Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Photochemistry and Photobiology A: Chemistry 164 (2004) 23–27

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Coordinative interactions in a dye-sensitized solar cell

Helena Greijer Agrell [a], Jan Lindgren [b], Anders Hagfeldt [a,*]

[a] Department of Physical Chemistry, University of Uppsala, P.O. Box 579, SE-75123 Uppsala, Sweden
[b] The Ångström Laboratory, Department of Material Chemistry, University of Uppsala, P.O. Box 538, SE-75121 Uppsala, Sweden

Received 11 November 2003; accepted 2 December 2003

Abstract

Resonance Raman scattering studies of a complete dye-sensitized solar cell (DSC) including iodine and lithium iodide in the electrolyte indicate that triiodide (I_3^-) exchange the SCN^- ligand of the dye bis(tetrabutylammonium) *cis*-bis(thiocyanato)bis(2,2′-bipyridine-4-carboxylic acid, 4′-carboxylate)ruthenium(II). The choice of cation in the iodide salt influenced the ligand stability of the dye. It was proposed that an ion pair $Li^+ \cdots I_3^-$ formation occurred which by a reduced electrostatic repulsion between I_3^- and SCN^- facilitated the exchange of these anions at Ru(II) of the dye. The additive 1-methylbenzimidazole (MBI) suppressed the SCN^-/I_3^- ligand exchange by forming a complex with Li^+. The concentrations of Li^+ and MBI have to be carefully balanced due to the SCN^- ligand exchange with MBI in deficiency of Li^+. In order to observe and understand the prevailing coordinative interactions between the components in a DSC, the use of characterization methods with which complete devices can be studied is necessary.

Keywords: Dye-sensitized solar cell; Raman scattering; Ligand exchange; Mesoporous, nanostructured

1. Introduction

The thiocyanate ion ligand in the dye-sensitized solar cell is believed to play an important role in the reduction of the oxidized dye [1]. Photoelectron spectroscopy experiments confirm that both Ru 4d and atomic orbitals centered on the SCN^- ligand, in particular S 3p wave functions, contribute to the frontier orbitals of the complex. Moreover, the SCN^- ligand attached to Ru through the N atom [2] points in the direction of the electrolyte and may facilitate reduction of the oxidized dye by iodide (I^-). At the cathode, the oxidized redox couple (I_3^-) collects an electron from the counter electrode.

In our previous work [3], using resonance Raman scattering (RRS), the amount of thiocyanate ion ligand coordinated to the dye bis(tetrabutylammonium) *cis*-bis(thiocyanato)bis(2,2′-bipyridine-4-carboxylic acid, 4′-carboxylate)ruthenium(II) (referred to as N719) was found to decrease with increased amount of iodine added or triiodide (I_3^-) formed in the electrolyte.

Very recently an article on in situ resonance Raman microscopy of a solid-state dye-sensitized photoelectrochemical cell appeared [4]. The authors found a time dependence of the Raman spectrum under open circuit conditions. The $111\,cm^{-1}$ Raman band from I_3^- was used as a probe band to follow the time dependence. The slower kinetics in this case as compared to earlier studies [3], was explained by the lower conductivity by the solid electrolyte and a less intimate contact in the dye/TiO_2 interface.

In the present work, also using RRS, we focus on coordinative interactions of the different components in a dye-sensitized solar cell and especially Li^+, I_3^-, SCN^- and the additive 1-methylbenzimidazole.

2. Experimental

2.1. Preparation of samples

The samples were prepared in an argon atmosphere glove box as described elsewhere [3]. The additive 1-methylbenzimidazole (Aldrich 99%) was dried over night at 40 °C (hereafter denoted by MBI) before added to the electrolyte. The electrolyte used in this study, consisted of 50 mM iodine (I_2), 500 mM lithium iodide (LiI) and 500 mM MBI in the solvent 3-methoxypropionitrile (hereafter denoted by 3MPN).

---

[*] Corresponding author. Fax: +46-18-47-13654.
E-mail addresses: helena.greijer@fki.uu.se (H. Greijer Agrell), jan.lindgren@mkem.uu.se (J. Lindgren), anders.hagfeldt@fki.uu.se (A. Hagfeldt).

1010-6030/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2003.12.015

2.2. Electrochemical and spectroscopic measurements

The overall light-to-electric energy conversion efficiency measurements were performed with a light drive 1000 lamp (type 1400-E2/1) through an infrared-blocking filter. The light intensity was 100 W m^{-2}.

The Renishaw System 2000 micro-Raman spectrometer equipped with a 514 nm argon laser (25 mW) and a 780 nm diode laser (25 mW) with 2 cm^{-1} resolutions was used in recording the Raman spectra. The solar cell was placed on the microscope stage and with an ultra long working distance 50× objective with 8 mm focal distance it was possible to focus through the glass on the active thin film. A macro-point objective was used to direct and focus the laser on solutions in vials. The scattered radiation was collected in a back scattering geometry. The power of the green laser at the sample surface is about 0.5 mW. The intensity of the laser is about 1×10^8 W m^{-2}. Thus, the solar cells in this work are exposed to a very high intensity of light, which for example, will accelerate light degradation mechanisms compared to normal operational conditions for a cell in solar light where the intensity at AM1.5 is 1000 W m^{-2}. However the solar cells show remarkable stability. In some measurements the solar cells are exposed to the green laser for 2 h without any observed molecular degradation or visible damage. It is noteworthy that the light dose on the solar cell after 2 h exposure to the green laser corresponds to more than 100 years in the sun.

3. Results and discussion

3.1. The thiocyanate ion ligand

As an internal reference for judging intensity differences of the CN stretching band of the SCN$^-$ ion we will use the CN stretching band from the solvent 3MPN and the 1612 cm^{-1} band from the dicarboxybipyridine (dcbpy) group. For an incomplete solar cell (hereafter denoted cell) without I_2 and LiI in the solvent the intensity of the CN stretching band of the SCN$^-$ ligand at 2105 cm^{-1} was higher than the intensity of the solvent nitrile peak at 2250 cm^{-1} (see Fig. 1). For a solar cell with an electrolyte consisting of 50 mM I_2 and 500 mM LiI in 3MPN the CN stretching band of SCN$^-$ has disappeared and we concluded that the SCN$^-$ ligand was no longer part of the dye (see Fig. 2A) [3]. However, from the RRS spectrum of a solar cell with 1-methylbenzimidazole (MBI) added to the electrolyte (Fig. 2C), it was obvious from the presence of the CN stretching band at 2105 cm^{-1} that the SCN$^-$ ligand was to a large extent still coordinated to the dye. The suppressing of the SCN$^-$ loss has been observed earlier with the additive 4-*tert*-butylpyridine (4TBP) (see Fig. 2D) [3] (the smaller band at 2173 cm^{-1} is probably a CN stretching band of the SCN$^-$ ligand coordinated to an electrolyte species).

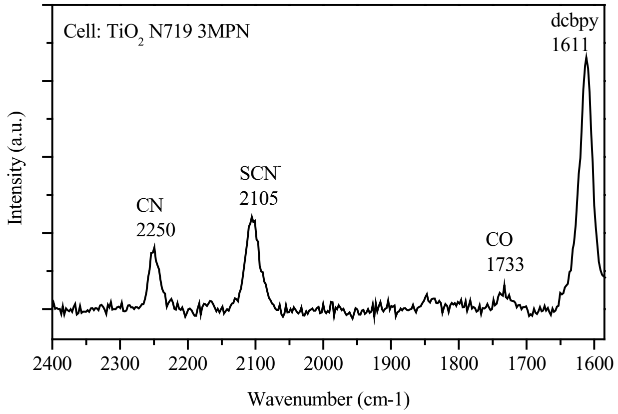

Fig. 1. A Raman spectrum of an incomplete dye-sensitized solar cell (cell) without I_2 and LiI in the solvent 3-methoxypropionitrile (3MPN). The excitation wavelength was 514 nm.

3.2. Interaction between 1-methylbenzimidazole and lithium ions

The additive MBI not only suppresses the loss of the SCN$^-$ ligand in the solar cell. As can be seen from the disappeared CN stretching band of SCN$^-$ in a cell without I_2 and LiI (Fig. 2B), MBI also seems to be able to replace the SCN$^-$ ligand from the dye.

To investigate if the lithium ions played a role in the protection of the SCN$^-$ ligand, a spectrum of a cell with

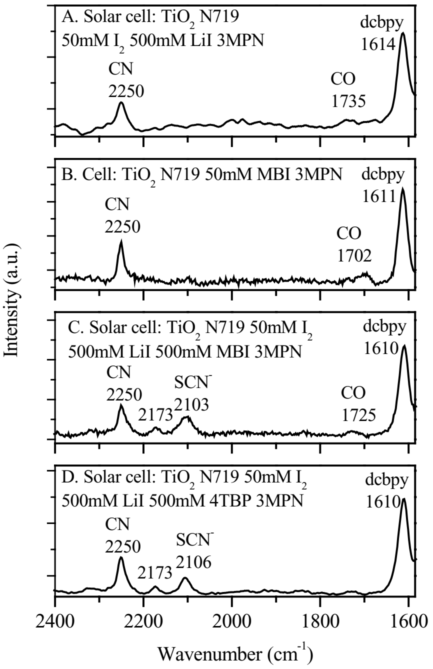

Fig. 2. Raman spectra of dye-sensitized solar cells with 50 mM I_2, 500 mM LiI in (A), 50 mM I_2, 500 mM LiI and 500 mM MBI in (C), 50 mM I_2, 500 mM LiI and 500 mM 4TBP in (D) and cell with 50 mM MBI in (B) in the solvent 3-methoxypropionitrile (3MPN). With 1-methylbenzimidazole denoted MBI and 4-*tert*-butylpyridine denoted 4TBP. The excitation wavelength was 514 nm.

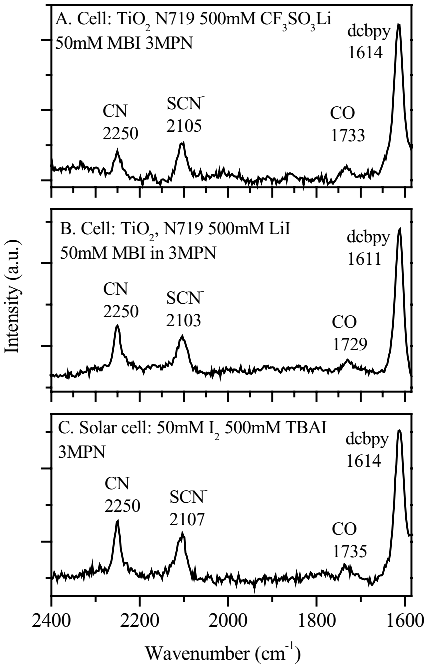

Fig. 3. Raman spectra of dye-sensitized cells with 500 mM CF_3SO_3Li and 50 mM MBI in (A), 500 mM LiI and 50 mM MBI in (B) and solar cell with 50 mM I_2 and 500 mM TBAI in (C) in the solvent 3-methoxypropionitrile (3MPN). Tetrabutylammonium iodide is denoted TBAI. The excitation wavelength was 514 nm.

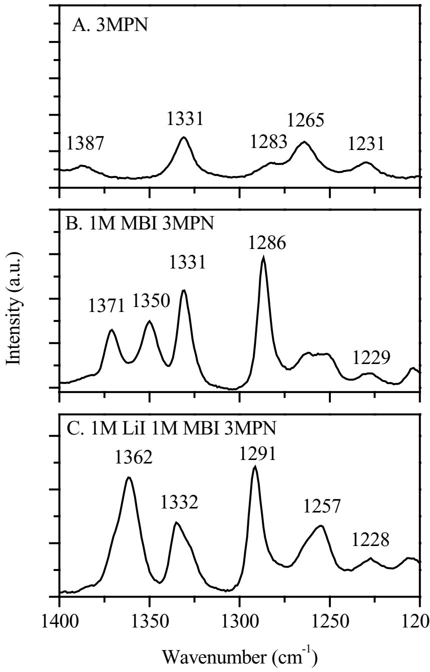

Fig. 4. Raman spectra of solutions (A) the solvent 3-methoxypropionitrile (3MPN), (B) 1 M MBI in 3 MPN and (C) 1 M LiI and 1 M MBI in 3MPN. With 1-methylbenzimidazole denoted MBI. The excitation wavelength was 780 nm.

500 mM lithium trifluoromethanesulfonate (CF_3SO_3Li) and 50 mM MBI was registered (Fig. 3A). When comparing the spectra 3A and 2B it was realized that the lithium ions did prevent the exchange of SCN^- ligands by MBI. The intensity of the CN stretching band from the SCN^- ligand was higher than the CN stretching band of the nitrile group in the solvent (Fig. 3A).

When LiI was added instead of $LiCF_3SO_3$ a CN stretching band from the SCN^- ligand is also seen but with somewhat lower intensity than for $LiCF_3SO_3$. In both cases, we suspected that a complex was formed between the lithium ions and MBI preventing MBI from replacing the SCN^- ligand. Therefore, Raman measurements of two reference solutions 1 M MBI in 3MPN and 1 M LiI, 1 M MBI in 3MPN were made. From Fig. 4, it can be seen that the Raman line at 1350 cm^{-1} from MBI (B) was shifted to 1362 cm^{-1} when LiI was added (C). The Raman line at 1371 cm^{-1} from the MBI (B) is probably seen as a shoulder of the Raman line at 1362 cm^{-1} (C). From this wave number shift it was concluded that Li^+ forms a complex with MBI.

3.3. Interaction between iodine and the thiocyanate ion ligand

In our earlier study it was suggested that a complex between I_2 and SCN^- was formed in the solar cell [3]. This suggestion was done in order to explain the disappearance of the CN stretching band of SCN^- in a solar cell containing LiI and I_2 in the electrolyte. A weak Raman band at 165 cm^{-1} was observed for the solar cell, which, by comparison to an aqueous solution of I_2SCN^- having a band at 160 cm^{-1}, was taken as an indication of the existence of the complex also in the solar cell.

In order to clarify this further we have in the present work made additional experiments now using the solvent 3MPN instead of water. In Fig. 5A, the Raman spectrum of a solution of I_2 and KSCN in 3MPN is shown. The formation

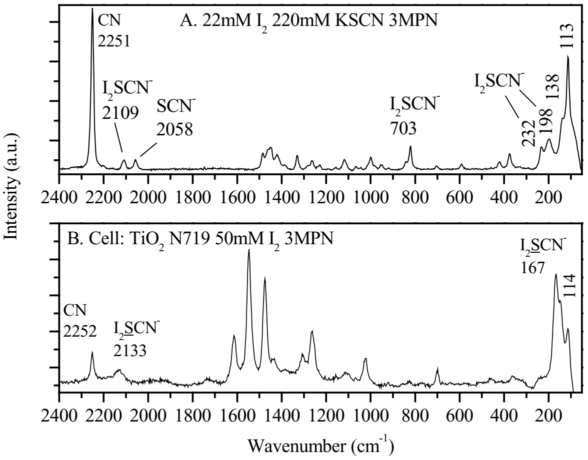

Fig. 5. Raman spectra of (A) a solution of 22 mM I_2 and 220 mM KSCN in the solvent 3-methoxypropionitrile (3MPN) and (B) a dye-sensitized cell with 50 mM I_2. The underline indicates coordination of I_2 to the sulfur atom. The excitation wavelength was 514 nm.

of I_2SCN^- can be seen from the shift in CN stretching frequency to 2109 cm^{-1} as compared to 2058 cm^{-1} in the free (solvated) SCN^- ion. Bands from I_2SCN^- are also seen at 232 and 198 cm^{-1}. However, no band close to 165 cm^{-1} can be seen as observed for the complete solar cell in Ref. [3]. In Fig. 5B, the Raman spectrum is shown from a cell containing the dye on TiO_2 and with I_2 added to the solvent 3MPN. The CN stretching band is now shifted from 2105 cm^{-1} in the pure dye (Fig. 1) to 2133 cm^{-1}, indicating an interaction between I_2 and the SCN^- ligand of the dye. Interestingly enough a strong band at 167 cm^{-1} is now observed. In this case, we know that the nitrogen atom of SCN^- is bonded to Ru(II) in the dye [2] and consequently I_2 has to interact with SCN^- via the sulfur atom. However, in the solution experiment referred to above I_2 has the choice to coordinate either to sulfur or nitrogen. Since, no band close to 167 cm^{-1} is observed in that case we conclude that I_2 is coordinated to the nitrogen atom in solution with 3MPN.

Returning now to the earlier study [3], it seems reasonable that the weak Raman band at 165 cm^{-1} in the solar cell can be identified as coming from a complex I_2SCN^- with SCN^- still attached to the dye. However, the weakness of the band and the fact that no CN stretching band from SCN^- could be seen leads us to conclude that only a small amount of I_2SCN^- is formed in the solar cell. We therefore believe that another mechanism is mainly responsible for the detachment of SCN^- in the solar cell. This is discussed in Section 3.4.

3.4. Coordination of triiodide ion

As concluded above, a complex I_2SCN^- is not formed to any appreciable extent in a solar cell containing LiI and I_2 in the electrolyte. In a cell with no I_2 added only a small decrease of the CN stretching band was observed [3]. The only remaining alternative seems to be that I_3^- is involved in the detachment mechanism. If, in particular, SCN^- would be exchanged by I_3^-, one would expect an enhanced resonance Raman scattering from I_3^-. That this is indeed the case can be shown by the comparison made in Fig. 6. From the intensities of the I_3^- band at about 114 cm^{-1} in cells with and without the dye (Fig. 6A and B), using the CN stretching band of the solvent as an internal standard, an enhancement factor of about 12 is found. In our earlier study [3], it was observed that some I_3^- was obtained from photooxidation of I^- by the dye. However, this occurred only to a small extent as compared to the formation of I_3^- when I_2 was added.

In Section 3.2, it was discussed how lithium ions could prevent MBI from detaching the SCN^- ligands from the dye by a complex formation $Li^+ \cdots$ MBI. We can now ask the question whether the lithium ions also play a role in the I_3^-/SCN^- exchange. We have therefore added tetrabutylammonium (TBA^+) iodide to the electrolyte instead of lithium iodide. It can be observed from Fig. 3C that the CN stretching band from SCN^- is seen although the intensity is about half of that in a cell with only the solvent and dye present (Fig. 1). Evidently Li^+ plays a role in the exchange process since no CN band is present in Fig. 2A for the LiI case. One can envisage an ion pair $Li^+ \cdots I_3^-$ formation which by a reduced electrostatic repulsion between I_3^- and SCN^- facilitates the exchange of these anions at Ru(II) of the dye. The much more bulky TBA^+ ion or $Li^+ \cdots$ MBI ion complex can be expected to be less effective in this respect.

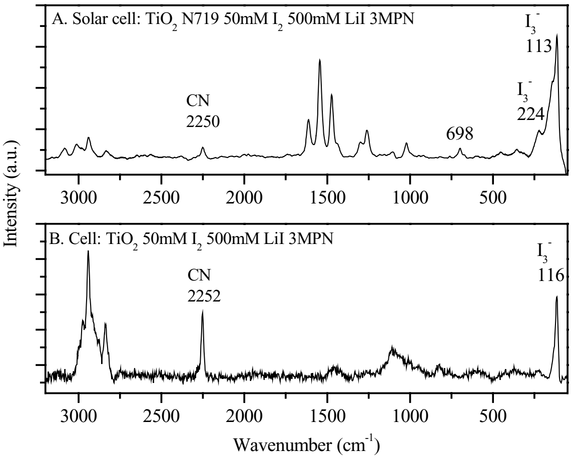

Fig. 6. Raman spectra of a dye-sensitized solar cell with 50 mM I_2 and 500 mM LiI in (A) and a cell without the dye with 50 mM I_2 and 500 mM LiI in (B) in the solvent 3-methoxypropionitrile (3MPN). The excitation wavelength was 514 nm.

In order to minimize the exchange of SCN^- in the solar cell with the additive MBI, it seems that the concentrations of Li^+, need to be carefully balanced with MBI. With excess of MBI relative Li^+, the SCN^- ligand is exchanged with MBI. With excess of Li^+ relative MBI, the ion pair $Li^+ \cdots I_3^-$ coordinates to and exchanges the SCN^- ligand in the solar cell.

3.5. Role of additives such as MBI or 4TBP for increased voltage of the solar cell

Higher open-circuit voltages of solar cells with the additives MBI [5–7] and 4TBP [8–13] were observed earlier as compared to without additives. Improving the voltage is of general interest and we will discuss different possibilities of increased voltage in relation to the observations of complex formation between the Li^+ and the MBI and the SCN^-/I_3^- ligand exchange in the present work.

The maximum voltage generated under illumination corresponds to the difference between the Fermi energy level of the TiO_2 and the redox potential of the electrolyte. Therefore, increased voltage can be achieved by (i) increasing the Fermi energy level of the TiO_2 and (ii) shifting the redox potential in the positive direction.

An increase of the Fermi energy level by a decreased back electron transfer from the TiO_2 surface by the addition of 4TBP is one model discussed in the literature [9]. The additive would then block the TiO_2 surface. Other mechanisms being discussed is a shift of the conduction band edge to higher energies by the adsorption of 4TBP itself at the TiO_2 surface [6] or deprotonation (by 4TBP) of the TiO_2 surface which is partially protonated during adsorption of the acidic dye [6,11].

The findings in the present study of complex formation between Li^+ and MBI, support a conduction band shift mechanism. In this mechanism, it is the cation of the electrolyte salt and possibly some effect by protons from the adsorbed dye, which influences the shift of the conduction band edge. Small ions such as Li^+ and H^+ having high affinity for the TiO_2 surface would shift the conduction band edge to lower energies as compared to larger cations having less affinity such as $Li^+ \cdots$ MBI, TBA^+ (tetrabutylammonium ion) and hexylmethylimidazolium cation. Thus, the role here for additives such as 4TBP and MBI would be to decrease the affinity of Li^+ for the TiO_2 surface. The solar cell with TBA^+ instead of Li^+ also showed 0.2 V higher open-circuit voltage than the solar cell without any additive (only LiI and I_2 in the electrolyte) in the present study. The use of the bulky counter ion TBA^+ instead of Li^+ in the solar cell also protected the SCN^- ligand better. For another large cation such as hexylmethylimidazolium iodide in the electrolyte high stability for solar cells was also reported [8].

Another possible contribution to the photovoltage change is a shift of the redox potential. From the observation of the exchange between SCN^- to I_3^- ligand in the solar cell one realizes that the concentration relation between I^- and I_3^- changes in the electrolyte. As a consequence, the redox potential changes according to the Nernst relation and hence an output voltage change is established. A decreased electrolyte concentration of I_3^- observed for a solar cell without any additive (only LiI and I_2 in the electrolyte) would lead to a more negative redox potential (increased concentration ratio of I^-/I_3^-) resulting in a lower output voltage, as compared to without any ligand exchange.

4. Conclusions

Coordinative interactions between different components in a dye-sensitized solar cell and especially with the additive 1-methylbenzimidazole (MBI) were studied with resonance Raman scattering. In a complete solar cell with iodine and lithium iodide in the electrolyte, triiodide (I_3^-) is found to exchange the SCN^- ligand of the dye bis(tetrabutylammonium) *cis*-bis(thiocyanato)bis(2,2′-bipyridine-4-carboxylic acid, 4′-carboxylate)ruthenium(II). The choice of cation in the salt influences the ligand stability of the dye. It is proposed that an ion pair $Li^+ \cdots I_3^-$ formation occurred which by a reduced electrostatic repulsion between I_3^- and SCN^- facilitated the exchange of these anions at Ru(II) of the dye. The much more bulky TBA^+ ion was as expected less effective in this respect.

From the RRS spectrum of a solar cell with 1-methylbenzimidazole (MBI) added to the electrolyte, it was obvious that the SCN^- ligand was to a large extent still coordinated to the dye. However, without Li^+ in the electrolyte MBI was also found to exchange the SCN^- ligand. We have shown that a complex $Li^+ \cdots$ MBI can be formed between the lithium ions and MBI preventing both MBI and $Li^+ \cdots I_3^-$ from replacing the SCN^- ligand. Therefore, in a complete solar cell the concentrations of Li^+ and MBI have to be carefully balanced in order to avoid SCN^- loss from the dye.

In the performance optimization of the dye-sensitized solar cell effects on both the efficiency and the stability need to be considered. This study points out the importance of characterization methods with which complete systems can be studied.

Acknowledgements

This work was financially supported by the Swedish Natural Science Research Council (NFR), the Swedish Foundation for Strategic Environmental Research (MISTRA), the Swedish National Energy Administration (Energimyndigheten) and the PSO-project under ELTRA project number 3629 (Denmark).

References

[1] H. Rensmo, S. Södergren, L. Patthey, K. Westermark, L. Vayssieres, O. Kohle, P. Brühwiler, A. Hagfeldt, H. Siegbahn, Chem. Phys. Lett. 274 (1997) 51–57.

[2] Md.K. Nazeeruddin, S.M. Zakeeruddin, M. Humphry-Baker, M. Jirousek, P. Liska, N. Vlachopoulos, V. Shklover, C.-H. Fischer, M. Grätzel, Inorg. Chem. 38 (1999) 6298–6305.

[3] H. Greijer, J. Lindgren, A. Hagfeldt, J. Phys. Chem. B 105 (2001) 6314–6320.

[4] U. Lavrenèiè Štangar, B. Orel, A. Šurca Vuk, G. Sagon, Ph. Colomban, E. Stathatos, P. Lianos, J. Electrochem. Soc. 149 (2002) E413–E423.

[5] G. Boschloo, A. Hagfeldt, Chem. Phys. Lett. 370 (2003) 381–386.

[6] G. Boschloo, H. Lindström, E. Magnusson, A. Holmberg, A. Hagfeldt, J. Photochem. Photobiol. A: Chem. 148 (2002) 11–15.

[7] P. Wang, S.M. Zakeeruddin, P. Comte, I. Exnar, M. Grätzel, J. Am. Chem. Soc. 125 (2003) 1166–1167.

[8] E. Rijnberg, J.M. Kroon, J. Wienke, A. Hinsch, J.A.M. van Roosmalen, W.C. Sinke, B.J.R. Scholtens, J.G. de Vries, C.G. de Koster, A.L.L. Duchateau, I.C.H. Maes, H.J.W. Henderickx, in: Proceedings of the Second World Conference, PVSEC, Vienna, 1998, p. 47.

[9] M.K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. 115 (1993) 6382–6390.

[10] M. Grätzel, K. Kalyanasundaram, Curr. Sci. 66 (1994) 706.

[11] G. Schlichthörl, S.Y. Huang, J. Sprague, A.J. Frank, J. Phys. Chem. B 101 (1997) 8141–8155.

[12] S.Y. Huang, G. Schlichthörl, A.J. Nozik, M. Grätzel, A.J. Frank, J. Phys. Chem. B 101 (1997) 2576–2582.

[13] A. Hinsch, J.M. Kroon, M. Späth, J.A.M. van Roosmalen, N.J. Bakker, P. Sommeling, N. van der Burg, R. Kinderman, R. Kern, J. Ferber, C. Schill, M. Schubert, A. Meyer, T. Meyer, I. Uhlendorf, J. Holzbock, R. Niepmann, in: Proceedings of the 16th European Photovoltaic Solar Energy Conference and Exhibition OB9.2, Glasgow, 2000.