SOLID-STATE SOLAR CELL BASED ON DYE SENSITIZED TiO$_2$/SnO$_2$: STUDY BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Regenerative dye-sensitized TiO$_2$ photoelectrochemical cells have been largely investigated in the last decade. The low cost production and good efficiency for energy conversion, reaching 10 %, make such devices a promising alternative for a new generation of solar cells [1-3]. Several techniques were used for understanding the processes involved in the working mechanism of such solar cells, including frequency resolved techniques like Electrochemical Impedance Spectroscopy (EIS), intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) [4, 5].

We are using EIS for investigating a *solid-state* version of regenerative dye-sensitized TiO$_2$ solar cells. These cells are assembled using a polymeric electrolyte based on the elastomer poly (epichlorohydrin-*co*-ethylene oxide), *Epichlomer-16* (Daiso Co. Ltd., Japan) [6, 7]. The best efficiency for energy conversion (η) that we have obtained was η = 2.6 % under 10 mWcm^2 (η = 1.6 % under 100 mWcm^{-2}). In spite of the lower performance, the substitution of a liquid electrolyte by a polymeric one is an advantage for such devices, preventing leakage and/or evaporation of the solvent. This contribution reports on the preparation of a regenerative TiO$_2$ / SnO$_2$ dye sensitized solar cell assembled with a polymer electrolyte and its investigation by EIS.

The TiO$_2$ / SnO$_2$ electrode was prepared by spreading aqueous suspensions of TiO$_2$ and of SnC$_2$O$_4$ onto a transparent SnO$_2$(F) electrode, followed by heating at 450 ℃. The porous electrode was sensitized with c*is*-[(dcbH$_2$)$_2$Ru(SCN)$_2$], where dcbH$_2$ = 4,4 -(CO$_2$H$_2$)-2,2 -bipyridine. A film of the polymer electrolyte was deposited by casting, using a solution of *Epichlomer-16* + NaI + LiI + I$_2$ in acetone. The assembly of the solid solar cell was obtained by pressing the CE:

(Glass) SnO$_2$:F | (TiO$_2$ / SnO$_2$)-dye || Epichlomer + NaI + LiI + I$_2$ || Pt | ITO (glass)
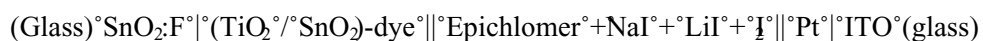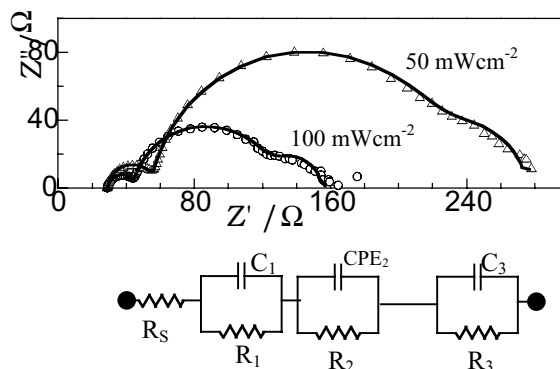
The performance of the cell was investigated employing a Xe lamp and cut off filters to avoid IR and UV radiation; the light intensity was varied using neutral density filters. Current-voltage curves revealed that under 10 mWcm^{-2}, the cell presented an open circuit potential V$_{OC}$ = 0.68 V, a short-circuit photocurrent I$_{SC}$ = 0.19 mAcm^{-2}, fill-factor ff = 0.65 and conversion efficiency η = 0.85 %. Under 100 mWcm^{-2}, V$_{OC}$ = 0.75 V, I$_{SC}$ = 1.83 mAcm^{-2} ff = 0.53 and η = 0.72 %. The performance of the cell can be considered reasonable for a *solid-state* version of the dye-sensitized solar cell, but was lower than the best results that we have obtained using a porous electrode consisting of only TiO$_2$ [7].

The EIS measurements were obtained by applying sinusoidal perturbations of – 5 mV over the V$_{OC}$, at frequencies from 10^5 to 0.02 Hz. Under illumination, the Nyquist diagram exhibited three semicircles, which depended on the intensity of illumination. In the dark, the system presented high impedance and the time constants were not well defined. Analysis using Boukamp software revealed that three parallel RC circuits in series, plus a resistance R$_S$, fit the impedance spectra.

A constant phase element (CPE) was used in substitution of C_2, and accounts for a *non-ideal* frequency dependent capacitance. In the Figure, experimental spectra were represented by symbols, and curves were obtained by fitting the spectra with the equivalent circuit. The resulting parameters are in Table.

Association of the elements of an equivalent circuit with the interfaces of the system is not straightforward, because dye-sensitized solar cells are complex systems consisting of several interfaces. To simplify the analysis, the porous electrode was considered as an ensemble of a network of particles of $TiO_2/°SnO_2$.

I_O/mWcm^{-2}	χ^2/(10^{-4})	R_S/Ω	R_1/Ω	C_1/μF	R_2/Ω	CPE_2/mFs^{n-1}	n	R_3/Ω	C_3/mF
100	2.4	29	15	17	84	0.85	0.89	28	48
50	3.0	29	26	17	175	0.73	0.92	45	36
10	5.6	30	46	17	700	0.50	0.93	78	29
dark	2.2	29	47	21	4.3×10^{-4}	0.0077	0.84	4.3×10^6	0.012

Since the measurements were performed at open circuit conditions, a high electron accumulation must be expected in the cell because photoinjected electrons were not extracted at the electrode contact [4, 5]. Thus, the capacitance associated with the semicircle verified at high frequencies, C_1, cannot be attributed to the interface between porous film and electrolyte. Also, C_1 behavior with light intensity would not be expected at the $Pt°|°$electrolyte interface, since concentration of I_3^- species in the CE may depend on light intensity. Thus, C_1 may be associated to the $SnO_2:F°|°TiO_2/SnO_2$ interface, and its small and constant value ($17°\_Fcm^{-2}$) is quite reasonable for the capacitance of the semiconductor $SnO_2:F$ film. Both the other two RC elements, related to the medium and low frequency responses, exhibited high capacitance that depended on light intensity. R_2CPE_2 can be associated to the $TiO_2/SnO_2°|°$electrolyte interface, where an accumulation of electrons and redox species is expected. At low frequencies, R_3C_3 elements can be related to the $CE°|°$electrolyte interface. The response of this interface at low frequencies may be related with the low conductivity of the polymeric electrolyte and the reduced mobility of I_3^- in such medium [7]. Finally, impedance spectra demonstrated the reasonable conductivity of our polymer electrolyte based on *Epichlomer-16* for application in a solar cell. Despite of the low efficiency exhibited by this regenerative solar cell, it might be used under low illumination conditions, such as indoor, for instance.

References
1. A. Hagfeldt, M. Grätzel, *Chem. Rew.,* **95** (1995) 49.
2. C.J. Barbé, F. Arendse, P. Comte, M. Jirousek, F. Lenzmann, V. Shklover, M. Grätzel, *J. Am. Ceram. Soc.* **80** (1997) 3157.
3. S. Pelet, J.-E. Moser, M. Grätzel, *J. Phys. Chem. B*, **104** (2000) 1791.
4. J. van Lagemaat, N.G. Park, A.J. Frank, *J. Phys. Chem. B*, **104** (2000) 2044.
5. G. Franco, J. Gehring, L.M. Peter, E.A. Ponomarev, I. Uhlendorf, *J. Phys. Chem. B*, **103** (1999) 692.
6. A. F. Nogueira and M.-A. De Paoli, *Sol. Energy Mater. Sol. Cells*, **61** (2000) 135.
7. A. F. Nogueira, M.-A. De Paoli, I. Montanari, R. Monkhouse, J. Nelson, J.R. Durrant, *submitted.*