

## Application Area: Energy

# Charge Extraction Method to Study Dye-Sensitized Solar Cells

### Keywords

Solar applications: DSC, charge extraction, Metrohm Autolab, photovoltaics, solar cells, Optical Bench

### Introduction

Among the different types of solar cells, the dye-sensitized solar cells (DSC) are attracting more and more interest because of their increasing performance 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  $\tau_n$  in the conduction band of  $\text{TiO}_2$ , for example, is shortened because of the back reaction of the photo-injected electron with iodine  $I_3^-$ . The rate of this back reaction must be slow in order to allow electrons to accumulate in the  $\text{TiO}_2$  conduction band and generate a photovoltage. On the other hand, the regeneration of iodine ions  $3I^-$  at the counter electrode must be fast, in order to prevent overpotential loss when current flows. In other words, the rate of 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 procedure is of help.

The charge extraction procedure consists of multiple cycles with the following steps:

- The light is switched OFF, and the cell is set at the short circuit voltage,  $V_{sc} = 0$  V.
- The light is switched ON for a defined time interval.
- 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 results in a decay time-dependent function from which the back reaction rate can be calculated.

### Experimental setup

The charge extraction experiment was performed on a Solaronix DSC, with a surface area of  $0.25 \text{ cm}^2$ . An Autolab PGSTAT204 equipped with an Autolab Optical Bench was used. The cell was connected to the PGSTAT in a two-

electrode configuration. The working and sense electrode leads were connected to the front of the cell, and the reference and counter electrode leads were connected to the rear of the cell. The light source had a wavelength  $\lambda$  of 627 nm (red color).

### The procedure

The NOVA procedure for the charge extraction is composed of following steps:

1. A two-second step in which the light is OFF and the potential is set to 0 V ( $V_{sc}$ ).
2. The potential is brought to the open circuit potential ( $V_{oc}$ ), 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 0 V ( $V_{sc}$ ) and the light is kept OFF. At this step, the charge is being extracted.

Figure 1 shows the potential and current behavior of the cell during the steps mentioned above.

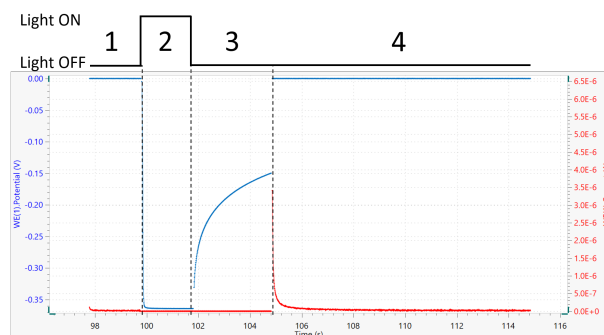


Figure 1 – Potential (in blue) and current (in red) vs. time, for a typical charge-extraction experiment.

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

The steps are repeated for 10 times. During the repetition of the experiment, all the parameters are kept constant while the decay time (step 3) increases by repetition. This experiment results in having the extracted charge versus decay time.

### Results

In Figure 2, an example of the potential (in blue) and the extracted charge (in black) from steps 3 and 4 are plotted versus time.

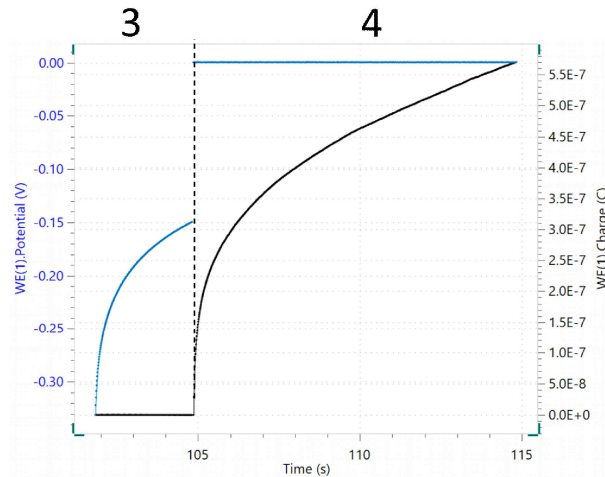


Figure 2 – Plot of potential (in blue) and extracted charge (in black) versus time, for the steps 3 and 4.

Here, the decay time was set to 4 s (step 3, from 101 s to 105 s), during which the potential changes, and no charge is collected. In step 4, the potential is brought to  $V_{sc}$  (0 v) and the charge increases.

### Calculation of the charge

The charge value of interest is the charge at the beginning of step 4, with the hypothesis that the charge would grow linearly vs. time.

The charge value of interest is therefore the value of the regression of the linear part of the charge versus time plot (the final part), extrapolated at the beginning of the step 4. In order to extract it, the inverse of the charge is calculated, plotted versus the time, and then a linear regression is performed. In the next step, the inverse of the extrapolated value at the beginning of the step can be collected. Figure 3 shows an example, where the blue line represents the inverse of the charge and in red is the linear regression.

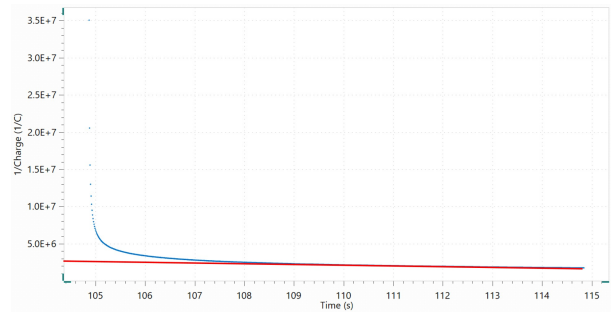


Figure 3 – Inversed charge vs. time plot. The red line represents the linear regression. The inverse of 1/charge at the beginning of the step is the charge value of interest.

The charge extraction and the relative linear regression are performed for each decay time.

Finally, the extracted charge is plotted versus the decay time, Figure 4.

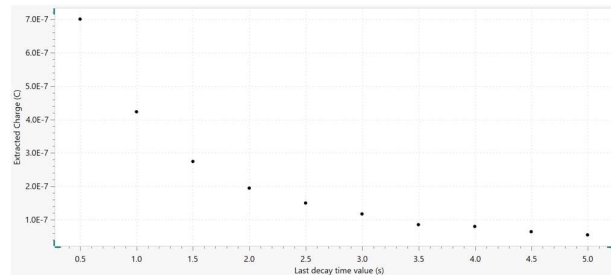


Figure 4 – Plot of the extracted charge vs. the decay time.

Here, it can be seen that the extracted charge decreases by increasing the decay time, since with a longer decay time more charges can recombine before being collected.

### Rate constant calculation

In order to have insights on the rate of the back reaction occurs, the rate constant can be calculated by linearizing the inverse of the extracted charge versus the decay time plot, Figure 5.

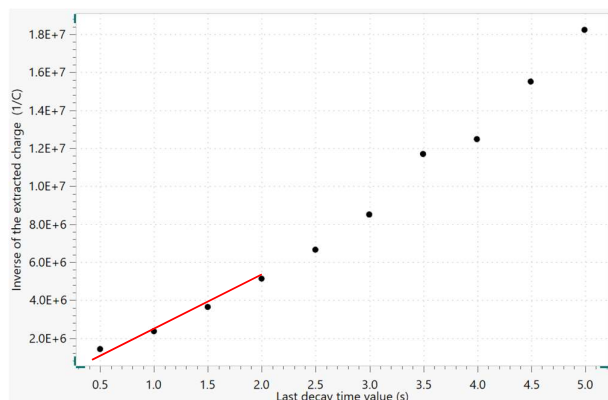


Figure 5 –Inversed extracted charge vs. decay time (black dots).

Here, it can be noticed that a linear relationship holds for the first four data points, 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 5. 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 PGSTAT and NOVA software can be used, together with the Metrohm Optical Bench, 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.

## References

- [1] L.M. Peter et al., *J. Electroanal. Chem.* Vol. 524 – 525, 127 – 136 (2002);
- [2] J. Bisquert et al. *J. Phys. chem. C*, Vol. 113, 17278 (2009);
- [3] N.W. Duffy et al., *Electrochem. Comm.* Vol. 2, 658, (2000).

## Date

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## For more information

Additional information about this application note and the associated NOVA software procedure is available from your local [Metrohm distributor](#). Additional instrument specification information can be found at [www.metrohm.com/electrochemistry](http://www.metrohm.com/electrochemistry).