

IMPERIAL COLLEGE LONDON

Quantifying Regeneration in Dye Sensitized Solar Cells

A Step Toward Red Absorbing Dyes having
Lower Energy Loss

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Abstract of Thesis

A limiting factor on DSSC efficiency is the lower fraction of the solar spectrum that is absorbed by the dye molecules developed to this point. Dye molecules that function well in DSSCs tend to have poor or no absorption to the red of 750 nm. Extending this absorption to the red by 100 nm, without losing efficiency in other ways, would result in a significant improvement in photocurrent. This challenge has proven difficult, in large part because of one slow reaction in the electron transfer cycle of DSSCs, the regeneration reaction. Better understanding of this reaction is thus critical. The kinetics of regeneration is understudied relative to the other processes in DSSCs, this is in part because the regeneration reaction produces no, as yet detected, measurable electrical signal. It must be studied by more difficult transient absorbance (TA) techniques.

The first step of this thesis focuses on isolating a reliable transient signal that reflects the regeneration reaction. This is made by upgrading the conventional TA system to also acquire transient electrical (TE) signals simultaneously (TA-TE). The system is used to characterize dye-sensitized solar cells (DSSCs) under 1 sun illumination whilst the cells are fully operational and their stability is monitored. The second step of the work consists of the development of a methodology and a kinetic model which uses the isolated regeneration signal and a range of complimentary measurements on operating cells, to determine the quantum yield and the associated intrinsic rate constants and orders of the regeneration reaction. This enabled understanding of the regeneration mechanism and its optional rate limiting steps. Finally, the use of steady state photoinduced absorption (SSPA), as a complementary or alternative tool to assess regeneration, is also questioned. SSPA is compared with the regeneration TA –TE and charge extraction measurements.

Declaration of Originality

Except where specific reference is made, the material contained in this thesis is the result of my own work. This dissertation has not been submitted in whole or in part of a degree at this or any other university, and does not exceed 100,000 words in length.

A. Y. Anderson

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Last but not least, again for accepting our relocation, for additional mental support and for visits that made home feel closer; family, former members of the club, and friends here, in Israel and around the world: Eyal & Dana, Anat, Ido, Tzach, Tal, Zohar & Noa, Aya & Noam, Tomer & Petra, Alon & Miri, Avner & Revi, Oren & Anat, Nadav & Hadar, Roy & Shani, Dani, Hilit, Gidi, Gil, Tal R, Hadas & Amit, Sian and the Barnes family, Nir & Karin, Aviv, Michael, Ran & Zoe, Avner & Galit, Izzy & Julie ...

Symbols and Abbreviations

DSSC	Dye-sensitized solar cells	PMII	1-propyl-3-methylimidazolium iodide
TA (TAS)	Transient Absorbance (spectroscopy)	PMITFSI	1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide
TE	Transient Electrical	GuSCN	Guanidinium thiocyanate
OC	Open Circuit	N719	<i>cis</i> -[<i>bis</i> (4,4'-dicarboxylate-2,2'-bipyridine)] (NCS) ₂ (NBu ₄) ₂ Ru(II)
SC	Short Circuit	dcbpy	4,4'-dicarboxy-2,2'-bipyridyl
CV	Constant voltage	N3	<i>cis</i> -[<i>bis</i> (4,4'-dicarboxy-2,2'-bipyridine)] (NCS) ₂ Ru(II)
CC	Constant current	V_{oc}	Open circuit voltage
TPV	Transient photovoltage	J_{sc}	Short circuit photocurrent
TPC	Transient photocurrent	Q	Charge
TPQ	Transient Charge	ε	Absorption extinction coefficient
S⁰	Ground state dye	τ_n	Electron recombination lifetime
S* or S^{+/*}	Excited dye	D_n	e ⁻ diffusion coefficient
S⁺ or S^{+/0}	Oxidized dye, sometimes also referred to as dye cation	IPCE	Incident photon conversion efficiency
[S⁺·I]	complex of oxidized dye and one iodide	ΔOD	Change in optical density (change in absorbance)
e⁻	Electron	AM1.5	Air mass 1.5 illumination
I[·]	Iodine radical	FF	Fill factor
I⁻	Iodide	FWHM	Full width at half maximum
I₂	Iodine	HOMO	Highest occupied molecular orbital
I₂^{·-}	Di-Iodine radical	LUMO	Lowest unoccupied molecular orbitals
I₃⁻	Tri-Iodide	VIS	Visible spectrum
TiO₂	Titanium Di Oxide	IR	Infrared spectrum
FTO	Fluorine-doped tin oxide	λ	Wavelength
TCO	Transparent conducting oxide		
MPN	3-methoxypropionitrile		

VB	Valence band	JV or IV	current voltage (curve)
CB	Conduction band	Ru	Ruthenium
k_{inj}	Injection constant	PC	Propylene carbonate
k_j	Collection constant	ACN	Acetonitrile
k_{rg}	Regeneration constant	TBA⁺	Tetra Butyl Ammonium ⁽⁺⁾
k_{decay}	Decay Constant	ClO₄⁻	Perchlorate ⁽⁻⁾
k_{edr}	Electron-dye recombination	Li⁺	Lithium ⁽⁺⁾
k_{eer}	Electron-electrolyte recombination	BZI	Benzimidazole
χ	Order of dependence in electrons	THF	Tetrahydrofuran
γ	Order of dependence in Iodide	TBP	4-tert-Butylpyridine
ν_{rg}	Regeneration observed rate	ND:YAG	Neodymium-doped Yttrium Aluminium Garnet (LASER)
Pt	Platinum	OPO	Optical parametric oscillator
SCE	Saturated calomel electrode	Ce	Cerium
SSPA	Steady State Photoinduced Absorption	$t_{1/2}$	Half life
PIA	Photoinduced Absorption	τ_{obs}	Observed lifetime - weighted average lifetime (from stretched)
InGaAs	Indium Gallium Arsenide	k_{obs}	Observed rate - effective rate constant (inverse τ_{obs})
I_0	Incident light before changes	Γ	Gamma function
I_n	Transmitted light	β	Stretched parameter
LED	Light emitting diode	τ_{ww}	The characteristic lifetime (Kohlrausch-Williams-Watts)
DAQ	Data acquisition (card)	n or [e-]	Total concentration of electrons
CE	Charge extraction	Os	Osmium
BG	Background Level	E_x	Excitation energy
Si	Silicon	MOSFET	metal oxide semiconductor field effect transistor
mpp	Maximum power point	OpAmp	Operational amplifier
tmpp	Theoretical mpp		
η	Conversion efficiency		

1 Introduction

Earth is “washed” with 162,000 TW flux of exergy from solar radiation whilst currently only 0.016 TW are converted to solar energy. Figure 1-1 shows the quantified values of the available terrestrial energy sources, the flow and distribution of global exergy flux, the accumulations and destruction of exergy and the amount that mankind harnessed for its uses. (Hermann 2006)

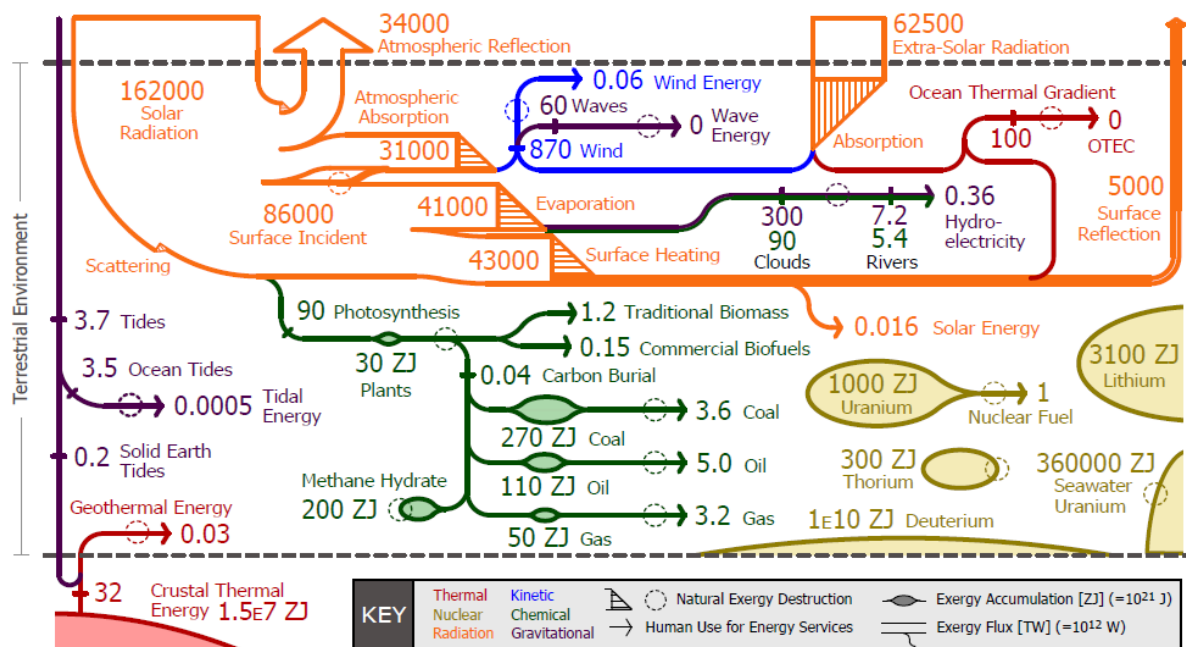


Figure 1-1 - Global Exergy Flux, Reservoirs, and Destruction.(Hermann 2006)

Exergy (*countable* and *uncountable*; plural **exergies**)

1. In thermodynamics, a measure of the actual potential of a system to do work.
2. In systems energetics, **entropy**-free energy.

From Wiktionary

1.1 DSSCs and the Regeneration Problem

Dye sensitized solar cells (DSSC) are a possible lower cost alternative to silicon based photovoltaics. (Kong 2007; Kroon 2007; Green, Emery et al. 2010) DSSCs operation, common materials, common configurations, alternative materials, alternative configurations, general characterization, advanced characterization and modelling were reviewed several times in the past and will not be the focus of this introduction. (Skotheim 1978; O'Regan 1991; Hagfeldt 2000; Bisquert J. 2004; J. Frank, Kopidakis et al. 2004; Kong 2007; Peter 2007; Snaith 2007; Gratzel and Durrant 2008; Ardo and Meyer 2009; O'Regan and Durrant 2009)

In general, in dye-sensitized cells, light absorption occurs in a monolayer of dye adsorbed on the surface between a transparent oxide electron conductor (nearly always TiO_2) and a semi-transparent electrolyte. High light absorption is achieved by using a thick film ($\sim 10 \mu\text{m}$) of nanosized oxide particles ($\sim 20 \text{ nm}$). The internal surface of the film is coated with the dye resulting in an absorbance near 100 % over the spectral width of the dye. A liquid electrolyte, which is virtually always iodide/tri-iodide in an organic solvent, is introduced into the pores. The TiO_2 /dye/electrolyte interface forms the critical charge separation component of DSSCs.

Figure 1-2 is presented in order to emphasize the large amount of combinations available under the concept of dye sensitized solar cell. It is often difficult to determine why a specific DSSC combination is better than another one, frequently a change in composition, intended to improve a specific property, causes undesired and uncontrolled changes in other properties. For example, there are currently major research efforts focused on synthesizing new dyes for DSSCs. The main goals for these new dyes are better light collection, electron injection, adhesion to the oxide and durability (Nazeeruddin 1993; Islam, Sugihara et al. 2003; Wang Peng 2003; Wang 2005; Jiang, Masaki et al. 2006; Handa 2007; Nazeeruddin 2007; Feifei Gao 2008; Reynal, Forneli et al. 2008; Snaith 2008; Yum, Jung et al. 2009). Changes to a dye to optimise these properties almost always cause an unavoidable change in two other properties, which are often not explicitly studied. These are the recombination of injected electrons (e^-) back to the dye cations (S^+) (Electron Dye Recombination (k_{edr} in Figure 1-3)) and the regeneration of S^+ by the electrolyte (k_{rg} in Figure 1-3).

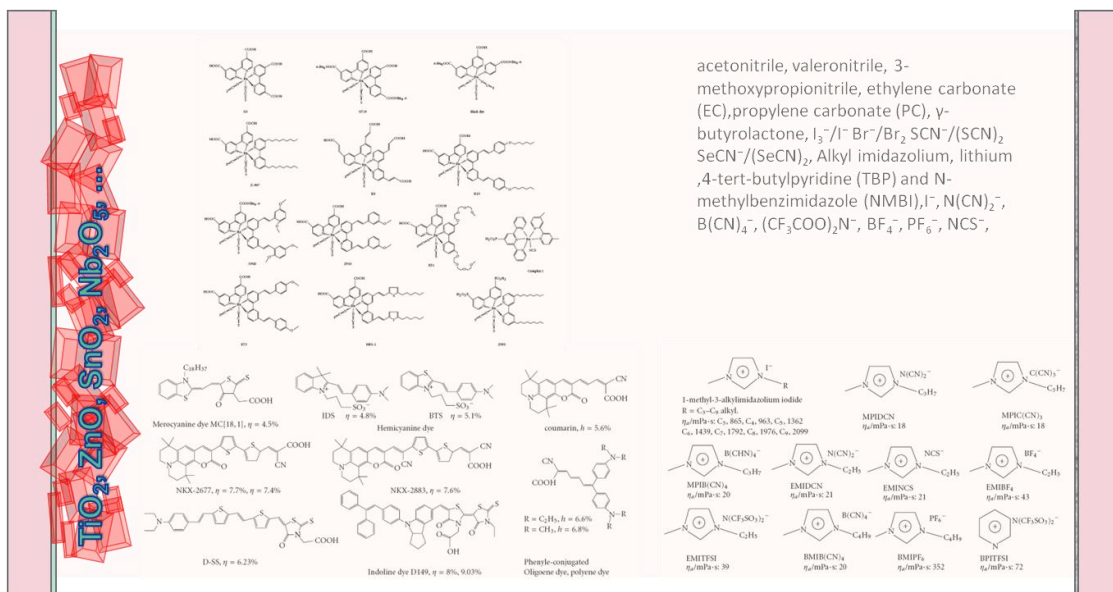


Figure 1-2 - part of the combinations available in dye sensitized solar cells. (Kong 2007) shown on a “sandwich” configuration of DSSC device. From top right and clockwise examples are shown for: solvents and redox couples, ionic liquids, organic dyes, semiconducting metal oxides and Ruthenium based dyes.

Figure 1-3 shows the context of k_{rg} and k_{edr} amongst the various energetic and kinetic transitions between the different components in a common DSSC. The driving force, ΔG , for the regeneration reaction is the energetic difference between the chemical potential of the electrolyte and ground state oxidation potential of the dye. $\text{Ru}(\text{dcbpy})_2(\text{NCS})_2$ ground state oxidation potential is positioned at 0.85 V vs. SCE (Nazeeruddin 1993; Islam, Sugihara et al. 2003). In highly efficient DSSCs, ΔG for regeneration is more than 0.7 V (Boschloo and Hagfeldt 2009) and thought to be associated with the highest energy loss of all the competitive kinetic steps taking place in a successful cycle of: light harvest, injection vs. dye decay (k_{inj} vs. k_{decay}) and electron collection vs. recombination ($[k_i \text{ \& } k_{rq}]$ vs. $[k_{eer} \text{ \& } k_{edr}]$).

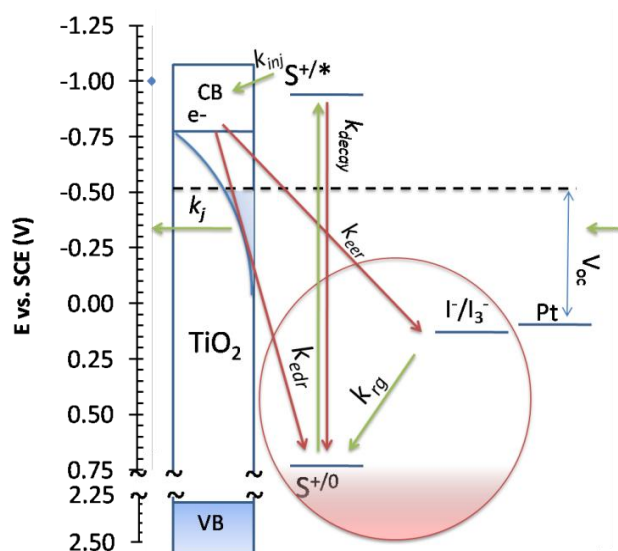


Figure 1-3 - Schematic of the energetic and kinetic relationships in DSSC, green and red arrows represent favourable and unfavourable reactions respectively. This study focuses on the encircled region: k_{rg} and k_{edr} the regeneration and recombination reaction rates.

In addition to the large loss in voltage and thus in efficiency, another limiting factor on DSSC efficiency, relative to competing technologies (e.g. silicon, CdTe), is the lower fraction of the solar spectrum that is absorbed by the dye molecules developed to this point (see Figure 1-4). Dye molecules that function well in DSSCs tend to have poor or no absorption at wavelength longer than 750 nm. (Nazeeruddin M. K. 2005; Gao, Wang et al. 2008; Reynal, Forneli et al. 2008; Cao, Bai et al. 2009) Extending this absorption to the red by 100 nm, without losing efficiency in other ways, would result in a significant improvement in photocurrent. (Hamann 2008; Snaith 2010) This challenge has proven difficult, in large part because of one slow reaction in the electron transfer cycle of DSSCs, the regeneration reaction. Better understanding of this reaction is thus critical for the future of DSSCs.

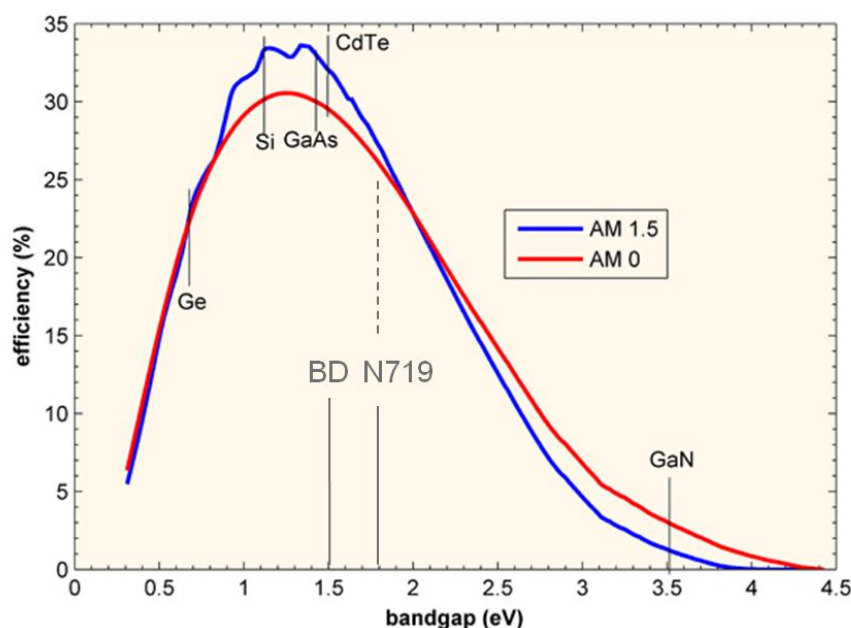


Figure 1-4 – Maximum solar cell efficiency as a function of the material bandgap for one-sun illumination. DSSCs performance and bandgap of Black Dye (BD) and N719 are loaded on the figure. The two dyes are typical Ruthenium based dyes commonly used in DSSCs. (Shockley and Queisser 1961; Honsberg and Bowden 2010)

1.1.1 The ideal cycle

The forward (desired) processes in the DSSC cycle are as follows (Figure 1-3). The photo-excited dye first injects an electron into the TiO_2 . The photo-oxidized dye is then regenerated (returned to the original state) by oxidizing an iodide ion in solution. This is the aforementioned kinetically challenging step. The net outcome of the absorption of 2 photons is the creation of two additional electrons in the TiO_2 , and one additional tri-iodide molecule in solution. During operation, the electrons diffuse to an electrical contact, from where they flow to the external circuit, through the load, and to a counter electrode in contact with the electrolyte. The excess tri-iodide diffuses to the counter electrode where it is reduced to iodide. The diffusion of iodide back into the pores of the TiO_2 layer completes the circuit. Quantum efficiency and energy losses can of course occur at any step of this process. For a general description of losses, see references (O'Regan, Durrant et al. 2007; Barnes 2009; Barnes, Anderson et al. 2009).

1.1.2 Injection

At the heart of DSSC function is the photo-oxidation and re-reduction of a dye molecule. As DSSCs have developed, it has proven relatively easy to manipulate the

conditions at the interface to achieve a near 100 % efficiency of the photo-oxidation (electron injection) step with relatively low energy losses, estimated to be ≤ 300 mV, for many classes of dyes. (Tachibana 2000; Haque 2005; Ardo and Meyer 2009) The key rate requirement at this step is that injection be at least 100 times faster than the natural decay of the dye excited state. This of course depends on the dye, but for the standard Ru complex dyes injection takes place on an ultrafast time scale (10^{-13} - 10^{-10} sec) and the natural decay is 10-20 ns. (Asbury 1999; Kallioinen 2001; Tachibana 2001; Koops, O'Regan et al. 2009)

1.1.3 Large Driving Force for Regeneration – Low Photovoltage

The re-reduction of the dye (i.e. regeneration) has proven difficult to study and optimize. The key rate requirement at this step is that the dye be regenerated by the electrolyte, before it is "regenerated" by an electron from the TiO_2 resulting in no net photocurrent. This latter reaction is referred to as "electron dye recombination" (EDR). Because of the nature of the iodide/tri-iodide redox couple, the regeneration reaction is complex and the rate constant is several orders of magnitude lower than the diffusion controlled limit. For example, dye regeneration by ferrocene in solution is approximately 3 orders of magnitude faster than that by iodide. (Cazzanti, Caramori et al. 2006) Luckily, reduction of the dye by the electron in TiO_2 (EDR) is also rather slow due to the low diffusion rate of the electrons in the TiO_2 (Schlichthorl, Park et al. 1999) and to the low concentration of electrons under operation (≤ 0.003 M) compared to the high iodide concentrations (≥ 0.5 M). Despite the concentration advantage, the current high efficiency dyes typically incorporate ≥ 600 mV thermodynamic driving force for the regeneration step. (Boschloo and Hagfeldt 2009) This driving force, related to the difference in the oxidation potential of the dye and the electrolyte, is dissipated as heat during the regeneration reaction and is a major loss in energy efficiency for DSSCs.

1.1.4 Slow Regeneration Limits the Use of Low Bandgap Dyes

This large required driving force is a major impediment to lower band gap dyes which absorb near infrared light. To reduce the band gap of the dye, either the reduction potential of the LUMO must become less negative, impairing the already optimized injection, and/or the HOMO must become less oxidizing, decreasing the driving force for regeneration. The thermodynamic driving force is in principle not directly related to the kinetics. It is, however, an expression of the difference in redox potentials that is required to make the regeneration proceed at a rate faster than that of EDR. Several examples of dyes with less positive

oxidation potentials, and much slower regeneration are known. (Onicha and Castellano ; Alebbi 1998; Clifford 2007) Although some counter examples have been cited in the literature, it is interesting that none of them, apparently, have red shifted absorption. (Sauvé 2000; Bessho, Yoneda et al. 2009) It appears that this large driving force is required to lower the activation barrier to regeneration to acceptable levels. As illustrated in Figure 1-5, a primary goal of regeneration studies is to understand this activation barrier and to find a way to catalyze the reaction by reducing it. There is insufficient data on the relation of dye redox potential and regeneration rate to map out a clear relationship at this time. Indeed, it is hard to change the redox potential of the dyes over a large range without including structural differences that could affect regeneration.

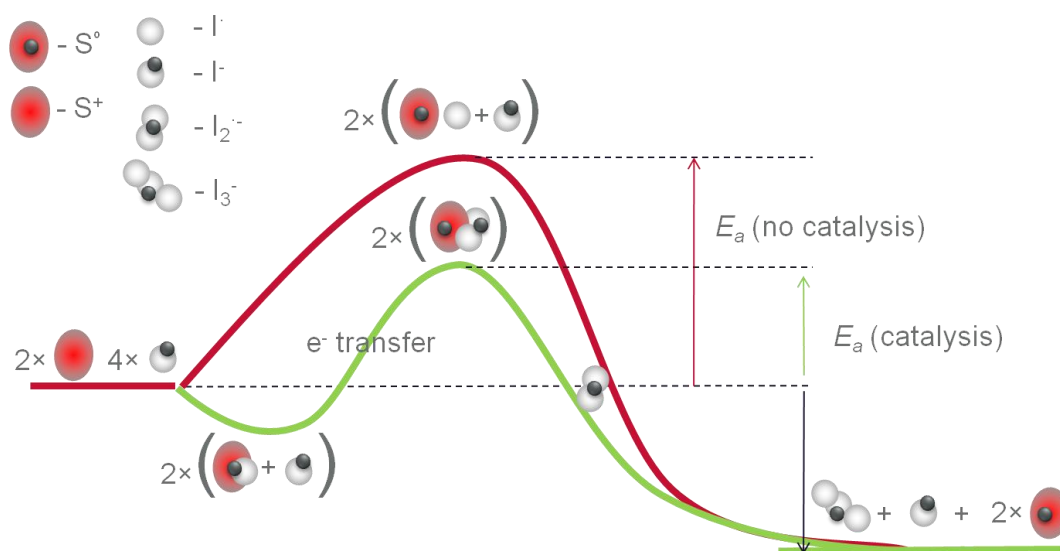


Figure 1-5 – Catalysing the regeneration reaction. The upper (red) route involves the formation of iodine atom radicals for the reduction of the oxidized dye, consuming the highest energy for regeneration. The green route shows that catalyzation of the formation of a lower energy intermediate, the Di-Iodine radical, on the dye itself reduces the activation energy (E_a) for regeneration and thus expected to result in higher performance for dye cells.

1.1.5 Qualitative Recombination and Regeneration Studies

The recombination reaction of injected e^- back to S^+ (EER) can be studied in redox inert electrolytes, since then there is no competition with regeneration and the recombination is the only route available for S^+ recovery ($S^+ + e^- \rightarrow S^0$). These experiments were conducted previously using externally applied bias potential to vary the e^- concentration in the TiO_2 and

transient absorption spectroscopy to probe S^+ relaxation. It was found that the recombination reaction is strongly dependent upon the accumulation of e^- in intraband/conduction band states of the TiO_2 film (Haque 1998; R. L. Willis 2002). However upon addition of redox active electrolyte, monitoring S^+ recovery becomes fiddly since the contributions of the two reactions are combined and expressed as a single process of S^+ loss.

The regeneration reaction and the level of competition with e^- recombination to the S^+ are key issues for understanding device performance. Commonly DSSC studies focus on the processes of light harvesting, injection and collection whilst regeneration is seldom studied explicitly and has never been quantified in working devices. This is because it is uncertain which species or intermediate limits the rate of the regeneration reaction and that the signal of regeneration, commonly measured using transient absorption spectroscopy (TAS), as said above, is often combined with that of the electron decay. In addition it can also be difficult to deconvolute the influence of the e^- back-reaction with the electrolyte (k_{eer}) from recombination to the S^+ (k_{edr}).

Qualitative regeneration studies have suggested possible routes for this reaction, as well as the possible regeneration rate limiting step. These studies have been made by: (a) changing the dye relative to the electrolyte (Alebbi 1998; Sauvé 2000; Kroeze 2006; Clifford 2007), (b) by changing the electrolyte relative to a fixed dye (Gregg 2001; Nusbaumer 2001; Oskam 2001; Sapp 2002; Cameron 2004; Nusbaumer 2004; Bergeron 2005; Hari M. Upadhyaya 2006) or (c) by changing the oxide in a same dye-electrolyte system (Nasr 1998; R. L. Willis 2002). Conceptually in (a), both regeneration and recombination may vary. In (b), recombination should remain constant while regeneration may vary. and in (c), regeneration should remain constant and recombination may vary. In each of the cases above the ratio between the rates of regeneration and recombination should change. It is important to remember that when this kind of changes are made, changes in spatial limitations (Kroeze 2006) or affinity between specific species (O'Regan 2009) may occur.

1.1.6 Preface to Regeneration mechanisms

This work considers iodide/tri-iodide (I/I_3^-) since, to date, it is the best performing redox couple; no other mediator or hole transporting medium is competitive at present. In the context of DSSCs, I/I_3^- is also the most studied redox couple and much relevant information and references can be found in a recent paper by Boschloo. (Boschloo and Hagfeldt 2009) Although the couple is extensively studied there is still some controversy over the reactions

mechanisms, the reactions rates and orders, the rate limiting step, and the final consequences for device performance (not to mention recombination).

Following regeneration there are several steps known to consume some of the initial energy provided by injection: It is thought today that the regeneration is followed by the disproportionation reaction (known also as dismutation), (Fitzmaurice 1991; Fitzmaurice 1993; Alebbi 1998; Nasr 1998; Pelet 2000; Walter 2001; Montanari 2002; Marton 2006; Clifford 2007; Gardner, Giaimuccio et al. 2008) Boschloo suggests that it is the disproportionation reaction that leads to a large loss in potential energy thus should be considered in the determination of regeneration driving force. This statement requires more empirical proofs. Following disproportionation small amount of energy is consumed for the diffusion of species to the counter electrode. Then a $2 e^-$ transfer on the counter electrode to reduce I_3^- and yield three I^- consumes additional amount of energy. The energy consumed in I_3^- reduction is small thanks to the catalytic behaviour of the platinum deposited on counter electrode. The platinum catalyzes the cleavage of I_3^- to form iodine radical atoms ($I^\bullet$) which are then easily reduced by the circuit electrons. (Papageorgiou, Maier et al. 1997; Wang, Moser et al. 2005; Bay, West et al. 2006; Khelashvili, Behrens et al. 2006). The rate of regeneration depends on the concentration of species available in the TiO_2 pores. Diffusion of “fresh” iodide to the pore and in the pores modulates these concentrations and also requires some energy. (O'Regan and Durrant 2009) The diffusion of species in the electrolyte, between the working and counter electrodes, is called mass transport or diffusion limitation and is dependent on parameters like solvent type, viscosity, cell thickness (Asano, Kubo et al. 2005; Hoshikawa 2006) and pore size (Papageorgiou 1996; Papageorgiou 1998; Cameron 2004). The first steps of regeneration, prior to the formation of $I_2^{\bullet-}$, are somewhat uncertain. After injection, S^+ must oxidise the electrolyte. There are several possible routes for this:

1.1.6.1 Iodine Radical

A direct reduction of S^+ by I^- to form S^0 may proceed via the formation of iodine radical ($I^\bullet$) in the solution. By using a high oxidation potential dye in solution (no oxide, no injection) ($S^+/S^0=1.36V$ vs. SCE) $[Ru(bpz)_2(deeb)](PF_6)_2$, where bpz is 2,2'-bipyrazine and deeb is 4,4'-(CO_2Et)₂-2,2'-bipyridine, Gardner et al showed that the dye's excited state decayed prior to the rise of $I_2^{\bullet-}$, the appearance of $I_2^{\bullet-}$ was three times slower indicating that it is not a direct reaction product of the excited state and that $I^\bullet$ is the only plausible

intermediate that could form in that time gap. (Gardner, Giaimuccio et al. 2008) $I^\bullet$ is hard to probe specifically and is known to have an oxidation potential which is higher than the ground state oxidation potential of most high performance dyes. Assuming that the measured value for $I^\bullet$ oxidation potential in water is approximately the same in organic solvents implies that $I^\bullet$ formation is energetically unfavourable in full dye sensitized solar cells. (Alebbi 1998)

1.1.6.2 [Oxidized-dye ·· Di-iodine anion radical] ion pairs formation

The S^+ forms an intermediate $[S^+, I_2^{\bullet-}]$ prior to the formation of free $I_2^{\bullet-}$. This was highlighted by Fitzmaurice et al. using colloidal TiO_2 with grafted $Ru(dcb)_3^{2+*}$ (dcb= 2,2'-biphenyl-4,4'-dicarboxylat) in acidic aqueous electrolyte solution. In that system they performed a transient kinetics study in 0.5 to 100 mM KI. The observations showed more intense absorption than would be expected for $I_2^{\bullet-}$ absorption. Fitzmaurice proposed that the excited state is expected to be better stabilized in water than in the less polar ethanol and concluded that the bipyridyl- $I_2^{\bullet-}$ charge transfer transition absorption (Person 1963) of a $RuL_3I_2^{\bullet-}$ ion pair is the most probable origin of their observed transient. (Fitzmaurice 1991)

1.1.6.3 [Iodide ·· Iodide] preformation

The idea of pairs formation was further developed by Pelet et al. It was suggested that the formation and dissociation of $[S^+, I_2^{\bullet-}]$ may be accelerated if either $[I, I]$ are formed prior to charge transfer or if $[S^+, I]$ is sufficiently long lived to allow the approach of a second I , which then enables charge transfer from I^- to S^+ . Pelet showed that a measured change in surface potential, changed from negative to positive, was correlated with accelerated dye bleach recovery which meant a faster regeneration. He suggested that small counter ions, which caused the change in surface potential, accelerated the preformation of $[I, I]$ and consequently the overall process. (Pelet 2000)

1.1.6.4 [Oxidized-Dye ·· Iodide] pair formation

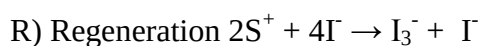
In a later study by Clifford et al, using $Ru(dcbpy)_2(CN)_2$ (dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl) ($S^+/S^0=1.0V$ vs. SCE) coupled with relatively low concentration of LiI (0.015M) a slow optical density rise (few microseconds, probed at 800 nm) was observed. Clifford proposed this as evidence for the slow formation of $[S^+, I]$ ion pair (see Pelet above). In the same work similar evidence was shown for $Ru(dcbpy)_2Cl_2$ and $Ru(dcbpy)_2DTC_2$ (DTC=diethyldithiocarbamate), (Clifford 2007) the signal rise of the last two dyes was faster

than the one observed for the $\text{Ru(dcbpy)}_2(\text{CN})_2$. However a noticeable rise time was not observed for the $\text{Ru(dcbpy)}_2(\text{SCN})_2$, the same dye used in this study.

1.1.7 Regeneration mechanisms and reaction orders

Reaction R (below) gives the overall regeneration reaction, taking into account the very strong binding between iodine (I_2) and iodide (I^-) (see equation 5-15 in section 5.7.8). Schemes R1-3 show various mechanisms that have been proposed for the reaction. It is reasonably certain that the reaction proceeds through di-iodine radical ($\text{I}_2^{\cdot-}$), requiring the participation of two I^- for each oxidized dye (S^+). A major division between the reaction schemes is thus whether the reaction is first or second order in I^- . In Scheme R1, which is assumed to be the most probable, after electron injection ($\text{S}^* \rightarrow \text{S}^+ + \text{e}^-$) there is a rapid formation of a complex of the oxidized dye and one iodide (R1a) without substantial charge transfer. (Clifford 2007) Then a second I^- approaches this $[\text{S}^+\cdots\text{I}^-]$ complex (R1b), charge transfer occurs, releasing the products S^0 and $\text{I}_2^{\cdot-}$. At this point regeneration is considered complete, as EDR cannot occur. Disproportionation of $\text{I}_2^{\cdot-}$ follows (R1c). Note that if R1a is effectively complete before R1b, the reaction will be first order in iodide, whereas if R1a reaches a rapid equilibrium, the order in I^- can be two. The same conclusion holds for step R1b; if R1b rapidly reaches equilibrium and step R1c is slow, then the overall reaction order in I^- can be two. In competition with the forward reactions is the EDR to the S^+ , and most likely to $[\text{S}^+\cdots\text{I}^-]$, as shown by reactions E1 and E2 respectively.

Scheme R2 assumes a precomplexation of two I^- before the regeneration, giving 2nd order in I^- . (Pelet 2000) Scheme R3 goes via direct oxidation of I^- to free iodine radical ($\text{I}^{\cdot}$), followed by binding of another I^- to form $\text{I}_2^{\cdot-}$. Again, equilibrium at R3a can give second order behaviour. It is important to realize that there is no "one and only" mechanism for regeneration. All of these reactions could function in different proportions in cells with different dyes oxidation potentials, solvent viscosities, etc.

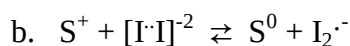


R1

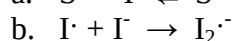
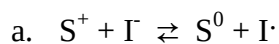
- a. $\text{S}^+ + \text{I}^- \rightleftharpoons [\text{S}^+\cdots\text{I}^-]$
- b. $[\text{S}^+\cdots\text{I}^-] + \text{I}^- \rightleftharpoons \text{S}^0 + \text{I}_2^{\cdot-}$
- c. $\text{I}_2^{\cdot-} + \text{I}_2^{\cdot-} \rightarrow \text{I}_3^- + \text{I}^-$

R2

- a. $\text{I}^- + \text{I}^- \rightleftharpoons [\text{I}^-\text{I}^-]^{-2}$



R3



E) Electron Dye Recombination

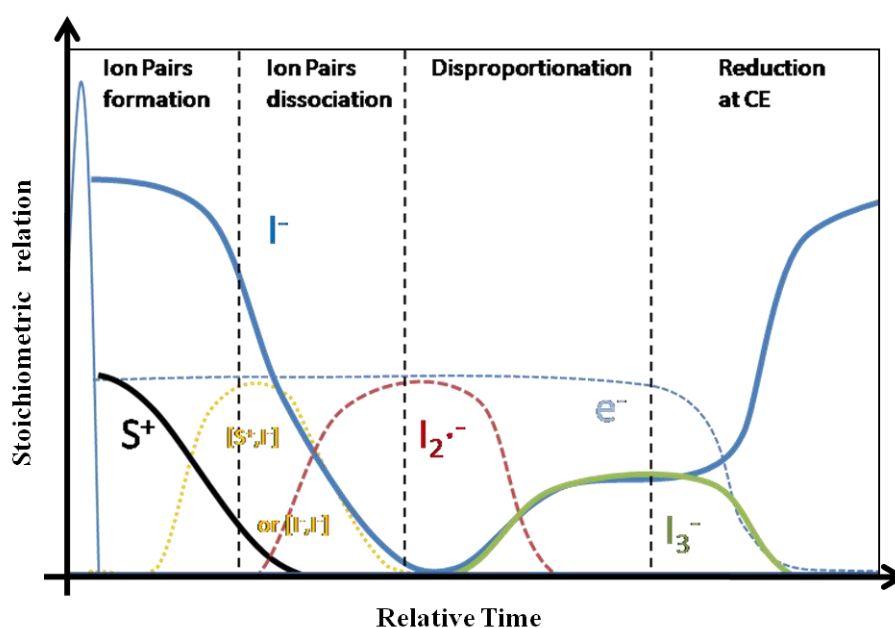
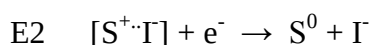
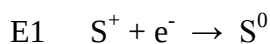


Figure 1-6 –The route of Ion pairs formation. Theoretical stoichiometric relation of regeneration related species as a function of relative time following dye excitation.

1.2 DSSCs Spectroelectrochemistry

Optical spectroscopy of dye sensitized solar cells is complex. When the cell is idle, overlaying on each other are the absorption spectra of several components. Once the cell is turned on, a mixture of new absorptions and disappearance of the initial ones are shuffled together. Changes in absorption occur in ground state, excited state, ions, charge transfer intermediates and complexes. Thus for each change in a dye sensitized cell component, the work of assigning absorption regions to species need to be repeated. For example at the probing region of $\lambda = 800 \pm 50$ nm there is evidence for the absorption of $\text{I}_2^{\bullet-}$ in water. (Hug 1981) At the same wavelength with TiO_2 colloid coated with the $\text{Ru}(\text{dcb})_3^{2+*}$ in water, $\text{I}_2^{\bullet-}$ had a six times larger molar absorption coefficient due to the charge transfer intermediate

$[S^0, I_2^{\bullet-}]$. (Fitzmaurice 1991) On contrary, in non-aqueous systems and with three dyes of the structure $Ru(dcbpy)_2X_2$, Clifford showed the formation of $[S^+, I^-]$, which dissociated without evidence for $I_2^{\bullet-}$. (Clifford 2007) The broad steady state absorption spectrum of TiO_2 in water, under applied bias voltage, indicated that e^- in the TiO_2 also absorbs light at this region (O'Regan 1991; O'Regan 1991; Rothenberger 1992). Finally, from Tachibana's work it is also known that $Ru(dcbpy)_2(NCS)_2$ shows an absorption for its S^+ and S^* states. (Tachibana 1996) following are the relevant spectra for this study.

1.2.1 Spectra of common DSSC's variables

1.2.1.1 Excited and oxidized $Ru(dscbpy)_2NCS_2$

As shown in Figure 1-7 the kinetics of S^+ can be tracked in near IR where $\lambda \approx 830nm$. Probing S^+ can be a measure of injection by its appearance and a measure of regeneration/recombination by its disappearance.

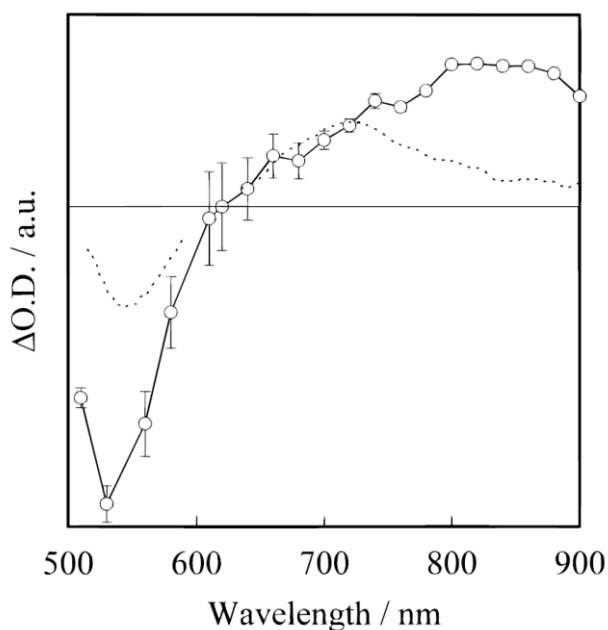


Figure 1-7 - Absorption difference spectra of the formation of cation (-o-) and excited (--) states of $Ru(dscbpy)_2NCS_2$ in ethanol solution. The difference spectrum for the excited state is taken at a time delay of 5 ps after 605 nm excitation in the absence of any electron acceptors. The cation state spectrum was obtained at a time delay of 10 μs after excitation of $Ru(dscbpy)_2NCS_2$ in the presence of the electron acceptor methylviologen (MV). The spectrum does not contain any residual contributions from the dye excited state which decays within nanosecond time scale. Contributions to this difference

spectrum of the MV anion have been subtracted from the transient data (Tachibana 1996).

1.2.1.2 Electrons in TiO_2

Figure 1-8 show the absorption spectrum of electrons in the TiO_2 , sometimes also called Ti^{III} . Electrons in the TiO_2 show a broad absorption spectrum that spans with gradually increasing amplitude from the UV region to the IR. Sometimes the absorption starts fading around 1000 nm. (O'Regan 1991; O'Regan 1991; Rothenberger 1992; Haque, Tachibana et al. 2000)

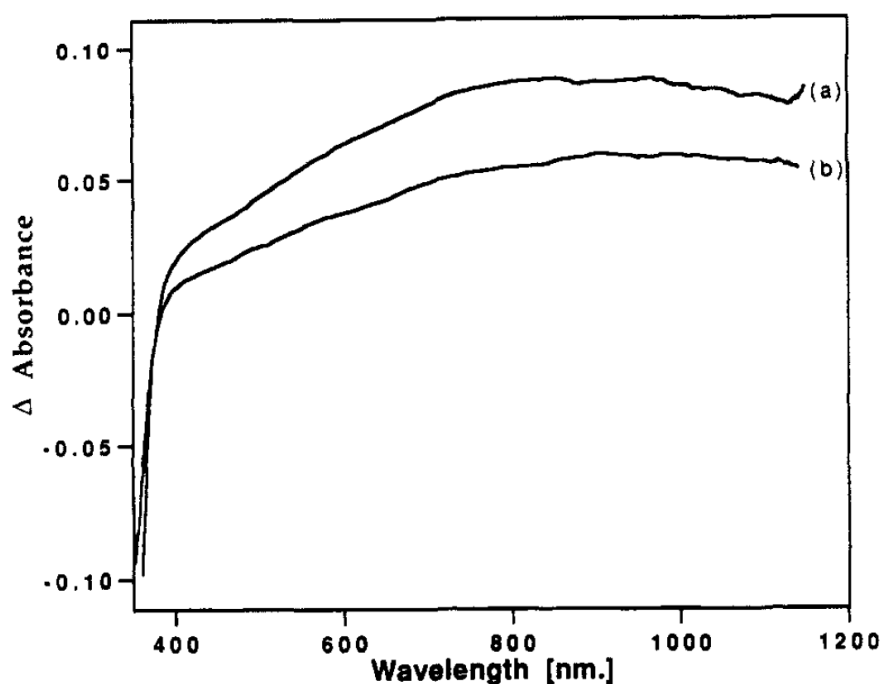


Figure 1-8 - (a) Difference optical absorption spectrum of a TiO_2 electrode in aqueous 0.2 M LiClO_4 (pH 3.0) measured at -1.00 and +1.0 V (SCE). (b) Difference spectrum of a TiO_2 electrode in aqueous 0.2 M LiClO_4 (pH 11.6) measured at -1.30 and +1.0 V (SCE) (Rothenberger 1992)

1.2.1.3 Iodine atom radical

The spectrum in Figure 1-9, of iodine radical ($\text{I}^\cdot$), shows a single peak around 260 nm ($\epsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}$) (Hug 1981). In device, this region is screened by the glass, the FTO and the TiO_2 band gap absorption.

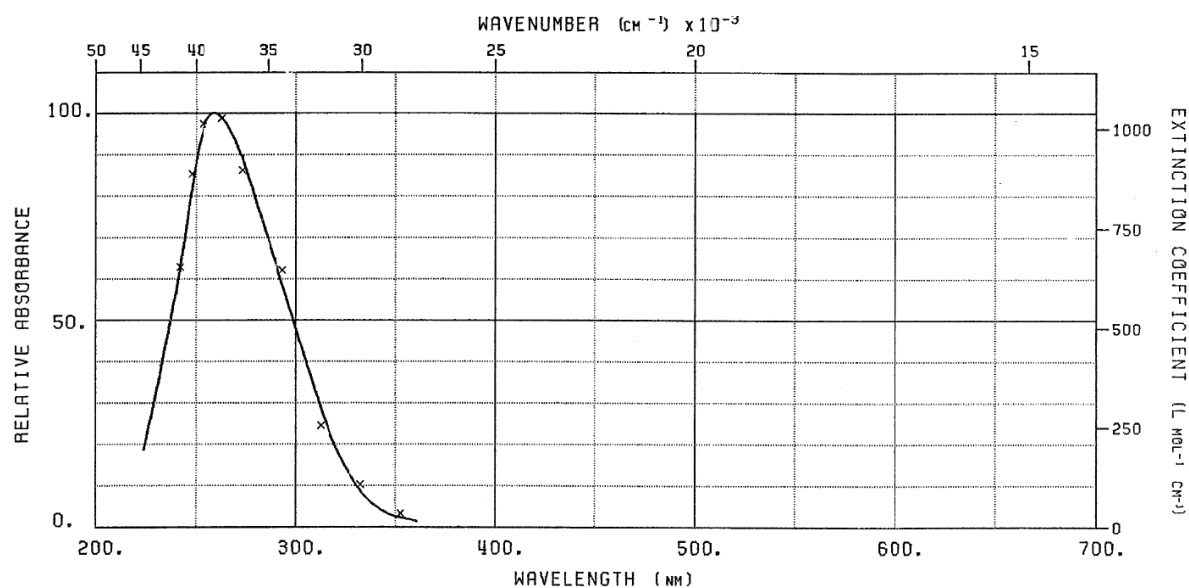


Figure 1-9 - the absorption spectra of iodine radical ($I^{\cdot}$) with single maximum around 260 nm ($\epsilon = 1000 \text{ M}^{-1} \text{ cm}^{-1}$). (Hug 1981)

1.2.1.4 Di-Iodine radical anion

The spectrum in Figure 1-10, of Di-Iodine radical anion, shows a primary absorption maxima around 390 nm ($\epsilon = 9500 \text{ M}^{-1} \text{ cm}^{-1}$) and a secondary broad peak around 745 nm ($\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$). (Hug 1981)

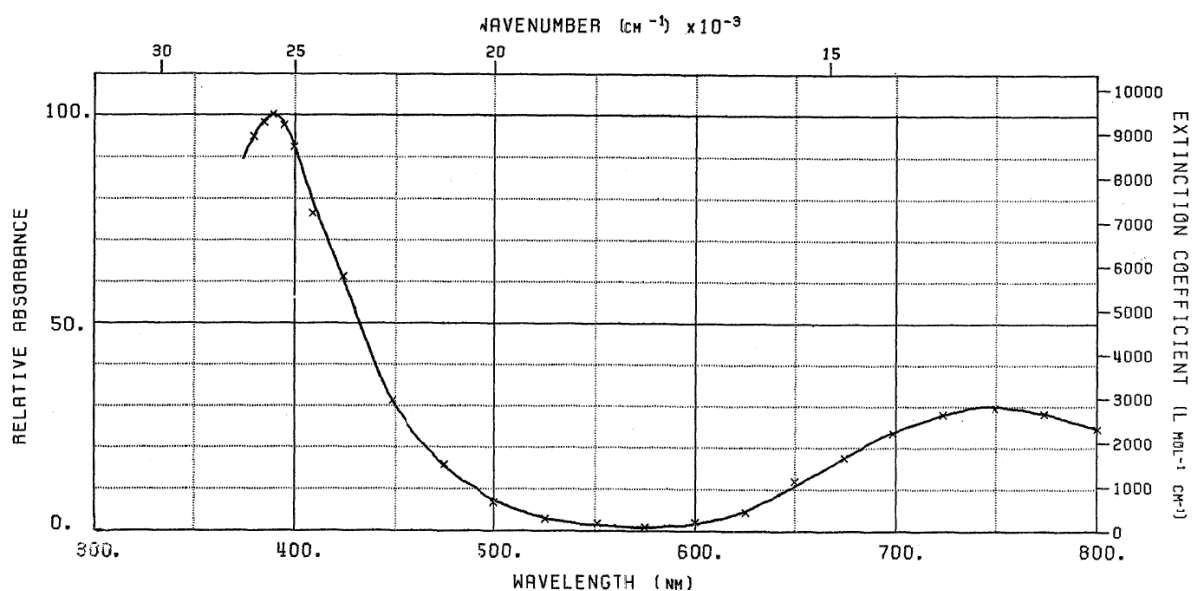


Figure 1-10 – absorption spectra of di-iodine radical anion ($I_2^{\cdot-}$) with primary maxima around 390 nm ($\epsilon = 9500 \text{ M}^{-1} \text{ cm}^{-1}$) and a secondary broad peak around 745 nm ($\epsilon = 3000 \text{ M}^{-1} \text{ cm}^{-1}$) spanning towards the IR. (Hug 1981)

1.2.1.5 Iodine, iodide and tri-iodide

Figure 1-11 shows absorption spectra of iodide (I^-), iodine (I_2) and tri-iodide (I_3^-) in acetonitrile. The rightmost peak of iodine, at $\lambda = 465$ nm, disappears once sufficient iodide was added to convert all iodine to tri-iodide.

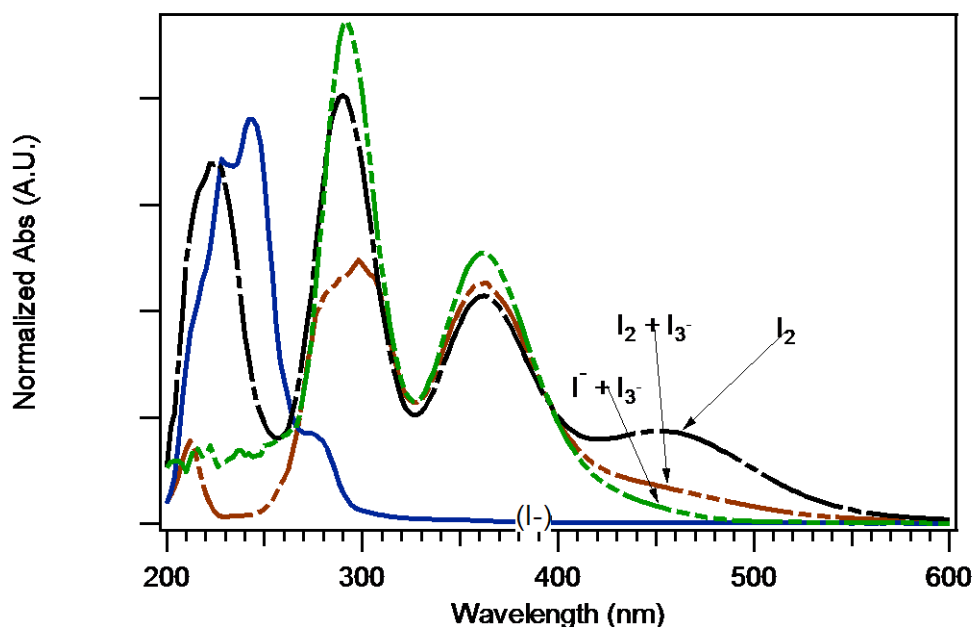


Figure 1-11 – Normalized absorption in acetonitrile of: Iodide (I^-) - 9×10^{-5} M tetra butyl ammonium iodide salt (TBAI). Iodine (I_2) - 4.6×10^{-4} M I_2 . Iodine and tri-iodide ($I_2 + I_3^-$) 2.3×10^{-4} M I_2 and 4.5×10^{-5} M TBAI. Iodide and tri-iodide ($I^- + I_3^-$) 3.65×10^{-4} M I_2 and 1.85×10^{-3} M TBAI. Unpublished data measured in Imperial college DSSC group and edited for the purpose of this chapter (Webster and O'Regan 2008).

1.3 The aims of this work and how the problem is addressed

The kinetics of regeneration has been little studied relative to the other processes in DSSCs. This is in part because the regeneration reaction produces no measurable electrical signal (as yet detected). It must be studied by more difficult transient absorbance techniques. The main objectives of this work are: To establish a solid framework for reproducible regeneration studies. To better understand the regeneration mechanism. To isolate and quantify the regeneration and electron-dye-recombination quantum yields under various conditions. To provide initial intrinsic numbers that rank dyes and interfaces in DSSCs and can be used to compare, model and predict future beneficial combinations. And finally, to try and optimize the way these numbers are obtained. These objectives are achieved in several steps, addressed in several planes that feed back into each other:

The first step, reviewed in experimental chapter - 2, is the technical development of the simultaneous transient absorption – transient electrical (TA-TE) setup. This setup does not just enable synchronised acquisition and control of both optical and electrical signals, it is also designed to minimize human errors, increase capacities and reproducibility, and monitor as many parameters as possible in order to extract the maximum information required. The way this information is stored enables the extraction of even more information retroactive. Monitoring the steady state photocurrent during TA-TE measurements revealed instabilities in cells assembled with propylene carbonate based electrolytes. These instabilities imposed serious difficulties in the interpretation of regeneration. Chapter 3, also experimental, tells the story of these electrolytes and the reasons that lead to the decision to drop the propylene carbonate and make the much more stable, state of the art, series of cells.

The results chapter 4 examines the type of signals that can be obtained by the TA-TE system and the merits of correlating electrical and optical signals. Using these observations, signals can be assigned to chemical species known to exist in the common configuration of DSSCs. The effects of poor and good regeneration are examined and the basis to the method and the model presented in chapter 5 are established. Chapter 5 gathers all the building blocks presented in the former chapters. The stable MPN series of cells is used and the kinetics of the oxidation of iodide is investigated using complete cells, under 1 sun illumination and at short circuit. A simple model and a method show that TA decays of the oxidized dye can be correlated with the short circuit current (J_{sc}) and electron concentration in the TiO_2 to determine the fundamental regeneration rate constant, as well as the order in iodide, the fundamental rate constant for electron dye recombination (EDR), and the apparent reaction order in total electron concentration.

Having the TA-TE setup arranged and a clear understanding of the kinetic model of regeneration ignited the development of the Steady State Photoinduced Absorption (SSPA) spectroscopy synchronised with steady state electrical measurements. The technicalities are mentioned in the experimental chapter 2 and further description of the method and results are shown in chapter 6. This concept is new and requires more exploration, experience and a development of an appropriate model, however it does already provide some new insights on regeneration studies and raises some questions on the accuracy and necessity of other techniques.

2 Experimental – Instruments Development and Techniques

2.1 Simultaneous Transient Absorption Transient Electrical (TA-TE) Setup

Figure 2-1 shows a photograph of the TA-TE setup, this setup is designed to acquire simultaneously optical and electrical signals and to obtain data on complete devices under operational condition. In order to enable maximum control and to obtain as much information as possible, both traditional hardware and software were reconsidered and reconstructed from scratch. The final result is a fully automated setup that, per sample, enables the acquisition of all the techniques and measurements described in this chapter. In practice TPV, TPC and CE measurements were also made with the transients electrical setup made by Dr. Brian C. O'Regan.

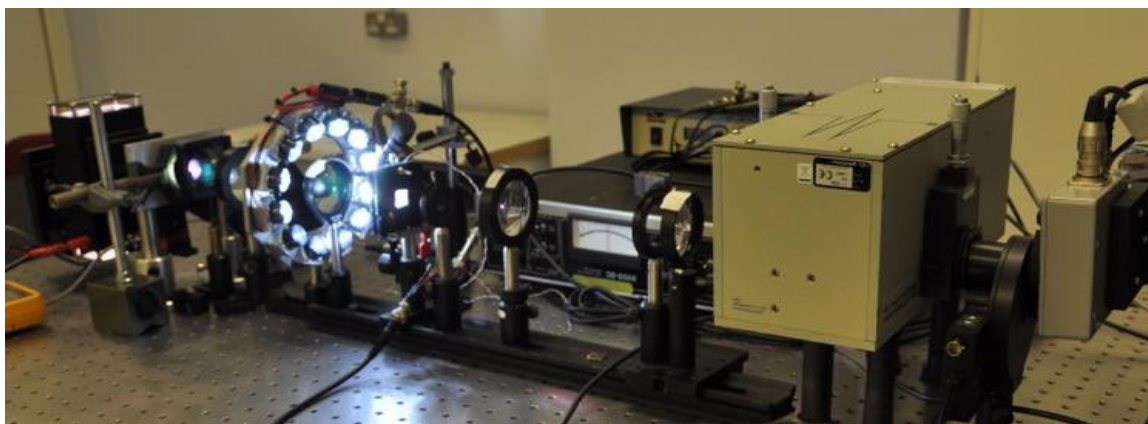


Figure 2-1 – Photograph of the simultaneous TA-TE setup.

2.1.1 TA-TE hardware

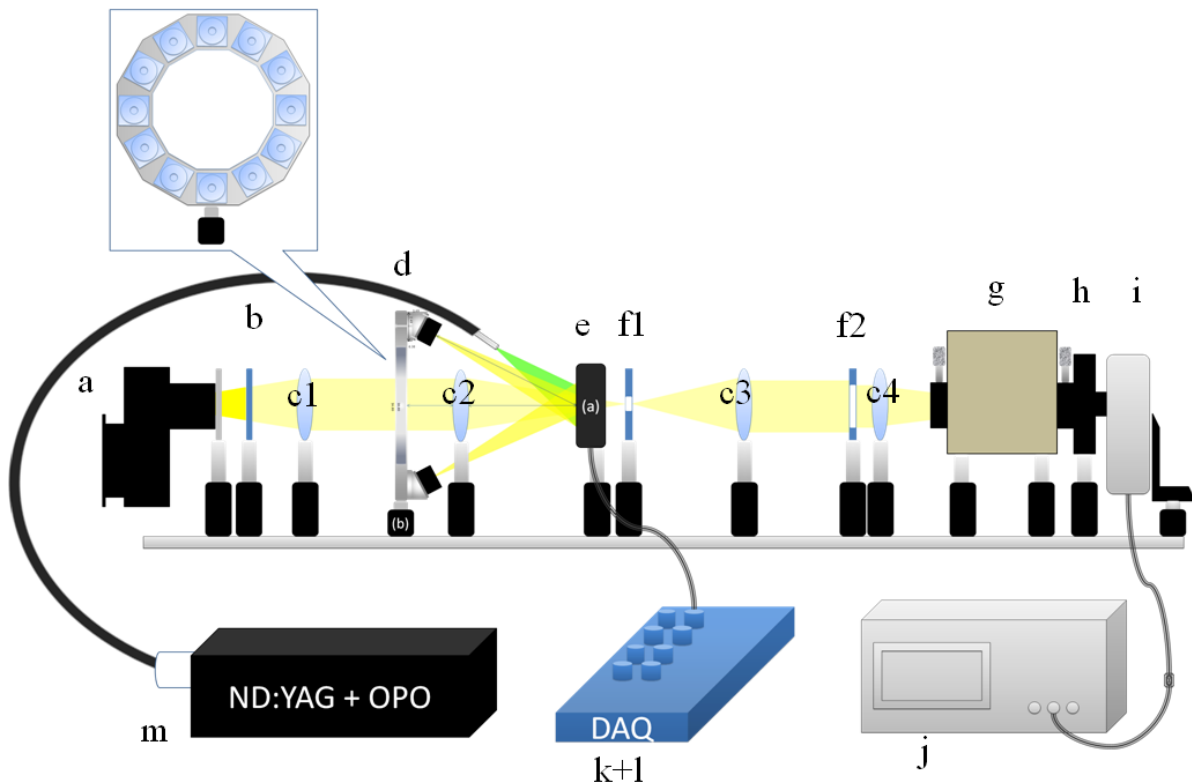


Figure 2-2 – Schematic drawings of the simultaneous TA-TE setup.

Figure 2-2 shows a schematic description of the TA-TE setup to date. When a different configuration of the setup was used, it is mentioned in the specific result chapters. The setup components (with references to their specifications) are as follows:

- a. **Tungsten Halogen Probe lamp source** - Bentham IL1. Controlled with current stabilized power supply - Bentham 605. (see 9.4)
- b. **Filters and shutter** - Holder/s for neutral density (ND), and/or bandpass (BP), and/or longpass (LP) optical filters. These are chosen according to the measurement requirement and usually are not changed during an experiment. A computer controlled shutter is located in this position as well. This enables the automatic recording of laser scatter and luminescence signals.
- c. **Lenses** - Set of four lenses to collimate (c1) and then concentrate (c2) the probe beam through the sample. Then to collimate (c3) again and concentrate (c4) the probe beam on the detector. Additional, fifth lens, is integrated in the probe light housing.
- d. **Bias Light** - Homemade array of LEDs which are focused on the sample holder and yet enables the probe beam and the excitation source to reach the sample with no

interruption. The bias light can generate up to two suns under given constrain that the LEDs emission spectrum is limited to the visible with intense bluish emission (9.5.2). The LEDs can be replaced if required. For the array design diagram and for the LEDs specifications see 9.5.1.

- e. **Sample holder with temperature and electrical probes** - Home made sample holder that can be easily positioned in the probe beam. The sample holder has three dimensional linear adjustments options + vertical rotation. The holder enables high reproducibility and easy replacement of samples. The sample holder is designed to mask a square cm solar cell, hence all cells are exposed to the exact conditions at the same location. The sample holder also connects the solar cell to the data acquisition card (DAQ) for the temperature and electrical monitoring with no need for alligator clips. A close-up photograph can be found in section 9.3.
- f. **Apertures** - the first aperture (f1) is positioned exactly at the focal point of lens c2. This position enables to control the amount of light that reaches the detector without altering the image. This location is very useful to reduce the amount of laser scattered light without reducing the probe beam intensity. The second aperture (f2) is positioned between lenses c3 and c4, where the probe beam is collimated. This position is useful to chop (from the image) the probe beam that does not go through the sample and causes oversaturation of the detector.
- g. **Monochromator** - the Cornerstone 130 1/8 m motorised monochromator is loaded with two gratings: the first has a blaze wavelength of 350 nm (9.6.1) to get maximum light throughput in the region where the tungsten halogen probe lamp is weak and the silicon detector is less responsive. The second grating has a blaze wavelength of 1000 nm (see 9.6.2) and is suitable for use with the infra red detector. Except the slits, the monochromator is fully software controlled.
- h. **Filter wheel** - the six positions filter wheel, Thorlabs FW120B, is currently loaded with 5 longpass filters: 280, 395, 495, 780 and 1000 nm (see 9.7.1). The filter wheel is also computer controlled and the appropriate filters are selected by the TA-TE software. At a given wavelength a LP filter minimizes the second order diffractions fooling the detector.
- i. **Fast detectors** - two Costronics detectors: first for the visible with 80 ns rise time - PVOT/D/V (see 9.8.1). The second for the IR region with 200 ns rise time - PVOT/D/IR (see 9.8.2). The detectors are easily interchangeable and use the same amplification box (see 9.8.3).

- j. **Oscilloscope** - any oscilloscope from the Tektronix TDS 200 1000 2000 series can be used to record the optical signals. If needed, the electrical output from the device can be connected, this is in the case that higher time resolution than the DAQ card provides is required. The TA-TE software avoids almost any user interaction with the oscilloscope.
- k. **Data Acquisition (DAQ) card** - the NI USB-6251 DAQ card (see 9.2 for specs) provides additional channels for analog inputs, analog outputs, triggers and digital outputs. The DAQ analog inputs are used to monitor transient and steady state electrical conditions. It also records the device temperature and the background level of the fast detector for optical density calculations. The digital channels are used to switch between electrical conditions. Digitals are also used to do simultaneous fast switching of electrical and bias light conditions (i.e. for charge extraction). Analogue and digital outputs are also used to control the operational amplifier circuit.
- l. **Operational Amplifier (Op-Amp) circuit** - the design of the homemade Op-Amp circuit, the circuit components and the table of operations' logics (Table 9-1) can be seen in section 9.1. The op-amp circuit enables to run JV curves directly on the TA-TE setup. It also enables to run the examined solar cell at constant current or constant voltage and to record the various electrical or optical transients originating from these conditions.
- m. **Laser + OPO + light guide + triggering photodiode** - for transients measurements the samples are excited with a ND:YAG laser (9.9.1). The excitation pulse can be tuned to any desired wavelength in the region of 410 – 2200 nm using an Optical Parametric Oscillator (OPO) (9.9.2), alternatively a 355 nm dedicated output can be used. A small fraction of the excitation pulse is diverted to excite the triggering photodiode (9.9.4); the triggering photodiode initiates any cycle of transient measurement and is connected to both the oscilloscope and the DAQ card. The remaining primary fraction of the excitation pulse is directed to a liquid light guide (9.9.3) that guides the pulse to the sample in the sample holder.

Appendix 9 in page 134 gathers all the aforementioned technical details.

2.1.2 TA-TE Software

Figure 2-3 shows the main panel of the TA-TE control software. The software synchronizes the acquisition of the transient optical and transient electrical signals. It also

analyzes some of the data to enable a live monitoring of steady state electrical stability, temperature and steady state absorption. A great emphasis is placed on reproducibility, automation and minimum human attention. This reduces the amount of efforts and increases the throughput.

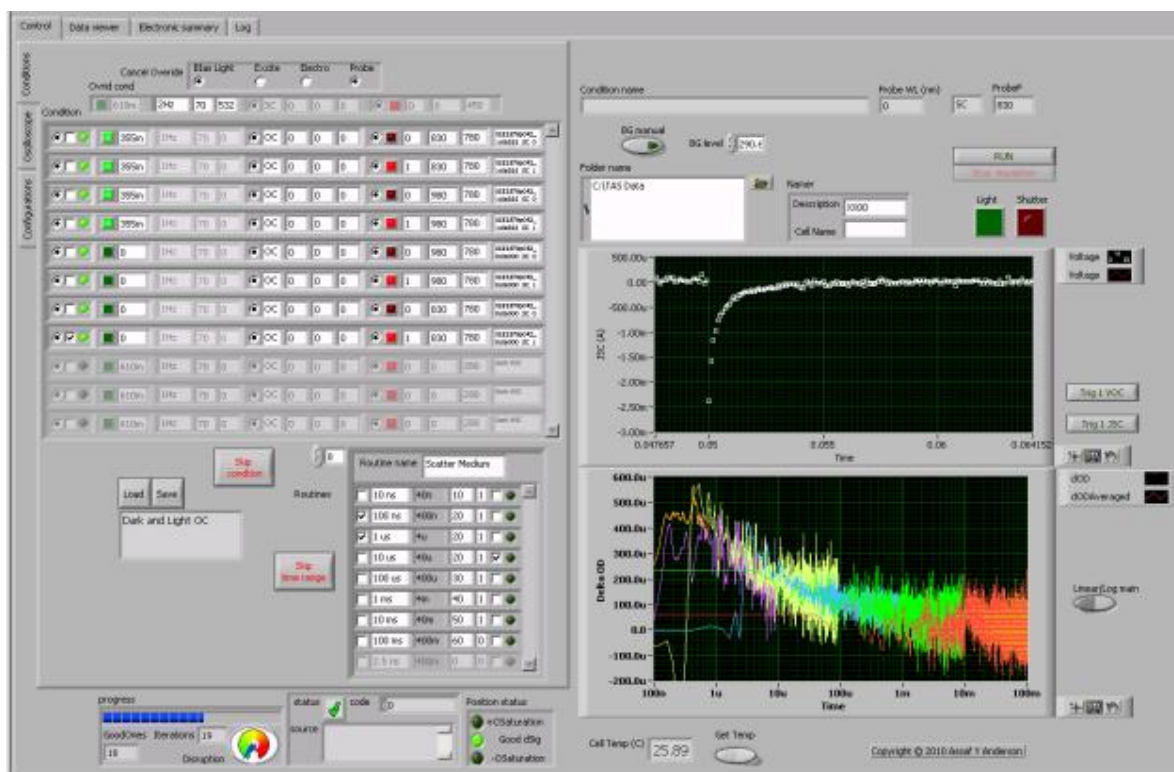


Figure 2-3 – Software, main window of the Simultaneous TA-TE Graphical User Interface (GUI).

The concept of the TA-TE software is to execute a queue of conditions where each parameter is stored with respect to the condition and the signal that originates from it. This is very useful for future references and for retroanalysis of results. The user can design an experiment where he can change any of the following parameters within an executed condition:

a. Bias light control

- a. Bias light On / Off.
- b. Bias illumination intensity, by controlling the current supplied to the LEDs array.

b. Excitation record (currently the direct control of the laser is disabled. However the software does store the parameters. The direct control of the excitation parameters has to be made from another computer), excitation parameters are:

- a. Q-switch repetition rate.
- b. Q-switch delay.
- c. OPO wavelength.

c. Electrical control

- a. Electrical condition (OC / SC / CC / CV).
- b. Constant current (CC) level or constant voltage (CV) level (the circuit supports these functions however currently CC / CV are disabled in the software).

d. Optical control

- a. Shutter open \ close.
- b. Reference to a set of oscilloscope routines to be executed per condition. These predefined routines specify the resolution, number of averaging and the number of segments that make a final concatenated oscilloscope signal.
- c. The probe wavelength (monochromator).
- d. Longpass filter (filter wheel).

2.1.2.1 Reproducibility

The user can add as many conditions as one can think of and save any configuration made to a set of conditions (and any other software controlled configurations) as an experiment. This is very useful for repeating or reproducing an experiment on a different sample, or on a series of samples and to establish standardization in the measurements.

2.2 Steady state electrical

Every time a solar cell is placed in the sample holder (2.1.1 e) it is connected to the DAQ card via the op-amp circuit (2.1.1 k+l). Connecting the cell in such a way enables control and measurement of the electrical (and optical) behaviour of the cell. The following are the steady state electrical conditions that can be applied on the cell. For each electrical condition the steady state electrical measurements that can be obtained is mentioned. The descriptions are given in the context of the DAQ + Op-Amp configuration:

Open Circuit (OC) –when the cell's electrodes are connected to an analogue channel on the DAQ card (see AI impedance values in 9.2), current doesn't flow and the cell voltage or photovoltage can be measured.

Short Circuit (SC) - In order to short circuit the cell, a digital channel in the DAQ card activates a transistor (metal oxide semiconductor field effect transistor - MOSFET), which

directs the current to a $2\ \Omega$ resistor. The voltage drop across this resistor is the measure of current (using $I=V/R$).

Constant Current (CC) and Constant Voltage (CV) – Relay-1 in the electronic circuit (Figure 9-1) switches the connection of the cell between the MOSFET circuit mentioned above and second sub-circuit, which can run in two modes on a dual op-amp. The op-amp is required due to the fact that the DAQ card is limited to a maximum current of 5 mA per channel and in some cases amplification assistance is required. In the second (op-amp) sub-circuit, relay-2 switches between the two modes (circuits), the CC and the CV:

The **CV** circuit will gain the necessary current to maintain the requested voltage. The current that the op-amp provides to the circuit is recorded. Dark and light extended JV curves and regular JV measurements make use of this circuit.

The **CC** circuit uses the same analogue output voltage channel as a control for the current level. This applied voltage is a result of the calculation of the requested current multiplied with the resistance of a resistor positioned on the input of the CC circuit ($1\ \text{k}\Omega$). The voltage that the circuit maintains in order to provide the requested current is recorded.

2.2.1 Device stability

TA measurements may take some time to accomplish (numerous averages are required per each routine and there are several routines per condition). One of the important requirements from TA measurements is that the sample and its environment did not change during the measurement. This will assure that the property under examination is a sole result of the pre-set conditions. Since the sample is wired to the electrical circuits, the examined electrical condition can be monitored and provide some indication on the stability and consistency during the measurement. Due to the fact that samples sometimes degrade, sometime improve and sometimes takes time to reach steady state equilibrium, this kind of monitoring has proven very useful as a tool to rank the quality and reliability of any of the measurement taken with the TA-TE setup. In many cases the electrical trend that a solar cell achieve after equilibration and within an hour of continuous measurement under one sun, can predict the solar cell life time.

Figure 2-4 is an example of the stability chart obtained during TA-TE measurement. In this example the cell showed good stability, i.e. the current did not show a noticeable change during the TA-TE measurements. Figure 3-4 and Figure 3-7 are more examples for

current stability during measurement. These figures show two series of cells: in the first series most cells showed severe degradation during measurement. In the second series several cells showed improvement in current during the first round of measurements, which led to a second round of measurements where the devices were more stable.

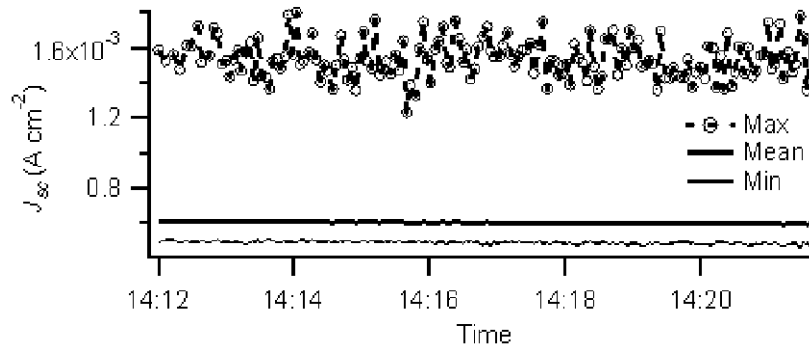


Figure 2-4 – An example chart of minimum, maximum and mean J_{sc} vs. Time of a solar cell that was measured in the TA-TE setup.

2.2.2 Temperature

A thermocouple (T- type) is attached to the solar cell when the cell is positioned in the sample holder. The thermocouple is connected to the DAQ card. The temperature is constantly probed during the TA-TE measurement. A live chart is presented during measurements and the results are also stored in a file. Temperature has huge influence on DSSCs behaviour in general and specifically on regeneration. The activation energy for regeneration deserves a temperature dependence studies by itself and the least that one can do is to note down the device temperature and its variation during the measurements.

Figure 2-5 shows the Temperature vs. Time chart for a device that was measured in the TA-TE setup. The temperature in this measurement shows a short rise and then decay, however it didn't change in more than one degree. In general, in this level of resolution (0.2 °C) several reasons can cause this type of behaviour. The focused probe beam (especially when it is unfiltered by ND, LP and/or SP filters) can heat the solar cell up to 45 °C whilst the room temp is 23 °C. In addition changes in bias illumination, open and closed shutter and variations in room temperature (i.e. when an A/C operates with a thermostat) can cause micro fluctuations in temperature. In this example (Figure 2-5), the rise is a trend hysteresis that follows a transition between conditions; the shutter was closed and the bias light was on, then

the conditions were inverted. Apparently the bias light in this example causes more heating than the filtered probe beam.

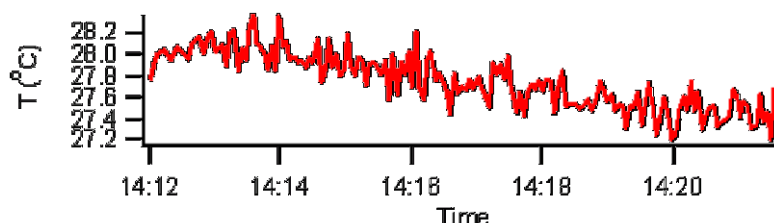


Figure 2-5 – An example chart of Temperature vs. Time of a solar cell that was measured in the TA-TE setup.

In order to assure minimum temperature effects during TA-TE measurements two precautions were taken: The first was to allow a short period of equilibration between conditions transitions. This period is a pause of measurements in the range of 1 to 30 seconds, depending in the contrast between conditions. The second precaution was to repeat the same measurement twice and use the first as an additional equilibration period which may provides additional data in case of need.

2.3 Transient Electrical Methods Using the TA-TE Setup

Every time a sample is excited, in parallel to the recording of changes in absorbance, an electrical signal is recorded. When the solar cell is open circuited, then this type of signal is called “transient photo voltage” (TPV). When the solar cell is short circuited the signal is called “transient photo current” (TPC). (O’Regan 2004) When TPV and TPC methods are mentioned here, the meaning refers to the part of the signal where it decays (after it reached the maximum). Other techniques like Photovoltage Rise Time (O’Regan 2006) or time of flight (Bondkowski, Bleyl et al. 1998; van't Spijker, O'Regan et al. 2001) may use other parts of the same signals that were acquired in similar ways. Although this kind of data may exist in the recorded signals, rise times and time of flight are out of scope in this work.

2.3.1 Transient Photovoltage measurement

The solar cell is open-circuited and is connected to a measuring device (DAQ analogue input impedance $> 10 \text{ G}\Omega$). The cell is subjected to a steady illumination from the bias light. These conditions form a steady-state equilibrium of injection, regeneration and

recombinations, but no collection. A constant photovoltage is established. On top of the steady state conditions an additional small perturbation of light photo-excites an additional small population of dye molecules, causing an additional population of electrons to be injected into the TiO_2 . This results in a small rise in the photovoltage. The small rise in photovoltage relaxes according to the rate of recombination of the injected electrons in the various recombination routes (Figure 1-3). At its simplest and easiest to analyze version, TPV decay can be fitted with a single exponential model to give the recombination lifetime (τ_n).

Recombination lifetime is a useful tool to measure the ability of a particular dye cell to maintain the separated charges. From materials point of view it can be used to rank the tendency of a treatment or a substance to enhance or suppress recombination, i.e. when different oxides, dyes, blocking layers and electrolytes combinations are used. One of the concerns in the use of TPV is the fact that TPV is not always obeying a single exponential model. In fact, in this work most of the decays were better described with a double exponential model and more precisely, a double stretched exponential (more about stretched exponential in chapter 5.7).

Figure 2-6 shows an example of a typical TPV decay recorded on the TA-TE setup. The decay is given in two different presentations a) on linear and b) on logarithmic time scales. The presentation on a logarithmic time scale makes it easier to identify that the TPV is biphasic.

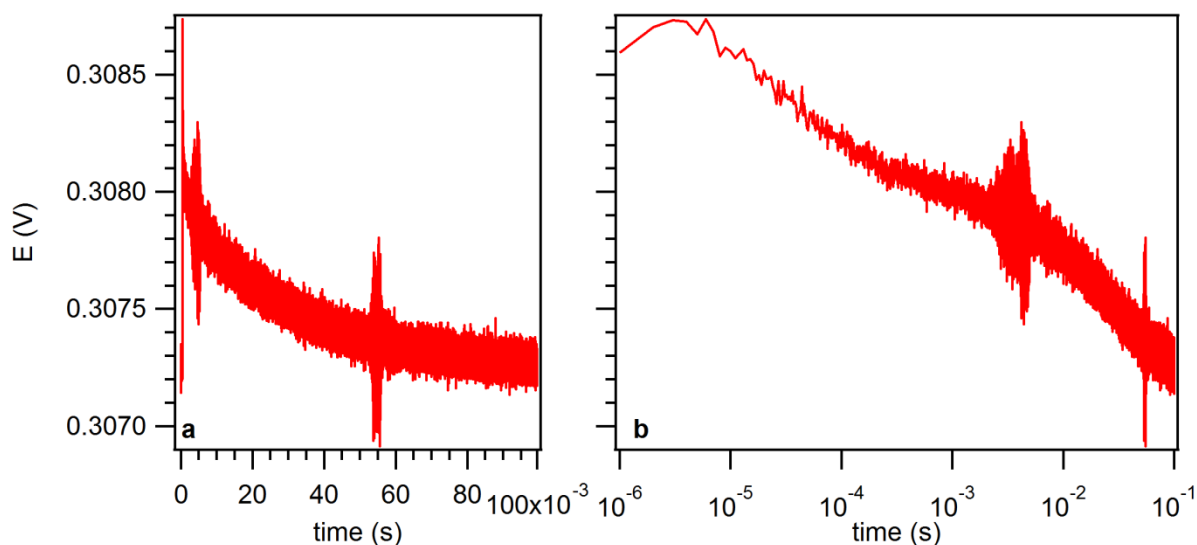


Figure 2-6 – example of a typical DSSC transient photovoltage (TPV) measurement in two different presentations: a) On a linear time scale. b) On a logarithmic time scale.

2.3.2 Transient Photocurrent - Transient Charge Measurements

Recording transient photocurrent decay is similar to TPV, except the fact that the cell is short circuited with a small resistor (2Ω in the TA-TE setup). The recorded voltage is translated to current by ohm's law. Unlike the TPV, the steady state equilibrium is not the same since under SC conditions collection is added up to the processes. By fitting TPC decay to a single exponential, the time constant τ_j can be obtained and this can be related to the chemical diffusion coefficient of electrons in the TiO_2 . (Barnes, Anderson et al. 2009) in this work TPC were not used directly but were converted to transient charge decays, or more accurately to “remaining charge that will be collected” curves. In order to do the conversion equation 4-1 is used. The conversion done in this work was in order to correlate optical and electrical signals of electrons in TiO_2 . Further details can be found in the results chapter 4.2.3.

Figure 2-7 shows an example of a typical TPC signal alongside its converted signal TPQ. The TPQ was obtained using equation 4-1.

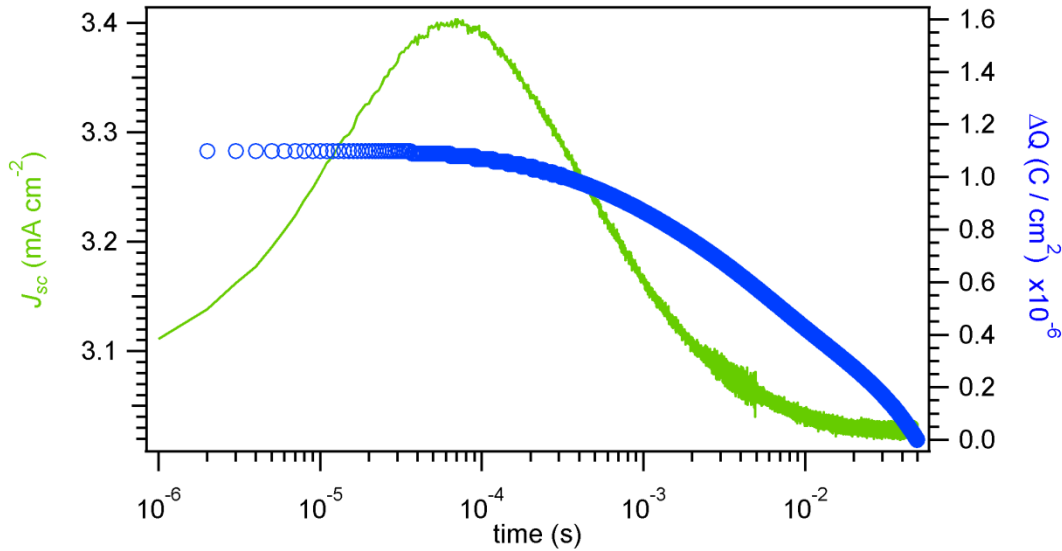


Figure 2-7 – example of a typical DSSC transient photo current and its derived transient “charge remaining that will be collected”

2.4 Charge Extraction

The solar cell is kept under a specific light intensity and is either open or short circuited. The cell is under these conditions for sufficient time to reach steady state equilibrium. In the case the cell is short circuited (SC), a fast solid state transistor (see 9.1.2) switch off the light following a computer command. In the case the cell is open circuited (OC), simultaneously when the light is switched off, another transistor switches the cell to short circuit. In both cases this action triggers a measurement of the current that leaves the cell. The measurement is carried for long enough until all the stored charge is extracted from the cell. An integral of this current signal, from time where light was switched off to “infinity”, gives the amount of charge that was stored in the cell. In the same way the charge can be measured under open or short circuit it can be measured under various bias voltages.

Further analysis of this kind of measurement would be to plot the resulting charge as a function of the resulting voltage or current that was obtained under various illumination conditions.

Charge extraction is a useful method to measure the amount of charge stored in a solar cell, formed under various operational conditions. Other optoelectronic measurements, obtained under the same conditions, can be related with charge to evaluate the effect of charge on processes that takes place in the cell under operation. The best examples are the relation of electron concentration in the TiO_2 with the observed recombination rate. Chapter 5

is another example of the relation of charge with regeneration and recombination. Charge extraction is a self consistent measurement. However, not always all the charge separated under steady state conditions can be extracted. Chapter 6 deals with the concern that some very fast recombination processes are faster than collection. Giving the picture that sometimes the extracted charge is lower than real. This kind of observation requires some attention when using CE technique.

Figure 2-8 shows a typical current vs. time decay. In this example the cell was short circuited prior to CE. In the case the cell was under OC conditions the charge is expected to be much higher. Figure 2-9 shows a series of charge extractions plotted against the voltages measured prior to each extraction. The different points were obtained under various illumination intensities.

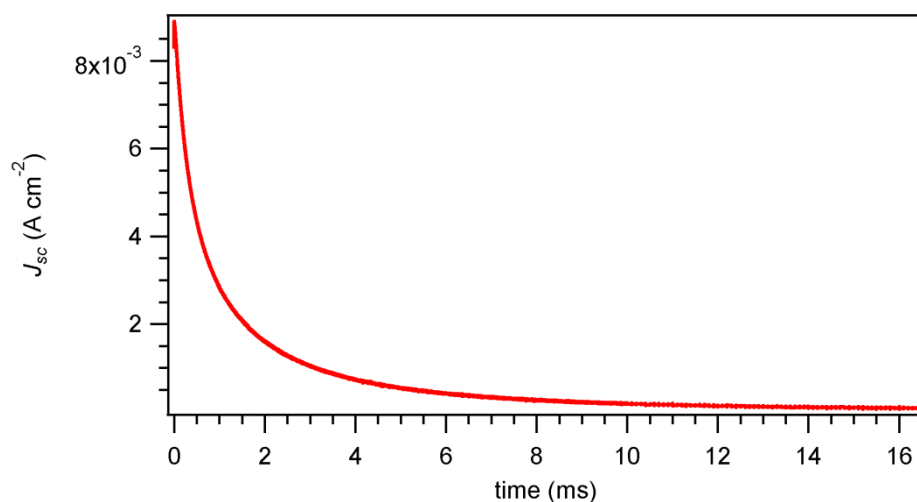


Figure 2-8 – an example of Current vs. Time decay following light switch-off. An integral of the decay gives the amount of charge (Q) in Coulomb (C) that was stored in the cell prior to extraction. This example starts from SC conditions.

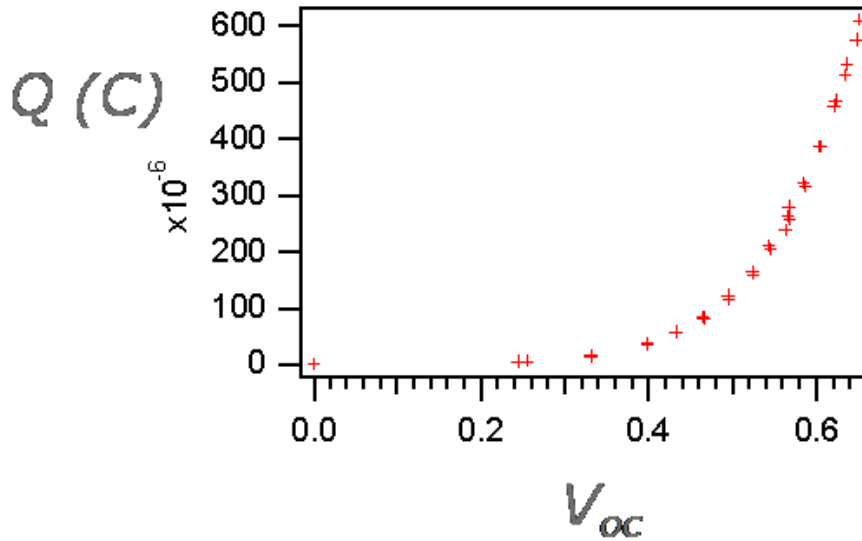


Figure 2-9 – Charge vs. Voltage formed under various illumination intensities.

2.5 Transient Absorption Spectroscopy

As per electrical transients (2.3), the cell is under a specific condition (i.e. Light intensity, OC/SC, etc.) and equilibrated. A pulse from the laser photo-excites a small fraction of the photoresponsive components of the solar cell, perturbing the steady state conditions. The chain of steady-state reactions (Figure 1-6 for example) is then shifted from its equilibrium, forming and consuming an additional part of the populations of the steady state species. The change in the populations is probed by optical path (TA-TE setup, see section 2.1) i.e.: the probe beam, lenses, apertures, longpass filters, monochromator and the fast detector. The actual TA signal is the change in optical density (ΔOD) in time (t) at a given wavelength (λ). ΔOD is obtained from the voltage changes of the fast detector, read on the oscilloscope (ΔV), and is calculated using equation 2-1:

$$\Delta OD(t) = -\frac{1}{\ln(10)} \frac{\Delta V(t)}{V_{BG}}$$

2-1

where V_{BG} is the background DC voltage, isolated by the detector's amplifier circuit (9.8.3) and is not affected by the small changes in absorption caused by the laser pulse. Additional useful information, references and history of TA techniques can be found in Yasuhiro Tachibana thesis. (Tachibana 2000)

The transient absorbance technique, applied to DSSCs, allows measurement of the formation and decay of chemical and electrical intermediates that absorb light. This is probably the most sensitive way to get information on the mechanisms that does not generate any measurable electrical signal. TA is a relatively complicated technique that requires a lot of practice and time in order to acquire and make sense out of the data. Furthermore, TA by itself is not always sufficient for assigning signals to species and/or for a quantifiable analysis. The combined TA-TE and automation of the acquisition is very helpful to ease the difficulty of the use of TA alone, as it used to be made previously.

Figure 2-10 is an example of a typical complete time TA decay recorded on the TA-TE setup. In this example the probe wavelength was 830 nm and the device was complete, regenerative, subjected to 1 sun bias illumination and open-circuited. Figure 2-11 shows full spectra, also recorded on the TA-TE setup. The spectra are of a device subset prepared by Mindaugas Juozapavicius, also measured under 1 sun equivalent bias illumination. Six representative points in time were chosen (see figure legend) from each of the 27 individual decays like the one in Figure 2-10. The decays were recorded between the wavelengths of 450 – 990 nm in 20 nm intervals.

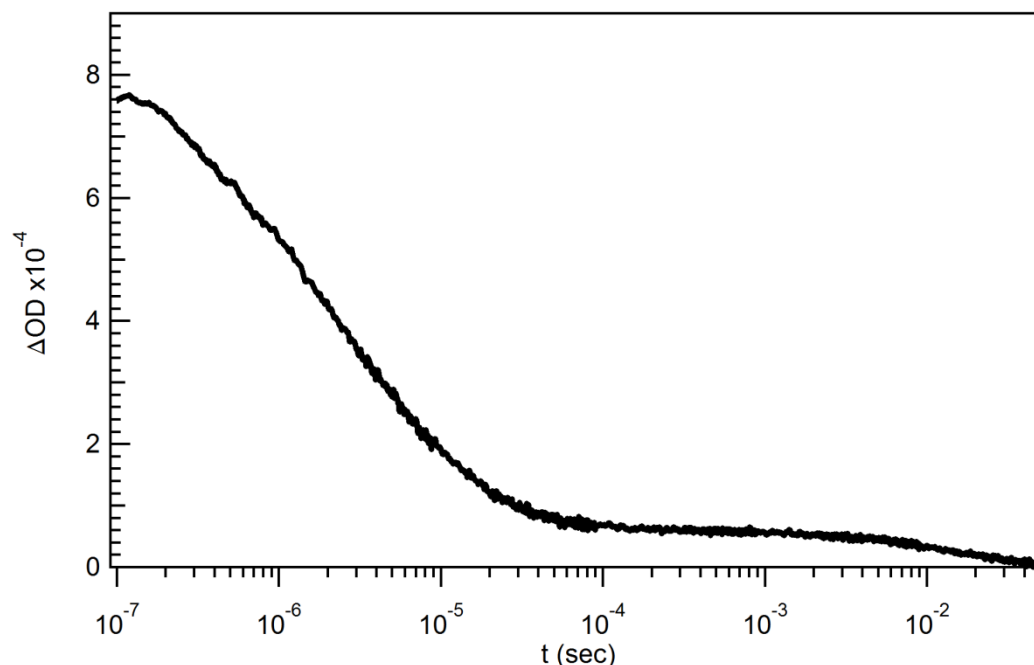


Figure 2-10 – example of a single TA decay, probed at the wavelength of 830 nm, under 1 sun bias light and OC conditions.

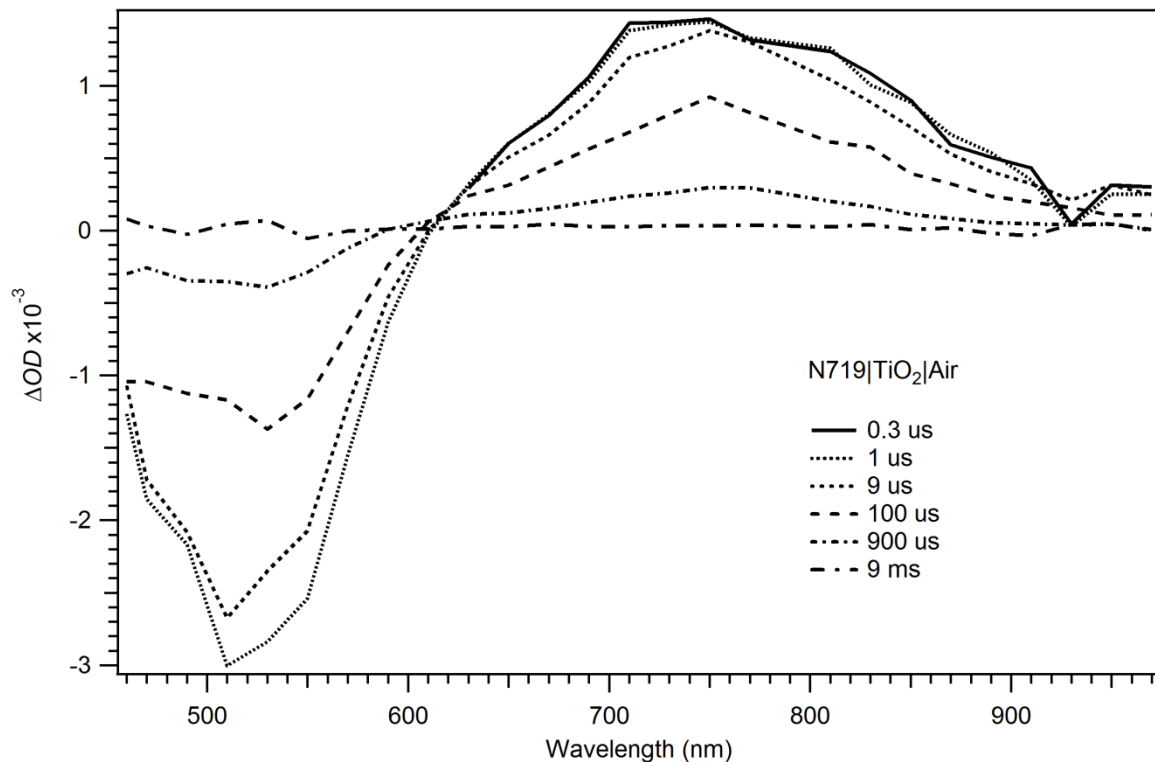


Figure 2-11 – example of spectra of a device subset; N719 dyed TiO₂. Measurement was taken under 1 sun equivalent bias illumination using the TA-TE setup. Device subset was made by Mindaugas Juozapavicius.

2.5.1 TA with Bandpass Filters vs. Monochromator

Early configurations of the TA-TE setup used bandpass filters instead of the monochromator. The motivation was to enable more probe light to reach the detector and hence to improve the signal to noise ratio and reduce the time for the acquisition of each signal. Other reasons were to enable a reasonable cost and dedicated setup for the study of regeneration. Conceptually, per photoelectrochemical system, first a spectrum is acquired in order to identify the regions where species absorb light. The spectrum has to be obtained in the microsecond system which has monochromators inline the optical probe beam path (see microsecond TAS configuration in Ivan Montanari and Yaushiro Tachibana theses (Tachibana 2000; Montanari 2002)). The second step is to go to the dedicated ‘bandpass system’ and make the study in 2-3 specific wavelengths, whilst changes are made in other parameters like: solar cells configurations (iodide concentration in this work), bias light and electrical conditions.

The TA-TE setup with the bandpass configuration was simpler and cost effective indeed. However in later stage when the monochromator was assembled in the TA-TE setup

instead of the bandpass filters, the system performance and signal to noise ratio didn't show a noticeable difference. The assembled monochromator was specified to enable accuracy and light throughput that are equivalent to a ± 10 nm bandpass filter. This was achieved thanks to the fact that the monochromator has two interchangeable gratings with blaze wavelengths that match the performance of the tungsten halogen lamp with either of the VIS or IR detectors (see 2.1.1 g). Furthermore the monochromator focal length is 1/8 m, which means it is less refined than a long focal length monochromator but more light goes through it. Yet, its accuracy is sufficient for the purpose of these studies. To conclude, the addition of the monochromator did not lessen the system performance. It enabled an automated acquisition of spectra for new systems; allowing computer controlled bias light and electrical conditions to be applied on spectra. Furthermore the addition of monochromator reduced the need to obtain a dedicated bandpass filter for each study and enabled the option to verify that no spectral shifts occurs when different iodide concentrations are employed, a measure that is harder to obtain using bandpass filters alone. See appendix 7 for various data obtained using the monochromator.

2.6 Steady State Photoinduced Absorption

The Steady State Photoinduced Absorption setup, as shown in Figure 2-12, makes the use of the TA-TE setup with some modifications. The visible steady state excitation source is the bias light array (9.5) whose intensity is under computer control. The bias light array operates in continuous mode (i.e. it does not flash). The tungsten halogen probe light (9.4) is attenuated with neutral density filters, and its visible region is blocked using long-pass 780 nm filter. This was done to avoid excitation of the dye by the probe light, allowing obtaining the reference beam intensity (I_0) when virtually no apparent process is occurring in the cell. Probe beam was detected using Si photodiode (9.8.1) for the 780 – 990 nm region or InGaAs photodiode (9.8.2) for the region of 0.7 – 1.7 μm . signals from the probing photodiode were recorded on a NI data acquisition card together with the current / voltage and temperature occurring from the exact same conditions that induced the changes in absorption. Currents at short circuit were measured over a 2 Ω resistor. Temperature was probed using a thermocouple attached to the solar cell.

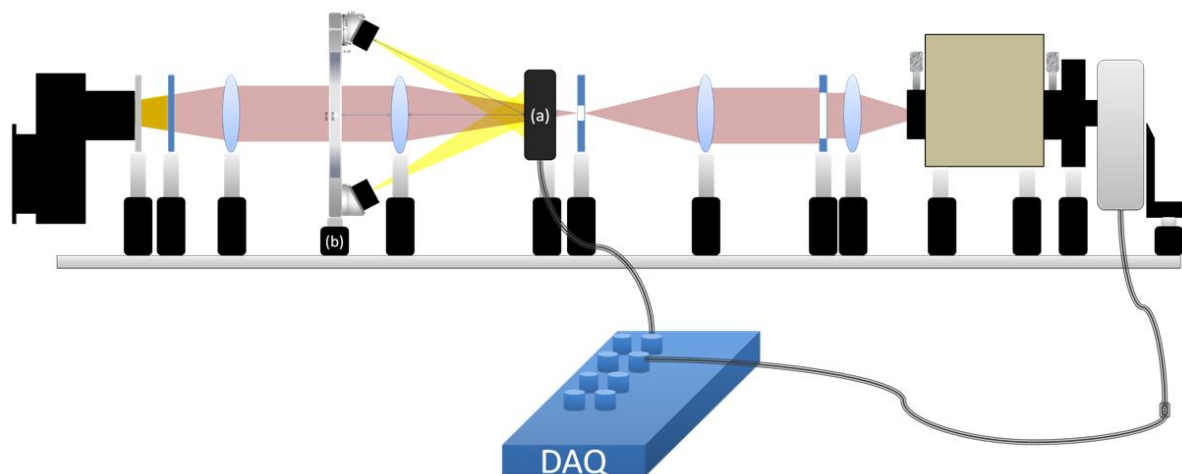


Figure 2-12 – schematic representation of the SSPA setup

Initially changes in absorption as a function of bias illumination intensities were obtained using band pass filters (either 830 ± 5 or 980 ± 5 nm) positioned after the sample. In this method, per wavelength, only the bias illumination was varied. Cycling dark to light allowed averaging. Upon addition of the monochromator (see 2.1.1 g), SSPA spectrums could be measured but the technique for doing so required some tuning (see below).

SSPA can be gathered as a spectrum to assign species to wavelengths, or in single wavelength to allow quantification and comparison to charge extraction etc.. When compared to spectra obtained using TA technique, SSPA is less sensitive to species that are short-lived and has low absorption coefficient. The following sections presents typical data obtained using SSPA. It includes two different techniques for obtaining spectrums (light cycles and wavelength cycles), followed by an explanation why the light cycle technique is better.

2.6.1 Light Cycles Spectrum Method

Figure 2-13 shows an IR spectrum obtained in the light cycles method. In this case, unlike the “wavelength cycles” (see 2.6.2), at each wavelength in the spectrum the illuminations cycle is carried out. Starting from dark (I_0), continuing through increments of light intensity (I_n), up to max illumination. Once the bias light increments cycle is complete, the monochromator proceeds to the next wavelength and the same illumination cycle is performed. After absorption is recorded for all wavelengths, the measurement is repeated several times to increase accuracy.

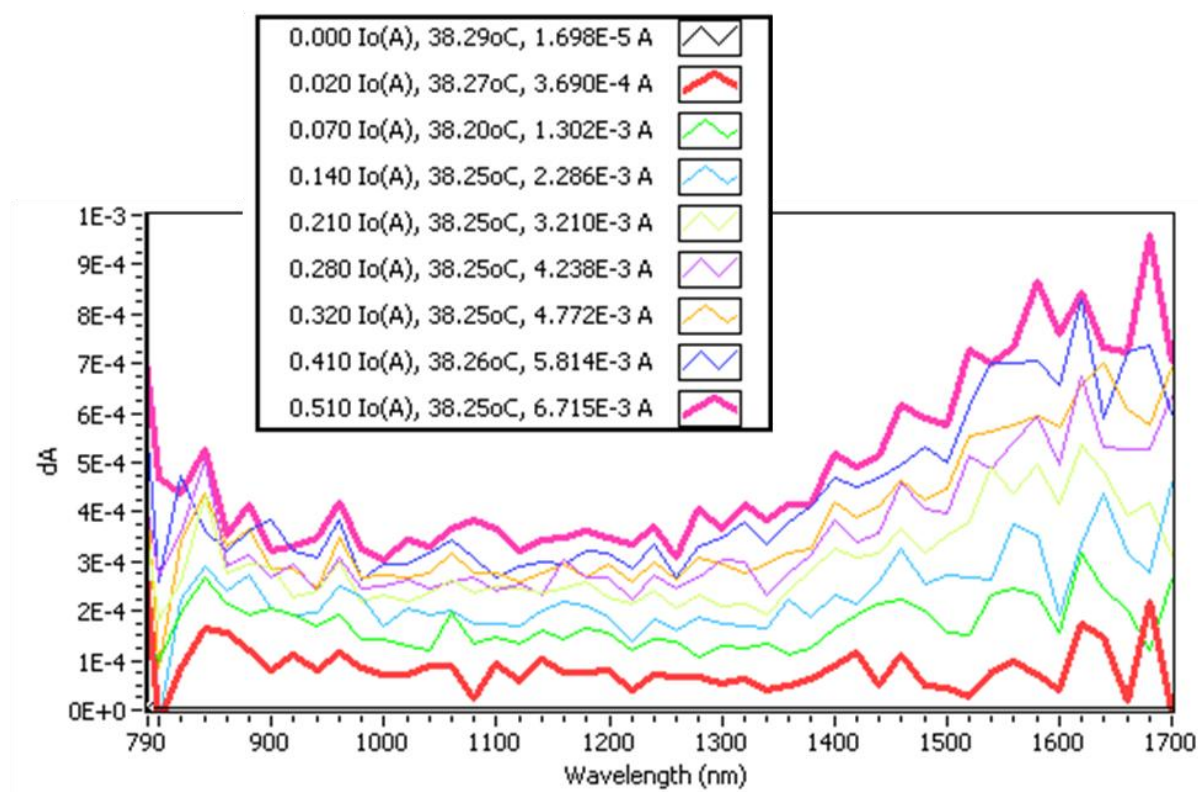


Figure 2-13 - Steady state photoinduced absorption spectrum. The spectrum was recorded using the “Light Cycle” method. The legend shows the illumination intensity (the applied current to the bias light by the power supply), the recorded temperature, and the recorded current for each line in the spectrum. The spectrum was recorded under short circuit for a typical DSSC device having 70 mM iodide in the electrolyte.

2.6.2 Wavelength Cycles Spectrum Method

Figure 2-14 shows an IR SSPA spectrum obtained in the wavelength cycle method. Starting from no bias light illumination (I_0), all wavelengths are scanned and the probe beam measured intensity is stored. Then the illumination intensity is increased (I_n) and the spectrum is scanned again. All wavelengths are scanned after each increment in light intensity until maximum intensity. Once all light intensities are complete, the measurement is repeated several times to allow averaging. The motivation for “wavelength cycles” was to keep the cell electrically stable for the maximum amount of time without making changes in illumination. In fact, as seen by comparing the temperature in the legends of Figure 2-13 and Figure 2-14, this method caused a distinctive temperature for each of the illumination intensities, resulted in distorted spectrums. The next section highlights this issue.

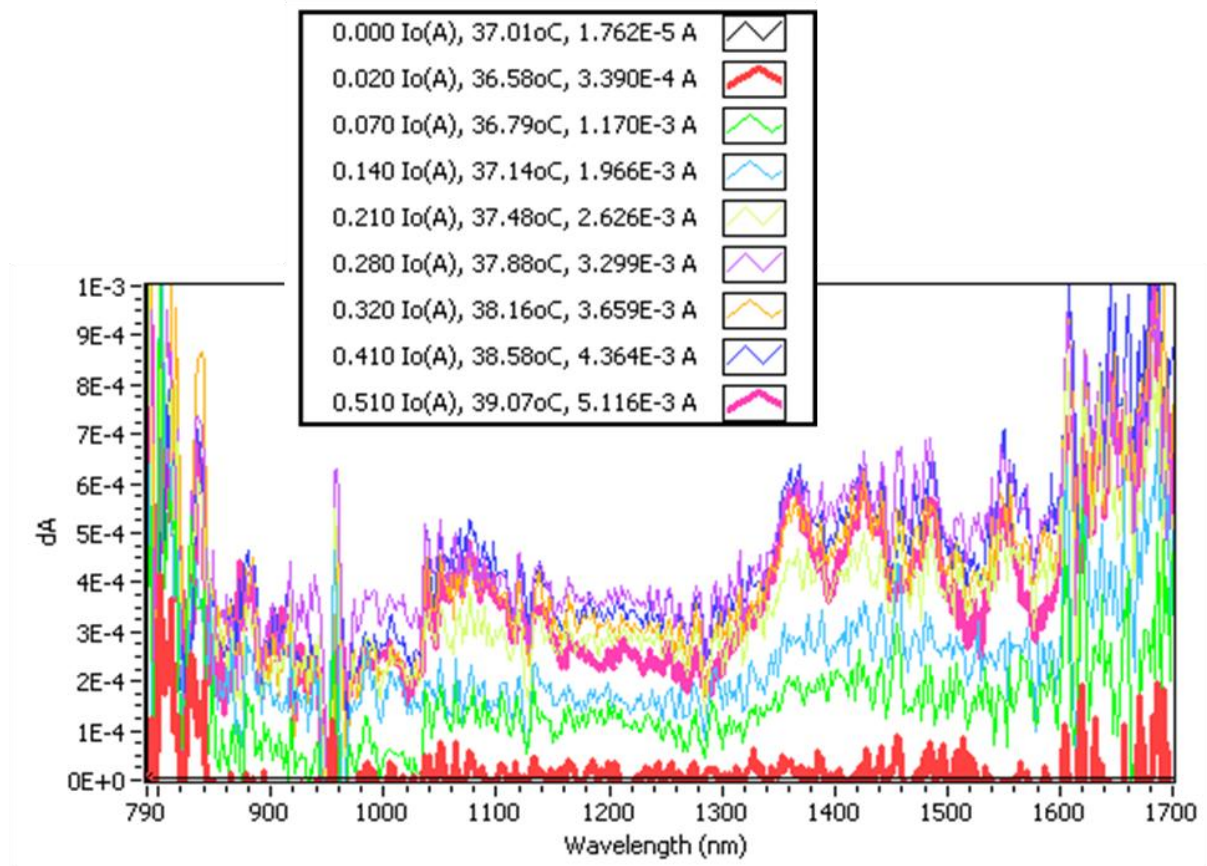


Figure 2-14 – Steady state photoinduced absorption spectrum. The spectrum was recorded using the “wavelength cycle” method. See Figure 2-13 for more information on cell and legend details.

2.6.3 Temperature and Electrical Measurements During Steady State Photoinduced Absorption – Resolving the Method for Spectrum Acquisition

Regardless of the method used (2.6.1 or 2.6.2), following any single measurement of light intensity, electrical and temperature measurements are also taken. The electrical and temperature values are averaged and stored per illumination intensity, discarding the wavelength dimension.

Figure 2-15 shows the averaged temperature and the averaged photocurrent together with its error bars (small errors), plotted against the approximated illumination intensity in ‘suns’. The photocurrent error bars are the standard deviation calculated from all the photocurrent measurements taken in a particular light intensity. The most obvious observation in this figure is the fact that in the light cycle method, the current followed the illumination intensity whereas the temperature remained almost constant. In the wavelength cycle method the situation was different; the averaged temperature had a

distinctive value for each of the light intensities. A comparison of the photocurrents between methods shows that these were also not exactly the same, although the same device and the same light intensities were used for both methods, the photocurrents in the wavelength cycle method were slightly lower and their error bars were slightly larger. A possible initial postulation is as follows: although it was noted above that in the wavelength cycle the cell does have a distinctive temperature for a given light intensity, yet, the initial temperature and the final temperature are different. This trend in temperature is reflected in the photocurrents behaviour; in both methods the examined device had a low regeneration performance and thus the photocurrents were more susceptible to changes in temperature. The outcome is the fact that severe changes occurred in the cell between the record of I_0 and the I_n . Making I_0 and I_n not related and causing the distortion of the spectrum in the wavelength cycle method.

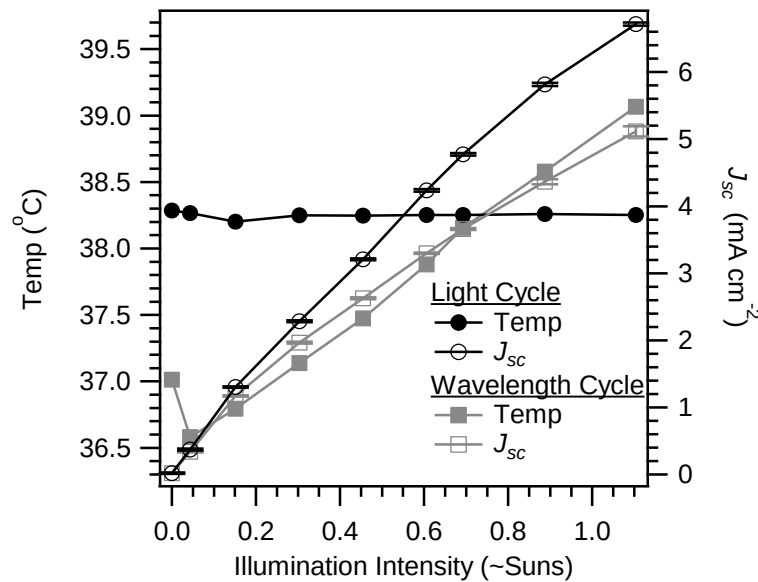


Figure 2-15 – Temperature (filled symbols) and photocurrent (J_{sc} , empty symbols) as a function of illumination intensity (~suns), measured during SSPA. Comparison between “light cycle” (circles) and “wavelength cycle” (squares). In light cycle the temperature is homogenous.

2.7 JV curves

Devices performance characteristics are obtained from JV curves. JV curves are measured with either the group’s solar simulator or on the TA-TE setup. The solar simulator is made of a 150 W xenon lamp (Sciencetech model SS150Wsolar simulator), equipped with an IR filter (water filter) and an AM 1.5 filter (Sciencetech). The Current and voltage are measured and controlled using a Keithley 2400 source meter. Measurements of JV-curves

on the TA-TE setup are made with the LEDs bias light array (9.5) and the current and voltage are measured and controlled using the DAQ card (9.2) aided with the homemade op-amp circuit (9.1). In JV, the current is measured as a function of voltage. The minimum requirement to obtain device characteristics is that JV is measured between zero volts and a voltage where the current equals zero amps and that the current measurement for each voltage step is sufficiently long to allow equilibrium. Another way of doing the measurement is as doing a cyclic voltammogram. This gives verification that the measured currents are the same when the curve crosses in the same voltage point twice, once on its way forth and once on its way back.

An example JV curve is shown in Figure 2-16, referring to the solid curve named ‘~1 sun’, the device performance characteristics are obtained, in this case, from the top right quadrant. The cell open circuit voltage (V_{oc} , in Volts) is the point where the curve cross the voltage axis and the current is zero. The short circuit current (J_{sc} , Amps cm^{-2}) is the point where the curve crosses the current axis and the voltage is zero. The theoretical maximum power point (tmpp, in Watts cm^{-2}) is the multiple of J_{sc} and V_{oc} . The actual maximum power point (mpp, also in watts cm^{-2}) is the point on the curve where the $J \times V$ is the highest. The voltage and current of maximum power can be noted (V_{mpp} and J_{mpp} respectively). The solar cell conversion efficiency (η , either as a fraction or in percentage) is the maximum power per unit area divided by the power per unit area output of the lamp, both measured at the same location with respect to the solar simulator beam. The fill factor (FF , fraction or percentage), $FF = mpp / tmpp$, is a number that reflects on the gap between the theoretical and actual power output of the cell.

JV measurements on the TA-TE setup gave a reasonable estimation of device performance and were mainly useful for internal comparisons within a series where the dye was the same for all cells. It was also useful for repeated measurements of the same cell along a long measurement, i.e. before, during and after simultaneous TA-TE. It is important to remember that the LEDs emission is not the same as an AM 1.5 emission, it covers mainly the visible region and almost has no emission in the infra red.

2.7.1 Dark and Illuminated Extended JV curves

The size of the JV window can be extended and can be measured under dark and illuminated conditions. This is useful in order to obtain additional information, for example the saturation current which is the ability of the electrolyte to shuttle charges. As the absolute

voltage is increased, the current increases until it reaches some saturation. There is an asymmetry in this measurement, depending on the polarity of the applied voltage. The following two cases are considered:

Diffusion limit in the pores: In the dark, as the working electrode is biased with positive potential, the TiO_2 is not conductive due to its n-type semiconducting characteristics. The oxidation current of the electrolyte (the reverse of the reactions shown in equations 5-11 and 5-12) occurs at the interface of the electrolyte and the transparent conducting oxide (TCO = FTO in this work). This oxidation is limited by the diffusion of species via the pores of the working electrode. Note: only works if the cell doesn't have blocking layer (i.e. the TCO is coated with thin layer of TiO_2).

Diffusion limit in the bulk: The second case is the case that the bias is reversed. Then the TiO_2 is negatively charged and conductive, it reduces the electrolyte at any position on the TiO_2 nanoparticles (the forward reactions shown in equations 5-11 and 5-12). In this case the diffusion is limited in the bulk of the electrolyte rather than in pores.

Regardless of the origin of diffusion limitation, either by the bulk-electrolyte or by the pores-electrolyte, once the light is switched on the maximum photocurrent a device can sustain is usually limited by either of these aforementioned barriers. Another type of information attainable from extended JV is the series resistance of the whole cell. This information is acquired from the slope of the curve in the bottom right quadrant in the case shown in Figure 2-16, before a saturation current is reached, series resistance is not considered in this work.

Dark and illuminated extended JV measurement is very useful and important for regeneration studies. It is important because it determines whether a DSSC's performance is degraded due to the lack of redox active species to shuttle charges in the electrolyte or whether a different problem, like regeneration efficiency, has to be addressed. Extended JV is very simple and requires the most basic equipment available for photoelectrochemistry studies. However, it enables just an initial estimation and in most cases further investigation is required.

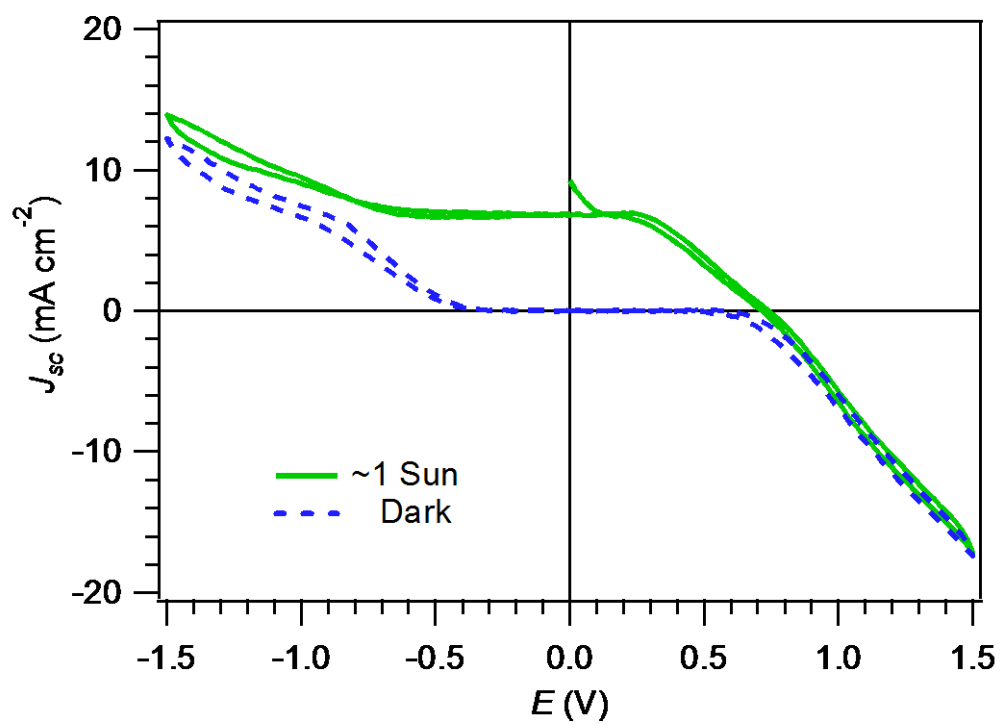


Figure 2-16 – dark and light cyclic voltammograms.

3 Experimental - DSSCs Devices Fabrication and Materials

The main focus of the research was to study regeneration from the electrolyte perspective, i.e. the effect of the reducing species concentration on the regeneration reaction. In order to do so, four series of cells were prepared. All cells components within a series were made and assumed to be constant, except their electrolyte. In order to achieve similarity in all components, well established techniques were used repeatedly, and for each series all device components were prepared in one batch.

3.1 Working Electrode

For the preparation of the working electrode, a TEC15 FTO glass was cleaned and dried. TiO_2 layers were synthesized as previously published, (Anderson, Gieselmann et al. 1988; O'Regan 1990; O'Regan 2009) using a readymade acid-batch colloidal paste. (Barbe', Arendse et al. 1997) The paste was spread on the FTO glass on double scotch tape spacer. Then the electrodes were air dried and went through the following steps of the thermal treatment: gradual temperature elevation, holding the electrodes at 450°C for 30 minutes, and cooling. Figure 3-1 shows a scanning electron microscope micrograph, published by Barbec et al, of the resulting film where a similar route for film preparation was used. A scattering layer was not used in this work's films to enable better transmission in the transient absorption spectroscopy. Before dyeing, the electrodes went through the TiCl_4 treatment.(Sommeling, O'Regan et al. 2006; O'Regan, Durrant et al. 2007) Un-dyed working electrodes were kept in a 120°C oven to avoid water adsorption.

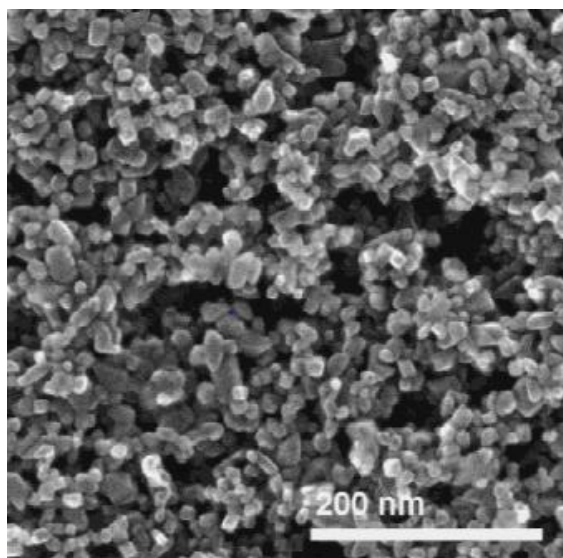


Figure 3-1 - SEM micrographs of films synthesized from colloid autoclaved at 250°C in a 0.1M nitric acid solution (pH 1).(Barbe', Arendse et al. 1997)

3.2 Dye

N719 dye - cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium) (see Figure 3-2 for structure) was dissolved in 1:1 ratio Acetonitrile:Tert-Butynol solution. This same dye solution was used for all the cells used in the four regeneration series cells.

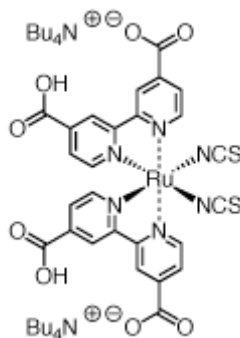


Figure 3-2 – N719 dye structure- cis-diisothiocyanato-bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) bis(tetrabutylammonium)(Solaronix 2010)

3.3 Electrolytes

The first three series incorporated the propylene carbonate solvent based electrolytes. In each series the variation was the concentration of iodide. Almost all cells within the first three series changed or lost performance immediately, resulting in irreproducible results. The

last series, the fourth one, incorporated state of the art electrolyte, based on MPN as a solvent and ionic liquids as a source of iodide. Alongside having the same components in any cell within a series, both PC and MPN series had the same ionic strength and the same concentration of additives and counter ions in the electrolyte. The only variation in each series was in the iodide concentration and its inert anion replacement.

3.3.1 The Propylene Carbonate based series

The first three series of cells were made using propylene carbonate (PC) as the solvent for backward compatibility with earlier studies made in the group.(Montanari 2002; Clifford 2007) Figure 3-3 shows schematic drawings of the molecular structure of the solvent PC as well as the rest of the series ingredients.

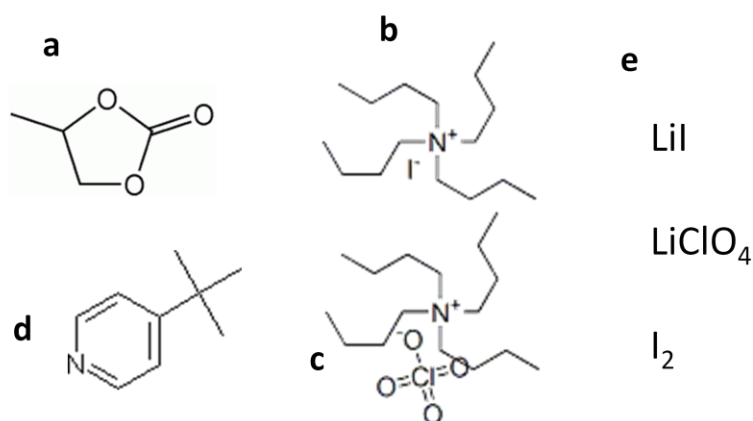


Figure 3-3 Ingredients of the PC based electrolytes series: a) Series solvent - Propylene carbonate (PC).(Wikipedia 2007) b) Primary iodide source salt – Tetra Butyl Ammonium Iodide (TBAI).(ChemicalBook 2010) c) Primary Inert anion source salt – Tetra Butyl Ammonium Perchlorate (TBAClO₄). (ChemicalBook 2010) d) 4-tert-Butylpyridine (TBP).(Chemexper 2010) e) Iodine (I₂), Lithium Iodide (LiI) and Lithium Perchlorate (LiClO₄).

The PC series of electrolytes were prepared as follows: 0.05 M iodine and 0.3 M TBP were dissolved in PC to make the primary solution. From the primary solution two secondary stock solutions were made. The first, the redox active, contained 0.1 M LiI and 0.6 M TBAI. The second, the redox inert, contained 0.1 M LiClO₄ and 0.6 M TBAClO₄. Both active and inert solutions had the same concentration of 0.1 M Li⁺, 0.6 M TBA⁺, 0.05 M I₂ and 0.3 M TBP whilst the redox active solution had 0.7 M iodide and the inert had 0.7 M ClO₄⁻. The series of solutions were prepared by mixing these active and inert stock solutions at different

volumetric ratios. For example to get 0.35 M iodide (which is also 0.35 M ClO_4^-) 1:1 volumes of the stock solutions were mixed. To get 43 mM iodide 1:15 volumes were mixed and so on. The specific concentrations used for each experiment will be mentioned where appropriate.

As was noted before, cells based on PC were unstable under illumination and rapidly showed significant loss in performance. Figure 3-4 shows the photocurrent stability recorded during TA-TE measurements. For further details on stability and device integrity during measurement see section 2.2.1, page 48. Each curve in the figure is approximately 15 minutes of measurement where the current is repeatedly sampled. Almost all the cells in the PC based series showed a rapid drop in current. Worst case occurred in devices expected to the best performance: In the first test after preparation of the 700 mM iodide-PC based cell, it lost 2.5 mA cm^{-2} within 9 minutes (Figure 3-4, 700 mM (a)). Curiously when the same cell was measured a day after it gave an improved initial photocurrent. However, again it lost photocurrent during measurement, this time a loss of 4 mA cm^{-2} within 17 minutes (Figure 3-4, 700 mM (b)).

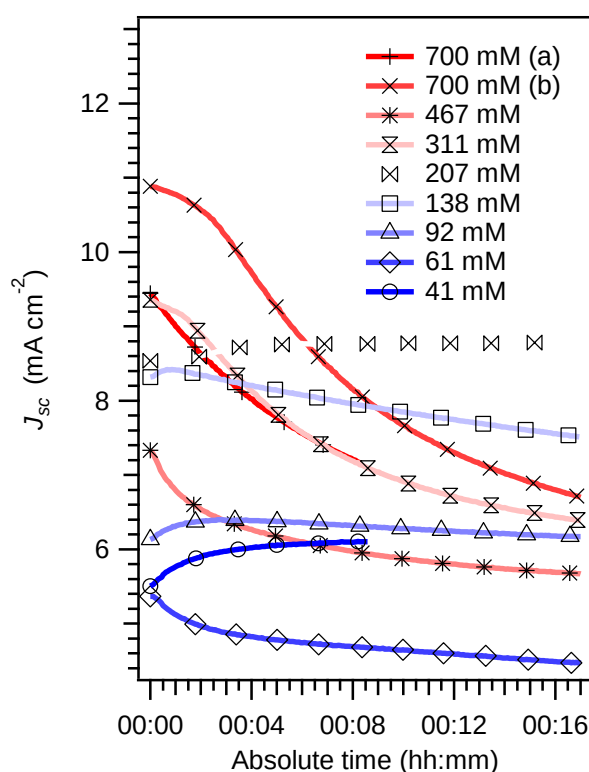


Figure 3-4 - stability during TA-TE measurements of cells having PC based electrolytes (third PC series). Each curve in this figure is a measurement on a device having the

noted concentration (in mM) of iodide. 700 mM (a) and (b) is the same device with a one day gap between measurements.

Many explanations can be given to the drop in current in cells that had PC based electrolytes. The quality of cell sealing probably plays a major role. Also the presence of TBA^+ , Li^+ can contribute to the effect. However there are some literature reports on the decomposition of PC in battery electrolytes. Figure 3-5 shows a proposed mechanism for the oxidation of PC on graphite electrodes. (Arakawa and Yamaki 1995) Although investigation was not made in this direction, similar process can take place in DSSCs as well.

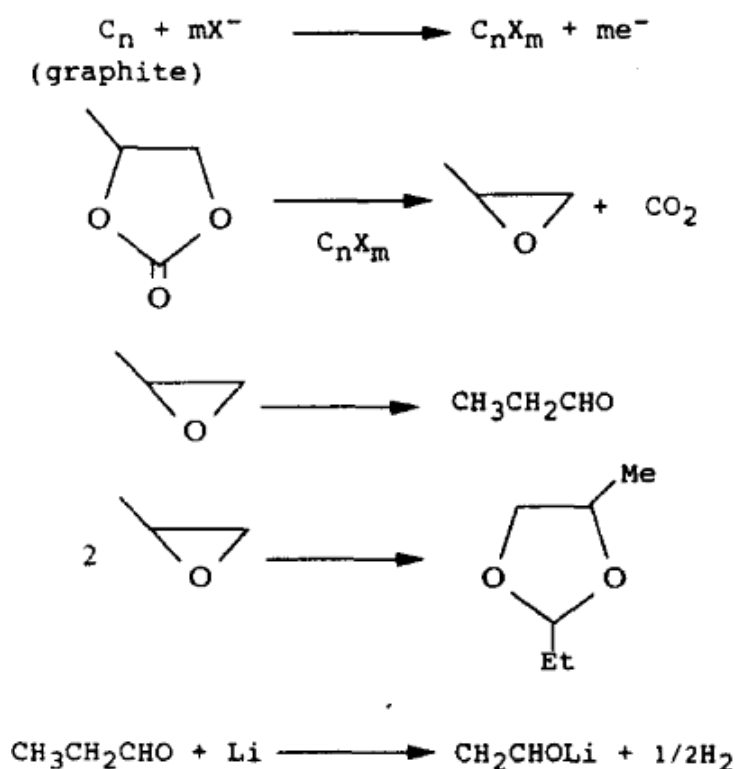


Figure 3-5 – Proposed mechanism for the oxidation of propylene carbonate. X^- is anion.(Arakawa and Yamaki 1995)

3.3.2 The 3-methoxypropionitrile based series

Given the failure of the PC based series an improved recipe for stable state of the art electrolytes was adopted (Wang, Klein et al. 2005) for the preparation of the MPN-iodide based series of electrolytes. Figure 3-6 shows schematic drawings of the molecular structure of the solvent MPN as well as the rest of the series ingredients.

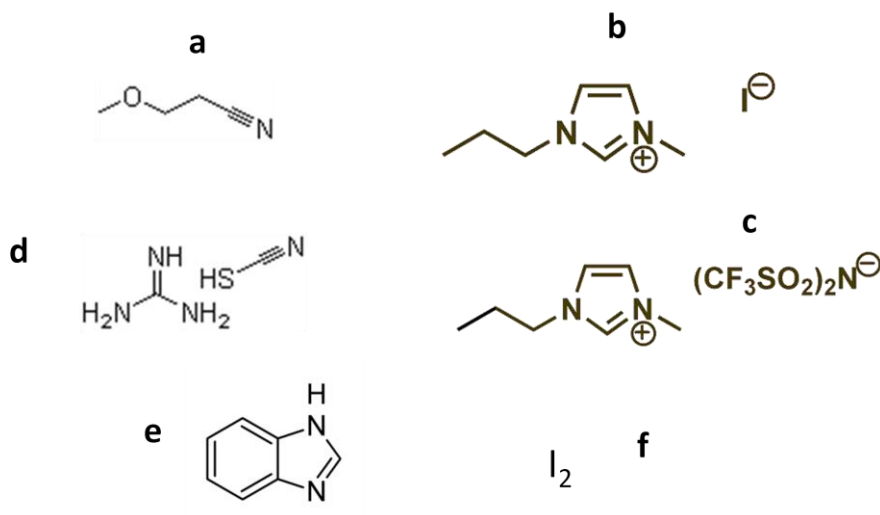


Figure 3-6 – Ingredients of the MPN based electrolytes series: a) Series solvent - 3-methoxypropionitrile (MPN)(ChemBlink 2010). b) Iodide source salt- 1-propyl-3-methylimidazolium iodide (PMII)(IoLiTec 2010) c) Inert anion source salt (iodide replacement to maintain ionic strength) - 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (PMITFSI)(IoLiTec 2010) d) Guanidine Thiocyanate (GuSCN).(ChemBlink 2010) e) Benzimidazole (BZI).(Wikipedia 2006) f) Iodine (I₂).

This series has proven very stable. Some particular degradation of cells made using this series can be assigned to poor sealing. Figure 3-7 shows the current stability recorded during TA-TE measurements (see section 2.2.1 in page 48 for more information on stability). Almost all the cells in the MPN based series either increased or maintained the initial current. Interestingly, cells with low iodide (i.e 46 and 70 mM) showed large improvement in photocurrents. These cells were also stable between measurements and at the moment of writing these lines most of the cells were stable for more than a year.

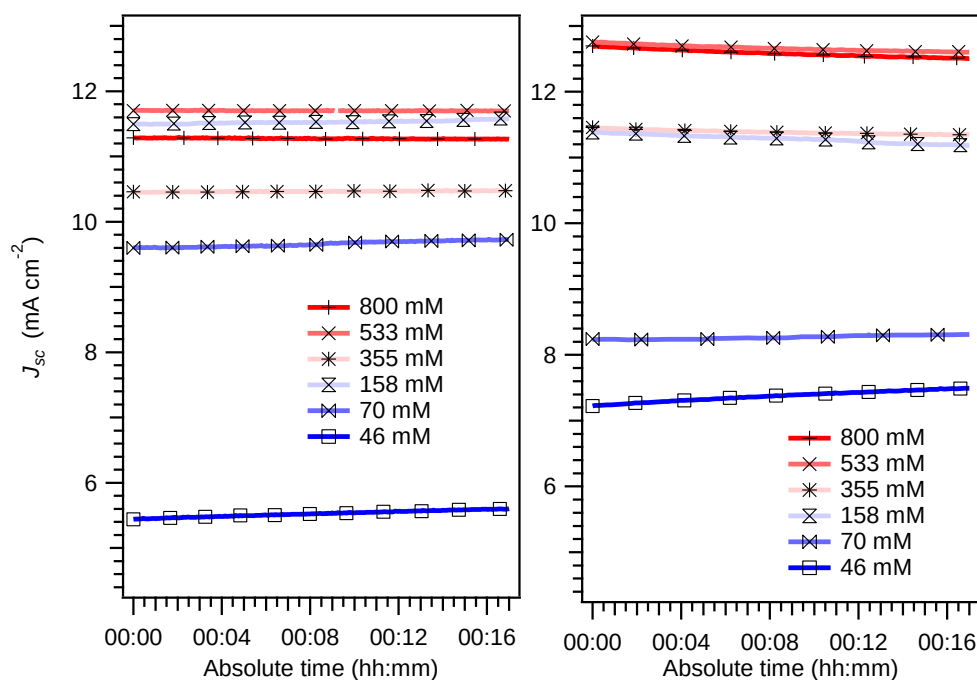


Figure 3-7 – Stability during TA-TE measurements with ~ 1 sun illumination of the cells having MPN based electrolytes. The left hand figure shows the stability during the first measurement following preparation. The right hand figure shows a repeated measurement taken 2 days later. Each curve in these figures is a measurement on a device having the noted concentration (in mM) of iodide.

3.4 Counter electrode

The requirement from the counter electrode in this research was two folds, on one hand it had to maintain a performance good enough not to degrade J_{sc} . On the other hand it had to enable enough transmitted light for the transient absorption characterisation. In the end a balance was found and approximately 15 μL of H_2PtCl_6 solution (5 mM in Isopropanol) were spread on FTO glass. The glass was heated at 400 $^\circ\text{C}$ for 20 minutes.

3.5 Device assembly

Cells were assembled by pressing the counter and working electrodes with a 25 μm thick double side adhesive gasket (Surllyn). The sealant was melted with a hot press at 120 $^\circ\text{C}$. After pressing and sufficient cooling, 3 μL of electrolyte solution was injected via pre-drilled holes. Then a covering glass was glued using another piece of Surllyn to seal the electrolyte injection holes. Silver paint was applied on the edges of the FTO glass to allow better contact with the various electronic measuring devices and reduce the series resistance.

4 Elucidating the Intermediates in Iodide

Oxidation

Simultaneously acquired transient absorption, photocurrent, and photovoltage signals are used to characterize operational dye-sensitized solar cells (DSSCs) under 1 sun illumination. At open circuit, the biphasic decay of both photovoltage and 980 nm absorption have identical decay profiles. The data show that, in devices incorporating N719 $[(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH})_2(\text{NCS})_2]]$ (dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl) as the sensitizer, the 950 – 1020 nm absorption can be assigned to electrons alone. This differs from some previous assignments. At short circuit, the comparison of the integrated photocurrent transient, electron absorption, and the absorption of the oxidized dye (830 nm) can be used to show relative loss of photocurrent to oxidized dyes. In addition, it is shown that, under operational conditions, there is no evidence for long-lived di-iodine radicals ($\text{I}_2^{\cdot -}$). Further, it is shown that the decay of the transient bleach at 560 nm, previously assigned to the bleach of the ground-state dye, contains additional long-lived bleach components that correlate with the electron transient. This calls into question the use of the bleach transients for kinetic studies of dye regeneration. The use of simultaneous transient absorption and electrical signals significantly increases the information available from transient absorption studies, at little extra cost in time or equipment.

4.1 Introduction

Dye-sensitized solar cells (DSSCs) present an interesting research topic not only from the point of view of increasing their contribution to future energy supplies but also as prototypes systems for other future nanoelectrochemical devices, such as for solar fuel production. DSSCs are photoelectrochemical systems where both electrical and chemical characteristics combine to define successful device operation. In this situation, simultaneous optical and electrical characterization of actual devices is of obvious relevance but has rarely been pursued. (van't Spijker, O'Regan et al. 2001; O'Regan, Durrant et al. 2007)

The transient absorbance (TA) technique, applied to DSSCs, allows measurement of the formation and decay of chemical and electrical intermediates that absorb light. Alternatively,

transient electrical (TE) characterization can detect changes in the quantity and position of charged species. TA has been routinely applied to DSSC research since its inception.(Desilvestro 1985; O'Regan 1990) For the most part, TA has been applied to partial systems composed of some subset of the complete devices. Examples include homogeneous dye solutions, TiO_2 /dye colloidal solutions, and dye-sensitized mesoporous films exposed to solution in cuvettes or behind covering glass. Usually these experiments are carried out under dark conditions. For example, difference spectra of the oxidized dye (S^+ , sometimes also referred to as dye cation) and excited dye (S^*) in solution (with and without e^- acceptor, respectively) were published in the past by Tachibana et al.(Tachibana 1996) The difference spectrum of S^+ in dye-sensitized film, immersed in 0.1 M LiI in propylene carbonate and measured with dark background conditions, was presented by Montanari et al.(Montanari 2002)

Transient electrical characterization is most successfully carried out on complete devices operating under illumination. The differences in the chemical environment at the photoelectrochemically active surface between complete devices and device subsets can limit the direct comparison of TA and TE results. Critical differences in electron concentrations and concentration profiles occur between a TiO_2 film in the dark and a device under operation. Another difference is the existence of concentration profiles of solution species across the device under operation,(Papageorgiou 1996) which are not present in solutions or device subsets. In devices at short circuit, diffusive gradients can cause the concentration of limiting species near the photoactive interface to be quite different from that in the original electrolyte. Another important difference is in the effect of the high surface area TiO_2 on the small volume of electrolyte in the actual device. For example, a typical cell has $2 \mu\text{L}/\text{cm}^2$ of electrolyte and a TiO_2 surface area on the order of $1000 \text{ cm}^2/\text{cm}^2$. A strong adsorption to the surface can fully deplete the electrolyte of a component initially present at 0.1 M. All these effects make the TiO_2 interface very different in a real device, compared with films in vacuum, neat solvent, or bulk electrolyte. Also, the application of TA on complete and functioning devices gives one the ability to correlate the transient observations with the device current, voltage, and fill factor, thus providing a firm footing for any conceptual models built up around the results.

Many electrical characterization techniques have been applied to DSSCs; this chapter focus on transient photovoltage and photocurrent measurements, as they can be directly compared to TA. Small perturbation transient photovoltage (TPV) and photocurrent (TPC)

decays are often used to measure the electron recombination lifetime (τ_n) and the e^- diffusion coefficient (D_n). (Barnes 2009; Barnes 2009; Barnes, Anderson et al. 2009) Typically, the diffusion length is calculated as $L_n = (\tau_n D_n)^{1/2}$. Recently, we observed that the diffusion length so calculated does not correlate correctly with measured photocurrents on the same devices. (Barnes 2009; Barnes 2009; Barnes, Anderson et al. 2009) This can lead to doubts concerning the transient techniques. For example, to what extent do the transient electrical measurements accurately reflect the charge concentration and movement in the TiO_2 film? This question is addressed in this chapter.

This chapter presents results of simultaneous measurement of TA and TE signals on working devices under operating conditions. In particular, it focuses on signals relevant to the recombination or extraction of electrons and the regeneration of oxidized dye molecules ($S^+ \rightarrow S^0$). The pump pulse used for the transient absorption also initiates electrical transients, and these are measured with a separate recording system. Bias illumination is provided and the ability to control the voltage on the cell. Using this system, initial results that illuminate the relationship of the electrical and optical signals is given. Good correlation is found between optical and electrical signals over a wide time range, solidifying the interpretation of both signals. Specifically, an optimized cell is examined, and one where an electrolyte component (iodide, I^-) has been decreased, inducing a large loss to a specific recombination pathway (electron to oxidized dye). Also a correlation is found between an optical and electrical signal not previously thought to be related.

4.2 Experimental

Titanium oxide colloids and films were prepared as previously published and as mentioned in chapter 3, using acid peptization. (Anderson, Gieselmann et al. 1988; O'Regan 1990; O'Regan 1991; Barbe', Arendse et al. 1997) $\text{TiCl}_4 \cdot 2\text{THF}$ (Aldrich) was used for the TiCl_4 treatment. (O'Regan, Durrant et al. 2007) Cells were fabricated as previously published. (O'Regan 2008) The device active area was 1 cm^2 and the TiO_2 thickness was $8.7 \pm 0.6 \text{ }\mu\text{m}$. FTO glass (tek-15) was the substrate for the working and counter electrodes. The latter was prepared using $15 \text{ }\mu\text{L}$ H_2PtCl_6 . The TiO_2 films were dyed with $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH})_2(\text{NCS})_2]$ (dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl) (N719, Dyesol) dissolved in a 1:1 ratio of acetonitrile/tert-butanol. The films were soaked in the dye solution for 3–4 days. Two identical cells were taken from the MPN series (3.3.2), varying only the concentration of the electron donor, iodide. The electrolytes were composed of 3-

methoxypropionitrile (MPN), 0.05 M I_2 , 0.3 M benzimidazole, and 0.05 M guanidinium thiocyanate. The iodide, as mentioned before, was changed by varying the ratio of 1-propyl-3-methylimidazolium iodide (PMII) to 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide (PMITFSI), keeping the total concentration of both at 0.8 M. The optimized device had 0.8 M PMMI, and the low iodide device had 0.07 M PMMI and 0.73 M PMITFSI. The MPN was high purity (99.85) from Dixie Chemical; other components were purchases from Sigma-Aldrich, Fluka, and Iolitec and used as received.

4.2.1 Difference Spectrum

Transient difference spectra (Figure 4-1) were acquired using a transient absorption technique similar to those previously published (see 2.5.1). (Tachibana 1996; Pelet 2000; Nogueira 2001; Montanari 2002; Clifford 2007) The pump was a nitrogen dye laser at 510 nm. The probe lamp was a 100 W quartz tungsten halogen lamp (Bentham IL1). White light from the probe lamp was directed at the sample, attenuated with neutral density filters to give ~ 1 sun illumination intensity. A single monochromator was used after the sample. The device used was as described above, but the electrolyte was 0.6 M 1-propyl-3-methylimidazolium iodide, 0.025 M lithium iodide, 0.04 M I_2 , 0.28 M TBP, and 0.05 M GuSCN in valeronitrile/acetonitrile, with a volume ratio of 15:85.

4.2.2 Transient Voltage/Current and Absorption

Simultaneous transient absorption and electronic transients (Figure 4-2) were measured on the TA-TE system. The tungsten halogen probe light was attenuated with neutral density filters, and its spectral region was constrained between 715 and 1000 nm using long-pass (LP715) and short-pass (Thorlabs FES1000) filters. This was done to avoid excitation of the dye by the probe light, allowing transients to also be measured in the “dark” condition. To simulate the 1 sun working condition, additional illumination was provided by 12 white LEDs (see section 9.5) whose intensity was under computer control. After the sample, the probe wavelength was selected using either 830 ± 5 or 980 ± 5 nm band-pass filters. The transient absorption was detected using Si photodiode (see section 9.8.1) integrated within a Costronics amplifier and recorded on an oscilloscope. Samples were pumped at a rate of 2 Hz using the 532 nm output of a ND:YAG pumped OPO (Opotek Opolette 355). The pump pulse energy was selected to cause a transient peak of ~ 0.5 m Δ OD at 830 nm for the 800 mM I^- device. This corresponds to ≤ 1 oxidized dyes formed per five particles. The energy was kept constant for the low I^- device. The cells were also connected

to a data acquisition (DAQ) card that allowed measurement of both the steady-state voltage/current caused by the bias light and the transient voltage/current created by the pump pulse. A computer-controlled switch allowed selection of open- or short-circuit condition. An attached power supply allowed in situ measurement of the cell IV to allow good cross correlation between transients and cell performance. Currents at short circuit were measured over a $2\ \Omega$ resistor. A thermocouple was attached to the cell to monitor temperatures during measurements. Measurements under 1 sun were performed with a device temperature of $29 \pm 0.5\ ^\circ\text{C}$.

For transient voltage/current and transient optical measurements at 560 nm, the probe light was attenuated with a $T = 63\%$ neutral density filter and its spectral region was constrained with a 500 nm long-pass filter and an infrared rejection filter. In this case, the probe illumination was approximately equivalent to 1 sun and the white diodes were not used. The 830 and 980 nm signals presented in Figure 4-3 were also measured in this configuration.

4.2.3 Transient Photocurrent to Transient Charge

The conversion of transient photocurrent to transient charge to be collected (Figure 4-2b,d) goes as follows: The laser flash causes a given number of electrons to be injected into the TiO_2 , Q_{inj} . Q_{inj} corresponds to the initial height of the TA at 980 nm. The temporal decay of the ΔOD at 980 nm corresponds to the amount of Q_{inj} *remaining* in the system, $Q_{\text{rem}}(t)$, as the charges disappear to recombination with S^+ , recombination to electrolyte, and transport (as photocurrent) out of the TiO_2 . On the other hand, integration of the photocurrent transient gives the part of Q_{inj} that has flowed out of the system (i.e., “collected”) up to time t , $Q_{\text{col}}(t)$ (eq 1). Integration over several seconds gives the total charge collected, Q_{tcc} . In an efficient cell, Q_{tcc} is close to Q_{inj} (Figure 4-2b). To convert $Q_{\text{col}}(t)$ into a charge *remaining* transient, we plot $Q_{\text{crem}}(t) = Q_{\text{tcc}} - Q_{\text{col}}(t)$. Thus, $Q_{\text{crem}}(t)$ is the part of the charge remaining in the system, at time t , which will be collected as photocurrent by the end of the transient. Equation 4-1 summarizes the above

$$Q_{\text{crem}}(t) = \int_0^\infty \Delta J dt - \int_0^t \Delta J dt$$

where $t = 0$ is the time of the excitation pulse and the photocurrent returns to its steady-state value J after a sufficiently long time, $t \approx \infty$.

4.3 Results and discussion

Figure 4-1a presents transient absorption difference spectra of a complete and functioning device, measured under ~ 1 sun illumination and open-circuit conditions at different times (t) after the excitation pulse. Figure 4-1b shows the complete decays at the major chosen probe wavelengths.

The spectra and its decay can be divided into three obvious sections with an isosbestic point around 660 nm. The bleach of the ground-state dye absorption appears at $\lambda < 650$ nm, peaking at 560 nm, which is near the absorption max of 535 nm. (Reynal, Forneli et al. 2008) (In the spectrum at 0.3 μ s, the bleach cannot be measured at $\lambda < 540$ nm due to the scattered light from the laser pulse.) At times < 100 μ s, the absorption between 700 and 890 nm can be assigned to the photooxidized dye superimposed on the absorption of the electron in the TiO_2 . The transient spectrum of the dye bleach and oxidized dye in the cell at $t < 100$ μ s looks similar to the transient spectrum of dye bleach and oxidized dye in a solution, presented by Tachibana et al. (Tachibana 1996) The absorbance at $\lambda > 920$ nm is thus assigned to only the electron in the TiO_2 . The oxidized dye is not expected to show a noticeable absorption at $\lambda > 920$ nm, the same as was shown for $\text{Ru(II)(bpy)}_2(\text{NCS})_2$ oxidized by Ce(IV) in acetonitrile. (Moser, Noukakis et al. 1998) Likewise, after 100 μ s, the absorbance between 700 and 890 nm is assigned to the electron alone. The spectrum between 700 and 1040 nm, at $t = 100$ and 900 μ s, matches the steady-state spectrum observed by applying potential to the TiO_2 electrode in water. (O'Regan 1991; O'Regan 1991; Rothenberger 1992) It is noted that this spectrum differs from that presented in Montanari et al.; (Montanari 2002) these earlier results were generated in a film facing bulk solution in a cuvette, and also without bias light, and thus are from conditions quite different from that inside the operating cell shown here.

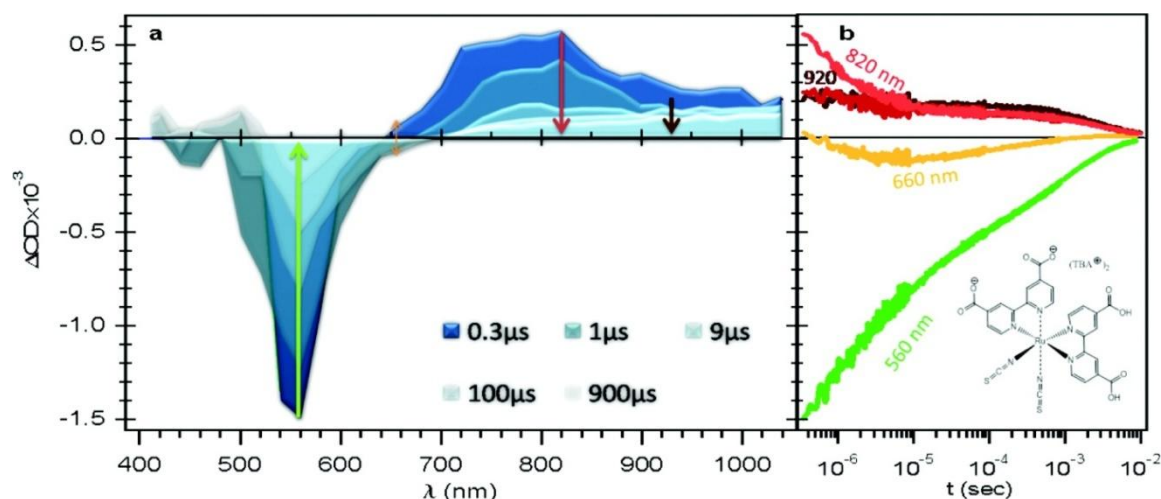


Figure 4-1- (a) Dynamic transient absorption spectra measured for a complete device. Measurement was taken under ~ 1 sun equivalent incident light intensity at open-circuit conditions. Spectra were taken after 0.3, 1, 9, 100, and 900 μ s, following a 510 nm laser excitation pulse. (b) Complete time decays for the example wavelengths.

Figure 4-2 shows the correlation between transient electrical and transient optical measurements. For Figure 4-2a,c, the cells were at V_{oc} (open circuit voltage) under 1sun illumination. The steady-state V_{oc} of the cell during the measurement is also shown. The transient voltage decays are plotted together with the 980 and 830 nm optical decays. In DSSCs, the voltage is proportional to the logarithm of the charge density.(O'Regan, Durrant et al. 2007) However, for the small perturbations used here, the logarithm is well-approximated by a linear function; thus, the absorbance and voltage are compared on linear axes. The normalization constants used will be discussed below. The cell shown in Figure 4-2a has the full iodide concentration and S^0 undergoes fast regeneration, and the cell shown in Figure 4-2c has low iodide and slow regeneration. The data show a strong similarity between the TPV and TA decay for both cases. Both voltage decay and TA decay (at 980 nm) are biphasic, and the similarity is good across the whole time scale from 1 μ s to 0.1 s (see Figure 4-2c, inset). The information contained in the voltage decay allows improved assignment of the TA 980 nm signal. The voltage is a measure of the Fermi level in the TiO_2 , and thus, the transient voltage can be assigned uniquely to changes in the TiO_2 electron concentration. Small changes in the solution redox potential may also occur, but these make very minor contributions.(Dor, Grinis et al. 2009) The high similarity of $\Delta V(t)$ and $\Delta OD(t)$ indicates that only electrons contribute significantly to the 980 nm TA signal. Fast disproportionation ($2I_2^{\bullet-} \rightarrow I^- + I_3^-$ ($k = 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$))(Rowley and Meyer 2009) combined

with a low absorption coefficient (Hug 1981) of $I_2^{\bullet-}$ minimizes the possible contribution of $I_2^{\bullet-}$ to the 980 nm signal. The species I_3^- , I_2 , I^- , $I^{\bullet}$, and S^+ show negligible absorption at 980 nm (Hug 1981; Moser, Noukakis et al. 1998; Kebede 1999) so that contributions to the TA signal are not expected.

Figure 4-2b,d shows similar data for the 1 sun illumination short-circuit condition. The cell J_{sc} (short circuit photocurrent) during the measurement is also given. In this case, the comparison of the TA signal (which measures charge concentration) to the photocurrent transient signal (which measures charge flux) requires additional steps. For this purpose, the photocurrent transient is integrated (over time) and it is reflected across the x axis to create a decay transient that is the “charge remaining that will be collected”, Q_{crem} (see the Experimental Section).

Figure 4-2b,d shows TA decay on the left axis compared to $Q_{crem}(t)$ on the right axis. The y -axis scaling has been chosen to maximize the overlap between TA and $Q_{crem}(t)$. The same scaling has been used in Figure 4-2b,d. Unlike the photovoltage case, the overlap can only be accomplished in the latter part of the transient, after 100 μs for the full iodide cell and after 1 ms for the low iodide cell (see Figure 4-2d, inset). At earlier times, the $Q_{crem}(t)$ amplitude is lower than the TA 980 nm. The difference corresponds to the charges that will not be collected, but instead, lost to recombination. This difference is much larger in the low I^- cell, showing large losses to ΔS^+ , as expected from the slower S^+ regeneration. This is also expressed in the lower photocurrent in this cell. In both cells shown, the $Q_{crem}(t)$ signal meets the TA 980 nm signal at the same time as the TA 830 nm signal meets the TA 980 nm signal. This point can be taken as the time at which there is no more excess S^+ from the pulse. (The 830 nm decay mainly contains a contribution from both the S^+ and the electron, when the excess S^+ has disappeared; the remaining absorption of the electron is similar to that at 980 nm.) The identical shape of the decays, after the disappearance of the excess S^+ , indicates that, after this time, both TA and $Q_{crem}(t)$ decays are signatures of the same process. Again, because the photocurrent transient is a measurement of electrons only, neither the TA 980 nor 830 nm contains a noticeable contribution from other intermediates, for example, $I_2^{\bullet-}$, after this time. This conclusion is strengthened by the fact that the shift in the TA 980 nm decay to shorter times between OC and SC is mirrored exactly by the shift in the TE decays.

The y -axis scaling (normalization) used in Figure 4-2 has been chosen to show a similarity in shape for purposes of assignment of the TA pulse. The scaling chosen for Figure

4-2b,d, implies a certain absorption coefficient for the electrons in the cell, under those conditions. The resultant value is $\epsilon_{(e^-)} = 1170 \text{ M}^{-1} \text{ cm}^{-1}$ (a cross section of $\sim 5 \times 10^{-18} \text{ cm}^2$), in good agreement with other results. (Boschloo and Fitzmaurice 1999; Safrany, Gao et al. 2000; Nguyen, Peter et al. 2009) Using this value, the normalizations used for Figure 4-2a,c imply a relation between the charge (from the ΔOD 980 nm) and the voltage, and thus, a cell capacitance. The capacitances implied are $\sim 3 \text{ mF/cm}^2$, similar to other measurements of capacitance in these cells. (Sommeling, O'Regan et al. 2006) It is noted here that the overlap of the latter part of the TA and $Q_{\text{crem}}(t)$ decay in Figure 4-2b,d does not necessarily indicate that there are zero recombination losses during this later phase. Electrons can recombine with I_3^- and with the background population of S^+ , during transport, and a different choice of the normalization constant would place the $Q_{\text{crem}}(t)$ transient lower than the TA 980 nm at later times. This cannot be resolved by transient analysis alone. Another advantage of doing the transient measurement on full cells is that the diffusion length can be measured separately by steady-state IPCE measurements. Our group is working on the integration of IPCE results and TA and will report on these results in the future.

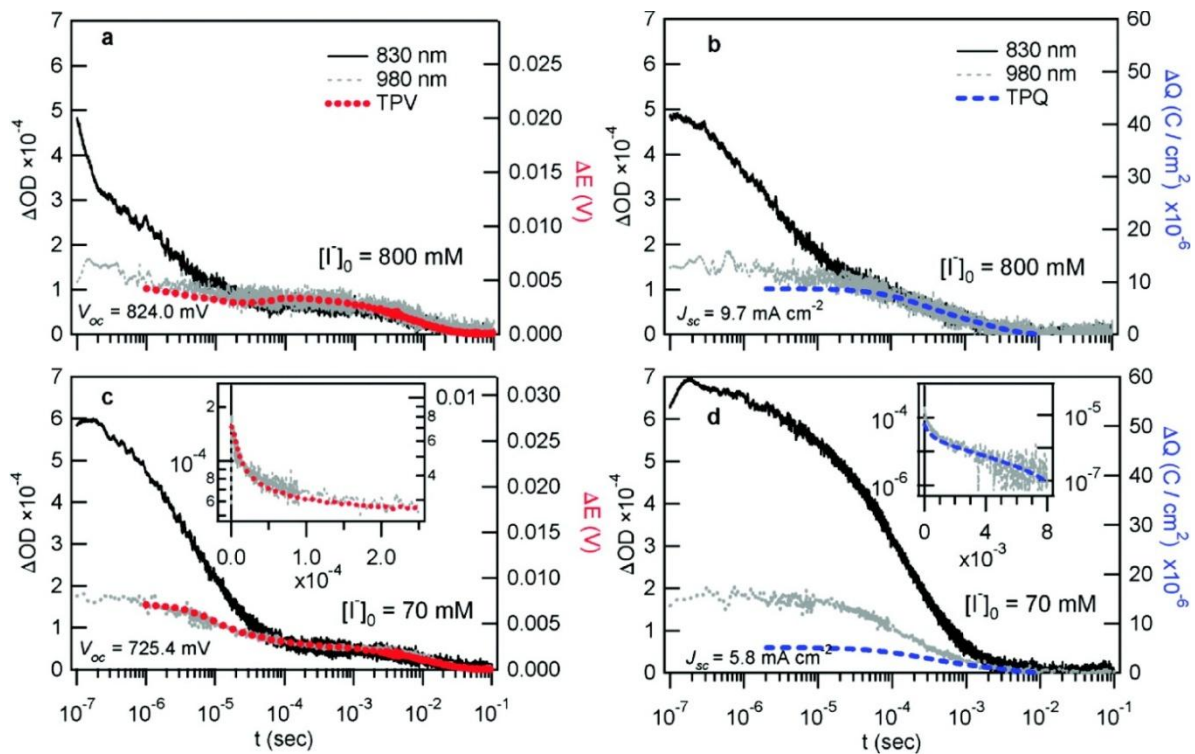


Figure 4-2 - Correlation between small perturbation optical and electronic signals. (a,c) Transient photovoltage decays ($\Delta E(t)$) for normal and poorly regenerating cells, containing 800 and 70 mM I^- , respectively. (b,d) Transient charge decays ($\Delta Q(t)$) measured under short-circuit conditions corresponding to the devices shown in (a) and

(c), respectively. The insets in (c) and (d) are the same plots of the 980 nm signal correlated with the corresponding electronic signal, plotted on $\log(\Delta OD)/\text{linear}(t)/\log(\Delta E/\Delta Q)$ scales. The inset in (c) highlights the match in the first 250 μs of the TPV decay. The inset in (d) shows that the 980 nm and the TPQ decays match at $t > 1$ ms. The ratio between e^- absorption and charge is $11.7 \text{ OD C}^{-1} \text{ cm}^2$ ($\epsilon_{(e^-)} = 1170 \text{ M}^{-1} \text{ cm}^{-1}$). In all cases, the measured signals were taken under the same conditions using the same excitation pulse.

4.3.1 Bleach

Apparent from Figure 4-1b is that the bleach at 560 nm decays much more slowly than does the absorption attributed to S^+ (measured at 820 nm, superimposed on the electron absorption). The longer lifetime of the apparent bleach at 560 nm has been noted before by Staniszewski et al. (Staniszewski, Ardo et al. 2008) This longer lifetime is unexpected, as the disappearance of S^+ by reduction would be expected to give S^0 directly, and thus, the bleach of the ground-state absorption should decay at the same rate as the S^+ absorption.

Figure 4-3a–d compares directly the apparent bleach signal (560 nm), the absorption of S^+ (830 nm), and the electron (980 nm), at both SC and OC. In the plots, the bleach signal is inverted and scaled to match the initial absorption of the 830 nm signal. A further unexpected connection can be observed. In all cases, the final decay of the bleach at 560 nm occurs at the same time as the final decay of absorption at 980 nm. Especially striking is the difference between open circuit and short circuit in Figure 4-3a,b. As the electrons leave the film as photocurrent, at SC, the 980 nm absorption decays ~ 10 times faster than it does at OC, and so does the bleach.

In Figure 4-3c,d, the low iodide causes most of the S^+ to decay by recombination to electrons. In this case, the bleach, 830 nm absorption, and 980 nm absorption decay more or less simultaneously. Again, the longer-lived electrons visible at OC are removed as photocurrent at SC and the decay of the bleach is accelerated. However, in the case of low I^- , the fraction of the bleach that has a long lifetime relative to the 830 nm is strongly reduced.

It has been suggested that the long-lived bleach is due to a blue shift of the dye ground-state absorption due to dissociation of a $(S-Li^+)$ when the dye is oxidized. (Staniszewski, Ardo et al. 2008) This blue shift disappears as the environment around the dye, perturbed by the cycle through S^+ , returns to equilibrium. The data in Figure

4-3 are not easily reconciled to this explanation. Although a blue shift seems plausible, it is found here that the source of the blue shift is not related to the cycle through S^+ . The relative decrease of the long-lived bleach when $[I^-]$ is low (Figure 4-3c,d) shows that S^+ molecules that are created, and then recombine with the electron from the TiO_2 , do not create this blue shift in the ground state. Instead, this data show that the blue shift is generated only when the dye is efficiently regenerated. Thus, the bleach is related either to the products of regeneration or to the electrons that remains in the TiO_2 when the dye is regenerated. Also, the suggested specific involvement of Li^+ in the bleach is eliminated because the electrolytes used here contained no Li. (Staniszewski, Ardo et al. 2008)

One possible explanation for the long-lived bleach concerns complexes of the dye and other species that might form during regeneration, causing a blue shift of the dye spectrum. The intermediate species might be $[S^+I^-]$, as suggested by Clifford et al., (Clifford 2007) or in the form of $[S^+I_2^{2-}]$, as suggested by Fitzmaurice et al. (Fitzmaurice 1991) The fact that the bleach decays at the same time as the electron in the TiO_2 is hard to explain within this explanation. This would require that the complex in question be stabilized by the electron and thus only dissociates when the electron has left the TiO_2 . A second possibility is that the electron alone is responsible for the long-lived bleach. The necessity of iodide electrolyte can be tested with similar experiments using other redox couples (e.g., ferrocene). If the bleach is still present, the explanations involving only the electron will be necessary.

4.3.2 The stark effect

Spectral shifts (4.3.1) have been observed by other groups. (Cappel, Gibson et al. 2009; Snaith, Petrozza et al. 2009) Not long after, the spectral shifts were assigned to the "stark effect", whereby the local electric field shifts the ground state absorption of dyes. (Ardo, Sun et al. 2010; Cappel, Feldt et al. 2010) In these later papers, which relate the Stark effect (Stark 1914) to transient absorption spectroscopy in DSSC, the interpretation of TAS measurements made in previous publications are challenged. First order Stark effect can explain the strong correlation of the apparent bleach (at 550 nm) and electrons (at 980 nm) finishing their decays simultaneously (Figure 4-3a-d). Yet, it is important to define the relative contributions to the apparent bleach due to real bleaching (expected to correlate with oxidized dyes) and due to Stark shifts of the ground state dyes (which diminishes with the disappearance of the temporal electric field). If there is a significant contribution from both effects, then the extent of each requires proper analysis. It is important to highlight that in

this work the cells were under 1 sun equivalent illumination, the perturbation was relatively small and was on top of these steady state conditions. In this case, the transient electric field is much smaller than the background electric field, and the Stark effect is expected to correspond to a minor wavelength shift. Small perturbations are not the characteristics of photoinduced absorption, electroabsorption or large perturbation TAS, as these start from dark conditions. For the future, once introduced, the Stark effect and the magnitude of the electric field that drives it will require further consideration in the interpretation of optoelectronic work. The implications for solar cells devices functionality, if any, may also require further assessment.

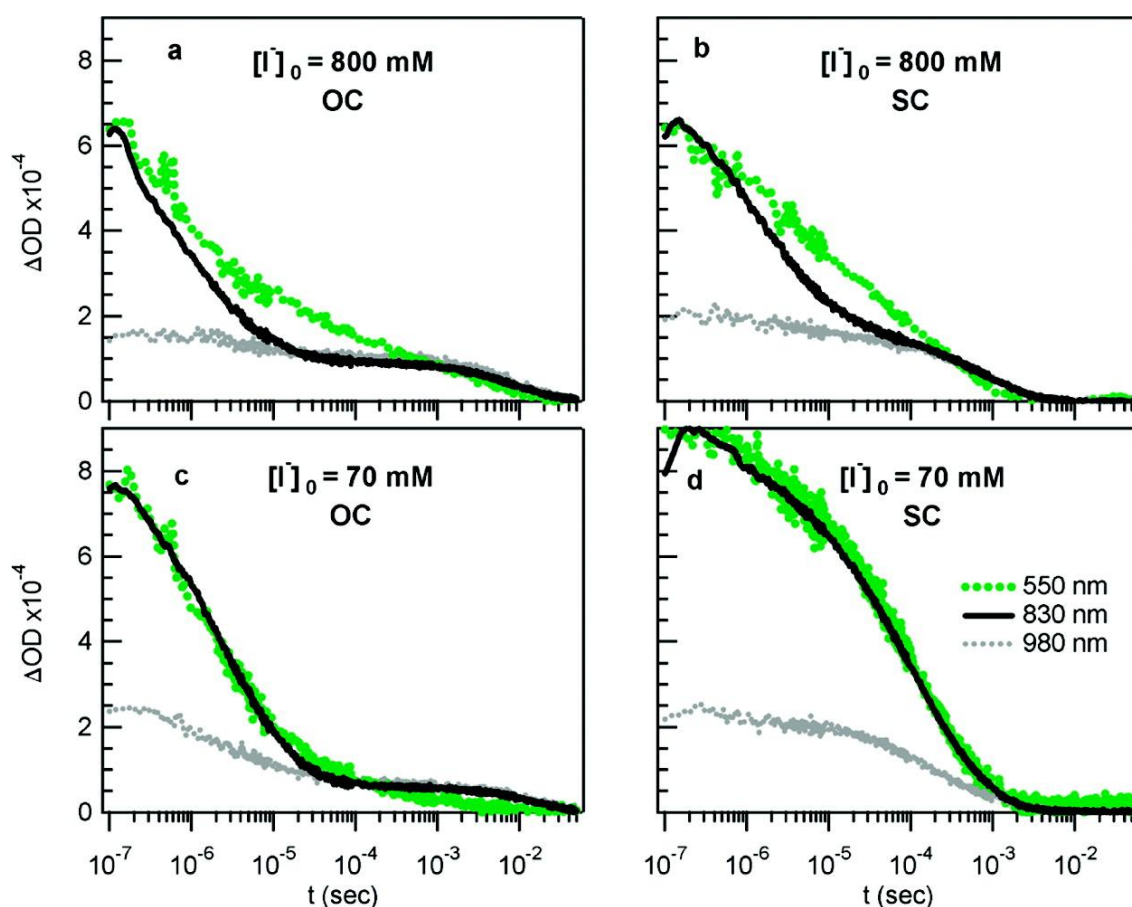


Figure 4-3 - Transient absorption correlation of the bleach signal measured at 560 nm to the superimposed oxidized dye (S^+) absorption, measured at 830 nm. The bleach signals were inverted and scaled such that their initial absorption will match the initial absorption of the 830 nm signal. The devices are the same devices used in Figure 4-2. The measurement was obtained under 1 sun illumination and either open or short circuit (OC or SC).

4.4 Conclusions

The long-lived signal, measured at the region of 920–1020 nm, is a direct proxy for the charge separated following injection. The decay under open circuit follows the photovoltage decay both in shape and in time. For the current configuration, $I_2^{\bullet-}$ does not have significant absorption in this wavelength range after $\sim 1 \mu\text{s}$. Such observation is highly important for regeneration studies because it enables a quantitative separation of oxidized dye absorption from that of e^- at the probe region of 800–840 nm.

Under open circuit, the e^- optical and electronic signals show a biphasic decay that can be correlated to the two recombination processes of e^- , either with S^+ (the fast phase) or with the oxidized species of the electrolyte (the slow phase). This has implication on transient photovoltage measurements and charge extraction because, at low time resolution ($>1 \mu\text{s}$), the fast recombination is missed out while the charge is at its highest concentration.

A correlation of e^- absorption under short circuit and the transient photocharge measured simultaneously reveals a simple method to quantify the charge separated and charge collected (or charge lost) in operational devices.

5 Quantifying Regeneration as a function of iodide

This chapter presents a proposition and application of a new experimental protocol for determining the kinetics of the oxidation of iodide (a.k.a. dye regeneration) in dye sensitized solar cells (DSSCs) using measurements on full cells under operating conditions. Transient absorption (TA) decays of the oxidized dye after a laser pulse are correlated with the short circuit current (J_{sc}) and electron concentration in the TiO_2 , measured during the TA experiment. Results for a series of cells with N719 $[(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH})_2(\text{NCS})_2]]$ (dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl), a standard electrolyte and varying iodide concentration allow one to fit for the fundamental regeneration rate constant ($k_{rg} = 7.8 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$), and to determine that the order in iodide, in these cells, is near 1 (0.98 ± 0.16), and clearly not 2. The rate and order allow to rank various reaction mechanisms and to discuss possible rate limiting steps that could be catalyzed to improve regeneration. The method can also give estimates of the fundamental rate constant for electron dye recombination (EDR) and the apparent reaction order in total electron concentration.

5.1 Introduction

In this chapter regeneration is studied using transient absorbance of the various species involved. Previous work has used similar techniques, and the relevant literature will be included in the discussion. What is new in this chapter's approach is that all measurements are made on complete functional devices under light bias and at short circuit, using the TA-TE setup (section 2.1 and described in chapter 4). This allows the measurement of the photocurrent quantum efficiency and the electron concentration at the same time as the transient absorbance decays. These two additional parameters allow determination of the fundamental regeneration and EDR rate constants as well as the order of the reaction for all reactants (see section 1.1.7). The determination of these rate constants allow one to make suggestions concerning the rate limiting step and its implications. Furthermore, the results are also useful for conceptual and numerical modelling of the cell. With the fundamental rate constants it is now possible to predict the flux of electrons recombining with the dye at any

potential and light level. This in turn allows modelling results to be more specific about the causes of V_{oc} and fill factor.

5.2 Method

Transient absorption decays are measured at 830 nm and 980 nm following laser pulse excitation of the dye. The cells are illuminated with 1 or 0.1 sun bias illumination, and are at short circuit. The cells contain the N719 dye, and a methoxypropionitrile electrolyte (see experimental). It is shown in the previous chapter that with this dye and electrolyte the 980 nm absorption is entirely due to electrons in the TiO_2 . The 830 nm absorbance contains significant contributions from TiO_2 electrons, the oxidized dye (S^+ and/or $[\text{S}^+\cdots\text{I}]$) (absorption coefficient $6000 \text{ M}^{-1} \text{ cm}^{-1}$) (Tachibana 2000) and a smaller contribution from I_2^- (absorption coefficient $2200 \text{ M}^{-1} \text{ cm}^{-1}$). (Hug 1981) The disproportionation reaction (R1c in section 1.1.7) was shown to be fast compared to the formation of I_2^- , (Grossweiner and Matheson 1957; Gardner, Abrahamsson et al. 2009) furthermore the additional light in this study gives a constant background concentration of I_2^- which speeds up the decay of this species. In this case the I_2^- concentration will track the S^+ concentration, and the I_2^- contribution to the 830 nm signal will not change the shape of the decay. I assume that to be the case in the following analysis: (Gardner, Giaimuccio et al. 2008; Rowley and Meyer 2009) By subtraction of the electron signal from the 830 nm absorbance, a decay of the S^+ species remains from which I extract the lifetime and rate constants. In this measurement I do not distinguish between S^+ and the possible $[\text{S}^+\cdots\text{I}]$ complex. The spectrum of the transient S^+ species measured in the presence of iodide is not strongly shifted from that of S^+ alone in iodide free electrolyte. (Tachibana 1996; Anderson, Barnes et al. 2010) This implies that the energy levels of $[\text{S}^+\cdots\text{I}]$, if present, are not significantly different from those of S^+ . It has been shown that EDR is not modulated even by large changes in driving force, (Kuciauskas, Freund et al. 2001; Clifford, Palomares et al. 2004) therefore it can be assumed that reaction E1 and E2 have similar rates. The decay of the S^+ species at 830 nm thus gives the combined rate of regeneration (via R1b, R2b and/or R3a) and recombination, whichever scheme is dominant. It is the dependence of the rate constant on other factors that can be used to distinguish between the mechanisms.

In practical terms, to remove the electron absorption from the 830 nm signal first the 980 nm decay is fitted with a single or double stretched exponential, depending on the transient. Then this fit is subtracted from the 830 nm transient absorbance and the resulting S^+

transient is fitted with another stretched exponential. The stretched exponential (eqn. 5-1) is a compact expression allowing one to fit some types of transient decays which occur over many orders of magnitude in time. The stretched exponential is equivalent to a weighted average of many single exponentials with a wide range of lifetimes. A specific probability distribution of lifetimes is required to create a stretched exponential, however there are many possible distributions of lifetimes that can give decays that are "stretched" over many orders of magnitude in time (see last paragraph of discussion). For any of these distributions, the weighted average lifetime can be calculated, and the inverse of this lifetime is the "effective rate constant" (i.e. $k_{obs} = 1 / \tau_{obs}$). This effective rate constant is the correct value for calculating flux of species in steady state situations using rate equations such as in eqn. 5-3. For the stretched exponential in particular, the weighted average lifetime can be calculated using eqn. 5-2. (Nasr 1998) (The gamma (Γ) function in eqn. 5-2 is defined in 5.7 Additional information - 5). Note that other distributions of lifetimes which fit the same transient decay (e.g. >10 distinct lifetimes) will result in approximately the same weighted average lifetime and rate constant. Another standard approach to compare stretched TA decays is the use of decay half time. This approach can be useful for discussing relative rate constants as long as the stretch parameter of the decays is similar. If the stretch parameter (β) differs significantly, decays with similar half times can correspond to very different weighted average lifetimes (see Figure 5-6 in Additional information - 5).

$$\Delta OD_{(t)} = \Delta OD_{(t=0)} e^{-(t/\tau_{ww})^\beta} \quad 5-1$$

$$\tau_{obs} = \frac{\tau_{ww}}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad 5-2$$

To extract the fundamental rate constants from the k_{obs} of the 830 nm signal, I begin with the assumption that the regeneration is first order in the concentration of the oxidized dye. This is reasonable as S^+ is immobilized, and is present in very low concentrations (< 1 per particle), thus the probability of 2 S^+ close enough to interact is very small. This assumption may not be valid for dyes where hole mobility occurs along the dye layer, however, this has not been found for N719. (Li, Nazeeruddin et al. Submitted) I also assume that reaction R1b does not form an equilibrium in this system. This assumption is justified in part by self consistency of the reaction order found (see discussion). Then the transient

absorption decay can be described by equation 5-3, allowing the reaction orders to be unspecified to include all the reaction schemes discussed above. Equation 5-4 for k_{obs} follows from equation 5-3.

$$-\frac{d[S^+]}{dt} = k_{rg}[I^-]^\gamma[S^+] + k_{edr}[e^-]^\chi[S^+] \quad 5-3$$

$$k_{obs} = k_{rg}[I^-]^\gamma + k_{edr}[e^-]^\chi \quad 5-4$$

Two separate equations (eqn 5-5 and 5-6) can be derived from equation 5-4 relating the measured J_{sc} and k_{obs} .

$$J_{sc} = J_{max} \eta_{rg} = J_{max} \left(1 - \frac{k_{edr}[e^-]^\chi}{k_{obs}} \right) \quad 5-5$$

$$J_{sc} = J_{max} \eta_{rg} = J_{max} \left(\frac{k_{rg}[I^-]^\gamma}{k_{obs}} \right) \quad 5-6$$

where J_{max} is the photocurrent that would be measured if regeneration was 100% efficient.

In this chapter k_{obs} and J_{sc} are determined for a series of cells with 5 different iodide concentrations (see experimental). Since electron concentration were also measured at short circuit for each cell (experimental), in principle equations 5-5 and 5-6 can be solved independently. However, it is found that the electron concentration, which is measured in-situ under operation, has less uncertainty than the free iodide concentration in the pores, which can and does differ from that in the source electrolyte (see below). For this reason first equation 5-5 is used to estimate J_{max} , k_{edr} and χ . The resulting uncertainty in J_{max} is small, indicating that J_{max} is indeed constant for the different iodide concentrations. This is consistent with observations that the injection efficiency and collection efficiency do not vary for this range of electrolytes. I use the so derived value of J_{max} , and the calculated free iodide concentrations to fit equation 5-6. I calculate the free iodide concentration using literature value for the strong association with iodine (eqn 5-7), but ignoring at this stage other

molecular associations and binding to the TiO_2 . This second fit gives us k_{rg} and the order of the reaction in iodide.

$$K_{eq} = \frac{[I_3^-]}{([I_2]_0 - [I_3^-])([I^-]_0 - [I_3^-])}$$

5-7

5.3 Experimental

Cell construction in this chapter is as described in chapter 3 and is identical to that in the group previous publications with the exception of the iodide concentration variation. Cells were fabricated using TEC15 FTO glass as front and back electrodes. TiO_2 layers were synthesized as previously and were $\sim 9 \mu\text{m}$ thick. (Barbe', Arendse et al. 1997; O'Regan 2009; Anderson, Barnes et al. 2010) The dye was bistetrabutylammonium *cis*-dithiocyanatobis(4,4'-dicarboxylic acid-2,2'-bipyridine)ruthenium(II) (N719). A first series of cells was made using propylene carbonate (PC) as the solvent for backward compatibility with the group earlier studies. (Montanari 2002; Clifford 2007) The standard (0.7 M iodide) example contained 0.6 M tetrabutylammonium iodide (TBAI), 0.1 M LiI, 0.3M tert-butylpyridine (TBP) and 0.05M I_2 . Lower iodide examples contained 311, 207, 138, 92, and 61 mM I^- , where TBAClO_4 and LiClO_4 were substituted for the iodide salts to keep the TBA^+ and Li^+ concentrations constant.

These cells were somewhat unstable under illumination (Figure 3-4), and another series was made for compatibility with today's state of the art electrolytes. These cells used 3-methoxypropionitrile as the solvent. The standard electrolyte contained 0.8 M 1-propyl-3-methyl imidazolium iodide (PMMI) 0.3 M benzimidazole, 0.05 M guanidinium thiocyanate and 0.05 M iodine. Lower iodide examples contained 533, 355, 158, 70, 46 and 0.0 mM iodide. 1-propyl-3-methyl imidazolium-bis(trifluoromethylsulfonyl)imide (PMMTFSI) was substituted for the iodide salt to keep the PMM^+ concentration constant. Consistent with literature, these cells have proven very stable (Figure 3-7). (Wang, Klein et al. 2005)

The current-voltage characteristics of the cells at "1 sun" were determined using a solar simulator based on a 150 W xenon lamp with AM 1.5 filter (Sci Tech) (2.7). Short circuit current as a function of light intensity was measured using an array of white LEDs.

The electron concentration in the TiO_2 at short circuit was determined by charge extraction technique (2.4). (Duffy, Peter et al. 2000; Barnes 2009)

The TA-TE in this chapter was carried out using a probe beam from the 100 W quartz halogen lamp (Bentham IL1) driven by constant current power supply (Bentham 605). Before the sample, the probe beam was attenuated with neutral density filters, and limited to the range 715 - 1000 nm with long and short pass filters. After the sample, the probe wavelength was selected using band pass filters. The transient absorption was recorded using Si photodiode (Hamamatsu S3071), a Costronics preamplifier-amplifier, and a Tektronix TDS 1012 oscilloscope. The pulse beam was 532 nm (Opotek Opolette 355 II), pulse width 3 ns, using a repetition rate of 2 Hz. The pulse energy was tuned to cause an absorbance increase of $\sim 5 \times 10^{-4}$ at 830 nm for the highest iodide member of a series. In this chapter's samples, this absorbance corresponds to less than one photo-oxidized dye molecule per particle. The pulse energy was kept constant for the other members of the series. To simulate working conditions, the samples were illuminated with a bias light (white LEDs) at intensities equivalent to 1 or 0.1 sun and held at short circuit. During TA measurements the cells were connected to the data acquisition system in order to measure the transient photocurrent, and also to monitor steady state current and voltage to insure TA data was taken only on stable cells. A thermocouple was mounted on the samples. Measurements were collected at 29 ± 0.5 °C for the 1 sun condition and 26 ± 0.5 °C for the 0.1 Sun (room temperature as 24 °C).

5.4 Results

Figure 5-1 shows the typical pattern of J_{sc} with iodide concentration. Typical DSSCs have 0.6 - 1 M iodide, however serious reduction in photocurrent does not begin until iodide is reduced below 0.2 M.

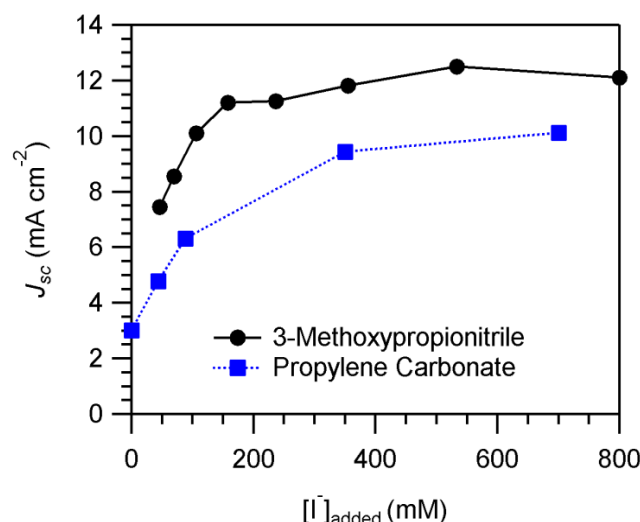


Figure 5-1 - 1 sun J_{sc} vs. concentration of added iodide. Cells containing the MPN and PC electrolytes.

Table 5-1 – Cell iodide concentrations and IV characteristics

	$[I^-]_{\text{added}}$ (mM)	$[I^-]_{\text{free}}$ (mM)	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF	η (%)
MPN	46	6×10^{-5}	7.45	0.697	0.32	1.68
	70	20	8.56	0.711	0.37	2.28
	106	56	10.1	0.720	0.39	2.87
	158	108	11.2	0.721	0.36	2.94
	355	305	11.8	0.735	0.33	2.93
	533	483	12.5	0.735	0.38	3.49
	800	750	12.1	0.748	0.40	3.59
PC	0	0	3.02	0.651	0.39	0.76
	44	4.6	4.78	0.698	0.39	1.31
	88	39.5	6.32	0.706	0.36	1.60
	350	300	9.43	0.726	0.36	2.44
	700	650	10.1	0.746	0.36	2.73

Table 5-1 gives the JV results as a function of the I^- concentration for the cells with MPN or PC electrolyte. The first column gives the concentration of iodide as added to the solution, in the second column I give the calculated "free" iodide concentration taking into account the complexation of iodide with iodine (eqn. 5-7). For cell 1, total $[I^-]$ 46 mM, the nominal 50 mM I_2 concentration gives effectively zero for the free iodide concentration. However, the cell was able to produce more than 60% of the maximum photocurrent, implying free iodide in the cell was much higher than calculated. Furthermore the first cell in

the PC based series had no initial added iodide, however this cell generated noticeable photocurrents which apparently had improved during operation. Iodine binding has been observed to several components of the cell, including the dye and solvent.(Kebede 1999; O'Regan 2009) In addition, the group I am in have found that the interaction of nitrile solvents and nano-porous oxides can result in the conversion of iodine to tri-iodide.(Li 2010) These factors combined reduce the iodine concentration, releasing free iodide which was bound in tri-iodide, or even creating free iodide when none was added. This apparently accounts for the current in low and no iodide cells. These observations were not expected and are currently under further study.

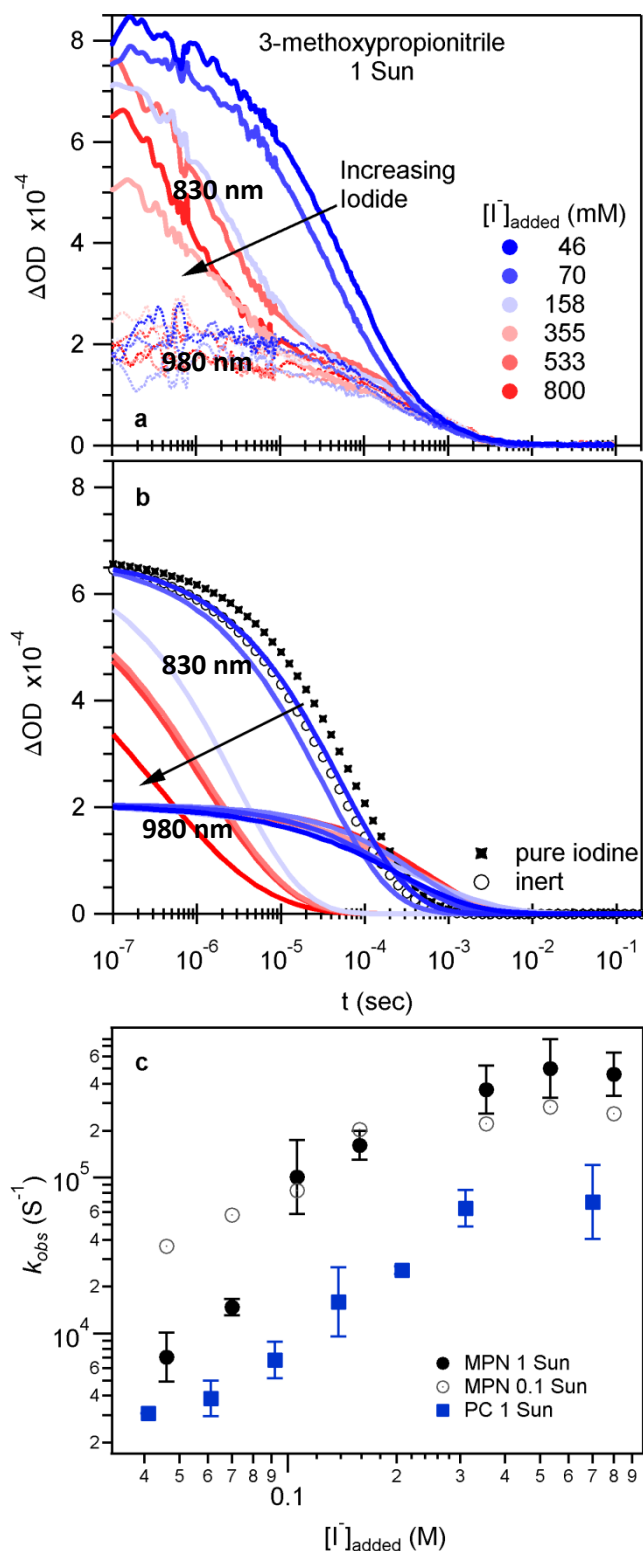


Figure 5-2 - a) Transient Absorption at 830 nm and 980 nm (Labelled) for cells containing various iodide concentrations in an MPN electrolyte. Bias illumination 1 sun. Short circuit condition. Pump laser 532 nm, with $\sim 150 \mu J cm^{-2} pulse^{-1}$. Repetition rate 2 Hertz. Typical averages 400. b) Fits, normalized to the same initial amplitude. c) observed rates, k_{obs} , as a function of added iodide.

Figure 5-2a shows the measured transient absorption decays for MPN cells at 1 sun bias and short circuit. Figure 5-2b shows the separated and fit results for the decay of electrons and S^+ . Also shown are two additional cells, one with no I^- , but the standard 50 mM I_2 , then other with no I^- or I_2 . Both cells contain all the other electrolyte ingredients detailed in the experimental. The TA results are broadly compatible with the other cells. For example, the only electron recombination pathway in the inert electrolyte cell is to the dye (Figure 5-7 in 5.7 Additional information - 5). Thus injection caused by the bias light leads to a higher electron concentration than in the 46 mM cell, or in the iodine only cell. This in turn causes the pulse induced S^+ transient to decay somewhat faster, as seen. (Note that cells with iodine/iodide were short circuited, whilst the inert cell behaves as if it is under open circuit regardless of the electrical configuration. It is the collection that reduces the electron concentration under short circuit). Figure 5-2c shows the extracted k_{obs} for the two electrolytes and for two bias light intensities for the MPN electrolyte (the PC and 0.1 suns MPN TA decays are presented in Figure 5-8 in Additional information - 5). As expected, the k_{obs} is slower in the more viscous PC electrolyte, however quantitatively the difference is larger than expected from the viscosity ratio of ~ 2 . Also note that the k_{obs} falls much more quickly at low iodide under 1 sun bias than under 0.1 sun. This is due to the gradient in iodide concentration when current is flowing through the cell. At 1 sun J_{sc} , the magnitude of the gradient becomes large, relative to the background iodide, when $[I^-]$ is $< \sim 0.2$ M (see below).

Table 5-2 - Measured and calculated regeneration parameters at 1 sun illumination, short circuit

$[I^-]_{added}$ (mM)	$[I^-]_{free}$ (mM)	J_{sc} (mA cm ⁻²)	k_{obs} (s ⁻¹ × 10 ⁴)	n (cm ⁻³ × 10 ¹⁷)	η_{rg}
46	6×10^{-5}	7.45	1.05	4.81	0.57
70	19	8.56	1.75	5.03	0.76
158	107	11.2	19.8	7.58	0.83
355	304	11.8	28.2	7.18	0.94
533	482	12.5	30.7	7.98	0.95
800	749	12.1	52.3	7.87	0.97

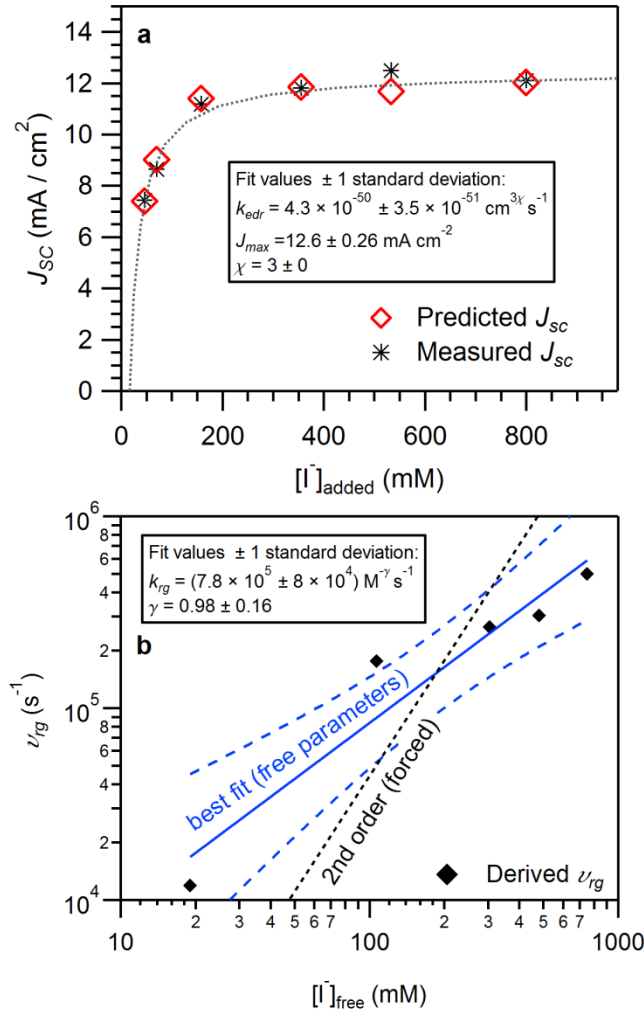


Figure 5-3 - a) Measured J_{sc} and predicted J_{sc} from best fit to equation 5-5. The solid line in the figure is the predicted J_{sc} based on the derived k_{rg} , k_{edr} , χ and γ and shows the predictive power of the model. It is not a fit, as the calculation requires extrapolating electron concentration between the measured cells. b) Calculated ν_{rg} vs. $[I^-]_{free}$ and best fit line. Dashed lines are 90% confidence bands around fit line. Dotted line is the "best fit" holding order of reaction in iodide to 2.

As described in the methods section, the short circuit current is measured during the transient absorption experiment, and separately the steady state background electron concentration in the film is measured under identical conditions using the charge extraction technique. Table 5-2 shows the measured and calculated values for the MPN cells at one sun. With this data, equation 5-5 (methods) can be used to fit J_{sc} , k_{obs} , and n , to determine the unknowns k_{edr} and χ . Figure 5-3a shows the measured and best fit J_{sc} . The fit is quite good, and J_{max} is well determined (12.6 mA cm⁻²). This indicates that the values of J_{sc} , k_{obs} , and electron density are measured without large errors. The data set I present has a small range in

electron density (Table 2), thus is cannot be used to determine separate values for χ and k_{edr} due to the covariance implicit in equation 5. This could be remedied by additional measurements at 0.5 and 2 suns to allow a larger range of electron density. The measurements at 0.1 suns are not useful as they all show essentially no losses to electron-dye recombination. Previous work has found a value near 3.0 for χ .(R. L. Willis 2002) and these cells also show a χ near 3.0 for the electron-electrolyte recombination. If the value of χ is held to 3.0, the uncertainty in k_{edr} is reduced, giving a value of $k_{edr} = (4.3 \times 10^{-50} \pm 3.5 \times 10^{-51}) \text{ cm}^{3\chi} \text{ s}^{-1}$.

Having determined J_{max} we can rewrite equation 5-6 to equation 5-8. We can then plot $\log(v_{rg})$ vs. $\log([I]_{free})$ and fit a straight line to find k_{rg} and the order of the reaction in iodide (Figure 5-3b). Despite some scatter in the data, the order of the reaction is found to be effectively 1.0 and k_{edr} is determined within 10%. It is noted that the best fit line of order 2 can be rejected with more than 90% confidence. The fit does depend heavily on the point associated with the 70 mM iodide concentration, as it is the only one with significant losses in J_{sc} . However the low noise in the transient decay in Figure 5-2a, the J_{sc} measurement and the value of J_{max} , all contribute to the placement of this point with high confidence. I have omitted the point for 46 mM I^- due to obvious formation of iodide in situ. However, an estimate of 5-10 mM free iodide, and a calculated v_{rg} of 6000 s^{-1} place this point squarely on the fit line already present.

There is scatter in the points in Figure 5-3b, and the source of this error is important for future improvements of the method. The source of the error can be narrowed down to a particular cause. The goodness of fit in Figure 5-3a, and the low uncertainty in J_{max} , mean that J_{sc} , and k_{obs} do not contain large errors. The only remaining parameter in equation 5-8 is the iodide concentration, thus errors in this parameter should be the main source of the uncertainty in k_{rg} .

$$v_{rg} = k_{rg}[I^-]_{free}^\gamma = \frac{J_{sc} k_{obs}}{J_{max}}$$

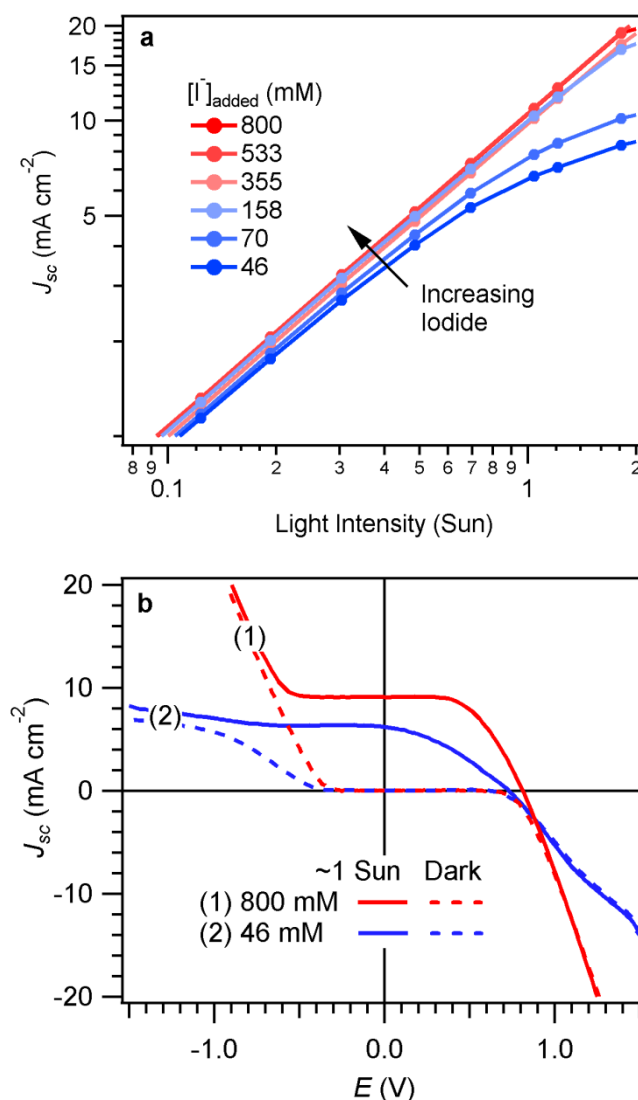


Figure 5-4 - a) Saturation of photocurrent at high light intensities at different iodide concentrations. b) Cyclic voltammograms showing the reverse bias ($E < 0\text{V}$) dark and light (~ 1 sun) current saturation in the low iodide cell but not the high iodide cell.

The uncertainty in the iodide comes from two sources. Under operation at short circuit iodide ions form a diffusion gradient from the counter electrode, where they are formed, into the pores, where they are consumed by the regeneration reaction. Based on the diffusion coefficient of I^- , at a current of 10 mA, the gradient across the cell is $\sim 0.01 \text{ M} / \mu\text{m}$. This does not significantly perturb the concentration of I^- in the pores when the starting concentration is large than $\sim 0.2 \text{ M}$, however for lower concentrations it becomes an issue. This is reflected in the trend of photocurrent with light intensity for the various I^- concentrations (Figure 5-4a). When the $[I^-]$ is low, and the light intensity is high, I^- depletion in the pores slows regeneration and current is lost to recombination. The same effect can be seen in the reverse bias dark current (Figure 5-4b) where the maximum iodide gradient

possible limits the dark current. Note the photocurrent for the low iodide cell is limited to a similar value as is the reverse bias dark current, supporting the assignment of the non-linear behaviour in Figure 5-4a to the iodide gradient.

Even were the issue of the iodide gradient resolved perfectly, there appears to be another source of error in the iodide concentration in the cells. In fact, as the calculation of v_{rg} does not involve the iodide concentration at any point, the inverse of Figure 5-3b can be fitted to find the predicted iodide concentrations in the pores (see Additional information - 5, Figure 5-9 and Figure 5-10). This fit also finds an order in iodide of one, however the predicted iodide concentration in different cells lies both higher and lower than the concentration originally added to the stock electrolyte. I believe this is due to the interaction of the very small quantity of electrolyte in real cells ($\leq 2 \mu\text{l} / \text{cm}^2$) and the large surface area of $\text{TiO}_2 / \text{dye}$ ($\geq 600 \text{ cm}^2 / \text{cm}^2$). For example, at a nominal iodide concentration of 0.2 M, only 0.4 μmoles of I^- are injected into a 1 cm^2 cell. A surface layer of adsorbed iodide on the TiO_2 , were such a layer to form, would require this entire amount.

5.5 Discussion

Table 5-3 - Literature values for the regeneration rate constant; various dyes, conditions, and measurement techniques

Dye	k_{rg} ($\text{M}^{-1} \text{s}^{-1}$)	Solvent	[I] (mM)	Additives	Configuration	E_x ($\text{cm}^{-2} \text{pulse}^{-1}$)	ref
$\text{Ru(L-H)}_2(\text{X})_2$	7.8×10^5	MPN	46 - 800	see experimental	1 sun SC (Anderson, Barnes et al. 2010)	150 μJ	this work
$\text{Ru(L)}_2(\text{X})_2$	1.6×10^5	PC	1 - 100	0.1 M Li^+ , ClO_4^- completes	films immersed in a cuvette	25 - 50 μJ	(Montanari 2002)
$\text{Ru(L)}_2(\text{X})_2$	1.4×10^8	PC	500	0.5 M Na^+ 0.05 M I_2	two-electrode cell	50 - 250 μJ	(Heimer 2000)
$\text{Ru(L)}_2(\text{X1})_2$	2×10^7	PC	500	0.5 M Na^+ 0.05 M I_2	two-electrode cell	20 - 25 mJ	(Alebbi 1998) a
$\text{Os(L)}_2(\text{X1})_2$	7×10^6	PC	500	0.5 M Na^+ 0.05 M I_2	two-electrode cell	20 - 25 mJ	(Alebbi 1998) b
$\text{Ru(L)}_2(\text{X})_2$	1.7×10^6 (s^{-1})	PC	100	Li^+/TBA^+ completes 0.1 M	film on glass + coverglass	1 mJ	(Pelet 2000)
$\text{Ru(L1)}_2(\text{L})^{2+}$	1.2×10^{10}	ACN	0 - 12	Na^+ same as I^-	SnO_2 films	5 mJ	(Nasr 1998)

Ru(L2) ₃	2.5×10^9	Water	0 - 0.4	K ⁺ same as I ⁻	Colloidal TiO ₂	35 mJ	(Fitzmaurice 1991)
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L = 4,4'-dicarboxylic acid-2, 2'-bipyridine

L1 = 2,2'-bipyridine

L2 = 2,2'-biphenyl-4,4'-dicarboxylate

X = thiocyanato

X1 = cyano

ACN = Acetonitrile

This is not the first study to report a regeneration rate constant for DSSCs. Table 5-3 summarizes some results from previous literature. Apparent from the table is an enormous variation in the k_{rg} determined. Some variation is contributed by the differences in the exact system measured. However it feels that problems with experimental methods also contribute to the variation. The main problem is the difficulty in separating regeneration and recombination using measurement techniques that can not measure electron density and/or photocurrent output of the cells. Some of the larger pulse energies used will have created large electron populations in the particles, which according to the results here will skew the results toward larger regeneration rate constants. For example Haque et. al. showed that in inert electrolyte the EDR accelerates from ~ 1 ms up to ~ 1 μ s (half-life) when excitation pulse energy was increased from 0.04 to 6 mJ cm⁻² pulse⁻¹. (Haque, Tachibana et al. 2000) Also some pulse energies may have been large enough so that all the iodide in the pores would be consumed before regeneration was complete. Lastly, as noted by Meyer et. al, measurements of the kinetics of the bleach in the ground state absorption of the dye can give erroneous results in systems where the stark shift of the ground state absorption is significant. (Anderson, Barnes et al. 2010; Ardo, Sun et al. 2010) To summarize, I believe the technique shown eliminates the majority of the uncertainty in the measurement, and the k_{rg} value (7.8×10^5 M⁻¹ s⁻¹) can supplant many of the previous estimates.

The goal of these studies of regeneration is to achieve sufficient understanding of the reaction to predict which dye structures and electrolyte compositions will favor fast regeneration with lower driving force. The end goal is to catalyze efficient regeneration with infrared absorbing dyes with less positive oxidation potentials. I can now ask, do my results cast any light on the reaction mechanism and limiting step of regeneration. Consistent with

previous studies, it is found a reaction order of 1 in iodide for the combination of N719 and the MPN electrolyte. Although the data are not complete, the very similar trend of k_{obs} and iodide concentration in PC also supports a reaction order of 1 in that solvent. A reaction order of 1 is most easily compatible with reaction schemes R1 or R3. In the following discussion the slowest important step is assumed to be reaction R1b first, further below other possibilities are discussed.

The reaction rate as a whole, and therefore the slowest step, is far below the diffusion limitation. Thus it is assumed that reaction R1b must go through a high energy and/or low probability activated state. First, the second I^- must approach the dye along the right vector to encounter the bound iodide. Further, whatever the net charge on $[S^{+}\cdots I^-]$, the partial charge on the bound iodide will certainly be negative. Thus the correct approach of the second iodide will be electrostatically unfavourable. On the other hand, the high dielectric and high ionic strength of the electrolyte will screen the electrostatic repulsion to a large extent. In the presence of high screening, it may be that progress through the activated state to the product state might occur with low probability during the lifetime of the activated complex.

It is clear that studies with different ionic strengths and different solvent dielectric constants will be necessary to determine the electrostatic contribution to the activation energy. The fortuitously large change in rate constants for the two electrolytes shown in Figure 5-2c can shed some light on this. The viscosity (2.1 cP) and dielectric constant ($\epsilon_r = 65$) of PC are both about twice that of MPN (1.1 cP, $\epsilon_r = 36$). (Ue, Ida et al. 1994) If formation of the activated complex was the limiting step, the viscosity effect should decrease collision frequency of the reactants and reaction rate by about 2. However, assuming the same charge on both reactants, the higher dielectric should increase the probability of forming the activated complex, cancelling out some part of the viscosity increase. Instead, as also observed in reference (Montanari 2002), the PC electrolyte shows a factor of ~ 6 slower regeneration over the whole range of iodide concentrations. At present, the effects of solvent and solute cannot be sorted because the two electrolytes differ by more than just the solvent, however, the large difference seems to favour a rate constant limited by transmission through the activated state rather than the formation rate of the activated state.

Other possibilities for mechanism and limiting reaction steps are now discussed briefly. The results in ref (Gardner, Abrahamsson et al. 2009) indicates that the oxidation potential of N3/N719 dye is not large enough to drive oxidation to $I^\cdot$. Scheme R3 is

considered unlikely to be dominant in this system. As mentioned before, the preformation of $[I^{\cdot-}I]$ (R2a) would result in a second order behaviour in I^- . A limiting equilibrium at reaction R1 would also result in second order behavior in I^- . Both of these are thus excluded by the results shown here. In reaction R1b, cage escape of the $I_2^{\cdot-}$ might be another candidate for the slow step, however I think my data can eliminate it. For cage escape to be relevant, the electron recombination with the caged $I_2^{\cdot-}$ must be similar to that with the S^+ state. What I find empirically is that the spectrum of the species, for which I measure the decay at 830 nm, is very similar to the photo-oxidized dye without I^- . It is the decay of this species which correlates well with the photocurrent. The formation of S^0 caged with $I_2^{\cdot-}$ would not likely have the same spectrum and therefore is not likely a relevant species in conversion of S^+ to a "non-recombining" form.

It may be noted that the cells here have near 100% regeneration at iodide concentrations less than half that used in standard electrolytes. One reason standard electrolytes contain higher I^- concentrations relates to the fill factor. Efficient regeneration under load (at the maximum power point (MPP)) requires higher I^- to offset the higher electron concentration and thus the faster EDR. With measurement of electron density vs. voltage, (O'Regan and Durrant 2009) and the kinetic parameters determined herein, it is possible to predict the regeneration efficiency at the MPP, and thus determine the required iodide concentration. (Barnes, Anderson et al. 2010) My work also highlights that studies of regeneration must carefully distinguish between the added I^- concentration, the free I^- , and the actual I^- concentration in the pores under operation. Improved accuracy will result from better measurement and control of these parameters, a project the Imperial College DSSC group hope to report on soon.

Lastly, I discuss briefly the interpretation of the magnitude of the stretch parameter. For these cells, the fit stretch parameter (β) was between 0.33 and 0.54. A stretched exponential in electron recombination has previously been associated with trap limited kinetics, however, that model is not easily translated to regeneration. (R. L. Willis 2002; Green, Chandler et al. 2005; Green, Palomares et al. 2005) One physical mechanism that can give rise to stretched decays is a range of activation energies for a reaction. A small spread of activation energies is then related to a much larger spread in rate constants via the exponential in the Arrhenius formula. If one assumes a Gaussian distribution of activation energies, then the FWHM required to approximate the decays in Figure 5-2 is ~ 0.1 to ~ 0.22 eV. Although the Gaussian model does not fit the data well, a variation of this magnitude in

activation energy can easily be imagined given the electrostatic and steric heterogeneity found in the porous TiO_2 structure. For example, the different facets of TiO_2 will have different surface potentials and there is more than one possible binding orientation for the dye. On top of this, under short circuit there will be a gradient of iodide concentration across the film (see Figure 5-5, Additional information - 5). The iodide gradient is probably heterogeneous in itself, with lower concentrations in areas with more constricted pores. It might be that one of differences between champion DSSCs and less successful attempts could be the degree of homogeneity in dye regeneration. A more narrow spread in regeneration rate constants will mean that significant electron recombination to the dye will only begin to occur at higher electron concentrations (thus higher voltages). This could mean a higher FF and possibly higher V_{oc} for less heterogeneous cells. The group I am in hope to explore the relation of the stretched decays and cell efficiency in the future.

5.6 Conclusions

Demonstrated is a relatively simple procedure that allows complete quantification of regeneration rate constants, orders and quantum efficiencies in operating cells. This is made possible by TA, J_{sc} , and charge measurements on fully operating cells under illumination. Similar measurements can be attempted using isolated TiO_2 /dye/electrolyte films or particles, however, without concurrent measurement of the electron density in the TiO_2 , it is not possible to correctly separate the effects of regeneration and recombination on the measured TA decays. Determination of the reaction order in these cells narrows down the choices of limiting reaction step. With small extensions to the data set shown, values of electron-dye recombination and its order in electrons could also be determined. I hope that accrual of similar data on other dye/electrolyte systems will give us the background required to find materials to catalyze regeneration and thus facilitate incorporation of NIR absorbing dyes in DSSCs.

5.7 Additional information - 5

5.7.1 Stretched exponential

In the measurements e^- are probed at $\lambda = 980$ nm and $S^+ \rightarrow S^0$ superimposed on e^- at $\lambda = 830$ nm. In order to get S^+ decay characteristic first I fit the e^- signal to a single stretched exponential, then I fit the 830 nm superimposed decay with a double stretched exponential,

whilst holding the fitting parameters obtained from the e^- signal. The simple case where 830 nm signal shows biphasic decay is described in the following equation:

$$\Delta OD(t) = A_{(S^+)} \cdot e^{-\left[\frac{t}{\tau_{ww}(S^+)}\right]^{\beta_{(S^+)}}} + A_{(e^-)} \cdot e^{-\left[\frac{t}{\tau_{ww}(e^-)}\right]^{\beta_{(e^-)}}}$$

5-9

where ΔOD is the change in optical density with time (t), A is the initial absorption, β is the stretching parameter and τ_{ww} is the characteristic relaxation time of the function.

Stretched exponential functions (eqn 5-9) are used to fit the observed transient signals since they are useful for describing the decay observed from an ensemble of single exponential decay processes with a distribution of different time constants. This situation is expected here because variation in the concentrations of e^- , S^+ , I^- , I_2 and I_3^- are established across the cell under working conditions (for example see schematic of I^- profiles in a cell at short circuit shown in Figure 5-5), creating different environments for the regeneration-recombination reactions to take place. This results in different decay time constants at different locations within the cell as expected from eq 5-2 and 5-3.

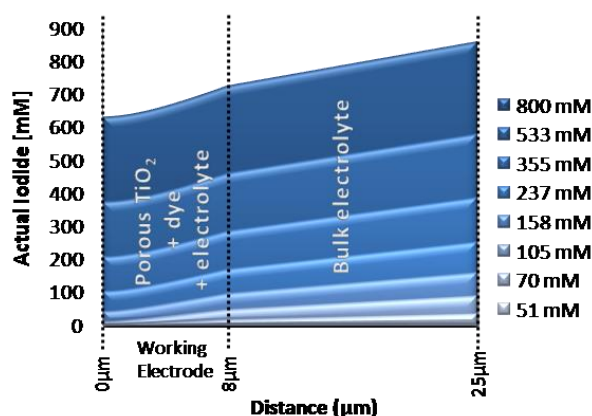


Figure 5-5 – Schematic of I^- concentrations profiles under short circuit, 1 sun illumination operating conditions for the various initial concentrations added to the electrolyte assuming diffusion coefficient of I^- in pores is half the bulk value.

5.7.2 The gamma function

The gamma function is defined as:

$$\Gamma\left(\frac{1}{\beta}\right) = \int_0^{\infty} u^{\frac{1}{\beta}-1} e^{-u} du$$

5-10

where u is a variable of the integration and here β is the stretching parameter as defined in the main text.

5.7.3 Why stretched exponential should be used instead of half life

Figure 5-6 is a simulated justification for using τ_{obs} instead $t_{1/2}$. All three decays presented in the figure and the following table has the same half life ($t_{1/2} = 1$ ms), however the nature of the decays is defined more accurately by stretched exponential decays and in the case of ‘simulated 3’ by exponential decay (i.e. $\beta = 1$). Using equation 1 in the main text the resulting τ_{obs} for the three simulated decays spans between ~ 1.4 ms for the non stretched decay and 750 ms to the decays when the stretching parameter $\beta = 0.2$.

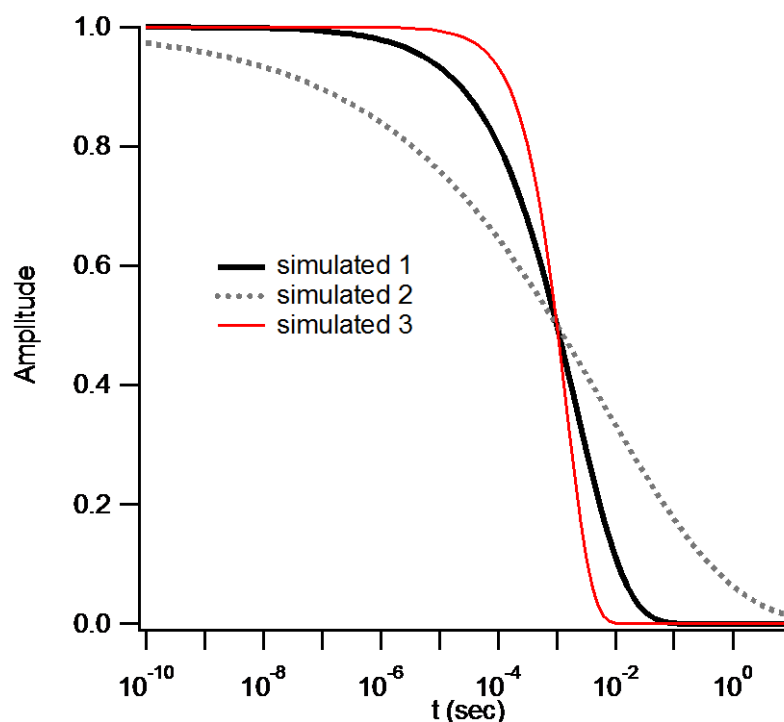


Figure 5-6 – example of three decays having the same half-life but different τ_{obs}

Table 5-4 - half-lives and fitting parameters for three different decays shown in Figure 5-6

	A0	τ_{ww}	θ	$t_{1/2}$	τ_{obs}
simulated 1	1	0.002081	0.5	1E-03	4.16E-03
simulated 2	1	0.00625	0.2	1E-03	7.50E-01
simulated 3	1	0.001443	1	1E-03	1.44E-03

5.7.4 TA response for sample without iodide/tri-iodide

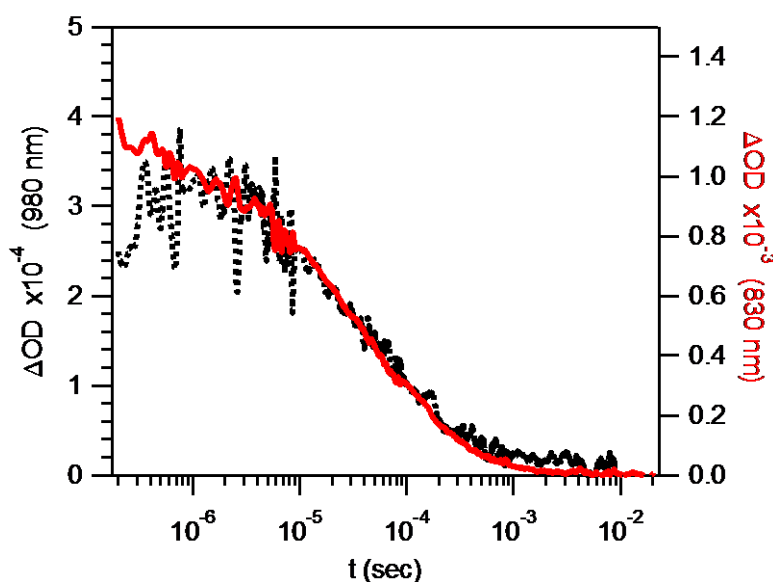


Figure 5-7 - Inert electrolyte cell. Electrons (probed at 980 nm) and dye cation (probed at 830 nm). Scaled axis TA decays. The figure shows that both species decay at the same time hence all injected electrons recombine with oxidized dyes.

Previous works showed that upon excitation charges can remain separated with a half life of a few milliseconds, depending on the concentration of e^- . (Haque 1998) Figure 5-7 shows that for a redox inert device, under one sun illumination (the device generates no photocurrent), the half-life both for the S^+ and for the e^- (probed at $\lambda = 830$ and 980 nm respectively) is ~ 15 μ s. The reason that the half-life is more than 3 orders of magnitude faster than the previously published values is because of the high e^- concentration generated at 1 sun illumination. I note at this point that the $t_{1/2} = 15$ μ s corresponds $\tau_{obs} = 80.1$ μ s (and $k_{obs} = 12489$ s^{-1}) and that the $t_{1/2}$ is used here in order to compare to the previous published values.

5.7.5 TA Decays for all devices and conditions used in the chapter

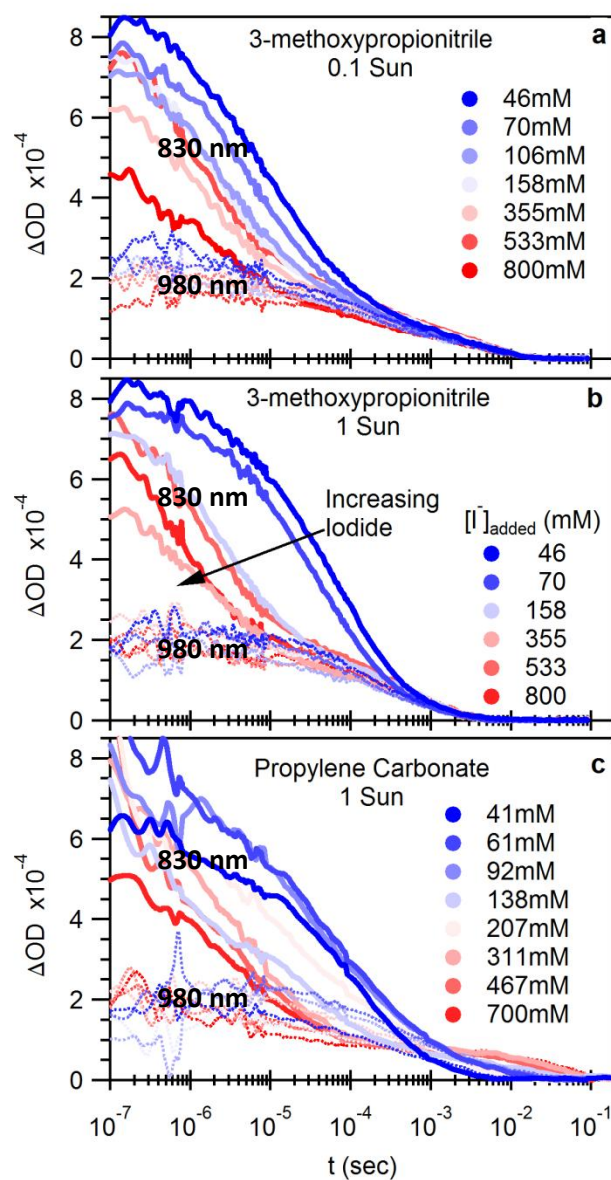


Figure 5-8 –TA decays of the (a) 0.1 sun MPN series, (b) 1 sun MPN and (c) PC series.

5.7.6 Estimation of the actual concentration in the pores

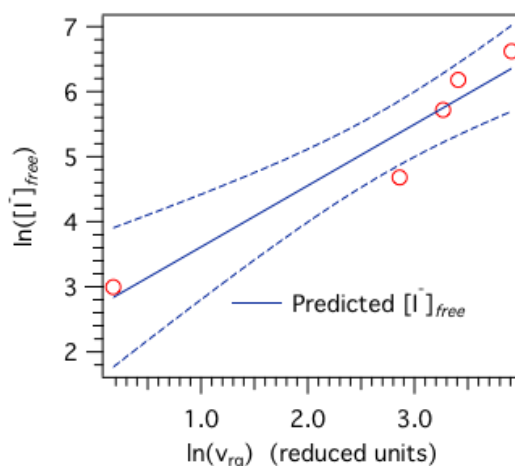


Figure 5-9 - Best fit of $\ln[I^-]_{free}$ vs. $\ln(v_{rg})$, using v_{rg} calculated by $J_{sc} \times k_{obs} / J_{max}$.

5.7.7 Comparison of measured and recalculated J_{sc}

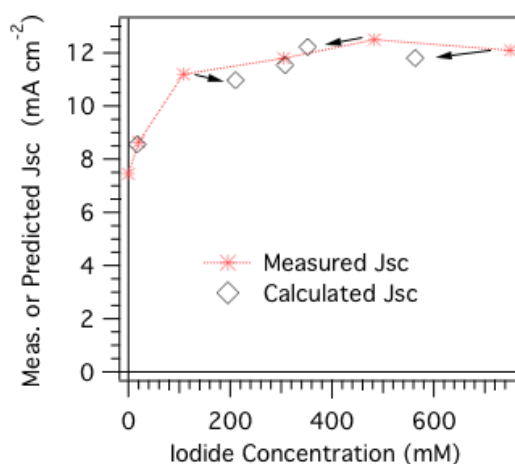


Figure 5-10 - Measured J_{sc} vs. iodide concentration as added. Calculated J_{sc} vs. estimated "real" iodide available in the pores from Figure 5-9. J_{sc} calculated using the predicted iodide, an order in iodide of 1, and the J_{max} and k_{rg} determined in the text. Arrows show the shift in iodide concentration predicted by the fit in Figure 5-9. Prediction of the J_{sc} is now good, but the iodide values found from Figure 5-9 are surprisingly different from those in the bulk solution before addition to the cell.

5.7.8 Redox potentials and the evaluation of the association constant for the PC series

Redox potential measurements of the electrolyte solutions were taken in order to find the free energy differences between the electrolytes midpoint potentials relative to the dye

ground state. Furthermore, from redox potential measurements the association constant, K , of iodine and iodide to give tri-iodide can be derived. Using K , the actual concentration of each of the species can be found. Calculations were performed in order to find K and the real concentration of the species by using the measured redox potential values presented in Table 5-5. (Note that once electrolytes are introduced to the cell potentials may shift).

Table 5-5 – summary of device characteristics and the externally measured redox potential of the electrolytes, obtained for the propylene carbonate series. Also shown are the initial and the calculated equilibrated concentrations of iodine, iodide and tri-iodide.

Initial [mM]		Equilibrated [mM]			Overall device performance					
$[I^-]_0$	$[I_2]_0$	$[I^-]$	$[I_3^-]$	$[I_2]$	JSC (mA/cm ²)	VOC (V)	Efficiency (%)	FF	E vs. SCE (V)	E ⁰ calc
0.0	50.0	0.0	0.0	50.0	3.86	0.651	0.83	0.39	0.512	
44.0	50.0	4.6	39.4	10.6	5.53	0.721	1.52	0.53	0.22	0.312
88.0	50.0	39.5	48.5	1.5	7.15	0.743	1.74	0.36	0.112	
175.0	50.0	125.5	49.5	0.5	8.04	0.744	2.04	0.42	0.094	
350.0	50.0	300.2	49.8	0.2	11.69	0.754	3.66	0.46	0.068	
700.0	50.0	650.1	49.9	0.1	12.1	0.801	3.47	0.6	0.061	0.083

The calculation goes as follows:

It was shown that the electro reduction of iodine to iodide proceeds in two reversible reactions (Popov 1958; Baucke 1971; L'Her 1975; Hanson 1987; Hanson 1987):



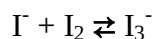
The two reversible reactions are also two halves of electrochemical cell reactions that are responsible for the equilibrated redox potential measured externally using a Pt wire and SCE. The standard potentials (ε^0) for each of these half cells can be described by the following equations:

$$\varepsilon^0_{(I_2/I_3^-)} = \varepsilon - \frac{25.7 \text{ mV}}{2} \ln \frac{[I_2]^3}{[I_3^-]^2} \quad 5-13$$

$$\varepsilon^{\theta}_{(I_3^-/I^-)} = \varepsilon - \frac{25.7 \text{ mV}}{2} \ln \frac{[I_3^-]}{[I^-]^3}$$

5-14

In the solution $\varepsilon^{\theta}(I_2/I_3^-) = \varepsilon^{\theta}(I_3^-/I^-)$ and these two half cells are interconnected by the association reaction,



5-15

but on the extreme concentrations one can assign the contribution to a measured potential as just a single half cell. So in order to find the two ε^{θ} , the following assumptions can roughly be made:

in order to find $\varepsilon^{\theta}(I_3^-/I^-)$ the assumption that $[I^-]_{\text{added}} \gg [I_2]_{\text{added}}$ is made, in this case $[I_3^-]_{\text{final}} \approx [I_2]_{\text{added}}$ and $[I^-]_{\text{final}} \approx [I^-]_{\text{added}} - [I_2]_{\text{added}}$.

in the same fashion, in order to find $\varepsilon^{\theta}(I_2/I_3^-)$ the assumption that $[I^-]_{\text{added}} \ll [I_2]_{\text{added}}$ is made, then $[I_3^-]_{\text{final}} \approx [I^-]_{\text{added}}$ and $[I_2]_{\text{final}} \approx [I_2]_{\text{added}} - [I^-]_{\text{added}}$.

In the current study, the concentration of $[I^-]_{\text{added}} = 0.7 \text{ M}$ represents the half cell $\varepsilon^{\theta}(I_3^-/I^-)$. For the other half cell and in the lack of an appropriate concentration, $[I^-]_{\text{added}} = 0.044 \text{ M}$ represents $\varepsilon^{\theta}(I_2/I_3^-)$. The calculated standard potentials are then 0.083V and 0.312V respectively (vs. SCE).

The association reaction (5-15) is thermodynamically characterized by the association constant, K , which is maintained constant at the assumed constant ionic strength (in the current series the ionic strength is maintained constant using a complementary redox-inert anion (ClO_4^-) instead iodide).

K is given using the following equation:

$$K = e^{\left\{ \frac{2(\varepsilon^{\theta}(I_2/I_3^-) - \varepsilon^{\theta}(I_3^-/I^-))}{3 \times 0.0257 \text{ mV}} \right\}}$$

5-16

Placing the calculated ε^{θ} values gives $K \approx 3.7 \times 10^2$ which is completely different from the literature published value of $10^{7.7}$ (L'Her 1975; Hanson 1987; Hanson 1987). The big

difference may rise from the fact that the $[I^-]_{\text{added}} = 0.044 \text{ M}$ electrolyte has too much iodide and the calculated standard potential for the half cell it represents should be higher. In addition the studied system includes other additives which their effect wasn't studied here and these additives weren't in use the literature studies where the much higher K was obtained.

Using the calculated K , the equilibrated concentrations can be calculated using equation 5-7.

The results per concentration are presented in Table 5-5 and in Figure 5-11 as well.

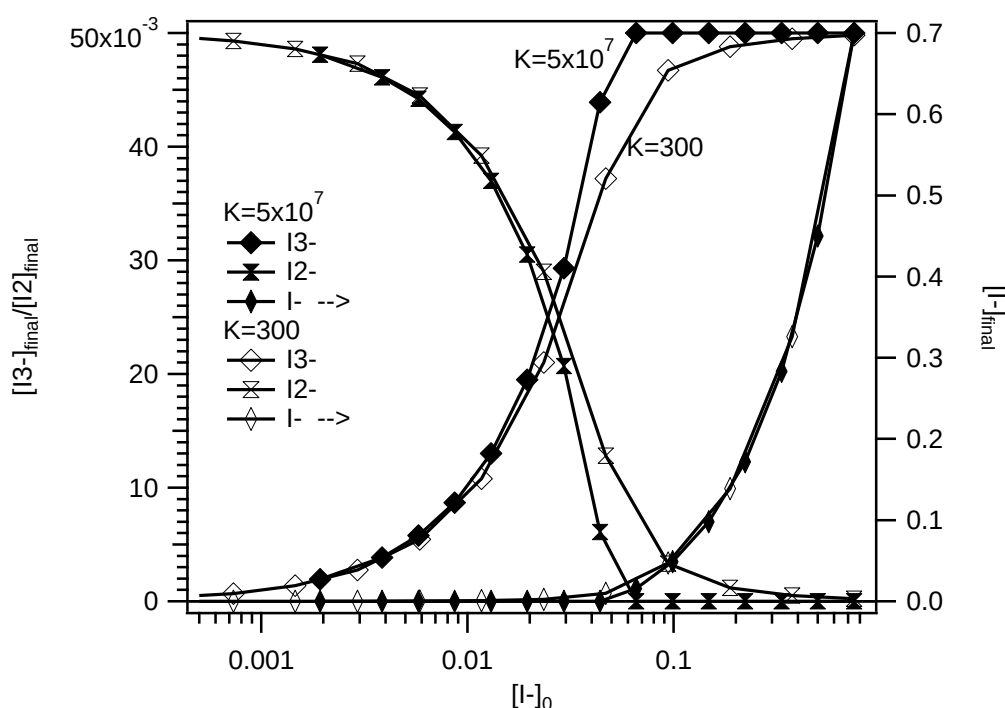


Figure 5-11 – Modelling of the real concentration of iodide, iodine and tri-iodide as a function of added iodide to a constant concentration of 0.05M iodine. The real concentrations were solved using equation 5-7 and association constant of $K=300$ derived in this research, compared to a previously published association constant of $K = 5 \times 10^7$ (L'Her 1975). The circles represent the compositions that were used in the propylene carbonate series of cells.

6 Non Extractable Electrons due to Slow Regeneration – a Comparison of Charge Extraction and Steady State Photoinduced Absorption

In this chapter the changes in the steady state absorption spectra under different illumination conditions are used to monitor the concentration of electrons and oxidized dye molecules in working devices. This information is compared with the concentration of electrons that can be extracted from the same cells, starting from the same conditions. The comparison of data collected using these complimentary techniques allows a simple determination of the conditions at which poor regeneration and mass transport start to limit cell performance. The comparison helps to constrain the possible sources of photocurrent loss in the cell and suggest that the charge formed in the cell, thus light harvest and injection, are independent on iodide concentration and does not play a noticeable role in device efficiency.

6.1 Introduction

Photoinduced absorption (PIA) was applied in the past on dye sensitized solar cells (Franco, Gehring et al. 1999; Kai, Schiff et al. 2002; Boschloo and Hagfeldt 2003; Ford, Avilov et al. 2005; Boschloo and Hagfeldt 2008; Cappel, Gibson et al. 2009; Snaith, Petrozza et al. 2009; Cappel, Feldt et al. 2010). It was shown to provide equivalent data to transient absorption (TA) spectroscopy. (Boschloo and Hagfeldt 2008) PIA uses an excitation source whose lifetime is much longer than the laser pulse used in TA. This longer excitation source can saturate the detector and hinder the signal. In order to overcome the issue a sinusoidal modulation of the beam is made and in some cases the excitation is done at a different region (wavelength) than the probe region. The two regions are sometimes separated with cut-off filters placed on the probe source. In this study absorption changes are probed in the infrared (IR) region whilst the photoinduction is made using a steady state visible light source (LEDs with cold white emission, see emission spectrum in Figure 9-9). These LEDs has virtually no emission in the probed region and thus are not expected to distort signals

detected there. In such configuration the system then can be very simple and incorporate cheap components relative to other systems. Either modulator or beam chopper accompanied with a lock-in amplifier are replaced with computer controlled power supply to drive the LEDs. This configuration allows the possibility that the LEDs can be illuminated (or not illuminate) as long as needed to reach equilibrium and that the continuation to the next step can be conditioned by meeting defined criteria. In this case the PIA can be considered as steady state absorption spectra under different illumination conditions and the abbreviation SSPA will stand for steady state photoinduced absorption.

Due to the nature of the SSPA, that sufficient time is allowed between changes in conditions, the resulting changes in absorption could be synchronously correlated with changes in device performance as well as changes in temperature. This allowed a quantitative correlation of charge extraction (Duffy, Peter et al. 2000; Barnes 2009) (see 2.4 for more details on CE) and SSPA on a common performance axis. Later, both charge extraction and SSPA were measured simultaneously, and the results could be plotted vs. the resulting device performance or vs. the applied illumination intensity. Simultaneous optical and electrical measurements were made for transients in chapter 4 and the concepts and merits are discussed in chapter 4 introduction. The effect of the temperature formed by different illumination methods during spectra acquisition is discussed in the experimental chapter (see section 2.6.3).

6.2 Method

Upon stable illumination and electronic condition (i.e. open/short circuit or load) of a dye sensitized solar cell a specific equilibrium is being established. This results in specific concentrations of the various species which are formed or consumed during operation. These species show changes in absorption if their extinction coefficient is large enough and they are relatively long lived. In this chapter, per probed wavelength, first the absorption obtained without bias illumination (I_0) is recorded, then the cell is illuminated with steady state bias light and the probe beam intensity is measured again (I_n). Increasing the bias illumination to different intensities allows obtaining several points which can be correlated with the photocurrent or photovoltage resulting under the same illumination. The change in absorption (ΔOD) is calculated using $\Delta OD = -\log(I_n / I_0)$.

Oxidised N719 dye has an extinction coefficient of $\epsilon_s^+ = 6000 \text{ M}^{-1} \text{ cm}^{-1}$, around the wavelength of $820 \pm 20 \text{ nm}$, (Tachibana 2000; Montanari 2002) however the life time of the

oxidized dye is relatively short (between 1 μs and several millisecond). Electrons on contrary, has approximately 6 times smaller extinction coefficient, $\epsilon_e^- = 1170 \text{ M}^{-1} \text{ cm}^{-1}$ (this extinction coefficient is reported for the region of $980 \pm 40 \text{ nm}$ for cells with porosity of ~ 0.63 , as used in here). (Anderson, Barnes et al. 2010) However, electrons life time is of the scale of several millisecond up to tens and even hundreds millisecond. Remembering that lifetime depends on the operation conditions (light intensity, open/ short circuit or load) and on the device configuration.

Equation 6-1 below describes the concentration of the oxidized dyes population as these reaches steady state equilibrium under steady state operation. In such conditions the flux of the formation of oxidized dyes, i.e. the injection rate, v_{inj} (M sec^{-1}), should be equal to the flux of the total processes that reduces the oxidized dyes (i.e. regeneration and recombination to the dye).(Anderson, Barnes et al. 2010; Barnes, Anderson et al. 2010) The flux of the dye-reducing processes is described here as a multiply of an observed rate, k_{obs} (sec^{-1}), times the concentration of the oxidized dyes population, $[S^+]$ (M):

$$0 = \frac{d[S^+]}{dt} = v_{inj} - k_{obs}[S^+]$$

6-1

It is shown in the previous chapters that per illumination and electrical condition, k_{obs} is a sum of the two competing processes. The two processes are functions of the rate and order of dependence. In the case of regeneration it is the order and dependence in the free iodide available in the system and in the case of recombination it is the order and dependence in the concentration of electrons in the TiO_2 . (see equation 5-4)

In devices configurations as used here, under 1 sun illumination and open circuit conditions the concentration of electrons accumulated in the TiO_2 is approximately ten times higher than that formed under short circuit, mainly due to lack of collection. In such case the combination of high flux of electron-dye recombination will reduce the accumulation of oxidized dyes in the system by some degree, i.e. k_{obs} is large whereas $[S^+]$ is small. This situation is less sensitive to dye regeneration. On contrary, once a cell is short circuited, collection reduces the concentration of electrons in the TiO_2 such that the electron-dye recombination becomes relatively negligible. This strengthens the contribution of fast

regeneration to deplete the accumulating population of oxidized dyes. If a cell experience a poor regeneration, then k_{obs} is small whereas $[S^+]$ is large.

It can be more accessible to normalize the concentration of electrons and oxidized dyes to terms of number of species per particle. Specifically in this work this normalization gives us a clue on the total amount of these species residing within the fundamental repeating unit of the active layer (a particle coated with dye molecules). Such normalization, in general, will also ease the comparison between the endless possibilities exist amongst photoelectrochemical systems. By doing so, factors like: porosity, area and thickness of the active layer are cancelled out. Since a comparison of steady state photoinduced absorption with charge extraction is made, the results of both the number of species per particle and the total concentration of species per cubic cm are shown. Equation 6-2 below gives the total concentration of any of the species in a cell, $[n_s]$ (cm^{-3}):

$$[n_s] = \frac{\Delta OD N_A 0.001}{\varepsilon d}$$

6-2

where ΔOD (arbitrary units) is the change in optical density. ε ($\text{M}^{-1} \text{cm}^{-1}$) is the absorption extinction coefficient for a probed species at a specific wavelength. d (cm) is the thickness of the cell active layer (which is also the length of the medium that the probe beam cross through). N_A is the Avogadro number. The conversion number 0.001 is L to cm^3 .

Equation 6-3 converts the concentration per cm^{-3} to number of species per 100 particles, $n_{s/p}$:

$$n_{s/p} = \frac{4 \pi [n_s] r^3}{3 \rho} \times 100$$

6-3

where r is the particle diameter in meters and ρ is the porosity.

Alternatively, the areal normalized charge Q , (C cm^{-2}) can be calculated using equation 6-4 for direct comparison with charge extraction:

$$Q = FV \frac{\Delta OD}{\varepsilon l}$$

6-4

where F is the faraday constant (96,485.3415 Coulombs) and V (cm^3) is the cell volume (ΔOD usually represent charged species in this kind of characterization).

6.3 Experimental

6.3.1 Experimental technique

The experimental details and the development of the various SSPA techniques, including an explanation of what not to do with respect to the acquisition method, are described in experimental chapter 2.6. Separate measurement of charge extraction is described in chapter 2.4. Here is a description of the procedure for the synchronized comparison of charge extraction and SSPA (SC) which makes the results like in Figure 6-4 and exactly as in Figure 6-5. Inherent in this procedure are the basics of SSPA and CE.

Procedure:

- a) The cell is short circuited and the bias light is turned off.
- b) The steady state dark-current is measured for later subtraction.
- c) Probe beam intensity without bias illumination (I_0) is measured.
- d) The bias light is turned on at a given illumination intensity I_n .
- e) The photocurrent steady state stability is checked.
- f) Temperature measurement is taken.
- g) I_n probe beam intensity is measured.
- h) The bias light is turned off at time t_0 , triggering a measurement of short circuit current decay, in similar to the charge extraction routine described in the experimental chapter (2.4).
- i) The averaged dark current ((b) above) is subtracted from the current decay.
- j) The pre-triggered points are removed from the current decay and are averaged to obtain the steady state current that makes the x-axis location in the figure.
- k) The current decay is integrated from t_0 up to a value between $0.1 < t < 4$ sec (depending on the system) in order to get the amount of extracted charge that could leave the cell.
- l) The change in absorption is calculated.

6.3.2 Device configuration

Cell construction in this chapter is the same as the MPN based series of cells described in 3.3.2. A brief reminder: cells were fabricated using TEC15 FTO glass as front and back electrodes. TiO_2 layers were synthesized as previously and were $\sim 9 \mu\text{m}$ thick. (Barbe', Arendse et al. 1997; O'Regan 2009; Anderson, Barnes et al. 2010) The dye was bis(tetrabutylammonium) *cis*-dithiocyanatobis(4,4'-dicarboxylic acid-2,2'-bipyridine)ruthenium(II) (N719). The cells used 3-methoxypropionitrile as the solvent. The standard electrolyte contained 0.8 M 1-propyl-3-methyl imidazolium iodide (PMMI) 0.3 M benzimidazole, 0.05 M Guanidinium thiocyanate and 0.05 M iodine. Lower iodide examples contained 533, 355, 70 and 46 mM iodide. 1-propyl-3-methyl imidazolium-bis(trifluoromethylsulfonyl)imide (PMMTFSI) was substituted for the iodide salt to keep the PMM^+ concentration constant.

6.4 Results

Figure 6-1 (a) shows the 46 mM iodide device under both OC and SC conditions. The differences between the OC and SC are considered; for the exact same configuration in chapter 4 the region of 980 nm was assigned to absorption of electrons in the TiO_2 . In Figure 6-1 (a), at 980 nm and under ~ 1 sun there is 8 times stronger absorption under OC than under SC. Figure 6-1 (b) shows a comparison of the electrical charge extraction as a function of light intensity for the 46 mM iodide device, obtained under OC and SC. At the intensity of ~ 1 sun there are 10 times more electrons under OC than under SC conditions. This clarifies the large differences between the SSPA spectra obtained under the two conditions. The discrepancy between the ratios obtained by the two techniques will be elucidated in the following sections.

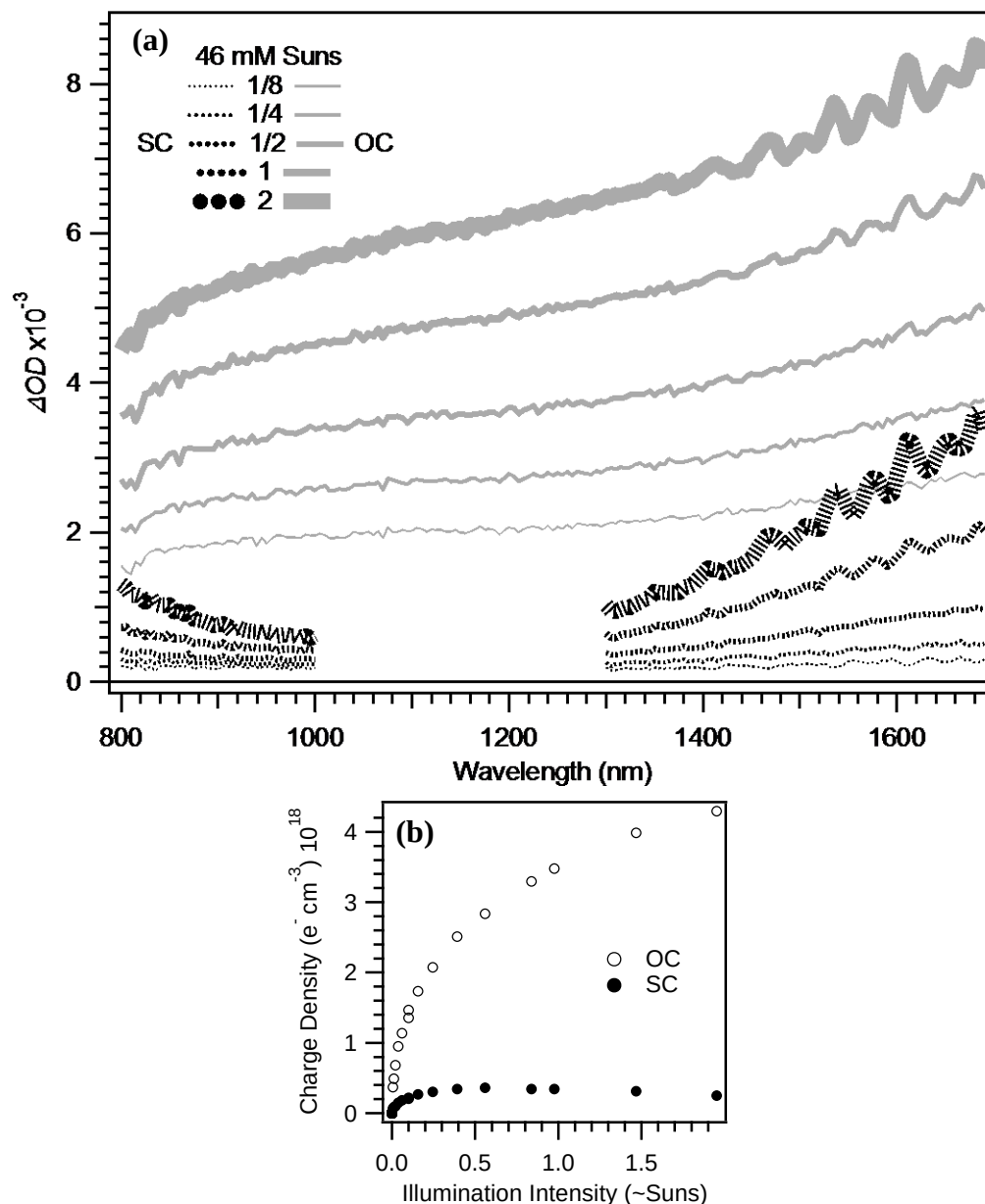


Figure 6-1 – (a) steady state photoinduced absorption spectra of a cell having 46 mM Iodide under both short and open circuit. Spectra were obtained under variable light intensities using the ‘light cycles method’ (2.6.1) device temperature was 32.5 ± 0.5 °C (Note that for the SC condition, data was not measured between 1000 – 1300 nm). (b) A comparison of electrical charge extraction for the 46 mM iodide device obtained from either OC or SC as a starting condition.

The absorption of electrons accumulated in the TiO_2 under OC complicates the identification of other absorption regions. Reducing the electrons accumulation in the TiO_2 by short circuiting the cell makes the identification easier. Figure 6-2 shows an example of steady-state photoinduced absorption spectra obtained for three devices under short circuit

conditions and different bias light intensities. The cell that has 46 mM added iodide (the same cell from Figure 6-1) has poor regeneration whereas the cell that has 70 and 355 mM iodide has reasonable and good regeneration respectively.

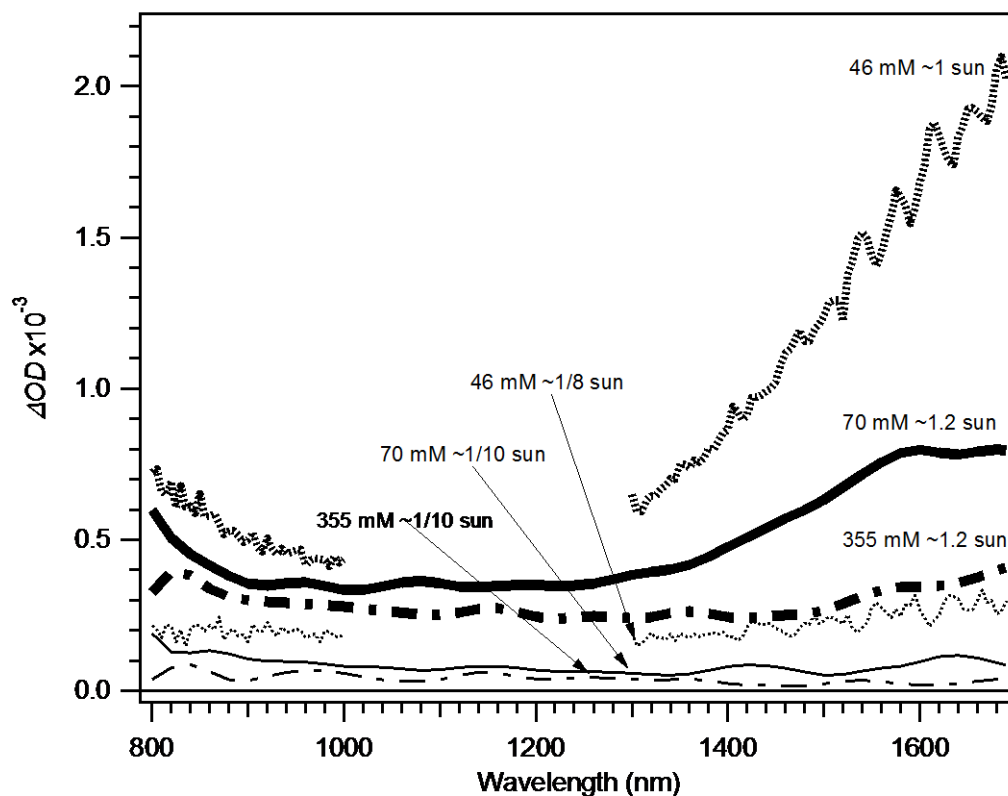


Figure 6-2 – Steady state photoinduced absorption spectra of cells having 46, 70 and 355 mM iodide under short circuit condition. Spectra were obtained under variable light intensities using the ‘light cycles method’ (2.6.1) where ‘70’ and ‘355’ had different illumination increments than the ‘46’ (see legends). ‘70’ and ‘355’ devices had a temperatures of 39 ± 0.5 °C and the ‘46’ was 32.5 ± 0.5 °C (note that for the ‘46’ SC conditions, data was not measured between 1000 – 1300 nm).

When the cells are under short circuit, the electrons absorption is reduced and new features are revealed. Under the lowest illumination intensity (approx tenth of a sun) the absorption spectrum for all devices under SC appears almost flat. Once the bias light illumination intensity is elevated, stronger absorption features evolve in the regions of 800 – 920 and 1250 – 1700 nm. See discussion for the relation of these absorptions to species.

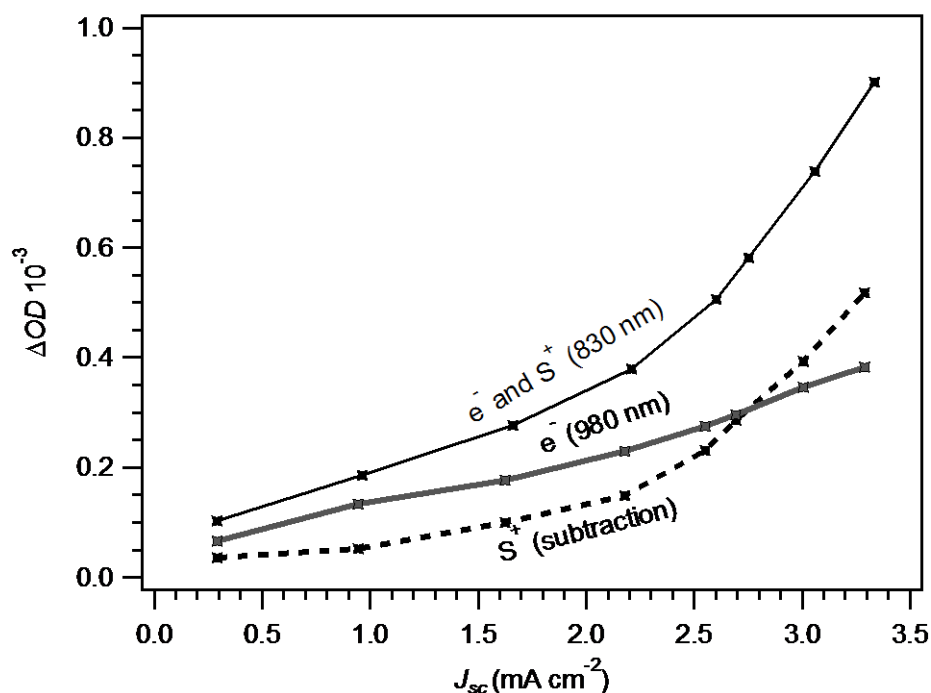


Figure 6-3 – example of raw data obtained with steady state photoinduced absorption for a dye sensitized solar cell having poor regeneration (46 mM iodide). The solid lines are changes in absorption (ΔOD) plotted vs. J_{sc} , both measured under the same conditions. 980 nm is a probe for electrons whereas 830 nm is a measure for both oxidized dye and electrons. The dashed line is a subtraction of the two absorptions to extract the absorption of oxidized dyes alone.

Figure 6-3 shows the changes in absorption of both electrons and oxidized dyes, plotted against J_{sc} . The measured cell, the 46 mM iodide, has the lowest regeneration of the series and hence was expected to have the largest accumulation of oxidized dyes population. Electrons are probed directly at $\lambda = 980$ nm whereas the oxidized dyes are a numerical subtraction of the 980 nm absorption from the 830 nm absorption, this assumes the absorption coefficient of electrons at these two positions does not change significantly. The 830 nm signal is also shown. This kind of presentation gives a general idea on the induced absorption at these two wavelengths, however it does not reflect on the ratio between oxidized dyes and electrons since the two have different absorption extinction coefficient.

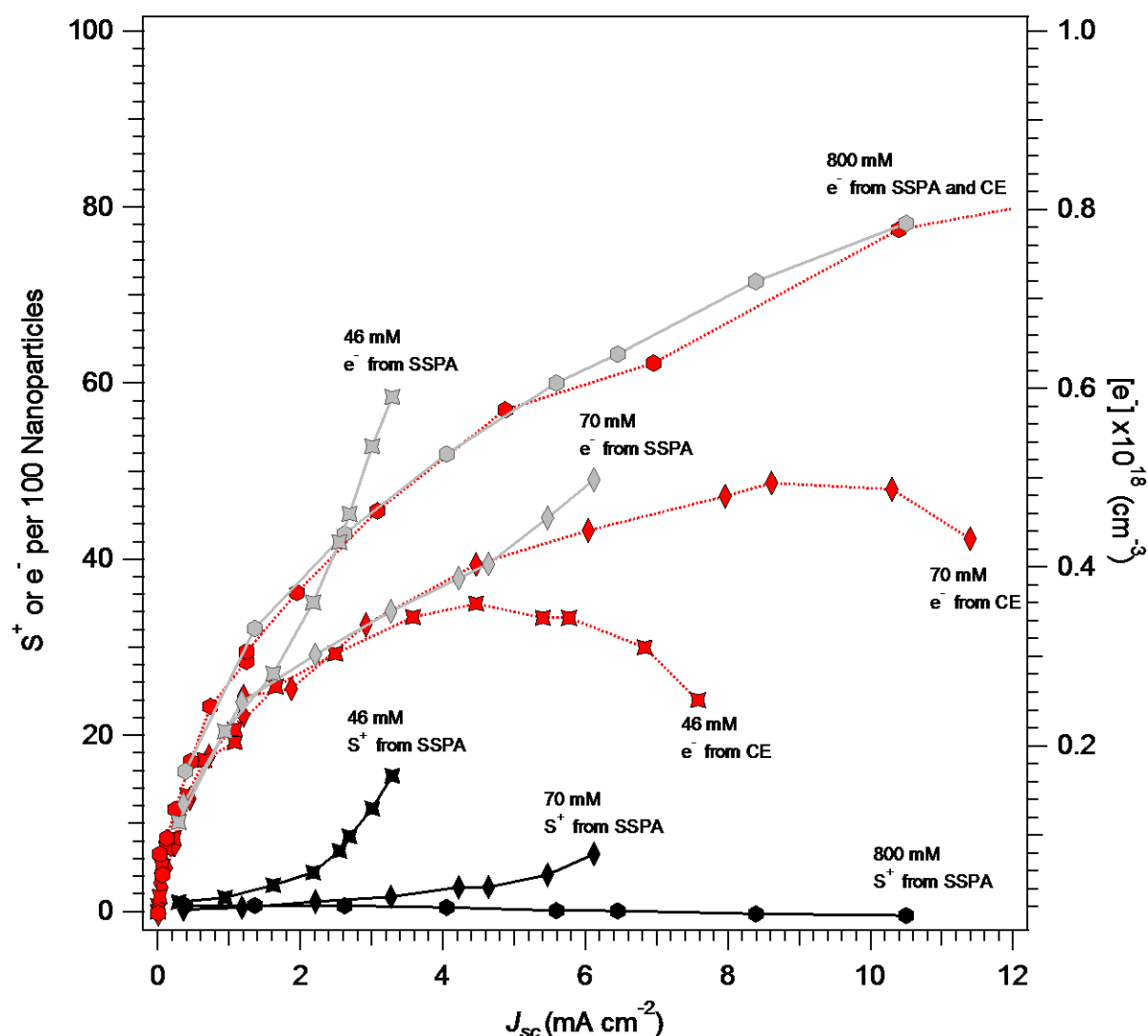


Figure 6-4 - Number of electrons and oxidized dyes accumulated per 100 TiO₂ nanoparticles at SC, plotted vs. measured J_{sc} . Obtained by varying illumination intensities and measuring the induced infra-red absorption and the short circuit currents for three different devices having different concentrations of iodide. The electrical charge was measured separately at a different time than the optical measurement.

Figure 6-4 shows either the number of species per 100 nanoparticles (left axis) or the density of species (right axis), both plotted against J_{sc} . The figure compares three different devices having different regeneration efficiencies. The figure also compares the concentration of electrons as they were measured separately by two different techniques: electrical charge extraction and the steady state photoinduced absorption (see method and experimental). The density of species and the number of species per 100 nanoparticles were calculated as

mentioned in the method section. This kind of presentation allows a comparison between the accumulated species, unlike the raw data presented in Figure 6-3.

Figure 6-5 shows another comparison of the electron concentration with two major differences: first, the electrons concentrations were measured simultaneously on the same setup under the exact same conditions, as mentioned in the procedure in the experimental section. This guarantees that the differences observed in Figure 6-4 are not due to any kind of changes occurred in the devices between measurements and/or changes in conditions that could occur in different setups. The second difference is that the results are presented as areal normalized charge vs. light intensity. Plotting against light intensity reveals the hindered variable of Injection; it eases the comparison of the charge formed in each device under equivalent illumination intensities.

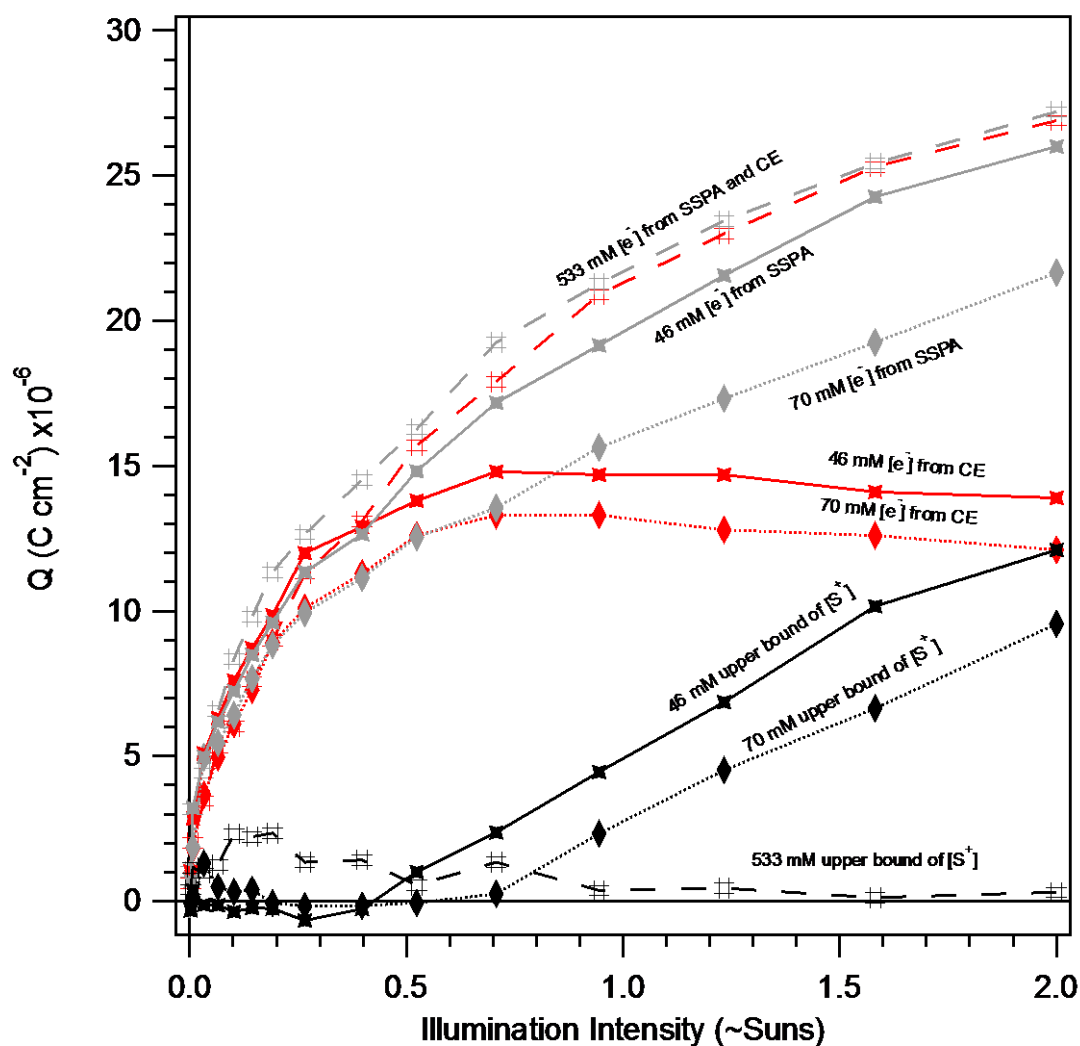


Figure 6-5 – Charge in the TiO_2 of working devices at SC, plotted vs. applied illumination intensity. Plot was obtained by varying illumination intensities and

simultaneously measuring the induced infra-red absorption, the short circuit currents and the extracted charge for three different devices, having different concentrations of iodide. The ‘upper bound’ charges of S^+ are the differences between the charges measured by the two different techniques for each point.

For the good regenerative devices in both figures (the 800 mM in Figure 6-4 and the 533 mM in Figure 6-5) the charge measured by the two techniques overlaps under all light intensities within the examined scope. For the 70 mM iodide cell the measured charge overlaps up to 4.5 mA cm^{-2} (~ 0.7 suns) and then a diversion between the values occurs. The same happens for the 46 mM cell where the diversion occurs at a lower light intensity and lower current, 1.5 mA cm^{-2} (~ 0.3 suns). Curiously, when looking at Figure 6-5, the optically probed charge in the 46 mM iodide device almost overlaps with the charge measured for the 533 mM device, at any illumination intensity.

6.5 Discussion

6.5.1 Assigning signals to species

The first region in Figure 6-1 (a), on average, is peaking at 830 nm. Previous works, using either transient absorption spectroscopy and PIA of N3/N719 or chemical oxidation of the uncarboxylated analogue $\text{Ru(II)(bpy)}_2(\text{NCS})_2$, showed that this 830 nm feature can be attributed to oxidised dye. (Tachibana 1996; Moser, Noukakis et al. 1998; van't Spijker, O'Regan et al. 2001; Boschloo and Hagfeldt 2008; Anderson, Barnes et al. 2010) At current stage the assignment of the second region is ambiguous. Some lines from the 70 and 355 mM iodide devices (see Figure 6-6 in the additional information for this chapter) may suggest that the feature has a maximum around 1600 nm, whereas the lowest iodide device, the 46 mM, seems to keep on rising beyond 1700 nm (the spectra are limited by the responsivity of the InGaAs detector). Comparing the spectra here with the ones obtained by van't Spijker using transient absorption spectroscopy raises even more questions regarding the nature of this peak. van't Spijker et al. showed that such feature (>1250 nm) originate from electrons in the transparent conductive glass, i.e. the fluorine doped SnO_2 (FTO). This was demonstrated by comparison of a dyed TiO_2 on FTO vs. a dyed TiO_2 on quartz (both in 10 mM KI / 1 mM I_2 solution). The quartz configuration did not show any absorption at the mentioned region. Here, however, the absorption at wavelengths > 1250 nm hardly exists in the best regenerative cell. Furthermore this feature seems to correlate with regeneration performances, respectively with the peak at 830 nm and not with the increased current that better

regenerative devices generates. In this situation it is more appropriate to assign the second region to oxidized dyes or to a combination of both oxidized dyes and electrons in the FTO (that peaks beyond the limitation of these spectra). In fact it is tempting to think that the 1600 nm feature should have existed also on the quartz configuration, if the spectrum was recorded in earlier times than 20 μ s. The reason to assume that can be reconciled with the fact that all three features in the spectrum of the quartz configuration had lower amplitudes compared to the ones recorded on FTO. In other words, the film on quartz had a faster decay of the 830 nm feature and a faster decay of electrons relative to the same configuration on FTO, suggesting that from some reason film on quartz has faster electron dye recombination, hence the origin of the disappearance of the > 1250 nm feature. Other directions for future work concern the fact that the spectrums sometimes appear somewhat wavy, this may be due to interference (Gaughlitz and Nahm 1991; Turrión, Macht et al. 2001) and/or due to electrolyte-electroreflection phenomena (Ferrer, Muraki et al. 1986; Boschloo, Goossens et al. 1997) and not just due to absorption of species.

6.5.2 Comparison of Charges measured by two techniques

The amount of charge measured by the two techniques overlapped pretty well for the good regenerative devices (533 and the 800 mM). The medium and slow regeneration devices (70 and 46 mM), reached a point where the electrons concentrations obtained by the two techniques diverge from each other. The concentration obtained by the steady state photoinduced absorption keeps rising as illumination is increased whereas the concentration that actually leaves the cell starts to decline. This diversion point occurs at lower current for the low iodide cell ($J_{sc} \approx 1.5 \text{ mA cm}^{-2}$) than for a cell with slightly higher iodide concentration ($J_{sc} \approx 4.5 \text{ mA cm}^{-2}$). The initial and simplified explanation can be attributed to the fact that some electrons don't leave the cell due to processes which are faster than collection. Examining the population of oxidized dyes shown in Figure 6-4 (measured at 830 nm and calculated as mentioned in the method) reveals that at low iodide concentration there is an accumulation of oxidized dyes. This accumulation can be qualitatively correlated to the mismatch between the charge extracted and the charge that exists in the device during steady state operation. The meaning for the previous chapter is that the ~ 1 sun charges used in the model for the low iodide devices were 23 % lower than real for the 46 mM device and 14 % for the 70 mM device and in general the real charges did not seem to change significantly as a function of iodide. This is reassuring because this is what the model in chapter 5 would predict and this was the initial motivation to make this kind of measurement. Furthermore it

suggests that electrical charge extraction should be treated with caution when regeneration studies are conducted and that when a change in slope and a decline of charge as a function of light intensity occurs, it can be a sign for regeneration issues.

6.5.3 Comparison of k_{obs} from the previous chapter

A direct comparison with oxidized dyes k_{obs} values obtained in the previous chapter (Table 5-2) can be made to check self consistency and the validity of the assumptions made for the model in chapter 5. Using equation 6-1 and the same injection flux of 12.6 mA cm^{-2} a calculation of accumulated oxidized dyes can be made. For the 46 mM device a k_{obs} of $1.05 \times 10^4 \text{ s}^{-1}$ is converted to $1.2 \text{ } \mu\text{C cm}^{-2}$. In the same fashion a $1.75 \times 10^4 \text{ s}^{-1}$ is converted to $0.72 \text{ } \mu\text{C cm}^{-2}$ for the 70 mM device. First a comparison of the numbers obtained in Figure 6-4 is made (note that the 1 sun for the SSPA in this figure are the points before the lasts): ~ 12 and ~ 4 oxidized dyes per 100 nanoparticles are equivalent to 6.31 and $2.28 \text{ } \mu\text{C cm}^{-2}$ and are 5.3 and 3.2 times more oxidized dyes than calculated from k_{obs} , respectively. This may suggest that the extinction coefficient of oxidized dyes of $6000 \text{ M}^{-1} \text{ cm}^{-1}$ used in eqn 6-2 is too low. Instead a value between 19000 and $30000 \text{ M}^{-1} \text{ cm}^{-1}$ may be more appropriate (the high number is consistent with the low iodide device).

In Figure 6-5 charge concentration was measured simultaneously by the two techniques, starting from the same conditions. In this figure the oxidized dyes were not measured at 830 nm . Instead, the estimation of $[S^+]$ is the difference between $[e^-]$ from CE and $[e^-]$ from SSPA at 980 nm . This assumes S^+ doesn't regenerate during CE and electrons recombine solely with S^+ , thus this estimate of $[S^+]$ is an upper bound. In this case the 1 sun calculated charges of oxidized dyes are now 4.45 and $2.33 \text{ } \mu\text{C cm}^{-2}$ for the 46 and 70 mM respectively, which are ~ 3.5 times larger than the ones obtained from k_{obs} . It is reasonable to assume that during CE some S^+ do regenerate and some electrons do recombine with other oxidizing species, thus the estimation of direct subtraction of charge values is too high. Lower numbers than this upper bound will get closer to the ones converted from the k_{obs} .

It is hard to put the finger on the source of discrepancy between the values obtained in this chapter and in chapter 5. It is important to remember that some time passed between the measurements and although the device seemed stable, some changes could occur. Furthermore, k_{obs} in chapter 5 reflect the behaviour of the steady-state population from the transient additional population formed on top of this same steady state population. Conceptually, by the assumptions made in chapter 5, this last statement should not have made

any difference, however the nature of each excitation could make the difference since the distribution of S^+ across the films (species profiles) is known to be different. Last option for explaining the discrepancy may be temperature differences. Although never thoroughly studied, temperature is expected to have an effect on regeneration performance due to the high activation barrier thought to exist. In this case several degrees difference may cause a 3 times difference in k_{obs} for the low iodide devices. Before final conclusion could be made it is probably better to make an experiment where all parameters are measured at the same time, under the same temperature and conditions. In any case the differences shown here are within the same order of magnitude.

6.5.4 Injection as a function of iodide

The question whether injection is affected by the presence of iodide is a subject for a reoccurring debate. In some configurations it was shown that iodide can quench the excited state of dyes and thus to alter injection. (Clark, Marton et al. 2006; Marton 2006) In other configurations it was shown that I^-/I_3^- do not have a significant influence. (Smeigh, Katz et al. 2008; Koops, O'Regan et al. 2009). The purpose of the work here wasn't to prove any of these previous works wrong or right. However the outcome of the comparison as shown in Figure 6-5 suggests that in two devices which are identical in all parameters but the concentration of iodide, the charges formed at any light intensity are the same and any changes if occurs falls within experimental error. The meaning is that although the photocurrent is subjected to iodide concentration, sufficient light is harvested and sufficient amount of electrons are injected to the TiO_2 to neglect light harvest as a function of iodide and injection as a function of iodide as a possible source for degradation in device efficiency. Furthermore it is eliminated here that even an accumulated population of oxidized dyes around the particle does not seem to have a conclusively effect on the accumulated charge. The fact that the same charge is formed doesn't mean that injection doesn't change but it supports the concept of kinetic redundancy where injection is dependent on the energetics of the conduction band of the TiO_2 . (Haque 2005) The meaning for this work is that the assumptions made in previous chapters are valid.

6.6 Conclusions

SSPA setup is simple and cheap. The analysis is straightforward and intuitive. The SSPA spectrums may be used to assign absorption regions to species and additional absorption peaks are found at 1460 and 1600 nm. A comparison of electron concentration

obtained by charge extraction and by SSPA reveals that charge extraction is a valid method for devices that shows reasonable regeneration in the examined illumination intensities. In the case that poor regenerating devices were examined, a mismatch in charge concentration was found. A critical point that shows the branching between extractable and non-extractable charges can be used to rank systems. The assumption that there are non-extractable charges is backed up by the fact that the oxidized dyes population can be also measured and quantified and the fraction of lost charges are in the same ball park of this accumulated population.

6.7 Additional information to chapter 6

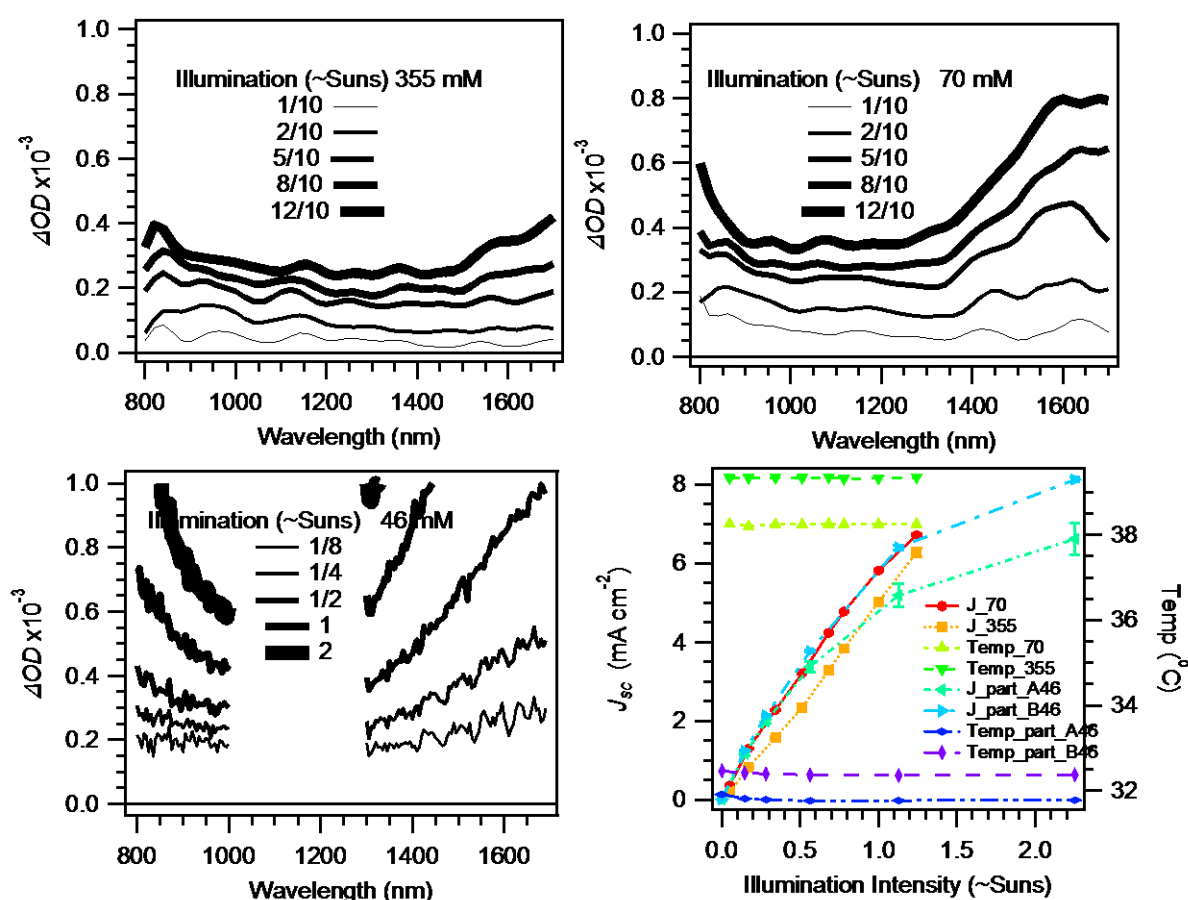


Figure 6-6 – data used to construct Figure 6-2. The bottom right figure shows the averaged temperature and the averaged photocurrents (± 1 standard deviation) as a function of light intensity.

7 Concluding Remarks

There are two pathways for improving single junction DSSCs. The first is to find an alternative or a solution for the large loss in potential that occurs in the iodine/iodide redox couple. The second route is to collect a larger fraction of the solar spectrum by minimizing the bandgap of the sensitizer thus increasing the maximum photocurrent achievable. We have started to conduct regeneration studies on IR absorbing dyes. Both as a step for implementing the regeneration model, the TA-TE setup and the concepts and techniques presented in this work, but also for the obvious goal, making efficient DSSCs. The idea was to find a dye with a bandgap smaller than 1.1 eV, where its excited state is positioned in the suitable region for the TiO₂ conduction band (CB). Then, using the suite of characterisations and advanced modelling available in the lab, to find holes in performance that can be filled with our expertise. Several IR absorbing (Ru^{II}/Os^{II} based) dyes were considered, usually with the common denominator of having one derivative of terpyridine (terpyridyl) ligand and one or no bipyridine derivative. (Onicha and Castellano ; K. Nazeeruddin, Pechy et al. 1997; Altobello, Argazzi et al. 2005; Chen, Liu et al. 2007) Such dyes have been known for more than a decade, however due to their low absorption coefficient in the visible region and low stability, these dyes have not made the quantum leap beyond the conventional and stable N3 (Ru(dcb)₂(SCN)₂) and its derivatives. Work is now in progress to examine examples of such dyes as well as IR organic dyes synthesised in other labs. The first dye to show up in our labs was an organic dye named VG5, a derivative of squarine (see structure in Figure 8-5).

Prior to the regeneration kinetic studies of the squarine IR dye VG5, several adjustments were required in order to get it to work properly. It appeared that squarine dyes tend to aggregate and requires co-adsorbing with a molecule like deoxycholic acid (a.k.a cheno). Further fine tuning was required involving adjusting the TiO₂ CB edge. A high Li⁺ concentration (1 M) was required to lower the CB such that injection will start occurring and become significant. Currents > 7 mA / cm² were achievable and seemed a promising starting point, even preliminary regeneration studies did not indicate a significant kinetic barrier and the electron dye recombination seemed long lived. However there were several drawbacks: when the iodide concentration exceeded a specific threshold the device performance started

to decline. This could be related to the reduction in the concentration of the inert counterion ClO_4^- corresponding to the increase in iodide required to maintain ionic balance. Alternatively, the reduction in current might result from the reduction in the driving force available as the negative shift in electrolyte redox potential (corresponding to the added iodide) approaches the conduction band of the TiO_2 which has been lowered with a high concentration of Li^+ . If this is true, then this is another challenge for low band gap dyes, the energy tuning window is small, and even when regeneration seems promising, high iodide concentration could paralyzed the device, meaning that regeneration would have to be faster to enable efficient cells with low iodide. Further tuning was considered, however a greater showstopper showed up: The dyes seemed to stop functioning after leaving VG5 cells in the dark for several days. The dye rejuvenated after some time under short circuit light soaking, but never reproduced their initial performances. Literature suggests that the squarine group in this family of dyes is weak and may fall apart. A complete report on this attempt should be published soon.

Hopefully, the work presented in this thesis has fertilized the ground for more straightforward regeneration studies in future. Finding the regeneration and electron-dye recombination rate constants, of combinations of both past and future dyes, semiconductors and electrolytes, are of obvious necessity for further development of DSSCs, although not before thorough studies of temperature dependant regeneration on state of the art DSSCs. These should reveal the regeneration activation barrier and the real competition between regeneration and electron-dye recombination.

8 Appendix- TAS spectra comparisons, collaborations and preliminary results

8.1 High vs. low iodide devices

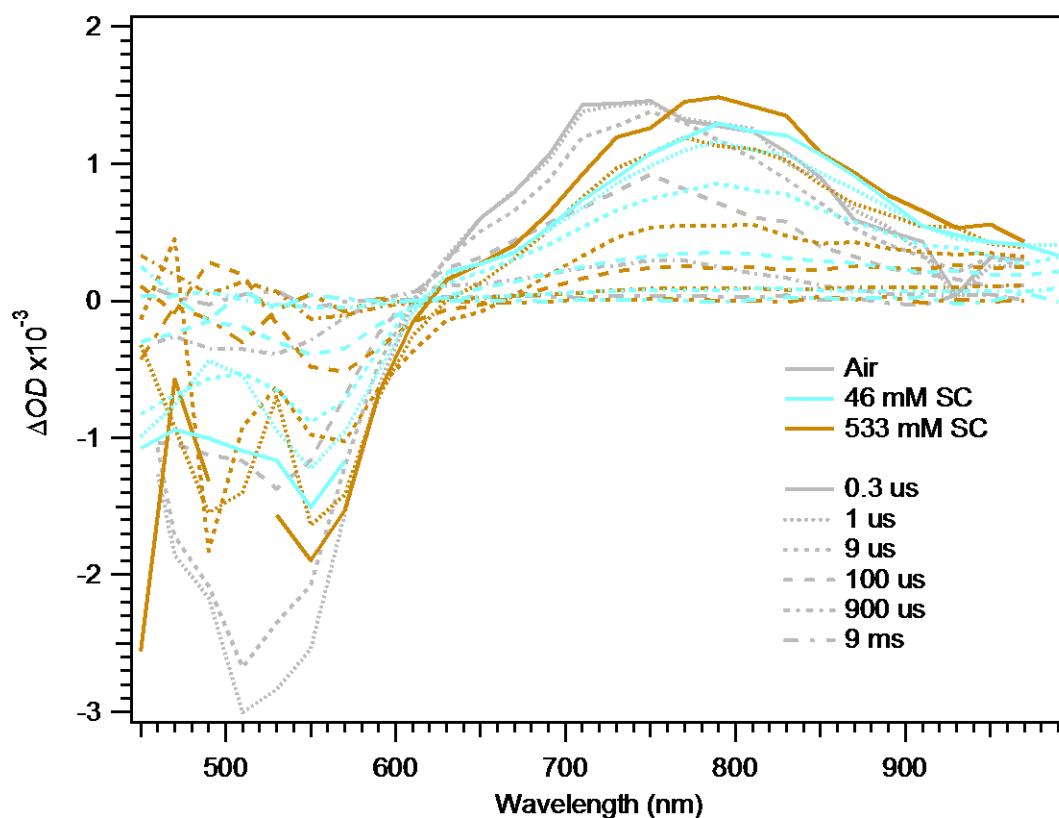


Figure 8-1 – verification that spectral shift doesn't occur when different iodide concentrations are used. Also loaded spectra acquired under air, shown in Figure 2-11. There is a greater shift between electrode in air and electrode in device than the effect of iodide concentration on spectral shifts.

8.2 Open vs. short circuit

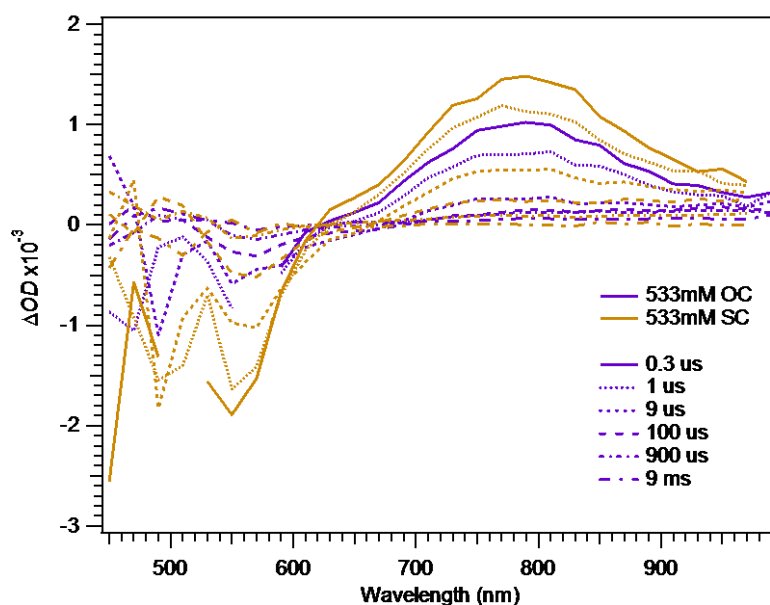


Figure 8-2 – a comparison of Open vs. Short circuit acquisition of difference spectra. Spectra were measured under 1 sun illumination for good regenerative device having 533 mM from the MPN series. (note that at early time and at)

8.3 TS4 dye in ACN based device – with and without Fc^+/Fc

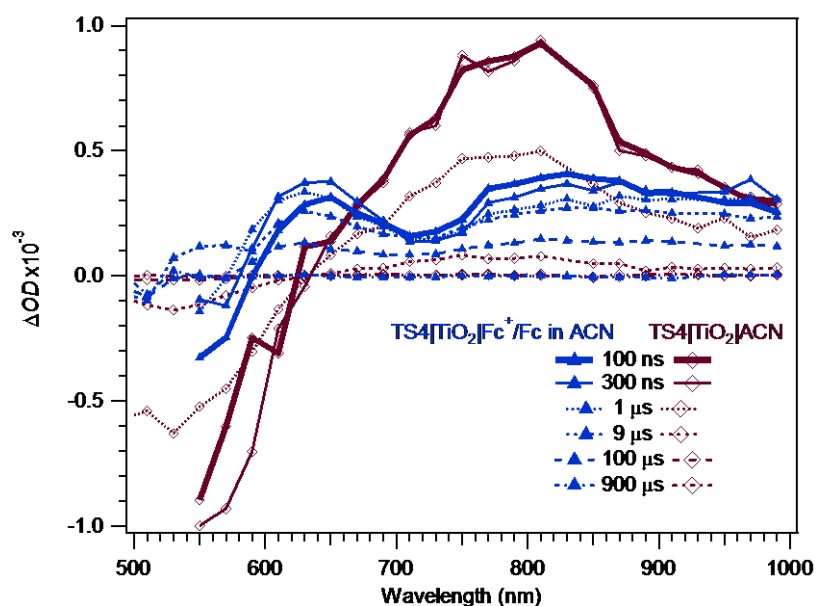


Figure 8-3 – done in collaboration with Andrea Listorti

8.4 N719 dye in – working electrode under Air / TPD

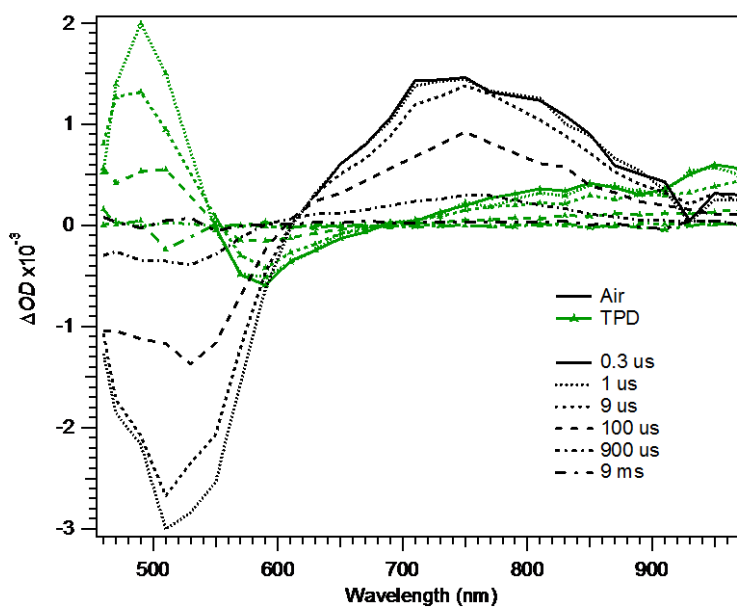


Figure 8-4 - *N,N'*-diphenyl-*N,N'*-(*m*-tolyl)-benzidine (TPD) as a hole transporting material. Done in collaboration with Mindaugas Juozapavicius.

8.5 VG5 - infra red dye in iodide based electrolyte

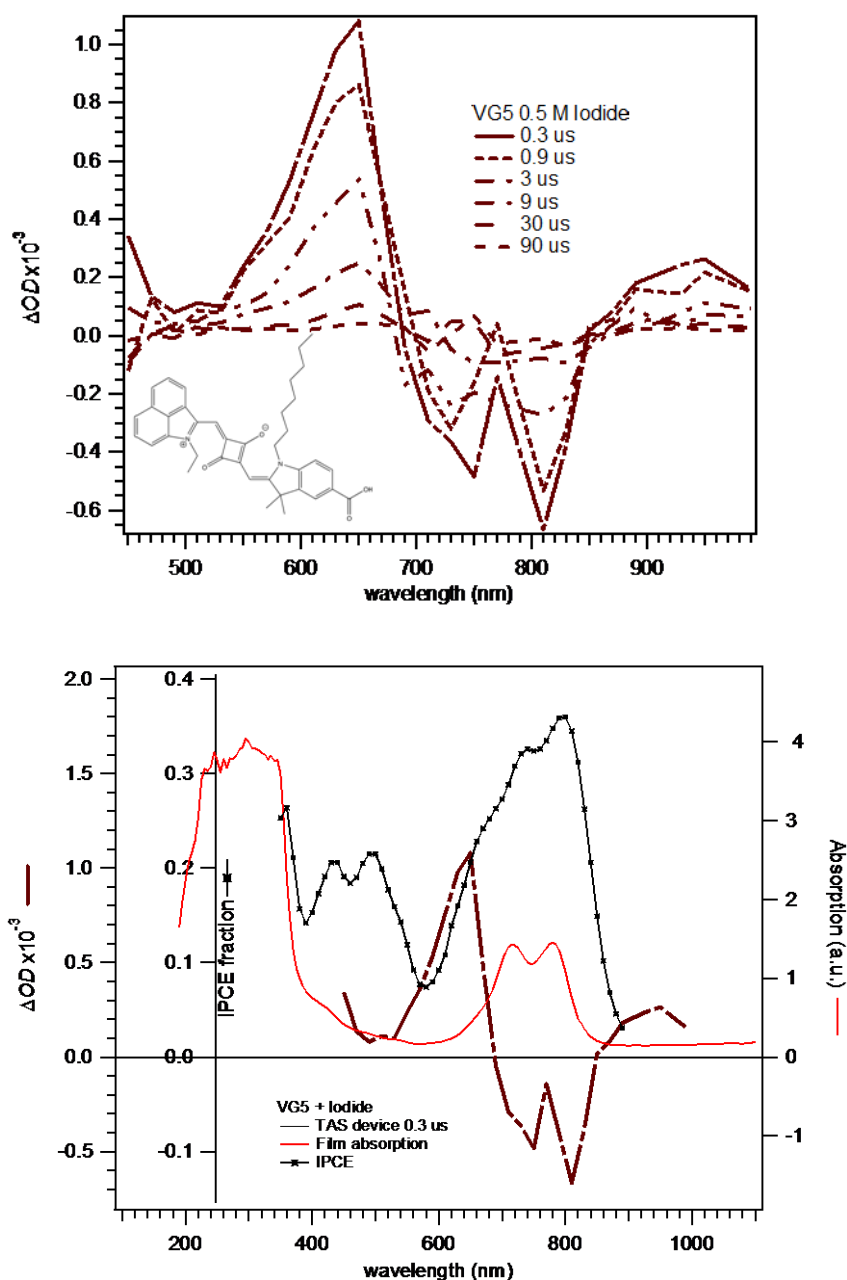


Figure 8-5 – Top – TAS spectra of VG5 based device with 0.5 M LiI in MPN electrolyte. Excitation at 430 nm, 10 Hz. 1 sun equivalent bias illumination. Bottom – VG5 spectrum at 0.3 μs compared with IPCE and the absorption spectrum of a dyed TiO_2 film. Done with Stefano Martiniani. Dye provided by Claudia Barolo from university of Torino, Italy.

9 Appendix- Technical Details and Components of the Simultaneous TA-TE Setup

9.1 Operational amplifier circuit

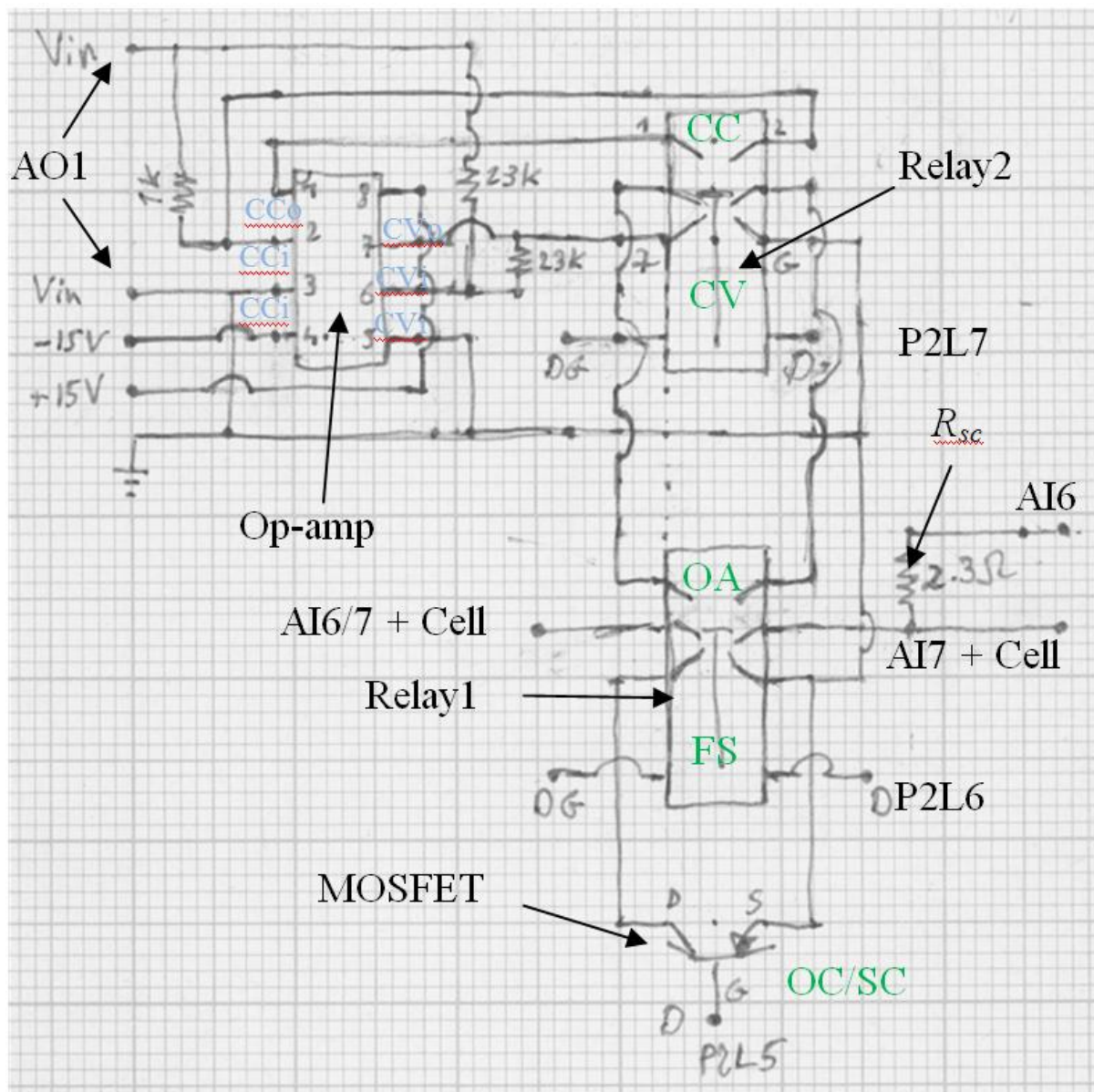


Figure 9-1 –“Home made” operational amplifier circuit + relays and fast solid state switch. FS – Fast Switch sub-circuit. OC / SC – Open Circuit / Short Circuit. OA – is the Operational Amplifier sub circuit. CV – Constant Voltage. CC – Constant Current.

Table 9-1 – the logics and controls required for each condition in the homemade op-amp circuit + relays.

	Digital				
	OC	SC	CV	CC	Channel
MOSFET	0	1	0	0	P2L5
Relay 1 (use OpAmp)	0	0	1	1	P2L6
Relay 2 (CV/CC)	0	0	0	1	P2L7
Record	V	A	A	V	
Record Channel	AI7	AI6	AI6	AI7	
Control Channel			AO1	AO1	

9.1.1 Operational Amplifier

LM358N/NOPB DUAL OP AMP - No. of Amplifiers:2; Op Amp Type: Low Power; Gain, Bandwidth -3dB:1MHz; Slew Rate:0.1V/ μ s; Voltage, Supply Min:3V; Voltage, Supply Max:32V; Termination Type: Through Hole; Case Style: DIP; No. of Pins:8; Operating Temperature Range: 0 °C to +70 °C

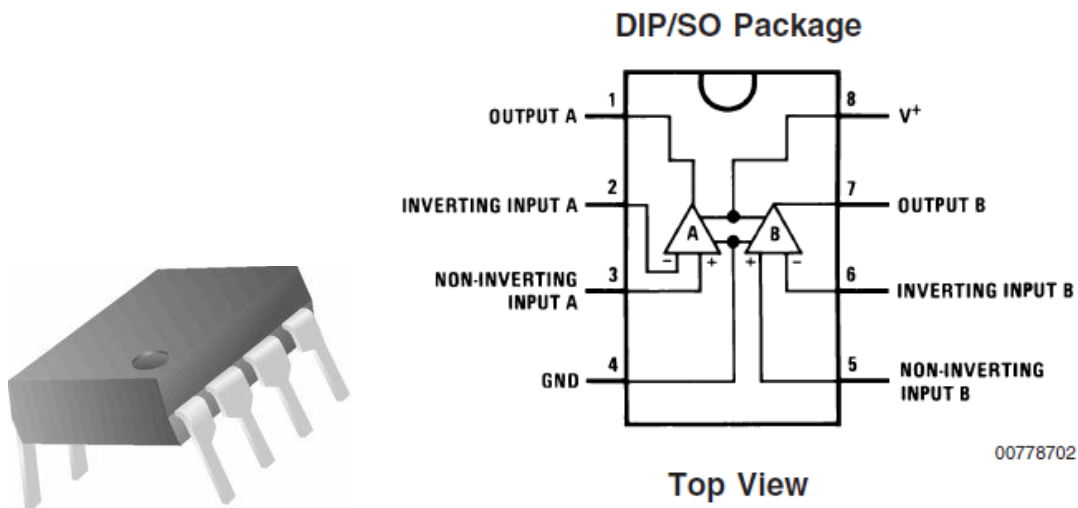


Figure 9-2 – LM358N/NOPB operational amplifier photograph (left) and connection diagram (right).

9.1.2 ZVN4306A - MOSFET, N, LOGIC, E-LINE

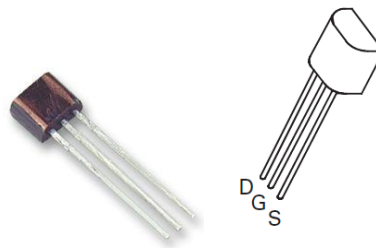


Figure 9-3 - ZVN4306A - MOSFET, N, LOGIC, E-LINE, photograph (left) and terminal assignemt (right)

Specifications

- | | |
|--------------------------------|------------------------------------|
| • MOSFET, N, LOGIC, E-LINE | • Lead Spacing:1.27mm |
| • Transistor Polarity:N | • Max Power Dissipation Ptot:0.85W |
| • Max Voltage Vds:60V | • No. of Transistors:1 |
| • On State Resistance:0.45ohm | • Power Dissipation Pd:0.85W |
| • Power Dissipation:0.85W | • Pulse Current Idm:20A |
| • Transistor Case Style:E-Line | • Termination Type:Through Hole |
| • No. of Pins:3 | • Transistor Type:MOSFET |
| • Case Style:E-Line | • Typ Voltage Vds:60V |
| • Cont Current Id:1.1A | • Typ Voltage Vgs th:3V |
| • Current Temperature:25°C | • Voltage Vgs Rds on |
| • Device Marking:ZVN4306A | Measurement:10V |
| • Full Power Rating | |
| Temperature:25°C | |

<http://uk.farnell.com/diodes-inc/zvn4306a/mosfet-n-logic-e-line/dp/9524924>

9.1.3 Relay

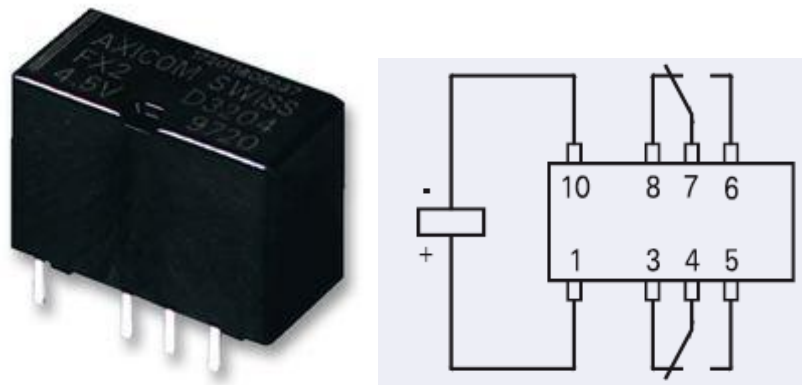


Figure 9-4 - FX2-D3223 - RELAY, PCB, DPCO, 5VDC photograph (left) and terminal assignment (right)

Specifications

- RELAY, PCB, DPCO, 5VDC
- Coil Type:DC Coil, Monostable
- Contact Configuration:DPDT
- Contact Current Max:2A
- Contact Voltage AC Nom:250V
- Contact Voltage DC Nom:220V
- Nom Coil Voltage DC:5V
- Coil Resistance:313ohm
- Cont Coil Power:80mW
- Relay Mounting:PC Board
- External Length / Height:10.7mm
- External Width:14.93mm
- External Depth:7.27mm
- Operating Voltage Range:3.75V to 12.5V
- Max Contact Current AC:2A
- Max Contact Voltage AC:250V
- Max Contact Voltage DC:220V
- Max Operating Temperature:85°C
- Min Temperature Operating:-55°C
- Mounting Type:PCB
- No. of Poles:2
- Series:FX2
- Approval Category:UL Recognised
- Contact Material:Palladium-ruthenium - gold covered
- Contact Resistance:70mohm
- Contact Style:2 form C
- Current Rating:2A
- DC Coil Power:80mW
- Dielectric Voltage Coil to Contact:1800V AC
- Dielectric Voltage Contact to Contact:1800V AC
- IP Rating:IP 67
- Insulation Resistance:1000Mohm

- Max Contact Current:2A
 - Max Switch Current:2A
- Max Switch Voltage:220V DC

Max Switching Power:60W

9.2 NI USB-6251 (BNC) Data Acquisition Card (DAQ)

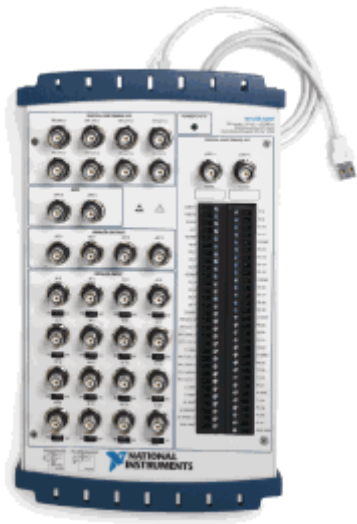


Figure 9-5 - USB-6251 (BNC) Data Acquisition Card (DAQ)

Specifications

Analog Input	(signal + common mode) ± 11 V
Number of channels	of AI GND
USB-6251 BNC 8	Input impedance
differential	Device on
ADC resolution..... 16	AI+ to AI GND..... $>10\text{ G}\Omega$
bits	in parallel with 100 pF
Input coupling DC	AI- to AI GND $>10\text{ G}\Omega$
Input range	in parallel with 100 pF
USB-6251 BNC $\pm 10, \pm 5,$	Device off
$\pm 2, \pm 1,$	AI+ to AI GND..... $820\text{ }\Omega$
$\pm 0.5, \pm 0.2, \pm 0.1\text{ V}$	AI- to AI GND $820\text{ }\Omega$
Maximum working voltage for analog	Input bias current.....
inputs	$\pm 100\text{ pA}$

Crosstalk (at 100 kHz)	USB-6221/6229 BNC.....	-90 dB
Adjacent channels	USB-6251/6259 BNC.....	-95 dB
Nonadjacent channels		

9.3 Cell holder



Figure 9-6 – Homemade Cell holder for the Simultaneous TA TE setup.

9.4 IL1 Tungsten Halogen probe beam

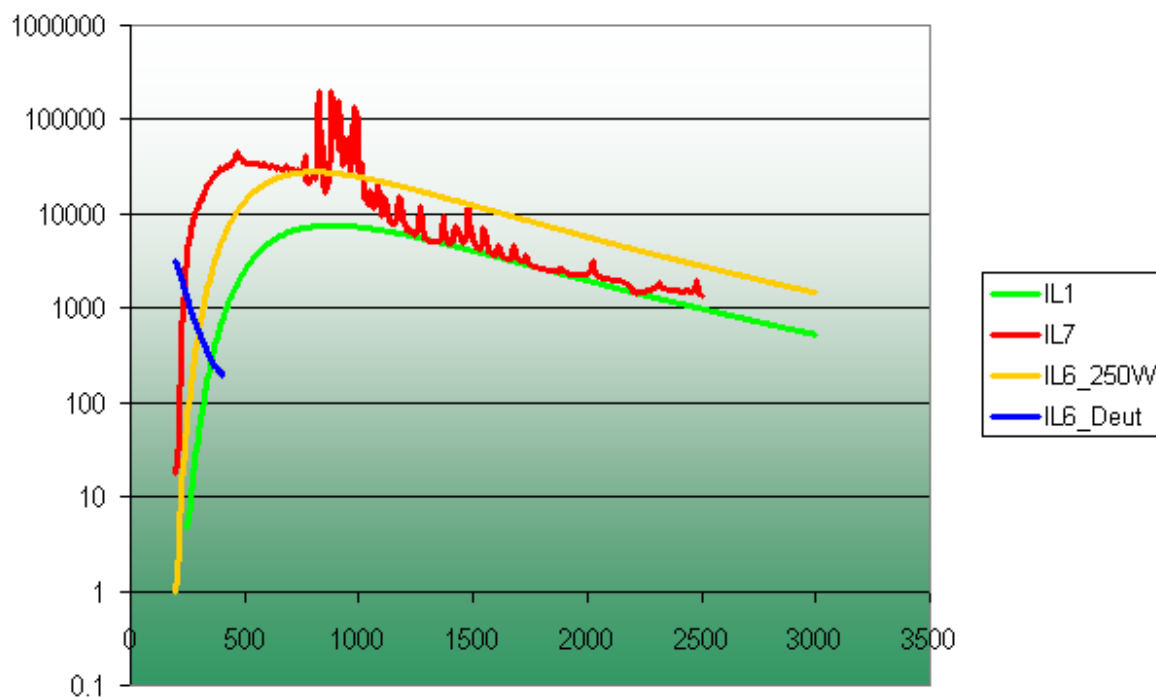


Figure 9-7 - Bentham IL1 light source emission spectra (Bentham website)

The IL1 is a general-purpose light source for use in the UV, visible and infra-red spectral regions from 350nm to 2.5mm.

A quartz halogen lamp controlled by a current stabilised power supply is employed.

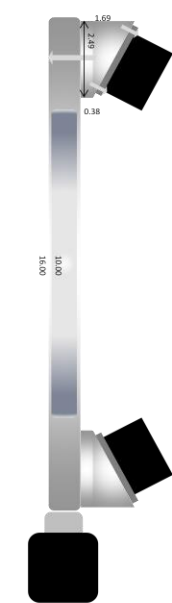
A single quartz condenser lens is used to fill the height and width of the slit and to match to the F/4 optics of the monochromator. The quartz halogen lamp is unsurpassed for stability by any other source and should always be used where it provides sufficient output in the wavelength region of interest.

Specification	
Stability of light output	Better than 0.1% over 8-hour period (when used with 605 p.s.u.)
Peak irradiance	1.3mW cm ⁻² nm ⁻¹ at 880nm
Lamp	100W quartz halogen

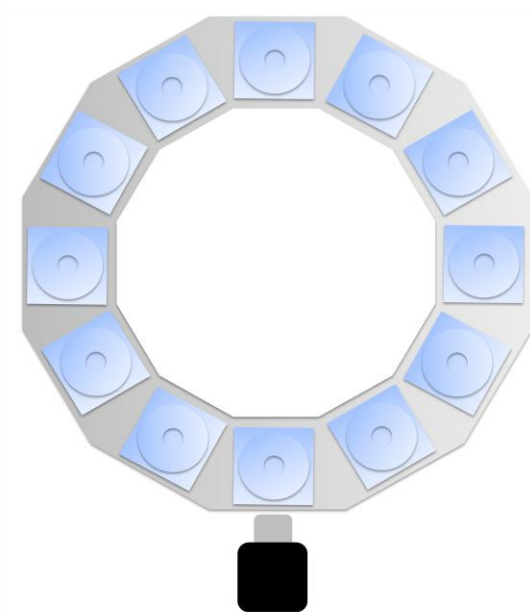
Horizontal adjustment	by screw slide
Vertical adjustment	by slackening nuts in T-slots
Lens	Single quartz condenser lens, adjustable focus
Power leads	1m long with spade terminals provided
Bracket for mounting 218 optical chopper is included	

9.5 Bias Light LED Array

9.5.1 Homemade Bias Light Array diagrams



Side



Front

Figure 9-8 – Home made Bias light LEDs array

9.5.2 LEDs emission spectrum and specification

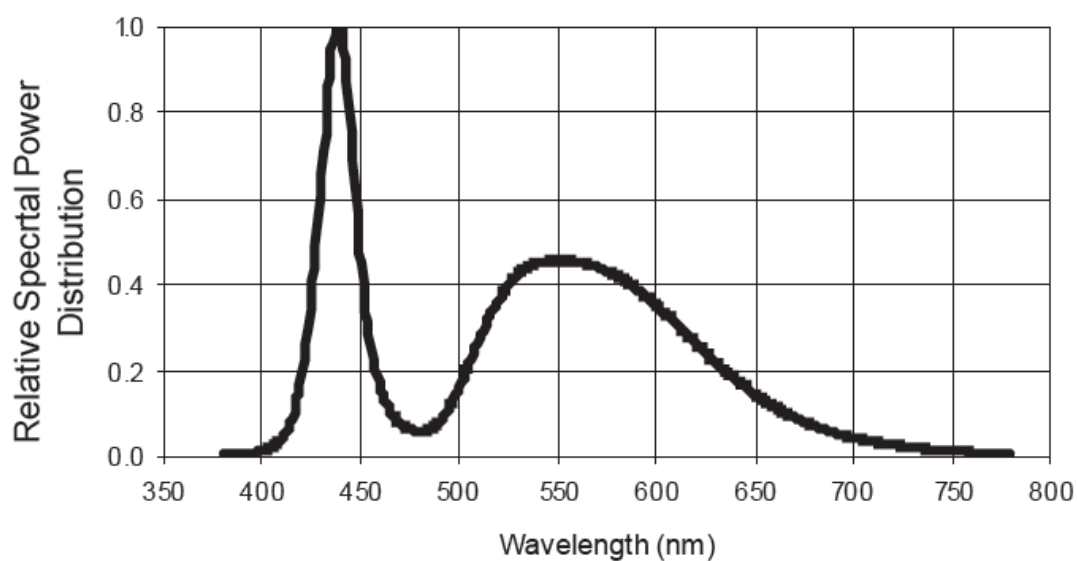


Figure 9-9 - LXHL-NWE8 white LED emission spectra (Luxeon website).

Table 9-2 - LXHL-NWE8 white LED specification table (Luxeon website).

LXHL-NWE8 Specifications	
Lumens @ 350mA	45 lm
Max Continuous Current	350 mA
Forward Voltage	3.42 Vf
Dominant Wavelength	5500 K
LED Type	Star/O
Radiation Pattern	Batwing
Weight	0.6g

9.6 Monochromator

9.6.1 Grating1 200 - 1600 nm

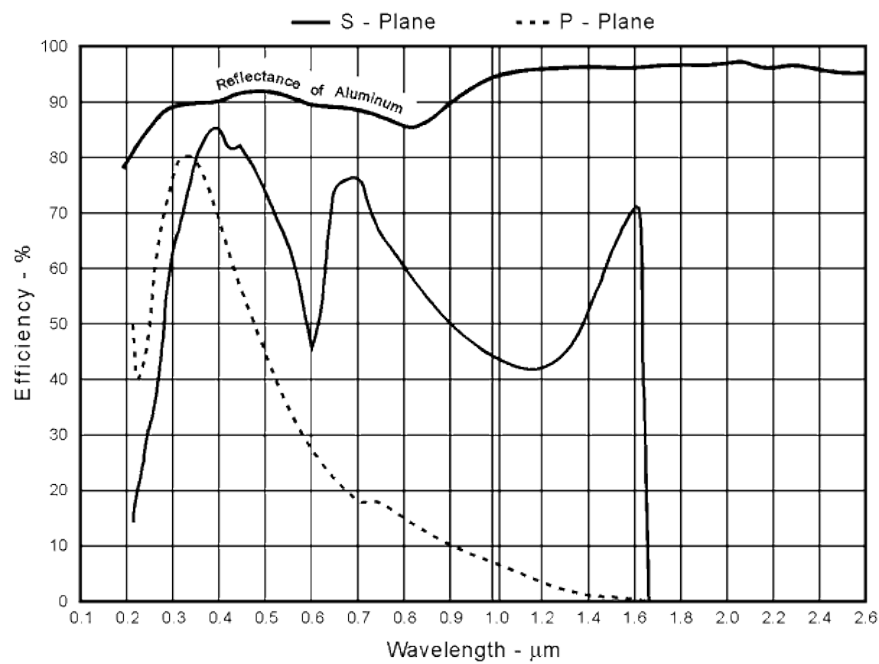


Figure 9-10 - Grating 74024 efficiency spectra, Ruled, 1200 l/mm, 350nm Blaze, 200-1600nm Primary.

9.6.2 Grating2 600 - 2200 nm

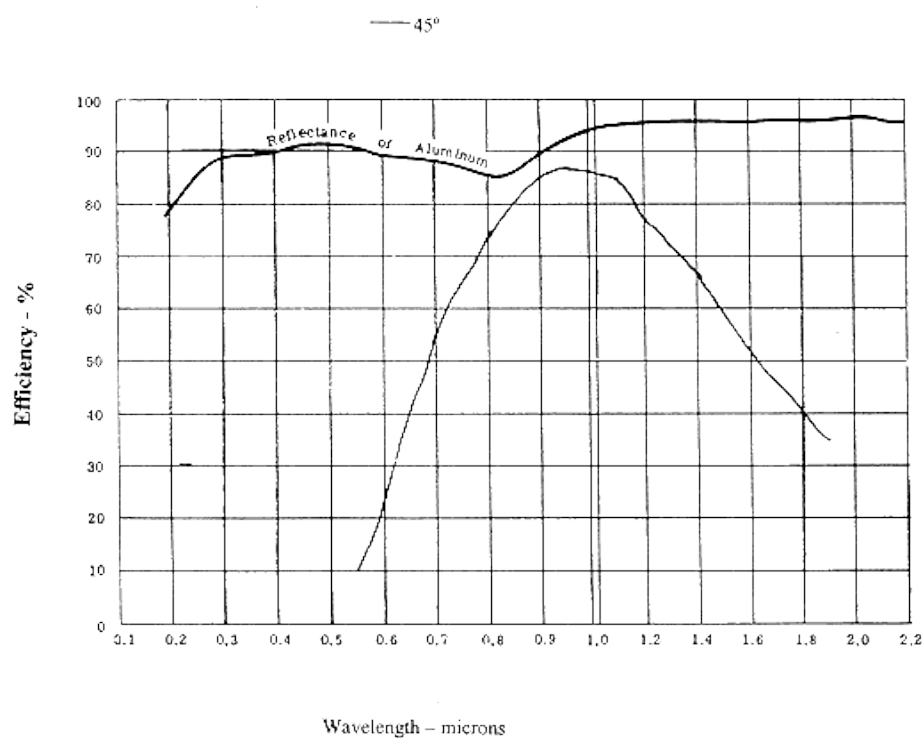


Figure 9-11 – Grating 74030 efficiency spectra, 45 deg polarisation, Ruled, 200 l/mm, 1000nm Blaze, 600-2200nm Primary.

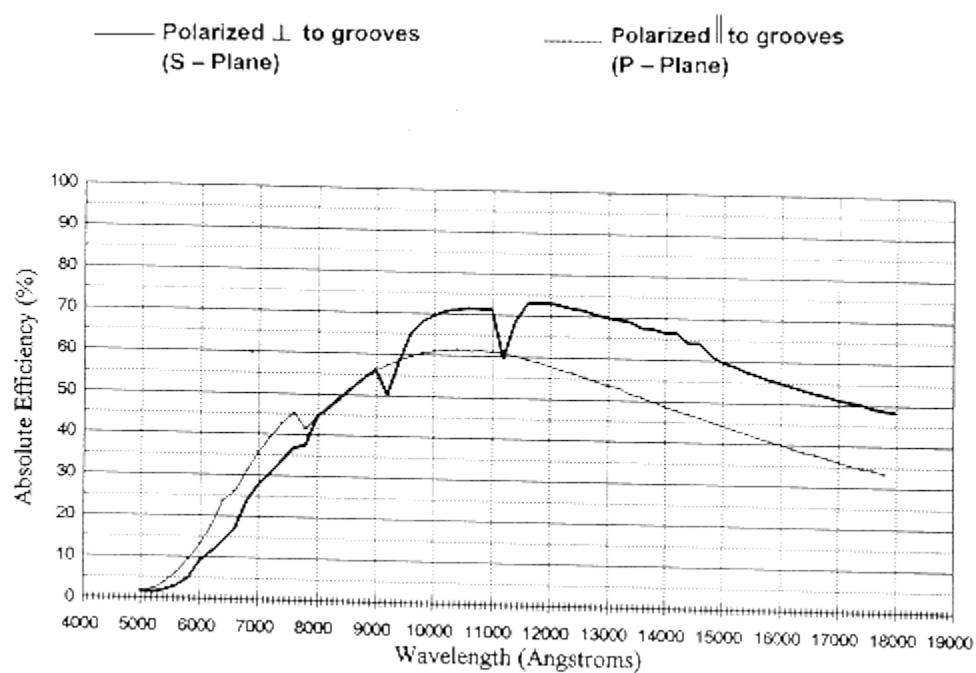


Figure 9-12 - 74030 S&P Grating efficiency spectra, Ruled, 200 l/mm, 1000nm Blaze, 600-2200nm Primary (74030).

9.7 Filter Wheel

9.7.1 Long pass filters

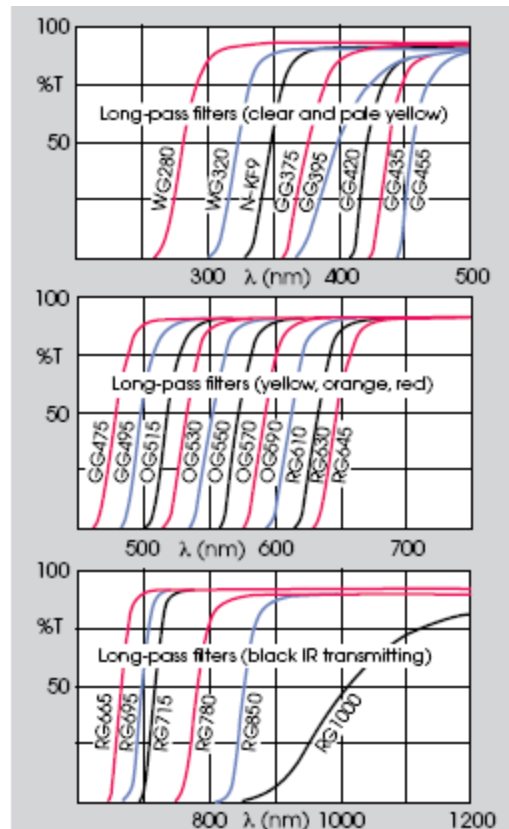


Figure 9-13 Glass colour longpass filters transmission spectra. (Comaroptics) currently the 280, 395, 495, 780 and 1000 nm filters are installed in the TA-TE setup. Wavelength listed is transition wavelength ($T = T_{max}/2$)

9.8 Probing detector

9.8.1 PVOT/D/V 80 ns visible range optical detector system

- (requires stabilised ± 12 V PSU ~ 200 mA from main amp module)
- High speed, large area, Si PIN photodiode
- Photodiode diameter: ~ 5 mm
- Spectral range 320 nm – 1060 nm
- Uses Hamamatsu S3071 low noise photodiode
- Risetime ~ 80 ns.

- Noise level/Delta OD detectable(full bandwidth, no averaging) $\sim 10^{-4}$
- Bandwidth DC – 10 MHz
- Transconductance gain: ~ 1 volt out for 10 microamp change in photodiode current

9.8.2 PVOT/D/IR 200 ns infra red optical detector system

- Detector/preamp head only (requires stabilised ± 12 V PSU ~ 200 mA from main amp module)
- InGaAs PIN Photodiode
- Photodiode diameter: ~ 2 mm
- Spectral range 0.7 to 1.7 μm
- Risetime ~ 200 ns.
- Noise level/Delta OD detectable....(full bandwidth, no averaging) $\sim 10^{-4}$
- Bandwidth DC - 3 MHz
- Transconductance gain: ~ 1 volt out for 10 microamp change in photodiode current

9.8.3 PVOT/M 80 ns main amplifier/PSU/digital lightmeter/variable filter module

- Noise level, ΔOD detectable (full bandwidth, no averaging) $\sim 10^{-4}$
- System transconductance gain: ~ 1 volt out for 25 nano-amp (10^{-9} A) change in photodiode current (or 40 MOhms expressed as a resistance)
- Risetime 80 ns.
- Frequency response DC to 10 MHz
- High Pass (coupling) filter select 10 μs – 100 μs – 1 ms – 10 ms – 100 ms – 1 s – 10 s - DC
- Low pass (smoothing) filter select 10 ns – 30 ns – 100 ns – 300 ns – 1 μs – 10 μs -30 μs

9.9 Excitation and triggering

9.9.1 Pump Laser specifications

Pump Laser Nd:YAG Flashlamp pumped

Pump Wavelength 355 nm

Pulse Repetition Rate (PRR) 20 Hz Lower rep rate can be selected

Pulse length 5 ns Nominal

Beam Diameter 3 (4) mm Nominal

External Trigger Lamp and Q-Switch, Flashlamp has to operate at designed PRR

9.9.2 Optical Parametric Oscillator parameters

Wavelength Tuning Range 410 - 2200 nm, No wavelength "gap" at degeneracy

Peak OPO Energy 4 (10) mJ, See Figure 9-14

Spectral Linewidth $\sim 4 - 7 \text{ cm}^{-1}$

Beam Divergence Vertical $\sim 2 \text{ mrad}$, Horizontal $< 10 \text{ mrad}$, FWHM

Polarization Signal: Horizontal, Idler: Vertical, Linear polarization

Computer Control All the laser and OPO functions, ON, OFF, Power, Rep-Rate, Tuning, Scan

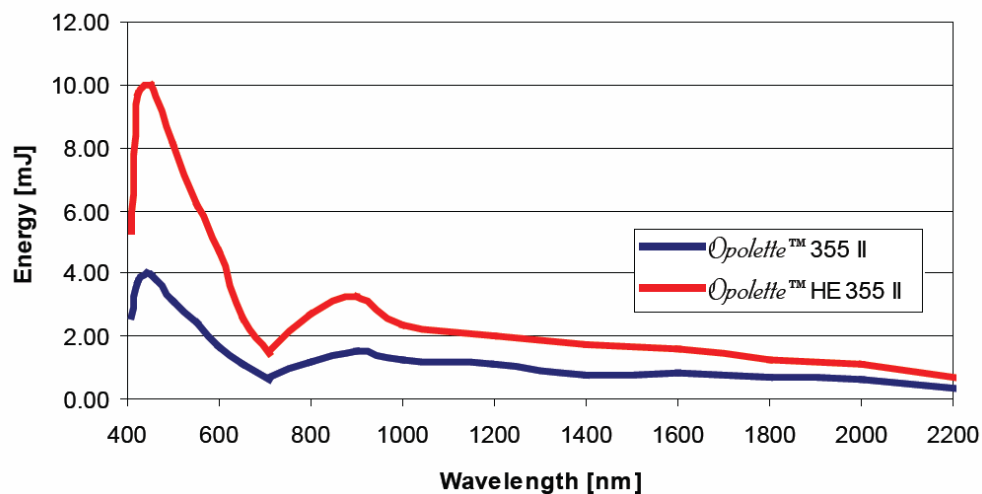


Figure 9-14 – Opolette™ 355 II Tuning Curve (Blue)

9.9.3 Light Guide

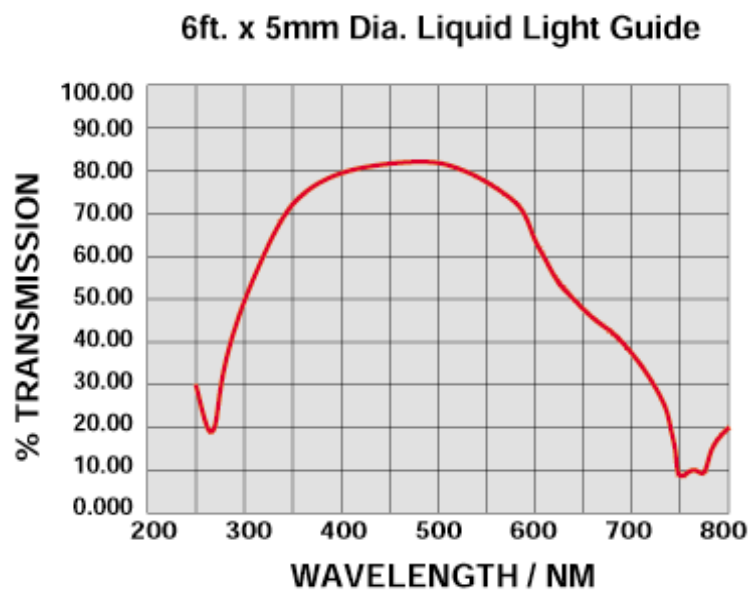


Figure 9-15 – Edmund Optics NT53-691 Liquid Light Guide transmission spectrum

9.9.4 Triggering photodiode

9.9.4.1 Triggering photodiode spectral response

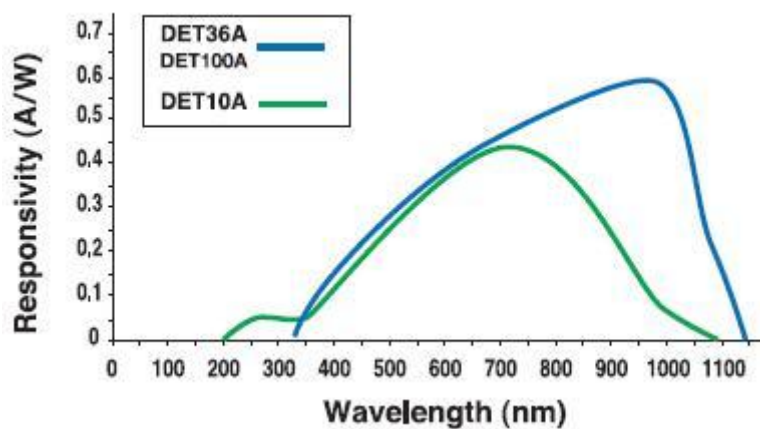


Figure 9-16 - DET10A/M - High-Speed Si Detector responsivity, 200 - 1100 nm, 1 ns Rise Time.

9.9.4.2 Triggering photodiode electronic circuit

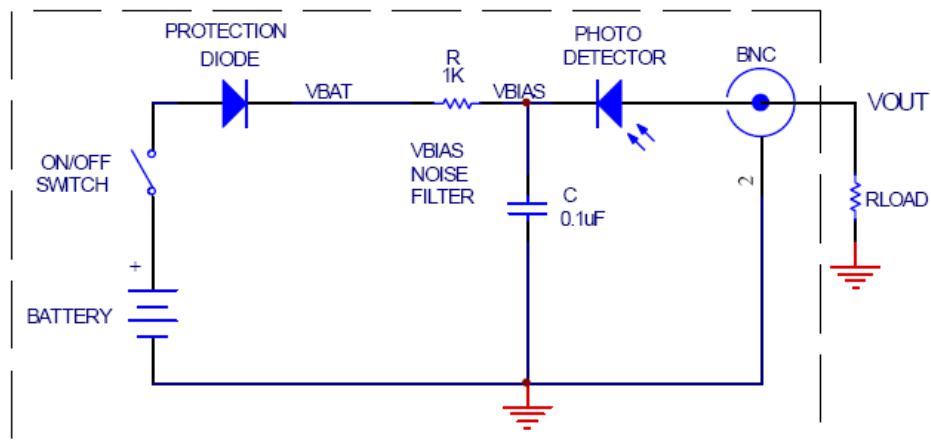


Figure 9-17 - DET10A/M Circuit schematic

List of Publications

- 1 Pollak, E., Anderson, A., Salitra, G., Soffer, A., Aurbach, D. The anomaly in the dependence of the electronic conductivity of activated carbon electrodes at different charging states. *Journal of Electroanalytical Chemistry* **601**, 47-52, doi:10.1016/j.jelechem.2006.10.028 (2007).
- 2 Barnes, P. R. F., Anderson, A. Y., Koops, S. E., Durrant, J. R., and O'Regan, B. C. Electron Injection Efficiency and Diffusion Length in Dye-Sensitized Solar Cells Derived from Incident Photon Conversion Efficiency Measurements. *Journal of Physical Chemistry C* **113**, 1126-1136, doi:10.1021/jp809046j (2009).
- 3 O'Regan, B. C., Walley, K., Juozapavicius, M., Anderson, A., Matar, F., Ghaddar, T., Zakeeruddin, S. M., Klein, C., Durrant, J. R. Structure/Function Relationships in Dyes for Solar Energy Conversion: A Two-Atom Change in Dye Structure and the Mechanism for Its Effect on Cell Voltage. *Journal of the American Chemical Society* **131**, 3541-3548, doi:10.1021/ja806869x (2009).
- 4 Barnes, P. R. F., Liu, L., Li, X., Anderson, A. Y., Kisserwan, H., Ghaddar, T. H., Durrant, J. R., O'Regan, B. C. Re-evaluation of Recombination Losses in Dye-Sensitized Cells: The Failure of Dynamic Relaxation Methods to Correctly Predict Diffusion Length in Nanoporous Photoelectrodes. *Nano Letters* **9**, 3532-3538, doi:10.1021/nl901753k (2009).
- 5 Genish, I., Irzh, A., Gedanken, A., Anderson, A., Zaban, A., Klein, L. Coating dielectric substrates by plasma-reduction of metallic ions in solvents. *Surface and Coatings Technology* **204**, 1347-1352, doi:10.1016/j.surfcoat.2009.09.029 (2010).
- 6 Anderson, A. Y., Barnes, P. R. F., Durrant, J. R. & O'Regan, B. C. Simultaneous Transient Absorption and Transient Electrical Measurements on Operating Dye-Sensitized Solar Cells: Elucidating the Intermediates in Iodide Oxidation. *The Journal of Physical Chemistry C* **114**, 1953-1958, doi:10.1021/jp910221j (2010).
- 7 Law, C., Pathirana, S. C., Li, X., Anderson, A. Y., Barnes, P. R. F., Listorti, A., Ghaddar, T. H., O'Regan, B. C., Water-Based Electrolytes for Dye-Sensitized Solar Cells. *Advanced Materials*, n/a-n/a, doi:10.1002/adma.201001703 (2010).
- 8 Anderson, A. Y., Barnes, P. R. F., Durrant, J. R. & O'Regan, B. C. Quantifying Regeneration in Dye Sensitized Solar Cells. *J. Phys. Chem.C* **Submitted** (2010).
- 9 Barnes, P. R. F., Anderson, A. Y., Durrant, J. R. & O'Regan, B. C. Simulation and measurement of complete dye sensitised solar cells: factors influencing device performance under light and dark conditions, interpretation of transient measurements and electron diffusion length. *Phys. Chem. Chem. Phys.* **Submitted** (2010).
- 10 Barnes, P. R. F., Anderson, A. Y., Juozapavicius, M., Liu, L., Li, X., Palomares, E., Durrant, J. R., O'Regan, B. C. Factors controlling charge recombination under dark and light conditions in dye sensitised solar cells. *Phys. Chem. Chem. Phys.* **Submitted** (2010).
- 11 Listorti, A., Rolandini J., A., Anderson, A. Y., Li, X., Barnes, P. R. F., Kisserwan, H., Ghaddar, T. H., Durrant, J. R. and O'Regan, B. C. Ferrocene electrolytes for dye-sensitized solar cells. **Manuscript in preparation** (2010).

- 12 Anderson, A. Y., Barnes, P. R. F., Listorti, A., Durrant, J. R., O'Regan, B. C. Non extractable electrons – a comparison of charge extraction and steady state photoinduced absorption in dye sensitized solar cells. **Manuscript in preperation** (2010).

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