C_{\text{Pt}}$ ) and the diffusion impedance of  $I_3^-$  ions ( $R_{I_3^-}$  and  $D_{I_3^-}$ ); they were found to be the same for both the full and half areas, i.e.,  $R_{\text{Pt}} = 2.4 \text{ } \Omega$  and  $C_{\text{Pt}} = 6.7 \times 10^{-5} \text{ F}$ , and  $R_{I_3^-} = 3.7 \text{ } \Omega$  and

$D_{I_3^-} = 8.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , respectively. Also the diffusivity of electrons in the titania electrode,  $D_{\text{eff}} (=1.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1})$ , is irrelevant to the area difference. Only  $Con$  (see its definition in the SI<sup>13</sup>) and  $k_{\text{eff}}$  varied with the irradiation area. Since the calculated curves fit very well the experimental values, the electron density and recombination reaction process are said to be mainly affected by the variation in the irradiation area.

The above findings are summarized as follows.

1. The EIS spectrum measured under dark conditions is quite different from that obtained under illumination. It is thus recommended that EIS measurements should be carried out under the same conditions as  $I$ - $V$  measurements are performed in order to get properly analyzed results concerning the electron-transport processes.

2. The main reason for the difference in the electron-transport performance attained between dark and illumination conditions was revealed to be the difference in the electron density prevailing in the cell under steady state between dark and illumination.

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