**Thermal stability of the DSC ruthenium dye C106 in robust electrolytes.**

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**Abstract**

We have investigated the thermal stability of the heteroleptic ruthenium complex C106 employed as a sensitizer in dye- sensitized solar cells. The C106 was adsorbed on TiO2 particles and exposed to 2 different iodide/triidode based redox electrolytes A and B at 80 ºC for up to 1500 hours in sealed glass ampules. Both electrolytes contain guanidiniumthiocyanate (GuNCS) and N-butylbenzimidazole (NBB) as additives. Electrolyte A: 1,3-dimethylimidazolium iodide (1.0M), I2 (0.15M), NBB (0.5M), and GuNCS (0.1 M) in methoxypropionitrile and electrolyte B: 1,3-dimethylimidazolium iodide/1-ethyl-3-methylimidazolium iodide/1-ethyl-3-methylimidazolium iodide/I2/NBB/GuNCS (molar ratio: 12/12/16/1.67/3.33/0.67) and sulfolane (1:1 v/v). The samples were prepared either in ambient air or under strict atmospheric moisture control in a glove box We extracted samples of the dispersion at regular intervals desorbed the dye from the TiO2 particles and analyzed its by HPLC coupled to UV/Vis and electro spray mass spectrometry. Samples prepared in the glove box gave the highest stability with a steady state photo anode surface concentration of 80% C106 intact and the remaining ~20% being the N-butylbenzimidazole (NBB) substitution products **3** and **4** formed by replacement of the thiocyanate ligand by NBB after 1500 hours of heating at 80 ºC. Samples prepared under ambient conditions gave a steady state C106 concentration of 60% of the initial value and 40 % substitution products. The C106 degradation was found to be independent of the degree of dye loading of the TiO2 particles and the ratio between the amount of dyed TiO2 particles and electrolyte volume. Assuming that this substitution is the predominant loss mechanism in a DSC during thermal stress, we estimate the reduction in the DSC efficiency after long term heat to be 12-24% depending on the degree of atmospheric control during the DSC fabrication.

**KEYWORDS** Dye-sensitized solar cells, thermal stability of sensitizer, C106, ionic liquid electrolytes, LC-MS

**1. Introduction**

Dye-sensitized solar cells (DSCs) have been studied extensively the last two decades ([Oregan and Gratzel 1991](#_ENREF_27), [Hagfeldt and Gratzel 1995](#_ENREF_8), [Grätzel 2005](#_ENREF_5), [Gratzel 2009](#_ENREF_4), [Hagfeldt, Boschloo et al. 2010](#_ENREF_7), [Peter 2011](#_ENREF_28)). From an economical point of view, DSCs are highly interesting because the manufacturing costs of DSCs are significantly lower than the costs of silicon cells ([Grätzel 2006](#_ENREF_6), [Hagfeldt, Boschloo et al. 2010](#_ENREF_7)). Furthermore, DSCs are very well suited for building integration *e.g.* as semi-transparent glass facades ([Hinsch, Brandt et al. 2009](#_ENREF_12), [Hagfeldt, Boschloo et al. 2010](#_ENREF_7),[Hinsch, Veurman et al. 2012](#_ENREF_14)). One of the success criteria required for commercial use of DSCs is high durability and stability under light soaking and thermal stress. While DSCs employing the ruthenium dyes N3, N719, Z907 and C106 with the general formula RuLL´(NCS)2 as sensitizers (see Figure 1) show excellent stabilities under light soaking conditions at 55-60˚C, early reports by Hinsch ([Hinsch, Kroon et al. 2001](#_ENREF_13)), Kroon ([Kroon, Bakker et al. 2007](#_ENREF_17)) and Sommeling ([Sommeling, Späth et al. 2004](#_ENREF_30)) raised some concern about the DSC stability at elevated temperatures (80-85 ˚C) in dark.



**Figure 1** Molecular structures of dyes, N3, N719, Z907 and C106

Wang *et al*. however, was able to prepare thermally stable DSCs with essentially no loss in efficiency after 1000 hours of heating at 85 ˚C by the application of the ruthenium dye K77 and a new type of electrolyte containing guanidiniumthiocyanate as an additive ([Wang, Klein et al. 2005](#_ENREF_31)). Recent thermal ageing stress tests at 80-85 ˚C of DSCs prepared with ruthenium dyes of general formula RuLL´(NCS)2 showed relative small efficiency losses in the range 0-30% and showed that it is possible to prepare reasonable thermally stable DSCs ([Sastrawan, Beier et al. 2006](#_ENREF_29), [Kuang, Klein et al. 2007](#_ENREF_18), [Goldstein, Yakupov et al. 2010](#_ENREF_3), [Harikisun and Desilvestro 2011](#_ENREF_10), [Hinsch, Veurman et al. 2012](#_ENREF_14)). Recently, Konto *et al.* observed a 70% decrease in the short current Isc after 1000 hours of heating at 80 ˚C in dark of a DSC prepared with N719 dye and an electrolyte comprised of 1-propylimidazolium iodide, iodine and guanidiniumthiocyanate in 3-methoxypropionitrile (MPN) ([Kontos, Stergiopoulos et al. 2013](#_ENREF_16)). The decrease in Isc could be reduced to 20% by application of tetraglyme as a solvent instead of MPN. Very recently (Marszalek, Arendse et al. 2013) showed a modest 20% efficiency loss after 1000 hours at 80 °C in dark of DSCs prepared by the ruthenium dye C106 and an ionic liquid-sulfolane composite electrolyte. The largely varying results on thermal ageing of DSCs at elevated temperatures in dark demonstrate that the performance loss of the DSCs depends on the dye, the electrolyte compositions and the DSC device fabrication procedure.

Degradation of thermally stressed DSCs has been attributed to I2 and I3- depletion ([Kontos, Stergiopoulos et al. 2013](#_ENREF_16)), degradation of the platinum catalyst on the cathode ([Lee, Lee et al. 2012](#_ENREF_19)), dye degradation and desorption from the TiO2 surface ([Sommeling, Späth et al. 2004](#_ENREF_30)) and electrolyte leakage ([Bari, Wrachien et al. 2011](#_ENREF_1)). Nguyen *et al.* Showed that RuLL´(NCS)2 dyes degrade thermally in dark by thiocyanate ligand exchange with nitrile solvents and nitrogen-additives like 4-*ter*t-butylpyridine and 1-methylbenzimidazole with half-life times from 150-300 hours at 85 ˚C in model experiments and in complete DSCs ([Nguyen, Ta et al. 2007](#_ENREF_21), [Nguyen, Degn et al. 2009](#_ENREF_23), [Nguyen, Andersen et al. 2010](#_ENREF_22)). The dye degradation reactions were estimated to account for about 40% of the efficiency loss of thermally aged DSCs prepared with N719 and an electrolyte comprised of I2 (0.05 M), tetrabutylammonium iodide (0.5M) and 4-*tert*-butylpyridine (0.5M) in MPN ([Nguyen, Andersen et al. 2010](#_ENREF_22)). Kontos *et al*., however, found no evidence of N719 dye degradation based on micro Raman measurements and attributed all the short current loss due to I3- depletion ([Kontos, Stergiopoulos et al. 2013](#_ENREF_16)).

 In order to solve these high temperature degradation issues, it is essential to ascertain the factors that control the DSC stability at elevated temperatures. This requires a rigorous analysis and estimates of possible degradation mechanisms including the above mentioned ones. The sensitizer is one of the key components of a DSC device whose stability is closely linked to that of the whole device.

 In this work, we have selected C106 as one of the most stable representatives of the heteroleptic RuLL´(NCS)2 complexes and studied its thermal stability at elevated temperatures in dark by model experiments in contact with two different redox electrolytes labelled “A” and “B”. DSCs using C106 with such “robust” electrolytes have previously been shown by Gao *et al.* to have excellent stabilities under light soaking conditions at 60 ºC ([Gao, Wang et al. 2008](#_ENREF_2), Marszalek, Arendse et al. 2013). Our aim is to estimate the efficiency loss of a ruthenium dye based DSC if dye degradation was the only thermal aging loss mechanism. The C106 thermal stress tests were performed as simple “test-tube” experiments ([Nguyen, Ta et al. 2007](#_ENREF_21), [Nguyen, Degn et al. 2009](#_ENREF_23), [Nguyen, Andersen et al. 2010](#_ENREF_22)) in which dispersions of C106-loaded TiO2 particles (TiO2|C106) in the electrolyte were heated in the dark at 80 ºC in sealed glass ampules. Hung-Lin *et al.* have shown that the water content in the electrolyte affects the stability of DSCs at light soaking ([Lu, Lee et al. 2011](#_ENREF_20)). In order to test this observation, samples were prepared under both ambient laboratory conditions and in a glove box under strict control of moisture and oxygen. After the thermal treatment, the dye loaded TiO2 powder was separated by centrifugation and C106 and its degradation products were desorbed from the TiO2 surface by a mild base treatment. The products identified and quantified by HPLC coupled to electro spray mass spectrometry (LC-ESI-MS).

**2. Experimental Section**

*2.1. Chemicals* The source of the employed chemical compounds, i.e. , N-butylbenzimidazole (NBB), guanidiniumthiocyanate (GuNCS), 3-methoxypropionitrile (MPN), sulfolane, 1,3-dimethylimidazoliumiodide (DMII), 1-ethyl-3-methylimidazolium iodide (EMII),1-ethyl-3-methylimidazolium tetracyanoborate (EMITCB) has been described previously ([Gao, Wang et al. 2008](#_ENREF_2)). C106 was synthesized according to Cao et al. (Cao, Bai, et al.). The TiO2 powder was prepared by the following method: Titanium dioxide paste prepared according to Ito *et al.* ([Ito, Murakami et al. 2008](#_ENREF_15)) was doctor bladed on a piece of glass followed by annealing at 450 °C and scratching off the powder.

Electrolyte A: DMII (1.0M), I2 (0.15M), NBB (0.5M), and GuNCS (0.1 M) in MPN ([Gao, Wang et al. 2008](#_ENREF_2)). Electrolyte B: DMII/EMII/EMITCB/I2/NBB/GuNCS (molar ratio: 12/12/16/1.67/3.33 /0.67) and sulfolane (1:1 v/v) (Marszalek, Arendse, et al. 2013).

2.2 *Preparation of dyed TiO2* (High-load): TiO2 (250 mg) powder, which had been dried at 450ºC for 30 min, was transferred to a glove box and added to a dye solution of 60 mg C106 dissolved in 125 ml of a mixture of 10% dimethylsulfoxide, 45% *tert*-butanol and 45% acetonitrile. After 12 hours of dyeing the TiO2 particles were collected inside the glove box by suction filtration. The red TiO2 particles were washed with methanol followed by removal of the supernatant. This process was repeated 3 times in order to remove any loosely bounded C106. Medium-loaded C106 TiO2 powder was prepared at ambient conditions by adding TiO2 (60 mg) to a dye solution of 1.66 mg C106 dissolved in 25 ml of 10% dimethylsulfoxide, 45% *tert*-butanol and 45% acetonitrile. After dye adsorption, centrifugation of the solution obtained the supernatant as colourless solution indicating that all the C106 was adsorbed on the TiO2 particles.

*2.3. Preparation of Samples* The1A-3A samples were prepared in glass ampules equipped with glass adapters for a vacuum line. TiO2 powder (10 mg) with either a high (samples 1A) or medium load (samples 2A and 3A) of C106 and electrolyte A (1ml) were transferred to the ampules. Dissolved air in the electrolyte was removed on a vacuum line by 3 freeze-pump-thaw cycles followed by flame sealing of the glass ampule. The 1G-3G samples were prepared inside the glove box by adding 10 mg of high C106 load TiO2 powder to the ampules together with either 1ml or 17 l electrolyte A or B. The ampules were taken out from the glove box protected with a rubber stopper and flame sealed outside the glove box.

*2.4 Thermal experiments* The sealed glass ampules were heated for 0-1500 hours in a GC-oven at 80 ˚C. After heating, the samples were stored in a refrigerator until the HPLC analysis.

*2.5 C106 extraction protocol* Thermal treated ampules were opened and the titan dioxide particles transferred to Eppendorf plastic tubes. The tubes were centrifuged and the supernatants were removed. The remaining dyed TiO2 particles were carefully washed by the addition of acetonitrile (1 ml) to each tube followed by vortex mixing, centrifugation and removal of the acetonitrile. The washing steps were performed 4 times. The C106 dye was extracted by addition of 500 l of Bu4NOH (0.1 M) in a 1:1 mixture of H2O:MeOH. The tubes were vortex mixed for 1 min followed by addition of dimethyl formamide (500 l) and continued vortex mixing for 1-2 min until the dyes have been removed from the surface of the TiO2 particles. The red colored base extracts were transferred to HPLC vials and analyzed immediately by LC-UV/Vis-MS.

*2.6 Product analysis* The LC-UV/Vis-ESI-MS equipment and setup used for the product analysis has recently been described elsewhere ([Hansen, Gervang et al. 2003](#_ENREF_9)). The analysis was performed with a Phenominex Phenylhexyl Kinetix analytical 10 cm column with an internal diameter of 2.1 mm. A 20 min gradient elution was performed with a flow of 0.2 ml/min and application of three solvents of A = methanol B = acetonitrile and C = HCOOH (1%), acetonitrile (5%) and water (94%). Initial eluent composition: 20% A, 10% B, 70% C. Final composition after 10 min: 20% A, 80% B and 0% C. The heated capillary temperature of the ESI was set to 200 ºC.

**3. Results and discussion**

The thermal degradation of C106 bound to the surface of TiO2 particles (TiO2│C106) was investigated at 80 °C in two “robust” electrolytes A and B with the same composition as reported previously by Gao and Marszalek ([Gao, Wang et al. 2008](#_ENREF_2)), (Marszalek, Arendse, et al. 2013). The composition of electrolytes is as follows, Electrolyte A: DMII (1.0 M), I2 (0.15M), NBB (0.5M), and GuNCS (0.1 M) in MPN ([Gao, Wang et al. 2008](#_ENREF_2)). Electrolyte B: DMII/EMII/EMITCB/I2/NBB/GuNCS (molar ratio: 12/12/16/1.67/3.33/0.67) and sulfolane (1:1 v/v). (Marszalek, Arendse, et al. 2013). The abbreviations and structures of the electrolyte components are shown in Figure 2. Oxygen free colloidal A or B solutions of C106 dyed TiO2 particles were heated for 0-1500 hours in dark in sealed glass ampules. The samples (see Table 1) were prepared under ambient (A) and glove box conditions (G) in order to test whether strict atmospheric control might improve the dye stability. The C106 dyed TiO2 powder was either dissolved in a “large” volume of electrolyte (1 ml) or in a small volume (17 l) in order to simulate the TiO2 to electrolyte ratio in a real DSC device. After heating the glass ampules at 80°C, the adsorbed C106 dye was extracted with a mild base from the TiO2 surface and an aliquot of the extract was analyzed by HPLC coupled to UV/Vis and electro spray mass spectrometry.



**Figure 2** Molecular structures of Electrolyte A and B components

**Table 1** Thermal TiO2│C106 degradation experiments performed at 80 ˚C in dark. The sealed samples prepared under ambient (A) and glove box conditions (G).

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Serie | Condition | Elec-trolyte | TiO2|C106pr. sample/mg | Volumeof elec-trolyte | Numberofsamples |
|  1A | Ambient |  Aa | 8.6-9.7b | 1 ml | 8 |
|  2A | Ambient |  A | 10c | 1 ml | 4 |
|  3A | Ambient |  A | 10c | 16.8 l | 4 |
|  1G | Glove box |  A | 10b | 1 ml | 5 |
|  2G | Glove box |  A | 10b | 16.8 l | 6 |
|  3G | Glove box |  Ba | 10b | 16.8 l | 6 |

aElectrolyte A and B composition: See text. bHigh dye load of TiO2c  Medium dye load of TiO2 .

*C106 degradation products* Figure 3 shows a HPLC chromatogram of the dye extract from the ampule of the experimental series 1A, which has been heated for 1464 hours in dark at 80 ˚C.



**Figure 3** HPLC chromatogram of a sample from the 1A series prepared at ambient conditions and extracted after 1464 hours of thermal treatment at 80 ˚C. The ordinate unit is in micro absorbance. The chromatogram was obtained in the max mode in the interval 400-800 nm.

Thermal degradation of C106 at elevated temperatures is similar to the degradation of N719 and Z907 and follows the general solvent and nitrogen additive substitution mechanism of RuLL´(NCS)2 complexes shown in eqs. (1)-(3) ([Nguyen, Ta et al. 2007](#_ENREF_21), [Nguyen, Degn et al. 2009](#_ENREF_23), [Nguyen, Andersen et al. 2010](#_ENREF_22)). (MPN = 3-methoxypropionitrile, NBB = 1-butylbenzimidazole).

[RuLL´(NCS)2] + MPN = [RuLL´(NCS)(MPN)]+ + NCS- (1)

[RuLL´(NCS)(MPN)]+ + NBB = [RuLL´(NCS)(NBB)]+ + MPN (2)

 [RuLL´(NCS)2] + NBB = [RuLL´(NCS)(NBB)]+ + NCS- (3)

 Degradation of the C106 dye is observed in the chromatogram shown in Figure 3. Beside the main initial dye C106 and its small C106 isomer (**2)** (initially present in the C106 synthesis product), four degradation products **3**-**6** are observed. The products were identified by their electro spray mass spectra (see Table 2) and their molecular structures are shown in Figure 4. The products **3** and **4** are isomers with the formula [RuLL´(NCS)(NBB)]+ which has two possible geometrical structures depending on which of the thiocyanate ligands in C106 is substituted by the NBB. The electro spray mass spectra of **3** and **4** are nearly identical and shows two ruthenium isotope clusters around the ions *m/z* = 1130 and *m/z* = 956 . These *m/z* values were assigned to the molecular ion [RuLL´(NCS)(NBB)]+ and the fragment ion [RuLL´(NCS)(NBB) - NBB]+ , respectively, with fully protonated carboxylic groups on the bipyridyl ligand L. (The carboxylate ion in C106 is protonated on the column due to the formic acid added to the HPLC eluent). In a similar way, the electro mass spectra of the peaks 5 and 6 were assigned to the solvent substituted products **5** and **6** with the formulary [RuLL´(NCS)(MPN)]+. The mass spectra of the two peaks are almost identical and contain the ions *m/z* = 1041 [M+] and *m/z* = 956 [M-MPN]+. The sensitivity of **3**-**6** in positive ESI-MS is much higher than the C106 sensitivity. This is probably related to the fact that the **3**-**6** compounds are “born” with a positive charge whereas the protonated form of C106 is neutral and has to attach a Na+ ion or to be oxidized in the electro spray needle to a charged Ru3+ complex in order to be detected in ESI-MS.

**Table 2** Characterization of observed C106 thermal degradation products in the thermal experiments.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Peak labela | **Rt min** | **max** **nm** | **MS1*****m/z*** | **Identification**b,c |
|  6 | 11.10 | 497 | 1041[M+], 956 [M-MPN]+ | [RuLL´(NCS)(MPN)]+ (**6 or 5**) |
|  5 | 11.50 | 497 | 1041, 956 | [RuLL´(NCS)(MPN)]+ (**5 or 6**) |
|  4 | 11.92 | 532 | 1130 [M+] , 956 [M-NBB]+ | [RuLL´(NCS)(NBB)]+ (**4 or 3**) |
|  3 | 12.10 | 534 | 1130 956 | [RuLL´(NCS)(NBB)]+ (**3 or 4**) |
|  2 | 13.10 | 540 | 1137[M+Na]+,1014,[M+], 956 [M-NCS]+ | [RuLL´(NCS)(SCN)] (**2**) |
|  C106 | 13.45 | 544 | 1137, 1014, 956 | [RuLL´(NCS)2] (**C106)**d |

aLabels of the HPLC peaks in Figure 3. bL is fully protonated. cThe molecular structures shown in Figure 4. dNa is substituted with H in the C106 structure.



**Figure 4** Molecular structures of C106 thermal degradation products. NBB = N-butylbenzimidazole, MPN = 3-methoxypropionitrile.

*C106 degradation kinetics* Figure 5 shows the relative product concentration profiles of C106+**2** (●), and its thermal degradation products **3** +**4** [RuLL´(NCS)(NBB)] (■) and **5+6 [**RuLL´(NCS)(MPN)] (▲) at 80 °C for the sample series 1A-3A and 1G-3G. The relative product distributions of the C106 reaction mixtures were calculated from the HPLC-UV/Vis chromatograms obtained in the max mode in the spectral range of 400-800 nm. The calculations are based on the following assumptions: a) All C106 thermal degradations products are observed in the HPLC chromatogram. b) All ruthenium degradation complexes have the same response factor or equivalently all of the ruthenium complexes have the same extinction coefficient at their respective maximum wavelength in the visible part of the spectrum.

The relative response factors of C106,and the substitution products **2-6** have not been experimentally obtained, however, it has previously been shown that the N719 derived 4-*tert*-butylpyridine substitution product [RuL2(NCS)(4-*tert*-butylpyridine)]+ has a response factor of 0.99 relative to N719 (Lund, unpublished results). This means that the substitution product is detected with the same sensitive by UV/Vis detector as N719. However, despite small variations may be anticipated between the response factors of the products C106 and **2-6** the relative concentrations were calculated based on the assumption a) and b). The sum of the chromatographic peak areas of C106 and **2-6** was reasonably constant within ±10 % which indicates that the assumptions a) and b) are reasonably fulfilled.



**Figure 5** Thermal degradation of TiO2│C106 at 80 oC. Relative product concentration profiles of C106+**2** (●), **3**+**4** [RuLL´(NCS)(NBB)] (■) and **5+6 [**RuLL´(NCS)(MPN)] (▲).

All the concentration profiles show a decrease of the initial concentration of C106 as a function of the heating time. The main degradation products are **3** and **4** with minor steady state concentrations of **5** and **6**. Notice that **5** and **6** were not found in the 3G experiments due to the fact that the B electrolyte did not contain MPN. After 1000 hours the profiles (except 3A) begin to approach a steady state equilibrium situation with time independent concentrations profiles. Both the electrolytes A and B contain guanidiniumthiocyanate (GuNCS) and the equilibrium situation is therefore anticipated based on the thermal substitution mechanism of RuLL´(NCS)2 complexes shown in eqs. (1)-(3). The experiments 1A and 2A are identical except that the 2A titanium dioxide powder had a medium dye loading of 2.6×10-4 mole C106/g TiO2 powder, whereas the TiO2 powder in 1A was saturated with a maximum load of C106 which estimated from HPLC was 3-5 times higher than the 1A powder dye load. The 1A and 2A profiles are, however, nearly identical and it is therefore concluded that the degree of TiO2 dye loading does not affect the C106 degradation kinetics. The 1G and 2G samples were prepared with 1 ml and 17 l electrolyte, respectively. The concentration profiles of 1G and 2G are nearly identical and it is therefore concluded that the amount of C106 dyed TiO2 powder vs. electrolyte volume does not influence the degradation kinetics.

 An interesting observation is that the equilibrium C106 concentrations after 1500 hours increases from 60% in the A series to 80 % in the G series. Careful sample preparation under strict atmospheric control in a glove box apparently helps to minimize the long-term thermal degradation of C106. The glove box sample preparation reduces the level of trace water in the samples.

The degradation of C106 in the two different electrolytes A and B can be compared in series 1G and 3G. As seen from Figure 5 there is no real difference between the concentration profiles and the C106 equilibrium concentrations are the same ([C106]eq = 80%). Electrolyte B contains less GuNCS (0.040 M) compared with electrolyte A (0.1 M), however the concentration ratio NBB/GuNCS = 5 is the same in both electrolytes and the [C106]eq values in the two electrolytes are therefore expected to be nearly equal. This is supported by the digital simulations of the degradation kinetics (see below).

*Simulation of C106 kinetics* The C106 degradation kinetics was simulated by applying the degradation mechanism eqs. (1)-(3) in the simulation program “Chemsimul” ([Olsen, Kirkeby et al. 2010](#_ENREF_26)) similarly to previous simulations of Z907 thermal degradation reactions ([Nguyen, Degn et al. 2009](#_ENREF_23)). The second order rate constants k1, k-1,k2, k-2, k3 and k-3 of eqs. (1) - (3) was obtained by fitting the simulations to the six concentrations profiles shown in Figure 6. The simulations of the 1A and 1G concentration profiles are shown in Figure 6 and the applied second order rate constants are shown in Table 3 including the rate data of the other series. Despite the heterogeneous nature of the C106 reactions, they are well simulated by homogenous based kinetics.



**Figure 6** Kinetic simulations of the concentration profiles of the C106 degradation experiments 1A and 1G. C106+**2** (▬), **3**+**4** (▬) and **5+6**  (▬). The applied second order rate constant are shown in Table 3.

**Table 3** Second order rate constants (M-1∙hours-1) of the C106 equilibrium reactions eqs. (1)-(3) at 80 °C.a

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | **1A** | **2A** |  | **3A** | **1G** | **2G** | **3G** |
| Electrolyte | A | A |  | A | A | A | B |
| Reaction volumeMPN | 1ml11.5 M | 1ml11.5 M |  | 17 l11.5 M | 1ml11.5 M | 17 l11.5 M | 17 l0 M  |
|  NBB | 0.5 M | 0.5 M |  | 0.5 M | 0.5 M | 0.5 M | 0.2 M |
| GuNCS | 0.1 M | 0.1 M |  | 0.1 M | 0.1 M | 0.1 M | 0.04 M |
| *k1* | 1E-05 | 4E-05 |  | 1E-05 | 1E-05 | 1E-05 | -d |
| *k-1* | 5E-03 | 5E-03 |  | 5E-03 | 5E-03 | 5E-03 | - |
| *k2* | 5E-03 | 5E-03 |  | 5E-03 | 5E-03 | 5E-03 | - |
| *k-2* | 5E-06 | 5E-06 |  | 5E-06 | 5E-06 | 5E-06 | - |
| *k3* | 9E-04 | 9E-04 |  | 1.1E-03 | 7E-04 | 6E-04 | 1.2E-03 |
| *k-3* | 8E-03 | 1E-02 |  | 1.0E-02 | 1.4E-02 | 1.4E-02 | 1E-02 |
| *K3*b | 0.11 | 0.09 |  | 0.11 | 0.05 | 0.043 | 0.12 |
| % C106 after 1000 h | 69 | 58 |  | 68 | 78 | 80.0 | 82 |
| % C106eqc | 60 | 52 |  | 61 | 75 | 77 | 64 |

a The second order rate constants k1, k-1,k2, k-2, k3 and k-3 were obtained by digital simulations of the concentrations profiles of Figure 6 assuming that the heterogeneous reactions (eqs.(1)-(3)) can be treated as homogenous reactions solution with a start concentration of C106 of 1mM .

b*K*3 = (*k*3/*k*-3)(100-%C106eq)/ (%C106eq). c % C106eq ≈ % C106 after 5000 h. d The B electrolyte applied in 3G does not contain MPN and eqs.(1) and (2) (see text) are therefore not involved in the degradation of C106 in the B electrolyte.

The second order rate constants shown in Table 3 supports previous similar findings for N719 and Z907 dyes with 4-*ter*t-butylpyridine ([Nguyen, Ta et al. 2007](#_ENREF_21), [Nguyen, Degn et al. 2009](#_ENREF_23))that *k*1<< k3 and *k*3<*k*-3 indicating a binding strength order to ruthenium, NCS- > NBB >>MPN.

If a NCS- salt had not been added to the electrolyte A, C106 would have degraded by the pseudo first order rate constant *k*´sub = *k*3[NBB] + *k*1[MPN] = 5.5×10-4 h-1 corresponding to a half-life time *t1*/2 equal to 1250 hours. ([MPN] = 11 M). This *t1*/2 is 4 times longer than *t1*/2 of the thermal degradation of TiO2│N719 in MPN and 0.5 M 4*-tert*-butylpyrdine (4-TBP) at 80 °C ([Nguyen, Ta et al. 2007](#_ENREF_21)). This shows that C106 in combination with NBB is less prone for thiocyanate ligand exchange than N719 in combination with 4-TBP. This is consistent with the recent results which show that NBB substitutes thiocyanate1.7 times faster in N719 than in C106; and 4-TBP exchange thiocyanate in N719 2.4 faster than NBB ([Nguyen, Ta et al. 2007](#_ENREF_21)). As seen from Table 3, preparation of the samples under glove box conditions reduces *k*3 and *K*3 and thereby increases the equilibrium surface concentration of C106.

*Dye degradation and DSC efficiency.* How does a reduction in C106 surface concentration to e.g. 69% of its initial value as observed in 1A (see Table 3) affect the photovoltaic power conversion efficiency of a DSC? As shown previously the N-methylbenzimidazole substitution product of N719, [RuL2(NCS)(MBI)]+, is itself a sensitizer with a DSC efficiency of ~40% of the value of DSCs prepared by N719 ([Nguyen, Lam. et al. 2011](#_ENREF_24)). The reduction of the initial N719 (or C106) surface concentration is not just a simple “dilution” process. Formation of the positive charged substitution product on the TiO2 surface, which competes with initial ruthenium dyes for the photons, change the photo anode properties e.g. decrease the electron diffusion lifetimes in the TiO2 (Andersen, Halme *et al.* 2011). The DSC efficiency therefore decreases. Preliminary measurements of efficiencies  of DSCs prepared with various amounts of N719 and its 4-*tert*-butylpyridine (TBP) substitution product RuL2(NCS)(TBP)+ correlates reasonable well to a linear correlation  = (t=0)\*((100-SUB%) + 0.40\*SUB%) (Nguyen, Lund, in progress).

 If it´s assumed that a similar reduction in efficiency of the C106 substitution product [RuLL´(NCS)(NBB)]+ as a sensitizer compared with C106, then the efficiency of a DSC cell prepared with C106 and the electrolyte A under ambient condition is expected to have an efficiency equal to (69 + 0.40×0.)% = 81% of its initial value after 1000 hours of heat treatment in dark at 80 °C. If the DSC is prepared under careful atmospheric and moisture control (*e.g.* in a glove box) with the application of electrolyte A, the efficiency of the cell is expected to decrease to (80 + 0.40×20) %= 88% of its initial value. If dye degradation was the only loss mechanism, the efficiency loss of the DSC may be estimated to 10-20% depending on the degree of atmospheric control during cell fabrication. This conclusion is likely to be valid also at 85 °C because the small temperature increase is expected to increase *k*3 and *k*-3 to the same degree keeping *K*3 and thereby the equilibrium surface concentration [C106]eq constant. While N719 substitute thiocyanate faster with N-additives than C106 (k3(N719) > k3(C106)) the same is true for the reverse reaction and K3 is therefore expected to be reasonably equal for all the RuLL´(NCS)2 complexes and the efficiency losses due to dye degradation approximately equal for all the RuLL´(NCS)2 dyes.

Compilation of recent literature data on long-term of DSC stability tests in dark at 80-85 °C is shown in Table 4. It´s seen that most of the reported efficiency losses after 1000 hours of heating relative to the initial efficiency are within the range of 10-30% which fits well with the expected loss due to dye degradation. The 0% loss reported by Hinsch *et al.* ([Hinsch, Veurman et al. 2012](#_ENREF_14)) is really impressive and smaller than expected from our analysis. Kontos *et al*. observed no N719-degradation by micro-Raman in their thermal ageing experiments ([Kontos, Stergiopoulos et al. 2013](#_ENREF_16)). However, recent results shows that the Raman spectra of N719 and its 4-*ter*t-butylpyridine substituted products are almost identical ([Hassing, Jernshoej et al.](#_ENREF_11) 2013); and it is therefore difficult to observe N719 thermal dye degradation by conventional Raman spectroscopy. Some of the performance losses observed by Kontos *et al*. may therefore be due to thermal dye degradation. Marszalek *et al*. prepared DSCs with the same dye and electrolyte (B) as used in this work and found a 20% efficiency loss after 1000 hours of thermal ageing at 80 °C which is exactly the same loss predicted from dye degradation data from this work. If all the C106 dye is degraded to the NBB substitution products **3** and **4** the Jsc is expected to be reduced to ≈50% (Nguyen, Lam et al. 2011). A C106 dye degradation of 30% will therefore be expected to decrease Jsh by ≈15% which is very close to the observed 13% reduction from 16 to14 mA/cm2. Furthermore, Marszalek *et al*. observed a decrease of the electron life time of the thermal stressed DSCs which may be explained by the formation of the N-additive substitution products which previously have been shown to decrease the electron lifetime in DSCs. (Nguyen, Lam et al. 2011). The above arguments supports the conclusion that the main reason for the performance loss observed in the work by Marszella *et al*. is due to C106 degradation. Similar thermal degradation is likely to occur in other DSCs based on RuLL´(NCS)2 dyes.

 The addition of a thiocyanate salt *e.g.* GuNCS to the DSC electrolyte is very important in order to minimize the efficiency loss during thermal ageing. The efficiency losses observed in previous earlier investigations ([Hinsch, Kroon et al. 2001](#_ENREF_13), [Sommeling, Späth et al. 2004](#_ENREF_30), [Kroon, Bakker et al. 2007](#_ENREF_17)) may be attributed to the lack of thiocyanate salt in the electrolyte.

**Table 4** Thermal stress tests of DSCs prepared with RuLL´(NCS)2 dyes.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Reference | Dye | N-additive(0.5 M) | GuNCS/M | temperature | Efficiency Loss after 1000 hours |
| Sastrawan 2006 | N719 | 4-TBP | 0 | 85 °C dark | 30% |
| Kuang 2007 | K77 | NMBa | 0.1 | 85 °C dark | 9% |
| Goldstein 2010 | N719 | ? | 0.1 (?)c | 85 °C 1 sun | 23 % |
| Harikisun 2011 | Z907 | Bb | 0.1  | 80 °C dark | 23% |
| Hinsch 2012 | C101 | NBB | 0.1 | 80 °C dark | 0% |
| Kontos 2013 | N719 | B | 0.1 | 80 °C dark |  20%d, 70%e |
| Marszalek 2013 | C106 | NBB | 0.04 | 80 °C dark |  20% |

aN-methyl-benzimidazolebBenzimidazolec The Dyesol EL-HSE was used as electrolyte.

The El-HSE electrolyte composition is unknown! dTetraglyme as solvent. e MPN as solvent.

**4. Conclusion**

Thermal degradation of C106 adsorbed on TiO2 particles was investigated by using two robust electrolytes at 80 ºC in sealed ampules. Both electrolytes contain guanidiniumthiocyanate and N-butylbenzimidazole as additives. Preparation of the samples under strict atmospheric moisture control in a glove box gave the best results with a steady state surface concentration of 80% intact C106 and ~20% N-butylbenzimidazole substitution products **3** and **4** after 1500 hours of heating at 80 ºC. The dye degradation was found to be independent of the degree of dye loading of the TiO2 particles and the ratio between the amount of dyed TiO2 particles and electrolyte volume. If dye degradation was the only loss mechanism in a DSC during thermal treatment the reduction in the DSC efficiency after long term thermal treatment may be estimated to 12%. The C106 dye stability therefore does not seem to be the limiting factor in full filling the requirements of the IEC 1215 standard thermal stress tests. In order to obtain a high thermal stability of C106 and other RuLL´(NCS)2 dyes thiocyanate salt addition to the electrolyte is essential.

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