Electrochemical Impedance Model of a (Low-cost) Dye-Sensitized Solar Cell

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Dye-sensitized solar cells (DSSCs) have been considered as a potential efficient tool for conversion of solar energy to electricity. DSSC's rely upon the presence of a semi-conductor (e.g. TiO_2) attached to the photoanode and a sensitizer (dye) for photogeneration of electrons at the SC interface. Most efficient DSSC's are based on Ru-organic coordination complexes as sensitizer, however the finite availability of Ru led to search for other dyes, being organic molecules or other metal-coordination complexes. The efficiency of the cell can be greatly affected by recombination of generated electrons by several processes in the cell, so co-adsorbents – organic molecules – can be added to the dye to hinder recombination of the electrons by shielding the TiO_2 surface. The present investigation deals with an impedance model tested for the case of a Ru-free organic sensitizer in the presence of one co-adsorbent amongst three different molecules at various concentrations. Best performances of the cell evaluated by i-V curves and impedance spectroscopy have been observed for co-adsorbent/dye ratio near 0.1, but in most cases, addition of the co-adsorbent was shown to improve both the exchange current density for electron collection at the anode and that of recombination phenomena, which contradicts the usual belief.

1. Introduction

Dye-sensitized solar cells (DSSC) are thin film solar cells, based on a semi-conductor and formed between a photo-sensitized anode and the electrolyte containing a redox mediator, which is regenerated at the cathode. The model version proposed by Grätzel and O'Regan (1991) was the first to exhibit appreciable efficiency with the use of an organic coordination complex of ruthenium. Because of their simple technology, their energy efficiency up to 13%, the possible use of printing techniques already existing in industry and their acceptable cost, DSSC's have been the topic of a number of works, patents and papers since then and demonstration examples have been installed, as for instance in the SwissTech Convention Center in the EPF Lausanne.

In its principle (Figure 1) DSSC produces electricity by solar light irradiation which is absorbed by the dye, often called sensitizer, S: S species at its fundamental state is excited to state S^*. The rise of energy level allows extraction of one electron and its injection into the conduction band of semi-conducting titanium oxide: electrons diffuse through the SC structure before being collected at the surface of the transparent photo-anode, and flowing in the external circuit as valuable electricity. The oxidized dye is regenerated by indirect electrochemical reduction at the surface of the Pt cathode, with the use of (I_3^-/I^-) couple as the mediator. Development of DSSC's is still hindered by the following issues to be solved: (i) the cost and availability of ruthenium which is the reference metal in the coordination complex because of its catalytic properties; use of metal-free organic dyes can partly solve the issue (Chen et al., 2005) even though their efficiency in energy conversion is far below those of many Ru-based sensitizers; (ii) a potential environment issue induced by the presence of acetonitrile and iodine in most electrolyte solutions in DSSC; (iii) the existence of side phenomena e.g. recombination of electrons in the bulk of mesoporous

TiO$_2$ or in the side-reduction of I$_3^-$ species at the TiO$_2$-electrolyte interface. The significance of recombination phenomena can be reduced by addition of co-adsorbent (Neale et al. 2005; Zhang et al. 2005), which is known to shield the uncovered TiO$_2$ surface by the presence of amphiphilic molecules, allowing in some cases higher voltage and photocurrent, together with more stable performance. In return electron extraction and injection may be hindered.
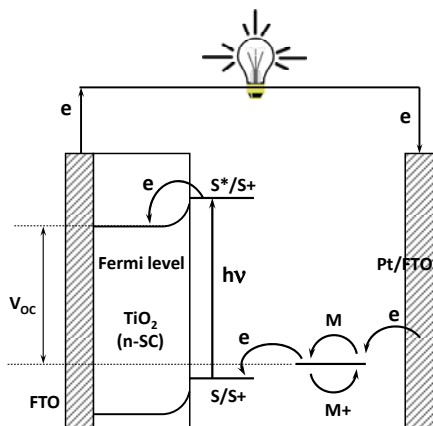

Figure 1: Principle of DSSC's with n-SC. Recombination reactions are not shown.

DSSC's are usually characterized electrochemically by I-V curve and electrochemical impedance (EI) measurements: for these two techniques, the power of the lamp is considered in the full emission spectrum. Current-Voltage curves give access to the energy yield, the open-circuit voltage, the maximal current density together with the fill factor. EI spectroscopy is known in the area as a powerful technique to give access to the rates of the various processes involved in DSSC operation, in conjunction with other transient electrochemical techniques. However, the EIS models encountered in the literature (Kern et al., 2002; Wang et al., 2005, Adachi et al. 2006) are not in full consistence with each other and the physical phenomena involved in DSSC's operation still need to be highlighted, in spite of the abundant recent literature (Wang et al. 2009, Li et al., 2012). The present investigation was aimed at observing the electrochemical behaviour of DSSC, for the example of a derivative of phenylcyanoacrylic acid – as considered by Yakhanthip et al. (2011) by i-V curves and EI spectroscopy, with the presence or not of a co-adsorbent amongst three different molecules. The developed EIS model was used to estimate the effect of the co-adsorbent concentration on the rates of energy transfer and electron recombination.

2. Experimental section

DSSC were prepared with 2x2 cm^2 FTO-glass plates (Solaronix). Platinum and and titania electrodes were screen printed using respectively Ti-nanoxide Ti/SP and Platisol inks (Solaronix) on the 6x6 mm^p active areas on the FTO-covered plates. The thickness of the TiO$_2$ layer was measured at 5 µm. Dipping solution for sensitization were 0.5 mM (diphenylamino)phenylcyanoacrylic acid (CyA) in acetonitrile. This Ru-free dye was selected as an example with acceptable performance in charge injection. Co-adsorbents were added at concentration ratio (Co-adsorbent/dye) varying from 0 to 1 in the dipping solutions: amongst the diversity of possible molecules, chenodeoxycholic acid (CDC), bis(4-methoxyphenyl)phosphinic acid (BMPP) and guanidinobutyric acid (GBA) were selected because they have already been tested with Ru-dyes (Neale et al. 2005; Zhang et al. 2005, and because of their very different amphiphilic/hydroscopic behaviour at the TiO2 surface, due to their very different chemical nature.
The mediating solution was the commercial AN50 I$^-$/I$_3^-$ electrolyte solution (Solaronix), with a content of iodide species at 0.05 M. The reproducibility in the cell preparation has been controlled by producing several replicates and performing all tests described below.
Experiments were conducted using a Solaronix Lumixo AM1.5 light engine as a solar simulator. As a matter of fact, the lamp used for experiments had an emission spectrum very similar to solar light, with around 7% energy in the near UV region, the rest being in the range 400-800 nm. The lamp was fixed on top of a 50 cm high chassis forming a cage, with four vertical Al plates 20 x 50 cm^2 fixed on it, to avoid illumination outside of the working area. Compressed air was continuously blown in the cage to avoid too significant temperature increase in the irradiated area: the temperature could be kept below 60°C to avoid

degradation of the DSSC's. The light power density was fixed at 50 mW cm^{-2} (AM1.0) for all tests described here.

I-V curves were recorded using a Keithley 2401 source meter and a Thorax light power meter. Electrochemical impedance measurements have been carried out with a PGSTAT 30 Autolab potentiostat under irradiation or in dark conditions with no bias (V=V$_{OC}$). As a matter of fact, scanning around the steady state of the DSSC with i=0, avoided progressive change in the excitation state of the dye and its regeneration by the mediator at the cathode. The voltage amplitude was 0.5 mV and the frequency was ranged from 10 kHz to 100 mHz with ten points per decade.

3. Impedance model DSSC

The electrons, once created after irradiation of the dye S through formation of oxidative form S$^+$ have to diffuse through the semi-conducting (TiO$_2$) layer: the corresponding resistance to the transport by diffusion is R$_d$. The diffusion impedance, whose expression derives from Gerischer's model involves also a specific rate ω_d, defined as in usual diffusion problem in electrochemistry (ω_d=L/D^2). However the so-called recombination of electrons can occur: (i) at the TiO$_2$-electrolyte interface, as clearly expressed by Wang et al. (2005) by formation of iodide ions I$^-$ from the triiodide species, (ii) by recombination with holes in the TiO$_2$ layer (since the semiconductor of n-type): this interpretation has been given in most recent papers of the Swiss group (Wang et al. 2009). Whatever the physical meaning and nature of the so-called "recombination" process, the corresponding impedance is expressed with two specific parameters: a charge transfer resistance, R$_k$, and a specific pulsation ω_k (equal to the rate constant). Altogether, the overall diffusion impedance related to electron diffusion and recombination, Z relies upon four parameters R$_d$, R$_k$, ω_d and ω_k, after expressions reported in previous papers (Wang et al. 2005; Adachi et al. 2006).

In addition to the electron transport to the anode – and their loss through recombination – two electrode reactions occur in the solar cell deposited on at the FTO surface, with charge transfer resistance R$_1$ and capacitance C$_1$. No control from I$_3^-$ ion to the cathode was considered here; (ii) at the anode, the electron collection at the interface TiO$_2$/FTO, with charge transfer resistance R$_2$ and capacitance C$_2$ in parallel. Finally, the cell has a non-negligible ohmic resistance, R$_{ohm}$. The overall equivalent circuit shown in Figure 2, involves the two above R-C loops in series with the ohmic resistance and the complex circuit related to electron transport and recombination, Z. The values of exchange current densities for the various electrochemical processes could be obtained from the resistance as shown for the case of electron collection by the FTO anode (subscript 2):
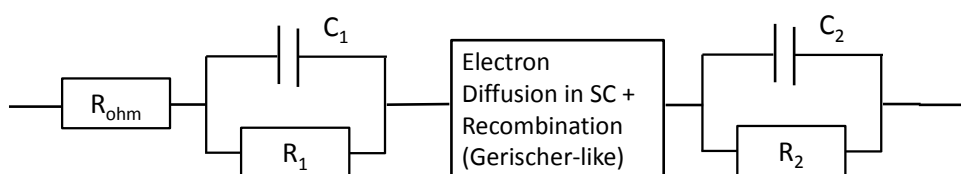
$$i_{0,2} = \frac{RT}{FR_2 S} \tag{1}$$

Figure 2: Equivalent circuit of DSS cells. The meaning of the various components is given in the text.

4. Results

4.1. i-V curves and cell electrochemical features

Figure 3 exemplifies the effect of co-adsorbents used with the dye. First because of the potentials of the mediator redox couple and the Fermi level of TiO2, the cell voltage was restricted to O.6 V or slightly less. Besides, for low voltages of the cell i.e. below 0.35 V, the current density remains at a high level, exhibiting a slight decrease with the cell voltage, then more significant current decay occurs, before decaying more rapidly to zero: whatever the nature of the co-adsorbent and its concentration in the impregnating solution, the open-circuit voltage (VOC) was in the order of 0.6 V. whereas lower concentrations just appear positive for the overall cell behaviour. For the case of CDC, co-adsorbent/dye concentration ratios between 0.1 and 0.5 appear promising, whereas concentrations near 0.1 or slightly below for the two other co-adsorbents (data not shown).

Filling factor, ff, is calculated from the integral under the i-V curve under the maximal electrical power: a decreasing variation of the current density with the cell voltage corresponds to ff=0, whereas a horizontal

current density profile with cell voltage up to VOC, will correspond to ff=1. It can also be observed that the effect of the co-adsorbent is not straightforward, i.e. its effect on the overall cell performance can be negative, in particular in the case of high co-adsorbent ratios (ratio near 1). For all the systems tested, filling factor was in the range 0.65-0.68, expressing the fact that at voltage below VOC/2, the delivered current density varies quite little from its maximal level at 0 V.
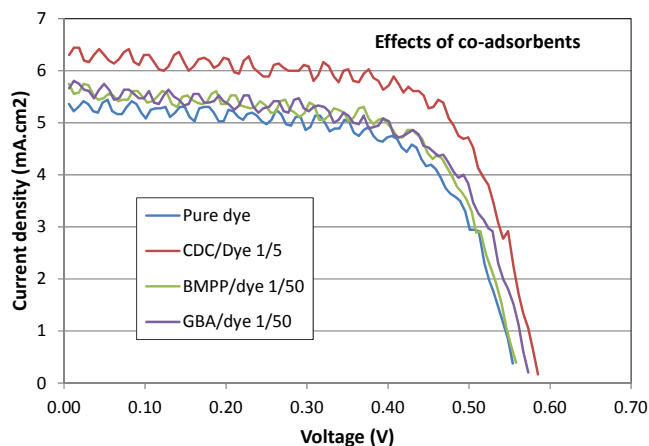

Figure 3: i-V curves of the solar cell depending on the co-adsorbent/dye concentration ratio.

The energy yield can defined as the product of V_{OC} by the maximal current density that can be deduced from the i-V curves over the light energy delivered by the lamp. Yield of energy conversion are in the order of 2% (Figure 4), corresponding to current density really below 10 mA cm^{-2} (Figure 3) and far below the performance of Ru-based sensitizers, as expected with a pure organic dye. Besides, the effect of the co-adsorbent nature and its concentration in the impregnating solution on the energy yield is also exemplified in this figure: the qualitative observations made from i-V curves (Figure 3) can be better quantified. Analysis of the result shows that (i) high co-adsorbent ratio, i.e. over 0.5 are detrimental to the cell efficiency, likely because of its too strong negative effect on electron injection and collection, (ii) the nature of co-adsorbent has a significant impact on its efficiency: presence of CDC allows improvement of the energy yield up to 27%, whereas addition of GBA results most often in poorer efficiency in energy conversion (Figure 4).
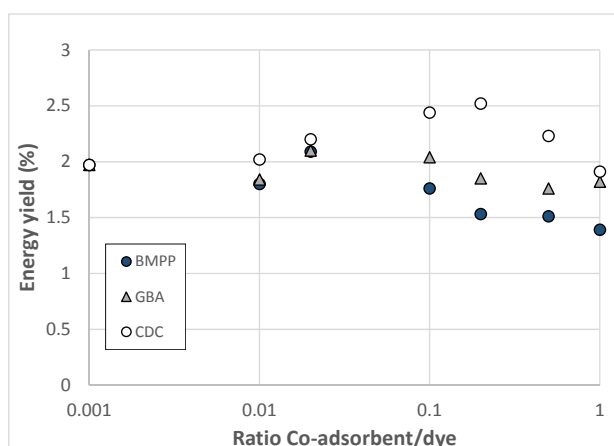

Figure 4: Energy yield of the solar cell depending on the nature and the amount of co-adsorbent.

4.2. Impedance spectroscopy

Examples of experimental spectra in Nyquist plot are shown in Figure 5 for the case of GBA. Two facts can be observed: (i) the effect of co-adsorbent although visible is not greatly significant – similar conclusions were observed for the other co-adsorbents (data not shown); (ii) the overall impedance of dye-co-adsorbent seems to exhibit a minimum – which should correspond to a maximum efficiency of the cell-

for a co-adsorbent fraction near 0.1 or 0.2 (Figure 5). The nature of the co-adsorbent impacts on the trend shown: high amounts of GBA and BMPP result in higher impedance of the cell, and decreasing the ratio inverts the negative effect of the co-adsorbents, whereas addition of CDC in any amount reduces the cell impedance. These observations are consistent with those drawn from the i-V curves (Section 4.1).
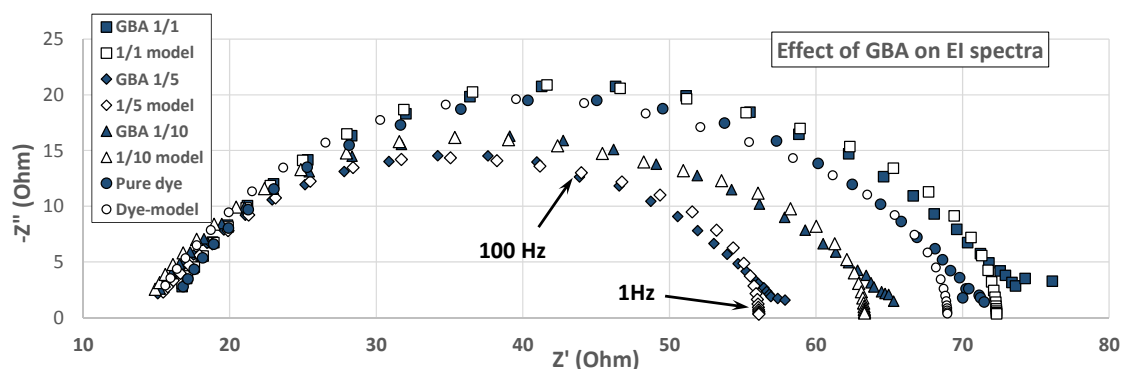

Figure 5: Impedance spectra of DSSC prepared mixed (CyA-GBA) at different dye/co-adsorbent ratios in the range 10 kHz-100 mHz: experimental data and EIS model

Because of the complexity of the equivalent circuit and the large number of parameters involved in the fitting, Interpretation of the spectra has been conducted with care. Preliminary simulation of simplified circuits with dummy components could guide in the development of the fitting procedure, considering both Nyquist and Bode plots. As a matter of fact, although only one loop can be observed in experimental spectra, the presence of all the components in the overall equivalent circuit (Figure 2) was shown to be required for satisfactory fitting of the data. Fitting the high frequency domain yielded estimates for the components of the two electrodes (R_1, C_1, R_2, C_2) and the ohmic contribution. Fitting the lower part of the spectrum led to estimates for parameters involved in the diffusion impedance. Then, fitting was refined for determination of all parameter values. The number of charge carriers in SC TiO_2, n_s, could be attained from the diffusion-related parameters (Adachi et al. 2006).

Figure 6 shows the compared influence of the various co-adsorbents, depending on their amount relative to the dye concentration. The results of the fitting are consistent with the global observation made above, while allowing more precise analysis of the phenomena, as explained below. Exchange current density at the FTO anode i_{02} is improved by addition of co-adsorbent, except with high amounts of GBA or BMPP; For CDC, i_{02} can be increased by 110% upon addition of 10-50% co-adsorbent. It was also observed from fitting of the numerous spectra that recombination rate, expressed by i_{0k}, could be also enhanced by addition of CDC, whereas slightly lower i_{0k} values were obtained for the two other co-adsorbents, in particular for BMPP. Further fitting tests with very different initial estimate for this current density did not affect the above observations: contrary to what is usually believed in the area, co-adsorbents do not always hinder the recombination, but globally favour the cell efficiency, the effect on i_{02} prevails often over that exerted by i_{0k}. The graph shown in Figure 5 on top right shows that the number of charge carriers in the SC are affected by the nature of the dipping solution (dye plus co-adsorbent), the higher density being obtained with CDC, which appears to be the most efficient co-adsorbent. Finally diffusion resistance R_d, deduced also from the diffusion circuit is little affected by the presence of any co-adsorbent (bottom right).

5. Conclusions

Based on a Ru-free organic sensitizer, the low-cost DS solar cells produced could be tested and modelled with respect to their electrochemical behavior by description of the various processes involved: for the model sensitizer used, (diphenylamino)phenylcyanoacrylic acid, the particular effect of co-adsorbent was examined. As a matter of fact, the compound added to the sensitizer in the dipping solution does not reduce the significance of recombination processes in all cases, but accelerates the injection process. Best results were obtained with chenodeoxycholic acid (CDC). The reason of this particular behaviour is likely caused to synergetic effect of this co-adsorbent with the dye investigated, in relation to the mesoporous TiO_2 phase employed. This behaviour somehow differing from the formerly reported effects, may be due to the chemical nature of the dye, a Ru-free molecule, whereas most papers rely upon N719 or comparable sensitizers. This is to be confirmed by ab-initio calculations. Besides, the EIS model developed is currently used, now with particular attention to the effect of the wavelength on the kinetics of the various phenomena, in a closer description covering electrochemistry and photophysics.
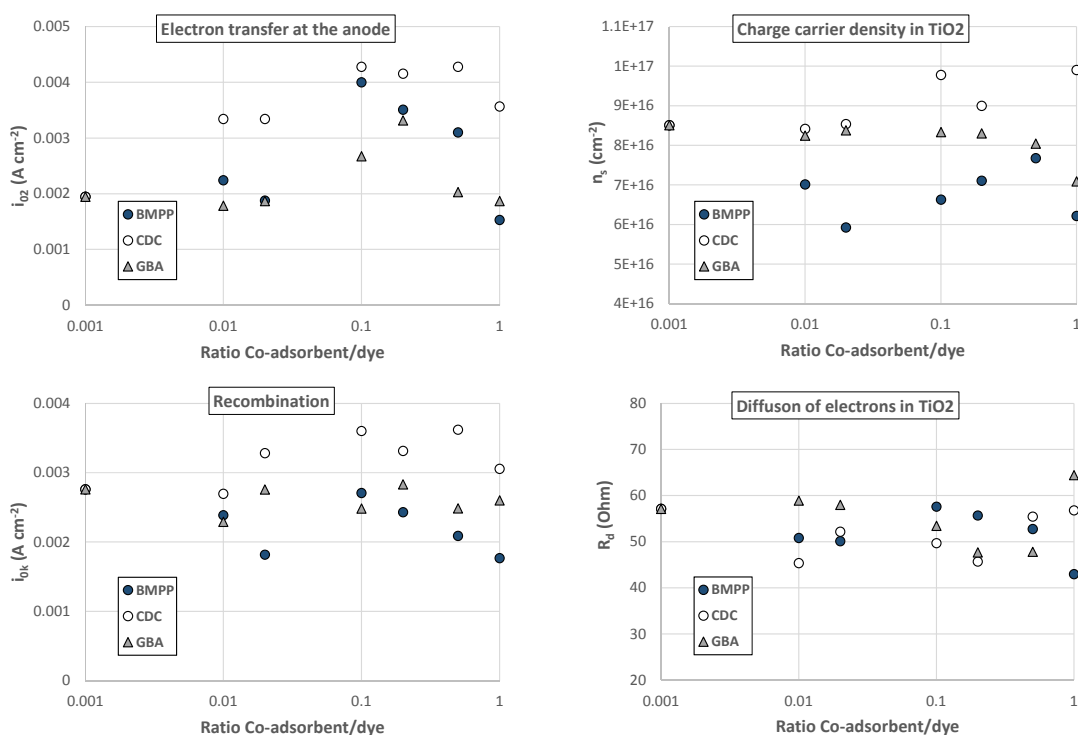
Figure 6: Variations of various electrochemical features of the cell with the co-adsorbent/dye ratio. Case of pure dye cell is shown on the graph for a ratio value at 0.001 for the sake of illustration with the semi-log plot.

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