

Continuity Equation for the Simulation of the Current-Voltage Curve and the Time-Dependent Properties in Dye-Sensitized Solar Cells – Supporting Information

Juan A. Anta^a, Jesús Idígoras^a, Elena Guillén^a, Julio Villanueva-Cab^b, Humberto J. Mandujano-Ramírez^b, Gerko Oskam^b, Laila Pellejà^c, Emilio Palomares^{c,d}

^a*Área de Química Física, Universidad Pablo de Olavide, E-41013, Sevilla, Spain.*

^b*Departamento de Física Aplicada, CINVESTAV-IPN, Mérida, Yucatán 97310, México.*

^c*Institute of Chemical Research of Catalonia (ICIQ), E-43007, Tarragona, Spain*

^d*ICREA. Barcelona. E-80810. Spain.*

Experimental details

TiO₂ cell: For optimized cell efficiencies, devices were made using 13 μm thick films consisting of a layer of 9 μm of 20 nm TiO₂ nanoparticles (Dyesol© paste) and a layer of 4 μm of 400 nm TiO₂ particles (scatter layer).¹ Prior to the deposition of the TiO₂ paste the conducting glass substrates were immersed in a solution of TiCl₄ (40 mM) for 30 minutes and then dried. The TiO₂ nanoparticle paste was deposited onto a conducting glass substrate (Hartford Glass inc. with 15 Ω cm⁻² resistance) using the screen printing technique. The TiO₂ electrodes were gradually heated under an airflow at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min and 500 °C for 15 min. The heated TiO₂ electrodes were immersed again in a solution of TiCl₄ (40 mM) at 70 °C for 30 min and then washed with ethanol. The electrodes were heated again at 500 °C for 30 min and cooled before dye adsorption. The DSSC active area was 0.16 cm². The counter electrode was made by spreading a 10 mM solution of H₂PtCl₆ in ethanol onto a conducting glass substrate with a small hole to allow the introduction of the liquid electrolyte using vacuum, followed by heating at 390 °C for 15 minutes. A batch of solutions of the dye at concentrations of 300 mM in ACN:ter-butanol was prepared and the film immersed at 4 °C overnight. The sensitized electrodes were washed with ACN and dried under air. Finally, the working and counter electrodes were sandwiched together using a thin thermoplastic (Surlyn) frame that melts at 100 °C. The electrolyte used consisted of 1 M buthyl-methyl imidazolium iodide (BMII), 0.05 M lithium iodide, 0.03 M iodine, 0.1 M guanidinium thiocyanate (GNCS) and 0.5 M tert-butylpyridine in a mixture of acetonitrile/valeronitrile (85:15).

The photovoltaic measurements were carried out with a 150W solar simulator from ABET© Technologies with the appropriated set of filters for the correct simulation of the 1.5 AM G solar spectrum. The incident light power was measured to be 1000 W/m² with a calibrated Silicon photodiode. The applied potential and cell current were measured with a Keithley 2400 digital source meter. Current versus voltage (I–V) curves were measured automatically with home-built Labview©

software. Incident photon to current conversion efficiency (IPCE) measurements were carried out with a home made set up, consisting in a 150 W Oriel Xenon lamp, a motorized monochromator and a Keithley 2400 digital source meter. An integrating sphere was employed in order to provide homogeneous monochromatic light distribution over the active area of the devices. In addition, photocurrent and irradiated light intensity were measured simultaneously.

ZnO cell: The dye-sensitized ZnO photoanodes used in this work² were fabricated on fluorine-doped tin-oxide-coated glass substrates (TEC15, Pilkington). Thin continuous ZnO blocking layers were deposited from a zinc acetate solution (0.1 M Zn [C₂H₃O₂]₂·2H₂O, 0.2 M C₂H₄O₆ in 25:75 (v/v) water/ethanol mixture) by spray pyrolysis. During deposition the substrate was held at ~ 350 °C. The precursor was sprayed in 15 consecutive 2 second bursts with a pause between each burst of 8 seconds³⁰. The ZnO paste for the semiconductor electrodes was prepared by mixing Evonik VP AdNano@ZnO20 (approximate nanoparticle size of 20 nm) and PI-KEM (approximate nanoparticle size of 50 nm) in 1:1 proportion. The nanopowder mixture was dispersed in water and ethanol (30:70) and stirred overnight to obtain a colloidal suspension of 30 wt%. For thin film preparation the suspension was spread onto the substrate with a glass rod using Scotch tape as spacer. The resulting film was then heated at 420°C for 30 minutes. The film thickness after sintering was around 8 μm and the active area of the cells was 0.64 cm². The films were immersed in an ethanolic solution 0.5 mM of the Ru-based dye known as N719 (Solaronix) for one hour. The photoanodes were then rinsed with the same solvents used for sensitization. Platinized counter electrodes were fabricated on TEC8 electrodes (Pilkington) by spreading 15 μl of Platisol (Solaronix) and subsequent annealing at 400°C for 5 min. Two small filling holes were previously drilled in the FTO glass. Photoanodes and counter electrodes were sealed together in a sandwich configuration using a hot-melt polymer (Solaronix, SX1170-25). The space between the electrodes was vacuum filled with the electrolyte. The electrolyte solution employed was 0.5 M LiI, 0.05 M I₂ and 0.5 M TBP in 3-methoxypropionitrile.

The ZnO devices were characterized using a solar simulator with AM1.5G filter (ABET). A reference solar cell with temperature output (Oriel, 91150) was used for calibration. Photocurrents, photovoltages, current-voltage curves and impedance spectra were carried out by means of an Autolab/PGSTAT302N station (Ecochemie) coupled with a FRA2 frequency generator module. EIS measurements were performed using a 10 mV perturbation in the 10⁻²-10⁵ Hz range. Zview equivalent circuit modeling software (Scribner) was used for fitting impedance spectra, including the distributed element DX11 (transmission line model).^{3,4} In the V_{oc} -lnI experiments, the intensity of the light was varied using Schott NG neutral density filters.

Numerical equivalence in the steady-state between the free density and the total density description

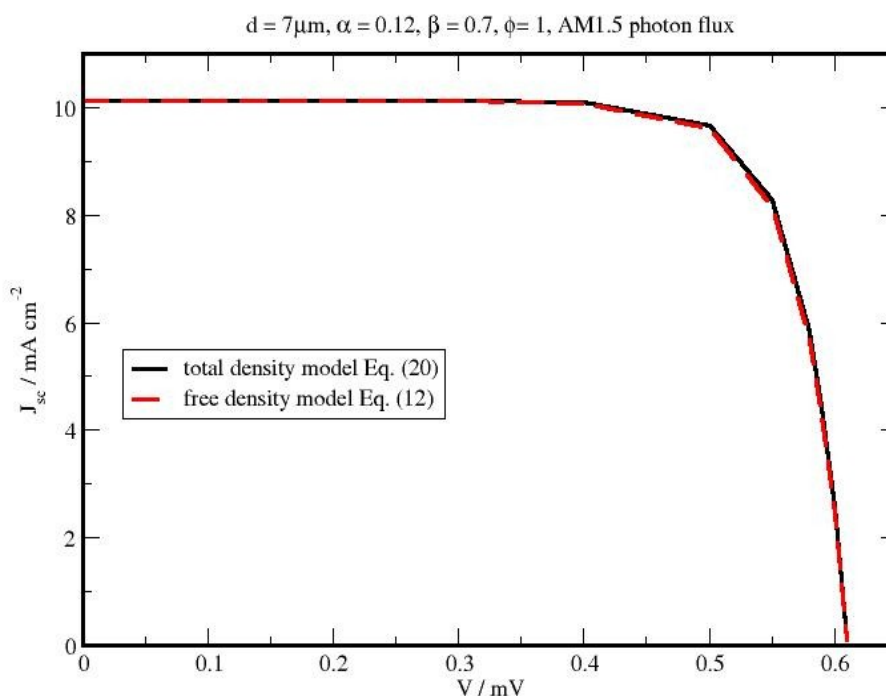


Figure S1. Simulation of the steady-state IV curve (with no series resistance) for the ZnO solar cell studied in the main text. Results for the total-density model (Eq. (20) in the main text) and the free density model (Eq. (12) in the main text) are shown. In both models, the dye loading and the recombination constant were adjusted to reproduce the short-circuit photocurrent and the open-circuit photovoltage, respectively. In both cases the calculation was carried out according to a recombination parameter of $\beta = 0.7$

Table S1. Correspondence between quantities in free and total electron density models

Term in continuity equation	Free electron density model: Eq. (14)	Total electron density model: Eq. (17)
Recombination	$k_0 n_c^\beta$	$k_n(n) = k_0 \frac{N_c^\beta}{N_t^{(\beta/\alpha)}} n^{(\beta-\alpha)/\alpha}$
Diffusion	$D_0 \frac{\partial^2 n_c(x, t)}{\partial x^2}$	$\frac{\partial}{\partial x} \left[D_n(n(x)) \frac{\partial n(x, t)}{\partial x} \right]$
Generation	Eq. (13)	Eq. (13)
Accumulation of electrons	$\frac{\partial n_c}{\partial t}$	$\frac{\partial n}{\partial t}$

Impedance Spectroscopy results for TiO₂

Impedance spectroscopy in the dark was used to extract the α and β parameters required for the model. In Figure S2 typical EIS spectra in the dark are shown. In Figure S3 the capacitance and the recombination resistances extracted from fittings of the spectra to the transmission model are plotted versus the applied voltage. Fittings to Eqs. (33) and (34) give $\alpha = 0.2$ and $\beta = 0.6$ respectively. See Refs⁵ for details. In Ref.² details for the impedance study of ZnO cells can be found.

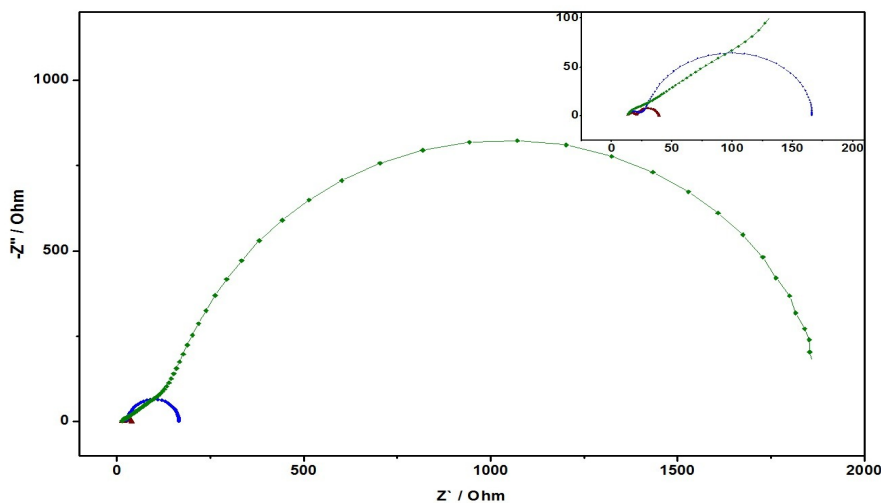


Figure S2. Nyquist plots for impedance spectroscopy measurements in the dark for the TiO₂-based DSC studied in this work. Data shown correspond to 600 mV (green), 700 mV (blue) and 800 mV (red).

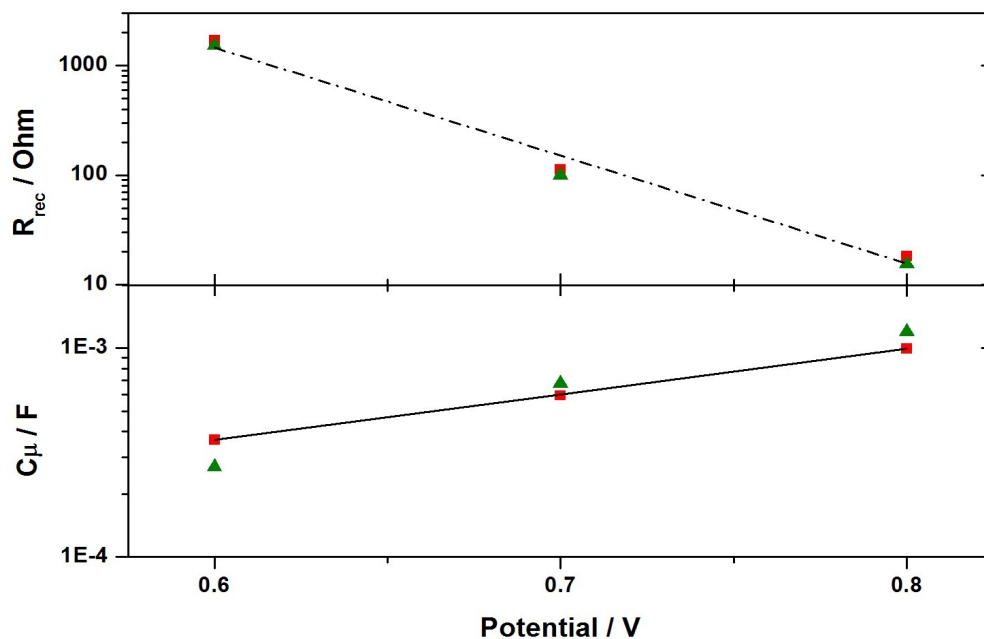


Figure S3. Recombination resistance (top) and chemical capacitance (bottom) as obtained from the impedance study of two TiO₂ cells studied in this work. Solid and dotted lines stand for fittings to Eqs. (33) and (34).

References

1. A. Reynal, A. Forneli, and E. Palomares, *Energy Environ. Sci.*, 2010, **3**, 805–812.
2. E. Guillén, L. M. Peter, and J. A. Anta, *J. Phys. Chem. C*, 2011.
3. J. Bisquert, *The Journal of Physical Chemistry B*, 2002, **106**, 325–333.
4. F. Fabregat-Santiago, J. Bisquert, G. Garcia-Belmonte, G. Boschloo, and A. Hagfeldt, *Solar Energy Materials and Solar Cells*, 2005, **87**, 117–131.
5. J. Navas, E. Guillén, R. Alcántara, C. Fernández-Lorenzo, J. Martín-Calleja, G. Oskam, J. Idígoras, T. Berger, and J. A. Anta, *The Journal of Physical Chemistry Letters*, 2011, **0**, 1045–1050.