Autolab Application Note PV04

Charge Extraction

Keywords

DSC, solar cells, charge extraction, photovoltaics

Introduction

Among the different types of solar cells, the dye-sensitized solar cells (DSC) are attracting more and more interest because of their increasing performances and low cost of production.

DSC performance mainly depends on the kinetics of the different processes governing the electron transfers [1-3]. The electron lifetime τ_n in the conduction band of TiO_2, for example, is shortened by the back reaction of the photoinjected electron with I_3^-. This back reaction must be slow in order to allow electrons to accumulate in the TiO_2 conduction band and generate a photovoltage. On the other hand, the regeneration of $3I^-$ at the counter electrode must be fast, in order to prevent overpotential loss when current flows. In other terms, the back reaction must be much slower than the $3I^-$ regeneration.

Therefore, it is of extreme importance to retrieve information about the mechanism and the kinetics of the back reaction. Here, the charge extraction method is of help. It consists of multiple cycles as follow:

- The light is switched on for a defined time interval.
- Then, the light is switched off and a decay time is defined.
- When the decay time is passed, the charge is collected.
- In the following cycle, the decay time is increased.
- The change in the extracted charge vs. decay time results in a time-dependent function from which the back reaction rate can be calculated.

Experimental

The charge extraction experiment has been performed on a Solaronix DSC, with a surface area of 0.25 cm^2. A PGSTAT204 + LED kit has been used, with a two-electrode configuration. Here, the working electrode and sensor leads were connected to the front side of the DSC, i.e. the anode, while the reference and counter leads were connected to the rear side of the DSC, i.e., the cathode. The light source chosen for the experiment had a wavelength λ of 627 nm (red color).

The procedure

The NOVA procedure for the charge extraction is composed as follows.

1. A two-second step in which the light is off and the potential is set to 0 V (V_{sc}, short circuit voltage); in order to discharge the cell.
2. The potential is brought to OCP (V_{oc}) and the light is switched on for two seconds.
3. The light is switched off and the built-up potential difference is recorded as it decays for a given amount of time, called decay time.
4. The potential is brought back to V_{sc} and the light is kept off. At this step, the charge is being extracted. The value of the charge at the beginning of the step is extrapolated via linear regression of the curve charge vs. time.

This routine is schematically shown in Figure 2.

The steps are repeated, increasing the decay time in step 3, at each repetition and a plot of the extracted charge vs. decay time is drawn.
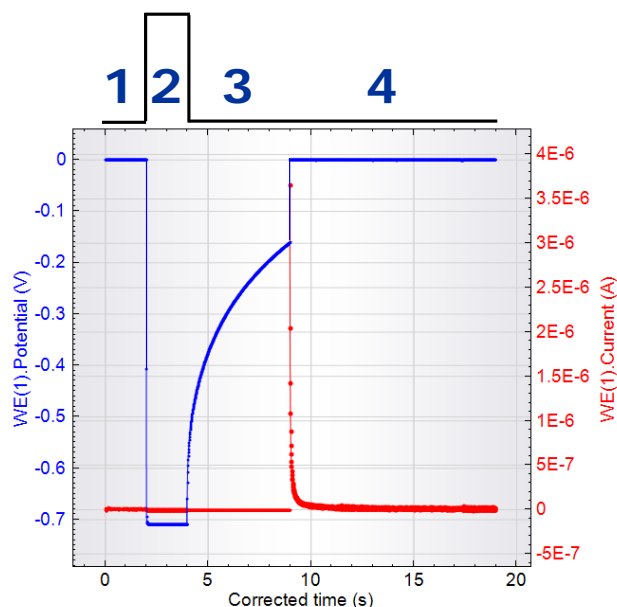

Figure 2 – Potential (in blue) and current (in red) vs. time, for a typical charge-extraction four-step routine, represented by the black line. For the description of each steps, please refer to the text.

Here, the potential (blue line) and the current (red line) are plotted versus time. The black line represents the light steps mentioned above, numbered as in the text.

Results

In Figure 3, an example of the potential (blue line) from the steps 3 and 4 and the extracted charge (black line) at the step 4 are plotted versus time. Here, it can be noticed that the decay time has been set to 4 s. In fact, the cell at OCP has let been relaxed for 4 s, in which the potential decays (step 3), and then brought to zero and the charge extracted (step 4).
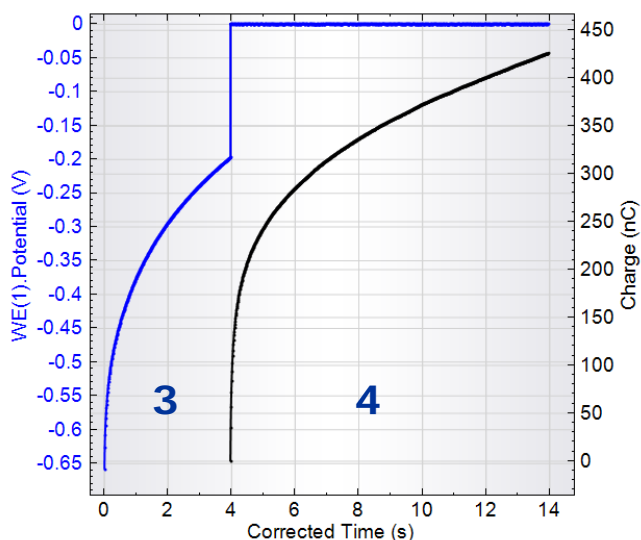

Figure 3 – Plot of potential (in blue) and charge (in black) versus time, for the steps 3 and 4.

Increasing the decay time, the amount of extracted charge after different decay time values can be compared. In Figure 4, the potential (in blue, plot above) at two different decay time values is shown, together with the relative extracted charge (in black, plot below). The thick line refers to the potential decayed for 0.5 seconds and the charge extracted is more than 900 nC (thick black line, bottom plot). The thin line in Figure 4, on the other hand, refers to a potential with a decay time of four seconds. The extracted charge afterwards reaches only 420 nC. Therefore, it can be concluded that increasing the decay time corresponds to a decrease of the extracted charge, since with a longer decay time more charges can recombine before being collected.
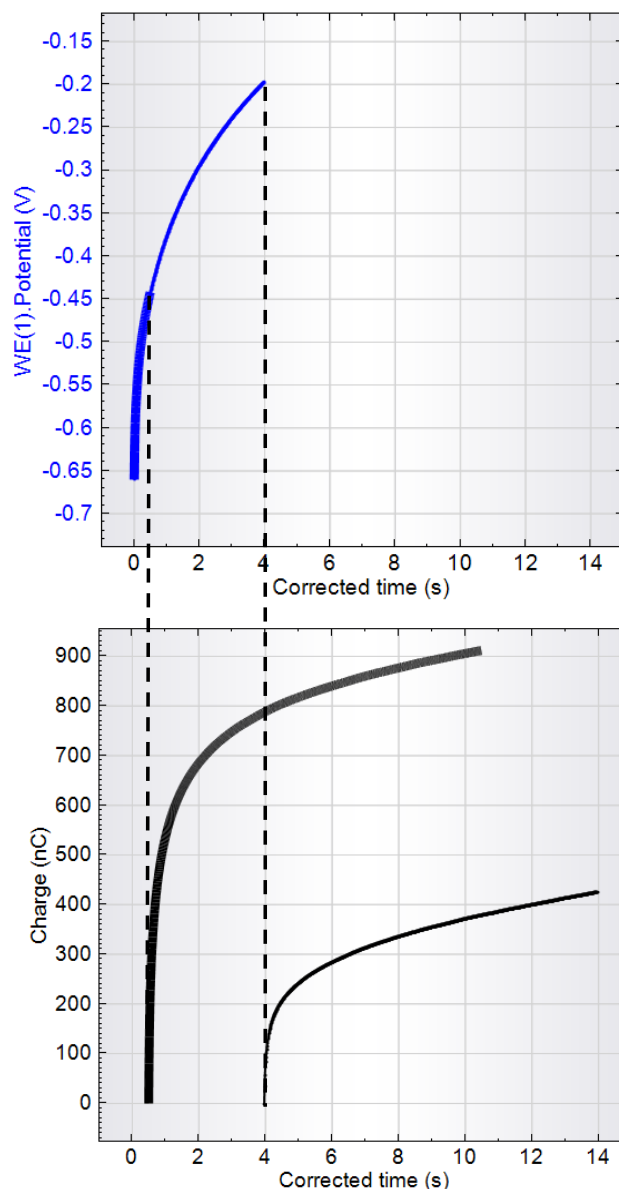

Figure 4 – A longer decay time for the potential (in blue, above) corresponds to smaller values of the extracted charge (in black, below).

Charge extrapolation

The charge value of interest is the one extrapolated at the beginning of the extraction. In order to calculate it, the inverse of the charge is plotted vs. time, and a linear regression is performed. An example is shown in In Figure 5, where the blue line represents the inverse of the charge and in red is the linear regression. Here, the time is shifted, so the beginning of the charge extraction is at t = 0 s.
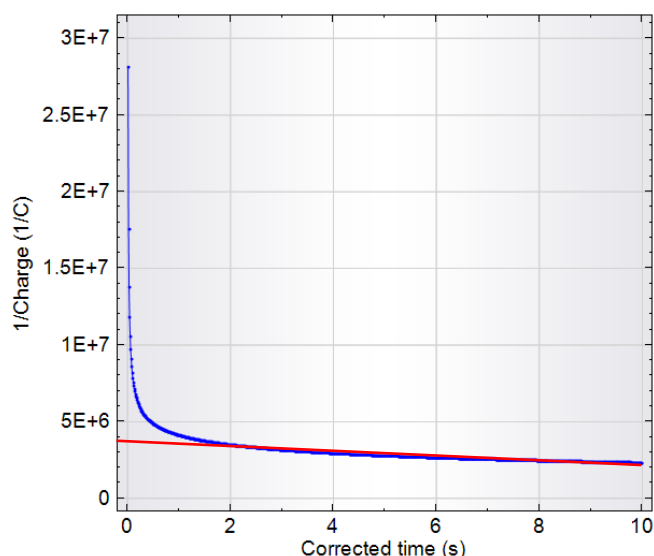
Figure 5 – Plot of the inverse of the charge vs. corrected time, in which the time when the charge starts to be extracted is set at zero. The red line represents the linear regression function. The inverse of the value at t = 0 s, is the charge wanted.

The charge extraction and the relative linear regression are performed for each decay time. Then, the extracted charge is plotted against the decay time, like Figure 6.
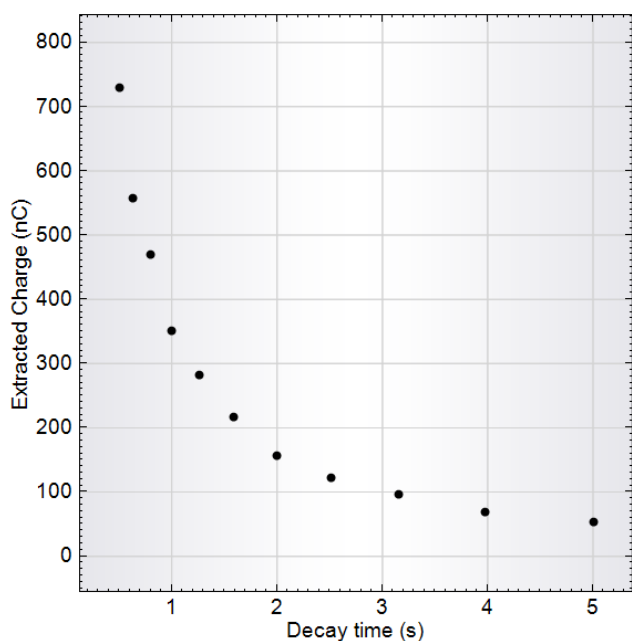

Figure 6 – Plot of the extracted charge, in vs. the decay time.

Rate constant calculation

In order to have insights of the rate constant of the back reaction, the plot in Figure 6 is being linearized, plotting the inverse of the extracted charge vs. decay time.
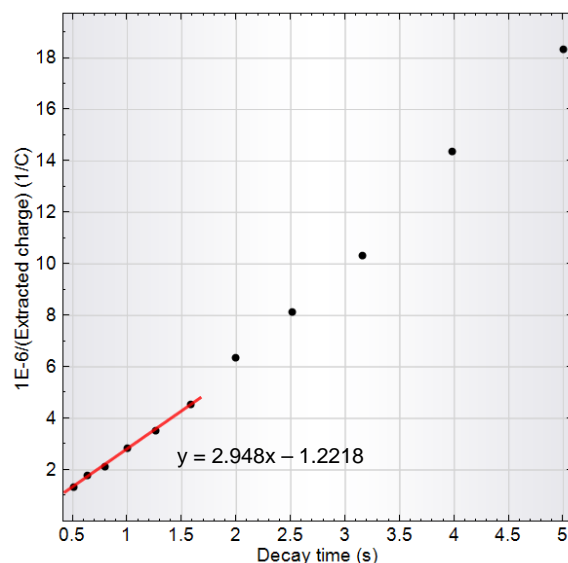

Figure 7 – Plot of the inverse of the extracted charge vs. increasing decay time (black dots), with the fit (red line) in the linear region. In addition, the equation for the fit is shown.

Here, it can be noticed that a linear relationship between the inverse of the charge and the decay holds only for short decay times, suggesting that the rate of decay varies with the square of the total electron concentration [1]. A linear fit is performed on the linear region of the plot; shown as a red line in Figure 7. The slope of the plot is related to the rate constant of electron decay, provided the electrons concentration. For insights of the calculation and explanation of the non-linear region, please refer to [1].

Conclusions

In this application note, it has been shown how Autolab and NOVA can be used, together with the LED kit, to retrieve kinetics information on electron recombination in dye-sensitized solar cells. After performing the test, NOVA allows to calculate automatically the linear regression of the data and to plot the following results.

Bibliography

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Date

21 July 2014