

Optimization of a Quasi-Solid-State Dye-Sensitized Photoelectrochemical Solar Cell Employing a Ureasil/Sulfolane Gel Electrolyte**

By Elias Stathatos, Panagiotis Lianos,* Angela Surca Vuk, and Boris Orel

A quasi-solid-state, dye-sensitized photoelectrochemical solar cell employing a gel electrolyte obtained by sol-gel chemistry is described. The gel electrolyte is based on a ureasil precursor (i.e., a poly(propylene oxide) oligomer end-capped by triethoxysilane groups through urea bridges) and sulfolane and it incorporates the I_3^-/I^- redox couple. It is shown that the combination of these two reagents prevents crystallization of KI, thus ensuring a long life for the cell and a satisfactory overall efficiency that surpasses 5%. Cell efficiency increases with temperature. Optimization of gel-electrolyte performance has been obtained by studying mobility with fluorescence-quenching techniques complemented by direct-current conductivity measurements.

1. Introduction

Dye-sensitized photoelectrochemical solar cells (DSPECs) are considered as the most promising low-cost option for the photovoltaic conversion of solar energy. Since the original model cell reported in 1991 by O'Regan and Grätzel,^[1] an ever-growing interest has been demonstrated by scientists of different disciplines so that a vast knowledge on these systems has already been accumulated. As a consequence, a more or less standard configuration of DSPECs has been established, as described in the multilayer structure appearing in Figure 1A. The functional components are sandwiched between two fluorine-doped tin oxide electrodes (FTO, $SnO_2:F$). A thin mesoporous TiO_2 film is deposited on the negative electrode. A dye-sensitizer is adsorbed and covalently bound on TiO_2 nanoparticles, typically *cis*-di(thiocyanato)-*N,N*-bis(2,2'-bipyridyl-4,4'-dicarboxylic acid)ruthenium(II) dihydrate $[RuL_2(NCS)_2] \cdot 2H_2O$.^[2] The counter electrode consists of FTO with thermally deposited Pt. Finally, the space between the TiO_2 /dye surface and counter electrode is filled with an electrolyte that typically contains the I_3^-/I^- redox couple, that makes a convenient combination with TiO_2 and $[RuL_2(NCS)_2] \cdot 2H_2O$.^[3,4] The overall efficiency of a DSPEC employing a liquid electrolyte is around 10%,^[2] that is, better than commercial photovoltaic cells based on amorphous silicon. However, some concern has been expressed recently as to the long-term stability of this type of DSPEC, owing to long-term sealing problems or solvent endurance against photochemical degradation. For this reason, an effort has been made to substitute liquid-electrolyte

cells by quasi-solid-state constructions. One such approach has been adopted by us, by proposing nanocomposite organic/inorganic gels, deposited by sol-gel chemistry, as hosts of the I_3^-/I^- redox couple.^[5-7] These materials gave a substantial improvement of the concept of the dye-sensitized solid-state solar cell (DSSC). DSSCs employing a gel electrolyte have a lower overall efficiency than liquid-electrolyte DSPECs, due to restrictions in ionic mobility. However, the advantages they offer compensate for the lower ionic conductivity. In this respect, and in order to obtain an appreciable ionic conductivity, it is necessary that the nanocomposite gel provides a percolating ion-conducting organic subphase and this is facilitated when a solvent is incorporated into the gel. The I_3^-/I^- redox couple is usually obtained by co-dissolving an iodide salt with iodine. A rather limited number of organic solvents containing polar functional chemical groups (for example, propylene carbonate, acetonitrile, etc.) can simultaneously dissolve an alkaline iodide salt and iodine. However, no solvent can be equally good for both substances, and for this reason crystallization, for example, of KI, has been a major source of deterioration of the cell. One approach to solve this problem is to use ionic liquids, for example alkylimidazolium iodides,^[8,9] which have low melting points and are liquids at normal temperatures. This approach has been very successful. However, it is not unique. We have recently studied combinations of nanocomposite gels with different functional solvents and searched for the "ideal" solvent for the KI/I_2 couple, which would be immune to the above problems and offer DSSCs with maximum efficiency and stability. We have thus found very encouraging results by combining ureasil gels with sulfolane. Cells made in this manner are stable and efficient, and are even more efficient when working at elevated temperatures.

2. Results and Discussion

The cells have the standard configuration shown in Figure 1A. The I_3^-/I^- gel electrolyte was synthesized using sol-gel chemistry and a ureasil precursor composed of a short poly-

[*] Prof. P. Lianos, Dr. E. Stathatos
Engineering Science Department, University of Patras
GR-26500 Patras (Greece)
E-mail: lianos@upatras.gr

Prof. B. Orel, Dr. A. Surca Vuk
National Institute of Chemistry
Hajdrihova 19, SLO-1001 Ljubljana (Slovenia)

[**] This work was supported by the following research grants: "K.KAPA-ΘEOΔΩPHΣ" of the University of Patras and the Greece-Slovenia Bilateral R&T Cooperation Program.

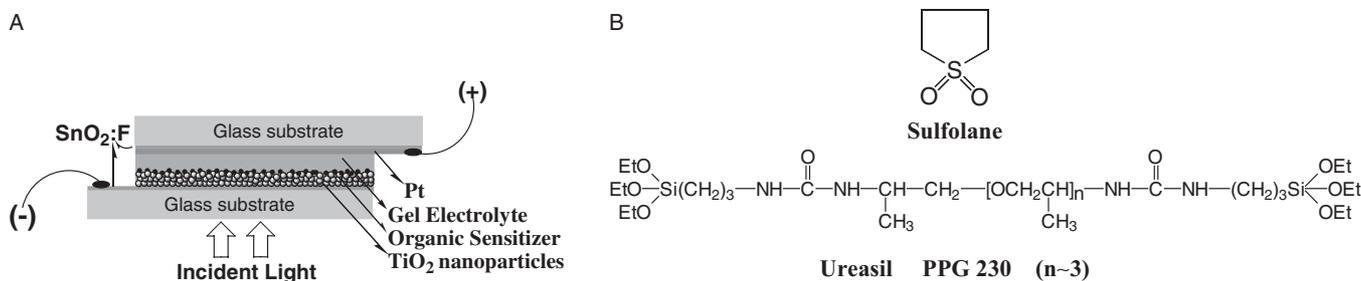


Figure 1. A) Standard configuration of DSPECs. B) Chemical structure of sulfolane and PPG-230 ureasil.

(propylene oxide) chain and two ethoxysilane end-groups bound by urea bridges (abbreviated PPG-230, see Fig. 1B for chemical structures of ureasil and sulfolane). Ureasil was mixed with various solvents, acetic acid and KI/I₂ and the gel was deposited as a thin film on glass slides. As usually happens with complex materials, the multitude of components creates a very large number of combinations that may lead the study away from the optimal conditions that are being sought. For this reason, we adopted a KI/I₂ content that has been proven successful in previous work, i.e., 0.5 M KI and 0.05 M I₂.^[6] These films were studied using scanning electron microscopy (SEM). Many solvents, for example propylene carbonate, acetonitrile, and mixtures of propylene and ethylene carbonate, produced films that clearly contain crystallites, as seen in Figure 2A. These crystallites were identified by in-situ elemental analysis as KI. However, nanocomposites made from ureasil and solvents such as propanediol, butanediol, poly(ethylene glycol) oligomers, and sulfolane did not reveal any crystallite formation (cf. Fig. 2B). The latter solvents were therefore judged appropriate for making DSSCs. However, only sulfolane was capable of offering cells with satisfactory photovoltaic efficiency and a long life. As a consequence, sulfolane was chosen as the “ideal” solvent for this application.

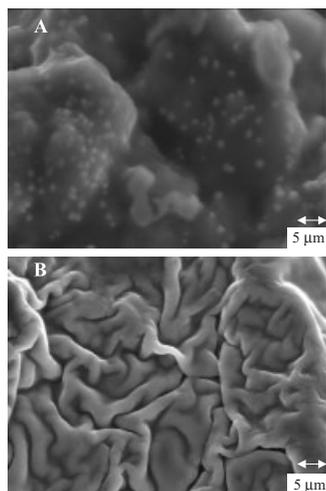


Figure 2. SEM images of nanocomposite films containing 0.5 M KI and 0.05 M I₂, made of ureasil and propylene carbonate (A), or ureasil and sulfolane (B). Both films present a rough surface. The film in (A) contains KI crystallites, as determined by in-situ elemental analysis.

The next step was to decide what proportion of ureasil and sulfolane would lead to optimal cell function. Since ionic conductivity is the basic criterion for this purpose, we studied gels made of ureasil and sulfolane by the following procedure. Ionic conductivity in a gel necessitates formation of a percolation cluster for the ion-conducting organic sub-phase. We employed time-resolved fluorescence probing to determine percolation by incorporating a fluorophore (pyrene) and a quencher (coumarin-153), both of which probe the organic sub-phases. By fitting the fluorescence decay profiles to a model of stretched exponentials, we obtained the non-integer exponent f , which is a measure of the restrictions imposed by the hosting material on probe mobility:^[5,10]

$$I(t) = I_0 \exp(-t/\tau_0) \exp[-C_1(t/\tau_0)^f + C_2(t/\tau_0)^2] \quad (1)$$

where $0 < f < 1$, C_1 and C_2 are fitted parameters and τ_0 is the decay time of pyrene in the absence of quencher. f is larger in less-restricted domains and it theoretically takes values ≥ 0.67 at and above the percolation threshold.^[11] The obtained values of f are plotted against the ureasil/sulfolane ratio in Figure 3. Curves are shown for four different temperatures ranging between 10 and 70 °C. The maximum probe mobility was obtained for a ureasil/sulfolane weight ratio equal to 0.35. Interestingly, the f values were found to be lower at higher temperature, which means that the reaction domain is a little more restricted at higher temperature. This is translated as a structural modification of the organic sub-phase with temperature. Apparently, in spite of the fact that the gel is solid, its organic sub-phase demonstrates a dynamic behavior, thereby providing functionality. The data of Figure 3 are complemented by dark DC conductivity measurements (measurements taken whilst light was excluded) on films containing KI and I₂ at the above-mentioned concentrations. Direct-current (DC) ionic conductivity measurements may, in some cases, be problematic because of polarization and continuous current decrease. In our case, after a current drop of about 15 % following application of the electric field, the current stayed constant. The dark DC conductivity values are plotted against ureasil/sulfolane weight ratio in Figure 4; all values were recorded after current stabilization. The results show an impressive similarity with the data of Figure 3. Not only do these data define the composition of choice (ratio of ureasil/sulfolane = 0.35) in an unequivocal manner, but they also promote the luminescence-quenching

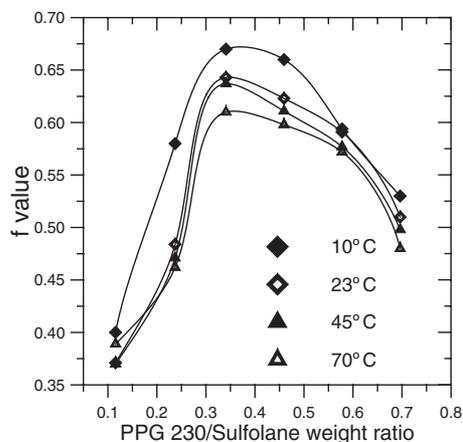


Figure 3. Non-integer exponent f -values at different temperatures versus gel composition: Pyrene concentration 1 mM. Coumarin-153 concentration varied between 2–5 mM. Measurements were made on films obtained by dip-coating sol on glass slides.

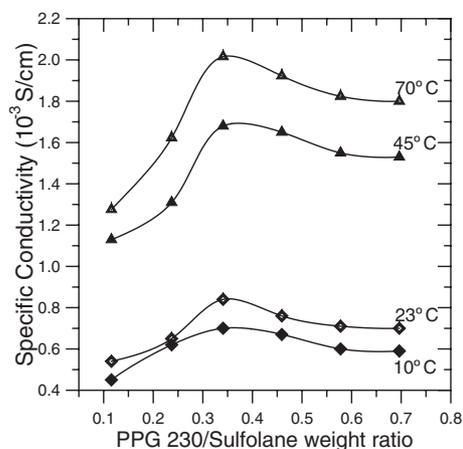


Figure 4. Dark DC conductivity values at various temperatures versus gel composition. Measurements were made on films sandwiched between two $\text{SnO}_2\text{:F}$ electrodes. Sol contained 0.5 M KI and 0.05 M I_2 .

procedure as a powerful tool for studying mobility in these complex systems. In this respect, it must be stressed that the position of the maximum at a given temperature is best described by fluorescence probing data than DC conductivity data, since the position of the maximum is sharper in Figure 3. In these instances it is a good idea to use both techniques.

Having determined the optimal gel composition we proceeded with the construction of solar cells and measured their efficiency at different temperatures. I - V curves are shown in Figure 5, while short-circuit current (I_{sc}), open-circuit voltage (V_{oc}) and overall efficiency (η) are tabulated in Table 1. As expected, the short-circuit current is highest at the highest temperature, in accordance with the conductivity data (cf., Fig. 4). The open-circuit voltage drops from 10 to 23 °C and thereafter decreases only slightly, meaning that it can be considered practically constant. A V_{oc} drop with increasing temperature has been detected and analyzed previously,^[12] and it is considered

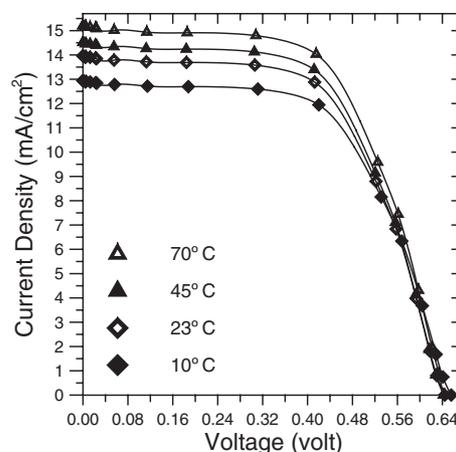


Figure 5. I - V curves for cells made with ureasil/sulfolane gel electrolyte at different temperatures.

Table 1. Values of short-circuit current, I_{sc} , open-circuit voltage, V_{oc} , and overall efficiency η for the cells employing a ureasil/sulfolane gel electrolyte at different temperatures.

T [°C]	I_{sc} [mA cm^{-2}]	V_{oc} [V]	η [%]
10	12.9	0.65	4.8
23	13.9	0.64	5.3
45	14.5	0.64	5.4
70	15.2	0.64	5.5

to be a complex function of the semiconductor Fermi level and electrolyte redox potential as well as the recombination rates of the electron-hole couples. The efficiency of the cell increased with temperature, although the variation is small in the range 23–70 °C, and it reached high values, ≥ 5.3 %, which is a very encouraging value for a quasi-solid-state cell.

An obvious question to ask for the above system is: what makes sulfolane a better component of the cell than other solvents of the same type? Sulfolane, also known as tetramethylene sulfone, is a high dielectric constant (43.16),^[13] non-protic solvent, which is a good solvent for both KI and I_2 . In addition, it has a high boiling point and a relatively high melting point (285 and 27 °C, respectively). It has been previously used as a plasticizer, in combination with high-molecular-weight poly(ethylene oxide), to make a gel electrolyte.^[14] In our system, gels of pure non-protic solvents, such as sulfolane, propylene carbonate, poly(ethylene glycol)-200, acetonitrile, etc., containing KI, I_2 , and mixtures of KI/ I_2 have been studied by UV-vis spectroscopy to determine the relative ratios of I^- , I_3^-/I^- , and I_2 by their characteristic absorption peaks around 220 (I^-), 300/360 (I_3^-), and 500 nm (I_2).^[15] Sulfolane and propylene carbonate distinguish themselves from the other solvents because they offer a balanced proportion of I^- and triiodide ion, while no I_2 is detected in these solvents. Figure 6 shows the absorption of two gel films containing ureasil and sulfolane or ureasil and

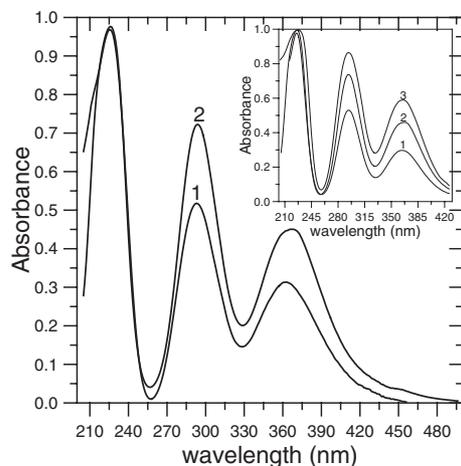


Figure 6. Absorption spectra of films made of ureasil and propylene carbonate (1) or ureasil and sulfolane (2). Both films contained 0.5 M KI and 0.05 M I₂, as measured in the original sol. Inset: Absorption spectra of the film containing sulfolane: fresh sample (1), after 5 h (2), after 5 days (3). All spectra have been normalized to the short wavelength peak.

propylene carbonate, both enriched with KI/I₂ at a molar ratio of 10/1. These spectra were recorded with freshly prepared samples. However, in a matter of hours we observed a deterioration of the films containing propylene carbonate, detected by either SEM or by cell performance, while those made with sulfolane were stable for months. As can be also seen in Figure 6, in the presence of sulfolane the relative quantity of triiodide ion increases with time. Obviously, the strong electron-donor properties of sulfolane (cf., Fig. 1) make this solvent favor triiodide formation.^[15] This is very important for the functioning of the cell since I₃⁻ is the main ionic conductivity vehicle through the cathodic dark reaction I₃⁻ + 2e⁻ → 3I⁻ on the counter electrode. Furthermore, the high boiling point of sulfolane keeps it from evaporating, while its plasticizing properties offer gels with excellent mechanical properties for the present application. These properties of sulfolane make it an excellent solvent for use in DSSCs.

3. Conclusions

Nanocomposite gel electrolytes made by the sol-gel method and incorporating the redox couple I₃⁻/I⁻ have been successfully employed with dye-sensitized solar cells, providing an overall efficiency higher than 5%. The gel electrolyte was made of ureasil and sulfolane, the solvent being necessary in order to obtain a substantial efficiency. The sol-gel procedure was catalyzed in the presence of acetic acid. However, gelation is mainly due to ambient humidity. The gel electrolyte is a dry gel and acts as a gluing substance that holds the parts of the cell together so that the whole structure can be considered as a quasi-solid-state cell. The optimal ratio of ureasil and sulfolane was determined by using dark DC conductivity and time-resolved fluorescence-quenching techniques, the latter proving to be a powerful tool to study nanocomposite gels.

4. Experimental

All reagents were purchased from Aldrich, except *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II) [RuL₂(NCS)₂], which was provided by Solaronix SA (Switzerland). SnO₂:F transparent conductive electrodes (8 Ω/square) were purchased from Hartford Glass Co., USA.

The ureasil precursor was synthesized by standard procedures as in previous publications [6,10]. TiO₂ film deposition and dye adsorption was done as in previous publications [5,6]. On top of the TiO₂/dye film we cast one drop of the sol, leading to a gel electrolyte. Then, a platinumized SnO₂:F electrode was placed on the top and squeezed against the titania electrode by hand. The two electrodes stuck together and the cell was ready to be used after one hour waiting time under ambient conditions. This time is sufficient for silica bonds to develop and hold the cell together. The sol was made by mixing ureasil and sulfolane at different proportions, at temperatures ranging between 27 and 30 °C. To 4 g of the mixture we added 0.7 g of glacial acetic acid which acts as a catalyst of the sol-gel process [6]. Gelling was essentially caused by environmental humidity. The fluorescence probe and quencher, as well as KI/I₂, were introduced by previous solubilization in sulfolane.

I-*V* curves were recorded by connecting the cell to an external variable resistor and measuring the current flowing through the resistor and the corresponding voltage across the resistor. The cell dimension for these measurements was 1 cm². Illumination was done by an Oriel 450W Xenon lamp. The illumination intensity was 100 mW cm⁻². Outdoors experiments using natural sunlight (performed in Patras, Greece) gave similar results with simulated light of equivalent intensity. Dark DC conductivity measurements were made by sandwiching the Ureasil/sulfolane/I₃⁻/I⁻ gel between two SnO₂:F slides and applying a 0.5 V electric tension. Time-resolved luminescence decay profiles were recorded with a single-photon-counting technique using an IBH nanosecond hydrogen flash lamp and ORTEC electronics. SEM images were obtained with a Jeol JSM 6300 microscope equipped with an EDS detector for elemental analysis (Oxford). UV-vis absorption measurements were made with a Cary 1E spectrophotometer. Temperature control in all cases was obtained by using water thermostated cell holders.

Received: April 21, 2003
Final version: July 22, 2003

- [1] B. O'Regan, M. Grätzel, *Nature* **1991**, 353, 737.
- [2] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Muel-ler, P. Liska, N. Vlachopoulos, M. Graetzel, *J. Am. Chem. Soc.* **1993**, 115, 6382.
- [3] A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, 95, 49.
- [4] G. Sauve, M. E. Cass, G. Coia, S. J. Doig, I. Lauermaun, K. E. Pomy-kal, N. S. Lewis, *J. Phys. Chem. B* **2000**, 104, 6821.
- [5] E. Stathatos, P. Lianos, C. Krontiras, *J. Phys. Chem. B* **2001**, 105, 3486.
- [6] E. Stathatos, P. Lianos, U. Lavrencic-Stangar, B. Orel, *Adv. Mater.* **2002**, 14, 354.
- [7] U. Lavrencic-Stangar, B. Orel, B. Neumann, E. Stathatos, P. Lianos, *J. Sol-Gel Sci. Technol.* **2003**, 26, 1113.
- [8] N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhote, A. Petter-sson, A. Azam, M. Grätzel, *J. Electrochem. Soc.* **1996**, 143, 3099.
- [9] G. R. A. Kumara, A. Konno, K. Shiratsuchi, J. Tsukahara, K. Tenna-kone, *Chem. Mater.* **2002**, 14, 954.
- [10] E. Stathatos, P. Lianos, U. Lavrencic-Stangar, B. Orel, P. Judeinstein, *Langmuir* **2000**, 16, 8672.
- [11] a) R. Rammal, G. Toulouse, *J. Phys. Lett.* **1983**, 44, L13. b) S. Alexan-der, R. Orbach, *J. Phys. Lett.* **1982**, 43, L625.
- [12] G. Kron, T. Egerter, G. Nelles, A. Yasuda, J. H. Werner, U. Rau, *Thin Solid Films* **2002**, 403-404, 242.
- [13] L. Jannelli, M. Pansini, *J. Chem. Eng. Data* **1985**, 30, 428.
- [14] S. Ozer, J. Jovorniczyk, C. A. Angell, *J. Electrochem. Soc.* **2002**, 149, A87.
- [15] Z. Kebede, S.-E. Lindquist, *Sol. Energy Mater. Sol. Cells* **1999**, 57, 259.