15.1.4.3 Regeneration of the oxidized photosensitizers

Electron transfer from the I^- ion into oxidized photosensitizers (cations), or regeneration of photosensitizers (Figure 15.9), is one of the primary processes needed to achieve effective charge separation. The kinetics of this reaction has also been investigated by time-resolved laser spectroscopy [48, 51]. The electron-transfer rate from the I^- ion into cations of the N3 dye was estimated to be 100 ns [48]. This reaction rate is much faster than that for charge recombination between injected electrons and dye cations. Thus, fast regeneration of the oxidized photosensitizer also contributes to the accomplishment of effective charge separation.

15.1.4.4 Recombination between injected electrons and tri-iodide ions (dark current)

Recombination of injected electrons with tri-iodide ions ($I_3{}^-$) on a semiconductor as shown in Figure 15.9, corresponding to dark current, is one of the primary processes in a DSSC (reaction [5]).

$$I_3{}^- + 2e^-(TiO_2) \rightarrow 3I^- \qquad [5]$$

This reaction can also occur on the SnO_2 surface because the nanocrystalline TiO_2 does not completely cover the TCO substrate, but predominantly occurs on the TiO_2 surface because of the high surface area of the TiO_2 relative to the SnO_2. This reaction contributes to the loss of PV performance in a DSSC analogous to the forward-bias injection of holes and electrons in a *p-n* junction. The V_{OC} in DSSC is obtained using the injection current, I_{inj}, as represented by the following equation, as well as *p-n* junction solar cells:

$$V_{OC} = \frac{kT}{q} \ln\left(\frac{I_{inj}}{I_0} + 1\right) \qquad (15.6)$$

where k is the Boltzmann constant, q is the magnitude of the electron charge, T is the absolute temperature, and I_0 is the dark current. I_{inj} and I_0 are represented by the following equations:

$$I_{inj} = q\eta\Phi_0 \qquad (15.7)$$

$$I_0 = q\, n_0 k_{et}[I_3{}^-] \qquad (15.8)$$

where η is the quantum yield for photogenerated electrons, Φ_0 is the incident photon flux, n_0 is the electron density on the conduction band of the semiconductor in the dark, k_{et} is the rate constant for recombination, reaction [5], and $[I_3{}^-]$ is the concentration of oxidized redox mediator, $I_3{}^-$, in the solution. From equations (15.6) to (15.8), we obtain the following equation:

$$V_{OC} = \frac{kT}{q} \ln\left(\frac{\eta\Phi_0}{n_0 k_{et}[I_3{}^-]} + 1\right) \qquad (15.9)$$

Usually, $\eta\Phi_0 \gg n_0 k_{et}[I_3{}^-]$ and equation (15.9) is simplified as follows [6, 12, 52, 53]:

$$V_{OC} = \frac{kT}{q} \ln\left(\frac{\eta\Phi_0}{n_0 k_{et}[I_3{}^-]}\right) \qquad (15.10)$$