Determination of the Electron Lifetime in Nanocrystalline TiO$_2$ Dye Solar Cells by the Analysis of Photovoltage Decay Measurements

Arie Zaban,[1] Miri Greenshtein,[1] Juan Bisquert[2]

[1]Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel.
[2]Departament de Ciencies Experimentals, Universitat Jaume I, 12080 Castello

Dye sensitized solar cells consist of a dyed nanoporous semiconductor photoelectrode permeated with a redox electrolyte[1]. When the cell is illuminated at open circuit, the free electron density in the semiconductor nanostructure, n, is affected by two main processes. (i) Electron photogeneration, that is achieved by electron injection from the photoexcited dye molecules attached to the semiconductor nanoparticles surface into the semiconductor conduction band (cb), i.e., photo-oxidation of the dye molecules. This photogeneration process can be maintained at a stationary rate because the reduced electrolyte species (electron donors) are able to regenerate the oxidized dye molecules. (ii) Recombination of the photogenerated electrons by reaction with electrolyte oxidized species. Therefore, n increases by photogeneration at a rate $G=\alpha I_0$ (where α is the absorption coefficient of dye molecules and homogeneous photoinjection is assumed) and decreases by recombination at a rate $U(n)$ that depends on the electron density in the electrode. The overall balance can be expressed by the kinetic equation

$$\frac{dn}{dt} = -U(n) + \alpha I_0$$

Under a constant illumination the solar cell reaches a photo-stationary situation in which the free electron density satisfies $U(n)=\alpha I_0$. Under these conditions, the photovoltage, V_{oc}, corresponds to the increase of the quasi-Fermi level of the semiconductor, E_{Fn}, with respect to the dark value, E_{F0}, which equals the electrolyte redox energy, $E_{Fn} = E_{redox}$. Therefore, it can be written[2]

$$V_{oc} = \left(E_{Fn} - E_{F0}\right)/e = \frac{k_B T}{e} \ln\left(\frac{n}{n_0}\right)$$

Here $k_B T$ is the thermal energy, e is the positive elementary charge and n_0 is the concentration in the dark. Clearly, the recombination rate has a major impact on the V_{oc} that is obtained at each light intensity.[3]

Information on the properties of the recombination process can be obtained from the correlation $V_{oc}(I_0)$ at the steady state. A much more sensitive method is to determine the characteristic time of recovery when the system is displaced from a steady state at open circuit, i.e. the electron lifetime, τ_n. In the dye solar cell area the dominant dynamic technique of this kind is the intensity-modulated photovoltage spectroscopy (IMVS), which measures the photovoltage in response to a small periodic modulation of the light intensity over a background steady state.[4,5]

Another way to probe the kinetics of recombination is to monitor the transient of V_{oc} during the relaxation from the illuminated quasiequilibrium state to the dark equilibrium. Although the V_{oc} decay method is fairly obvious, as far as

we know, it has not been fully developed for the study of dye solar cells. The reason for this could be that the photophysical magnitudes in this system undergo a huge variation as the steady state is varied. Indeed, the results of IMVS showed that the electron lifetime changes exponentially over orders of magnitude as the steady-state varies from V_{oc}=0V to the upper limit ~0.8V.[4,5] Therefore, large perturbation techniques, involving vast changes of the parameters, will in principle be much more difficult to interpret than those techniques that function by a small perturbation over a steady state, such as IMVS. Moreover, in general (e.g. in IMVS) the results of frequency domain and time domain techniques will not be simply the Laplace transform of each other, because the large perturbation techniques in the time domain involve an evolution through nonequilibrium states that are very different from the steady states probed by the small perturbation frequency techniques.

We report here on a new powerful tool to study the electron lifetime in dye solar cells by monitoring the transient of V_{oc} during the relaxation from the illuminated quasiequilibrium state to the dark equilibrium. The V_{oc} decay technique is based on a sandwich type dye sensitized solar cell. The cell is illuminated to a steady voltage after which the illumination is turned off using a shutter. Placing neutral density filters in the illumination path enables a systematic change of initial steady state conditions. Thus, open circuit photovoltage decay is recorded as a function of the starting steady state equilibrium.

The V_{oc} decay method has certain advantages over the frequency or steady state-based methods: (a) it provides a continuous reading of the lifetime as a function of V_{oc}; (b) it is experimentally much simpler and (c) the data analysis is outstandingly simple (basically, it consists in two derivatives). We shows that the electron lifetime, τ_n, obtained from the time domain large perturbation method of V_{oc} decay, is in fact in excellent accordance with the IMVS results reported in the literature. The coincidence, which is not fortuitous, will be discussed. We will derive an elementary and potent procedure to extract the fundamental information on the electron lifetime from the measured V_{oc} decay curves, and we introduce a parameter β that governs the change of the lifetime over a broad variation of internal conditions in the solar cell.

References

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