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2000 Hours Photostability Testing of Dye Sensitised Solar Cells using a Cobalt Bipyridine Electrolyte

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DSSCs incorporating Co(II/III) tris(bipyridine) redox couple in acetonitrile and the Z907 dye were subjected to $\geq$2000 hours of light soaking at 20 ^{o}C and ~1 sun light intensity from white LEDs (~no UV component). Initial energy efficiencies were near 6.3%. After 2000 hours, the best acetonitrile based cells maintained ~66% of the initial efficiency. Both J_{SC} and fill factor (FF) declined, while the V_{OC} remained highly stable. In comparison, the best Z907/cobalt cells with 3-methoxypropionitrile (MPN) as a solvent, maintained 91% of the initial efficiency after 2000 hour light soaking. Only FF declined in MPN based cells. In follow up testing of similar ACN cells at the maximum power point, at 30 ^{o}C, the best cells maintained 97% of the initial efficiency after 300 hours. Impedance, J_{SC} vs. intensity and charge extraction data are consistent with a decrease in the Co(III) concentration, or a restriction in Co(III) diffusion, during light soaking.

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Introduction

The dye-sensitised solar cell (DSSC) has potential for producing low cost electricity.[1] DSSCs are reviewed elsewhere.[2–4] The most common redox couple used in DSSCs is iodide/triiodide (I^-/I_3^-). The certified record efficiency of iodide based DSSCs is 11.4%.[5] Alternative redox couples based on cobalt polypyridine complexes have gained attention after publication of a cobalt based DSSC with an efficiency of 12.3%.[6] The main advantages of cobalt redox couples include higher open-circuit potentials, lower visible light absorption, and less tendency to corrode metal components than iodine/iodide.

The stability of DSSCs is a critical aspect for commercialisation. For the evaluation of DSSC long-term stability, a minimum of 1000 h of continuous illumination at "1 Sun" is a common benchmark.[7] 1000 hours continuous exposure near 1 sun is roughly equivalent, in absorbed photons, to 1 year outdoor exposure, at the optimum tilt, in SE England (our location), or about 6 months in an arid location in Spain or the US. In previous publications, the stability of cobalt based DSSCs has been reported up to 100-500 h at 1 sun, showing rather poor stability.[6,8,9] DSSCs based on cobalt electrolyte in acetonitrile have been reported with 10% efficiency decrease after 220 h light soaking at 1 Sun and 30 °C.[6] Studies on 3-methoxypropionitrile/cobalt based DSSCs reported over 50% efficiency loss after 500 h at 1 Sun and 40 °C.[8] Aqueous cobalt based DSSCs were reported with 30% efficiency loss after 60 h at 1 Sun.[10] In another study, acetonitrile/cobalt based DSSCs were reported to show 80% efficiency loss after 100 h. This result was used as a control with respect to a new hexadentate cobalt complex, said to be more stable.[9] We report herein on the stability of cobalt electrolyte based DSSCs up to 2000 hours at ~1 sun equivalent (without UV). This is roughly equivalent to an outdoor test of 2 years at our location. Our data demonstrate that current cobalt electrolyte DSSCs, while not stable yet, can have much greater stability than previously reported. We also investigate the light soaking induced changes in the cell characteristics with electrochemical impedance spectroscopy (EIS) and transient and charge extraction measurements.

The DSSC components used herein were selected on the basis of commercial availability and frequency in the literature. We have used Co(II/III) tris(bipyridine), $Co(bpy)_3^{2+/3+}$, because it is the most frequently used cobalt polypyridine derivative for DSSCs. In addition, only well-established additives such as Li^+ and 4-*tert*-butylpyridine were used.[11] Our purpose is to measure the stability of the electrolyte, so the ruthenium sensitizer Z907 was selected due to commercial availability and high long-term stability.[12–16] Z907 does not give the highest efficiency cobalt DSSCs, but the organic dyes used in record cobalt DSSCS may introduce additional instability. In the interest of simplicity we have also avoided the use of very small cells, anti-reflective front films, and back reflectors, all methods used to increase efficiency of record cells. For these reasons our cells start with lower efficiency than the record cells published elsewhere. This should not change the stability characteristics of the electrolyte itself. Acetonitrile solvent was tested, as it is used in record cobalt based DSSCs due to it's low viscosity. Due to it's volatility, acetonitrile is difficult to contain on the long term. As we wished to study the chemical photostability of the electrolyte, rather than the stability of the cells to leakage, the cells were held at 20 °C during exposure. We also developed an improved sealing method. None the less leakage and/or diffusion out through the seal occurred in most cells eventually. Despite these problems, some cells survived the 2000 hour test.   We focus on the best cells in this paper, rather than the average, as a "proof of principle" concerning the photochemical stability of the cobalt electrolyte in DSSCs. Although by no means perfect, the promising results should encourage further work on cobalt based DSSCs and their stability.

Experimental

All chemicals were purchased from Sigma Aldrich unless otherwise stated. Transparent conductive fluorine-doped tin oxide (FTO) glass (TEC 15 and TEC 8) was purchased from Hartford Glass (Indiana, USA). TiO_2 nanoparticle paste (DSL18NR-AO) was purchased from Dye-Sol (NSW, Australia).

$[Co(bpy)_3](PF_6)_2$ and $[Co(bpy)_3](PF_6)_3$ complexes were synthesised according to previously reported literature.[17] Methanolic solution of 2,2'-bipyridine was added dropwise to an aqueous solution of $CoCl_2 \cdot 6H_2O$ and stirred for 1 h. Work-up with excess KPF_6 formed a precipitate which was filtered, washed with methanol, and dried under vacuum to obtain the $[Co(bpy)_3](PF_6)_2$ complex. Oxidation to

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Co(III) was performed via addition of a molar equivalent methanolic bromine. The solution was filtered, evaporated under vacuum, redissolved in methanol and filtered. The oxidised product was precipitated with excess potassium hexafluorophosphate. The precipitate was filtered, washed with water and dried under vacuum to obtain the $[Co(bpy)_3](PF_6)_3$ complex.

DSSCs were fabricated using standard procedures from previous studies.[17,18] A compact TiO_2 layer was deposited on transparent conductive fluorine-doped tin oxide (FTO) glass substrates by spray pyrolysis.[19] Substrates were treated with $TiCl_4$ by heating at 70 °C for 30 mins.[20] The porous, nanocrystalline TiO_2 films (Dyesol 18NR-AO) were tape-cast and sintered at 450 °C for 30 mins in air. Average film thicknesses were 6.4 μm. The final cell geometry had a 1 x 1 cm active area. The electrodes were immersed and sensitised overnight in 0.3 mM Z907 solution in 1:1 mixture of acetonitrile and tert-butyl alcohol. Counter electrodes were coated with H_2PtCl_6 solution in iso-propanol, dried in air for 2 mins and then heated to 390 °C for 20 mins. Electrodes were sealed together with a Surlyn (Solaronix, Switzerland) gasket using a heat press set at 120 °C. The electrolyte was injected into pre-drilled holes in the counter electrode. The filling holes were sealed with a microscope coverslip and two layers of Surlyn; one on the cell, and one pre-attached to the coverslip. A thin TiO_2 layer was previously deposited on the non-conductive side of the counter electrode and on the coverslip to promote adhesion to Surlyn. The filling holes were then additionally covered by Bynel and a piece of 1 mm microscope slide, and finally all the edges were covered with epoxy. (We do not claim that all this sealing was in fact necessary. Some cells lacking the Bynel and microscope slide survived the 2000 hour test without leakage.) Two different electrolytes were used: "ACN" (acetonitrile with 0.2 M $[Co(bpy)_3](PF_6)_2$, 0.04 M $Co[(bpy)_3](PF_6)_3$, 0.5 M 4-*tert*-butylpyridine and 0.1 M $LiClO_4$), and "MPN" (3-methoxypropionitrile with 0.2 M $Co[(bpy)_3](PF_6)_2$, 0.1 M $Co[(bpy)_3](PF_6)_3$, 0.5 M 4-*tert*-butylpyridine and 0.1 M $LiClO_4$). A total of 10 cells (6 ACN and 4 MPN) were used for the long term stability study.

Current-voltage (*J-V*) characteristics were measured using a solar simulator consisting of a 150 W Xenon lamp with an AM 1.5 filter and an IR water filter (Sciencetech SS150W) . The light intensity was calibrated for each series of *JV*s using a silicon photodiode (model PBW21) to 1000 Wm^{-2} AM1.5G simulated solar spectrum. The current and voltage was measured and controlled using a Keithley 2400 source meter. Temperature in the solar simulator was not regulated, but did not exceed 35 ^{o}C.

Light soaking was carried out at ~1 sun equivalent illumination provided by white LEDs. The output spectrum of the LEDs is given in the supporting information (figure S9). "One sun equivalent" was determined at the start of the experiment by adjusting the output power of the LEDs to give the same cell photocurrent as measured under the solar simulator. Stability of LED illumination was checked by comparing the photocurrent under LED illumination with that using the calibrated solar simulator described in the previous paragraph. The LEDs provide no UV illumination, thus the photostability results are roughly equivalent to 1 sun outdoor illumination with a UV blocking layer. The important point is that the number of photons absorbed by the dye, per unit time, is approximately the same under the solar simulator and light soaking device. In the light soaking device, the cells were kept at open circuit, with the substrate electrode side facing the LEDs. The cells were maintained at ~20 °C using a water cooled metal block.

The initial efficiency in the data that follows corresponds to the *JV* parameters measured within one day of fabrication, before any light soaking. During light soaking, the cells were removed approximately every 5 days for *JV* characterisation with the solar simulator. The *JV* was performed within a few minutes after removal from the light soaking. Prior to each *J-V* measurement, the J_{SC} stability was monitored for 10 seconds. Cells with J_{SC} that drifted significantly during 10 seconds were discarded from the experiment. Each *JV* was measured cyclically starting from 0 V going to +1 V then -1 V and return, with a moderate scan rate of 0.08 Vs^{-1}. Further discussion regarding the requirement for standardised *JV* measurements is given in the Supporting information. In most cases, EIS, transient and charge extraction measurements were performed after *JV* characterisation. The total time out of the light soaker amounted to ~1.5 hours, every 5 days.

Electrochemical impedance spectroscopy (EIS) was measured using an Ivium CompactStat potentiostat. EIS spectra were measured at ~1 Sun (white LEDs) and V_{OC} (~0.8 V). The amplitude of the AC perturbation was 10 mV. The frequency of the AC perturbation ranged from 100 kHz to 0.1 Hz. A standard DSSC equivalent circuit was used to fit the EIS spectrum.[21–24] Further discussion of the equivalent circuit is given in the Supporting Information.

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Charge extraction from short circuit measurements were made by setting the cell to short circuit, reaching a steady state under illumination, then switching off the illumination using a fast solid state switch. The subsequent current decay in the dark is integrated to estimate of the quantity of charge stored within the cell under short circuit conditions.[18,25,26] A series of light intensities ranging from 0.1 - 2 Suns was provided using white LEDs. Steady state J_{SC} vs light intensity was also recorded over the same intensity range.

The above stability experiment was started with 6 ACN cells and 4 MPN cells. After light soaking for 322 h and 254 h, respectively, two cells (ACN3 and ACN4) were intentionally removed from light soaking to test cell regeneration in the dark.   Other than *JV* and transient characterisation, performed as above, about every 5 days, these two cells were kept at open circuit in the dark at room temperature. At a point near 350 h, the water cooling system for the light soaking system failed. Due to this, all the remaining 8 cells were subjected to light soaking at ~60 °C for ~12 h. These particular cells were not designed to withstand heating, and several of the cells leaked during or after the accidental heating. Cells which visibly leaked were removed from the experiment.   Three ACN and three MPN cells survived the heating episode.

More recently, an automated maximum power point (MPP) tracking device has been designed and constructed in house. The MPP tracking device is capable of measuring and applying a different MPP voltage to 8 different cells. Illumination is provided by the same LEDs used in the V_{OC} light soaking.   In the MPP system the voltage on each cell is adjusted every hour to keep the cell at the MPP.   Every four hours a *JV* is taken of each cell, after which the cell is returned to the MPP voltage. Eight new cobalt cells have been started on the MPP stability test. This test has been carried out with only fan cooling. The temperature of each cell has been measured to be between 30 and 32 °C.   The experiment has been carried out for ~300 hours at this point.

Results and discussion

Figure 1 shows the evolution of performance parameters for three of the most stable cobalt electrolyte DSSCs, light soaked at ~1 Sun equivalent (20 °C and open circuit). Data for additional cells are shown in figure S1, supporting information. Two of the best cells contain the ACN electrolyte and one the MPN electrolyte (see experimental section). Overall, after 2000 h of light soaking, the efficiency of the ACN cells decreased by 34 %, and the efficiency of the MPN cell decreased by 10 %.   An early decrease in the fill-factor (FF) caused most of the decrease in overall efficiency, followed, in the ACN cells, by a slow decline in the photocurrent. The open-circuit potential (V_{OC}) was completely stable for all cells. During most of the experiment the cells were actively cooled to 20 °C, however there was a brief cooling failure at about ~300 h light soaking. This resulted in the cells temporarily being heated to ~60 °C for ~12 h while light soaking at ~1 Sun. Although some of the cells were lost due to leakage of electrolyte during the hot period, the heating apparently did not accelerate degradation for those that did not leak.
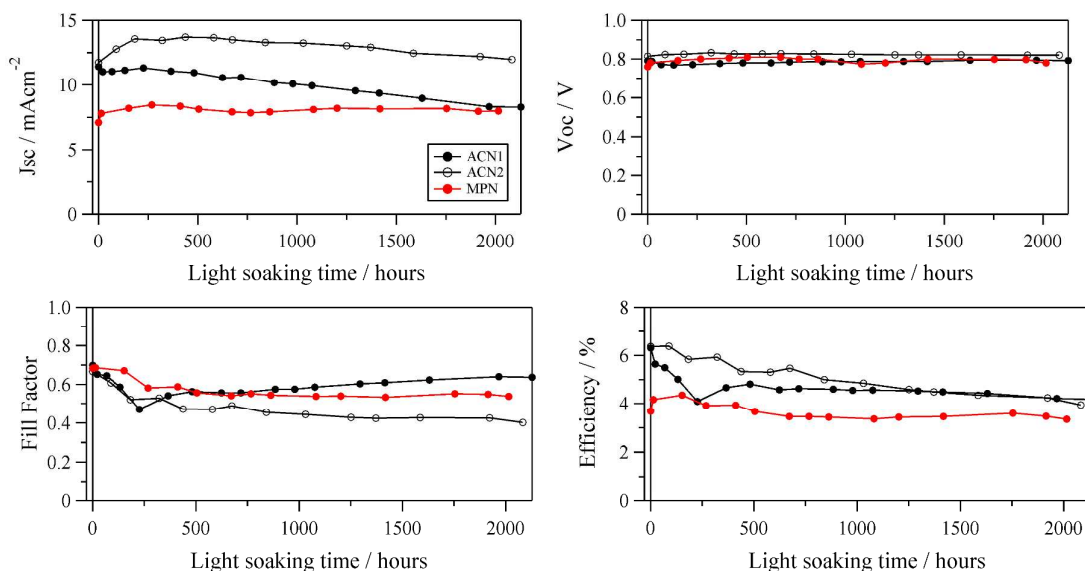
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Figure 1. Performance parameters of cells subjected to 2000 h continuous light soaking at 1 Sun equivalent (LED illumination) and 20 °C.　Electrolyte compositions ACN and MPN are given in the experimental. *JV* parameters measured under AM1.5 illumination from a solar simulator.
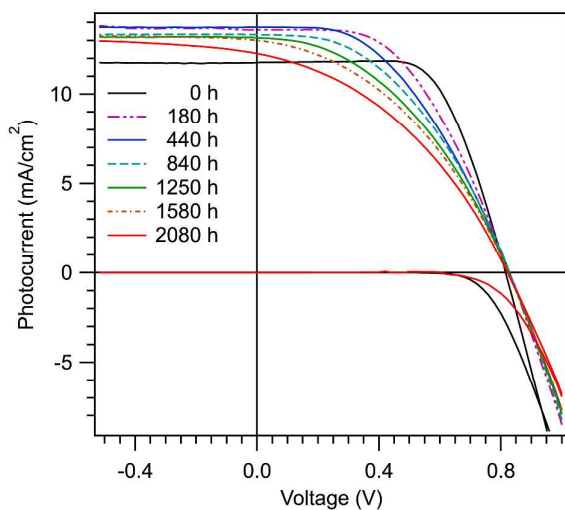

Figure 2. Evolution of the photocurrent vs voltage during continuous illumination at 1 sun equivalent for cell ACN2. Electrolyte composition given in experimental.

Figure 2 shows the evolution of the *JV* of cell ACN2 during 2000 h of light soaking. Initially there was a rapid increase in photocurrent, accompanied by an increase in series resistance. After ~200 hours the photocurrent stabilised and there was a slow degradation of fill factor.　The decrease in fill factor was caused by further increases in the series resistance and worsening ideality (curvature) of the *JV*. After 2000 hours, the J_{SC} decreased ~10% from the maximum value, but the reverse bias plateau photocurrent decreased only 5%. This latter is important in that is shows that photocurrent generation was virtually unchanged. No shunting is observed in the initial or final dark current curves, thus the low fill factor is caused by changes in the way recombination losses increase as a function of increasing potential. We return to this issue further below.

The above measurements under illumination at V_{OC} do not test the stability of the counter electrode (CE) to electrical bias and current flow because no current flows through the CE. We specifically excluded current flow through the CE because we wished to examine the electrolyte stability. However,

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because changes in the counter electrode can effect the series resistance and fill factor, we have examined another set of cells held at the maximum power point (MPP). The cells tested were identical to those in fig. 1 except that in this experiment we included cells with different initial Co(III) concentrations. Figure 3a shows typical JV results after 1000 hours of 1 sun equivalent illumination. The temperature of the cells was ~30 °C in this case. First, the results indicate that the stability of the cell with 0.04 M Co(III) was no worse at the MPP than it was at Voc (fig. 2).   This indicates that the counter electrode is not unstable to current flow. Second, the cell with the highest initial Co(III) concentration was the most stable, and there is a correlation between stability and Co(III) concentration.
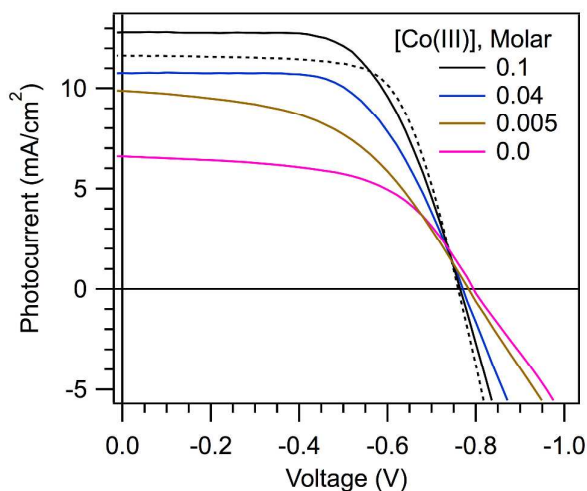

Figure 3.   Final *JV*s of cells held at the maximum power point for 1000 hours of 1 sun equivalent illumination. Electrolytes identical to fig. 1 except for varying [Co(III)].   Final JVs have been normalised for the differences in the initial 1 sun JV for each cell (<10%). Dotted line is the initial *JV* of the 0.1 M Co(III) cell, to which the others were normalised.

We also tested the ability of the continuously light soaked ACN cells to recover from the early decrease in FF when placed in the dark. Cells ACN3 and ACN4 were removed from the light at 322 h and 254 h, respectively. The cells were thereafter kept in the dark (~21 °C, open-circuit) except to measure the *JV*. Figure 4 shows the parameter evolution of these cells. (Note these cells were not subjected to the brief heating mentioned above.)   In the dark, the FF did improve somewhat, however the J_{SC} gradually decreased. Overall, the efficiency was stable in the dark, thus did not return to the value measured before light soaking.
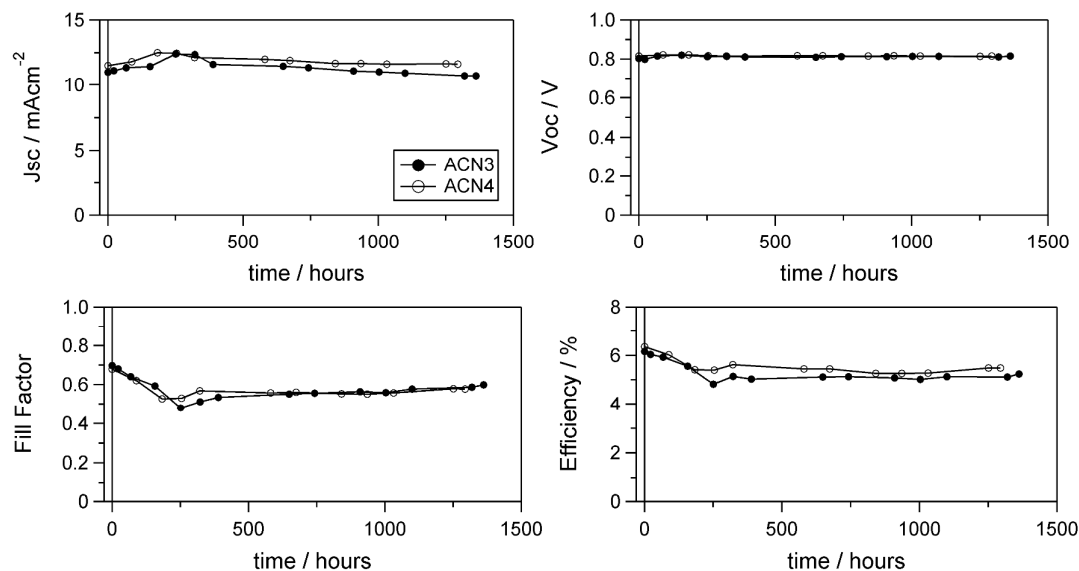
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Figure 4. Performance parameters of ACN cells first light soaked then placed in the dark. Cells ACN3 and ACN4 were initially light soaked at 1 Sun for 322 h and 254 h, respectively. From these points, the cells were kept in the dark (21 °C, open-circuit).

Electrochemical impedance spectroscopy (EIS) was used to examine the light soaked ACN cells. Analysis details given in supporting information figures S2-4 (supporting information). From the EIS we extracted the counter electrode charge transfer resistance (R_{CE}) and the Nernst diffusion resistance (R_D) of the electrolyte. R_D is inversely related to the ionic conductivity. For cell ACN2, after an initial 35% increase in R_{CE} in the first 90 hours, R_{ce} remained constant for the rest of the experiment (Table S1). On the other hand R_D increased continuously through the experiment, similar to the decreasing trend in FF. Figure 5 shows the correlation between the diffusion resistance and the FF of the cells, over time. The strong correlation indicates that changes in the electrolyte are connected to the degradation in the fill factor seen under illumination. An alternative explanation, that the decreased fill factor in figures 1-4 is related to increased recombination, can be ruled out. The charge transfer resistance of the TiO_2 electrode increased steadily during illumination (Table S1, supporting information). This corresponds to a decreasing recombination rate constant with illumination time. Small amplitude photovoltage transients also confirmed a decreasing recombination rate constant with time (Figure S5).

An increase in the measured diffusion resistance could be caused by a decrease in the concentration of the ions, an increase in the electrolyte viscosity, or blockage of the porosity of the TiO_2. In previous publications, an increase in R_D with light soaking was observed for iodine based DSSCs. A decrease in the triiodide concentration was found to be correlated with the increasing R_D.[27] We note, however, that in Figure 2 the increase in series resistance is by itself not sufficient to explain the loss of fill factor. A series resistance correction, applied to the last *JV* in Figure 2 recovers less that a third of the lost fill factor.
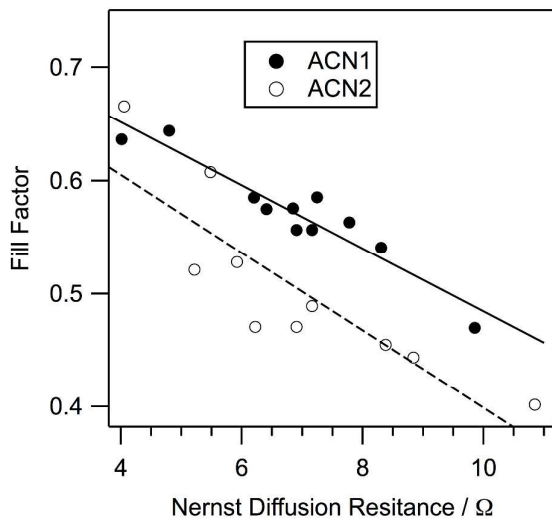
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Figure 5. Correlation of light soaking induced changes in the electrolyte diffusion resistance (R_D), from EIS, with changes in the cell fill factor (FF) from the *JV*.   Lines are linear fits.
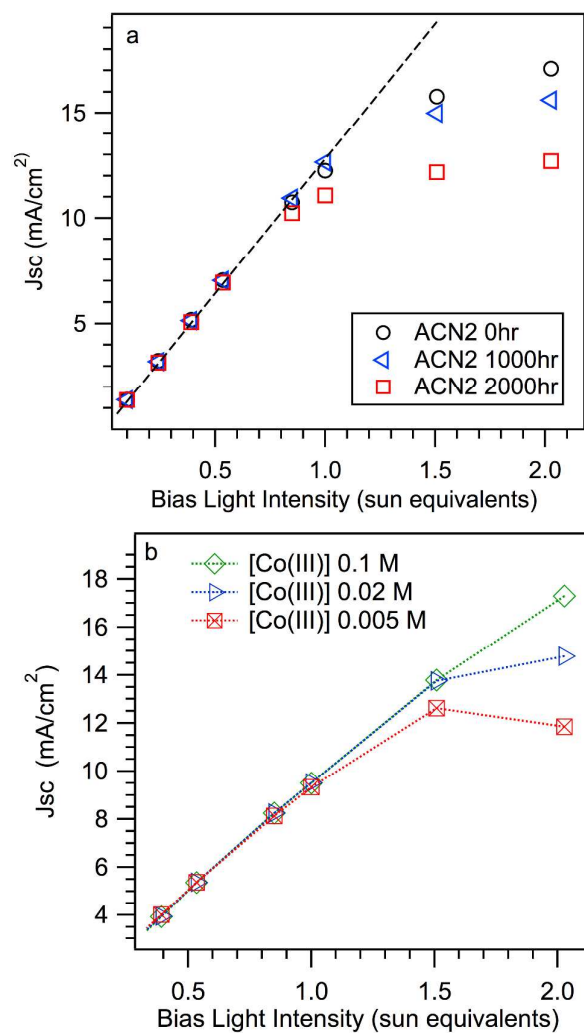
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Figure 6. a) Evolution of J_{SC} vs. light intensity with illumination time for cell ACN2 (0.04 M Co(III)). b) J_{SC} vs light intensity for different Co(III) concentrations. Data in b) have been normalised at 0.5 suns (normalisation coefficients ≤7%). Illumination from white LEDs.
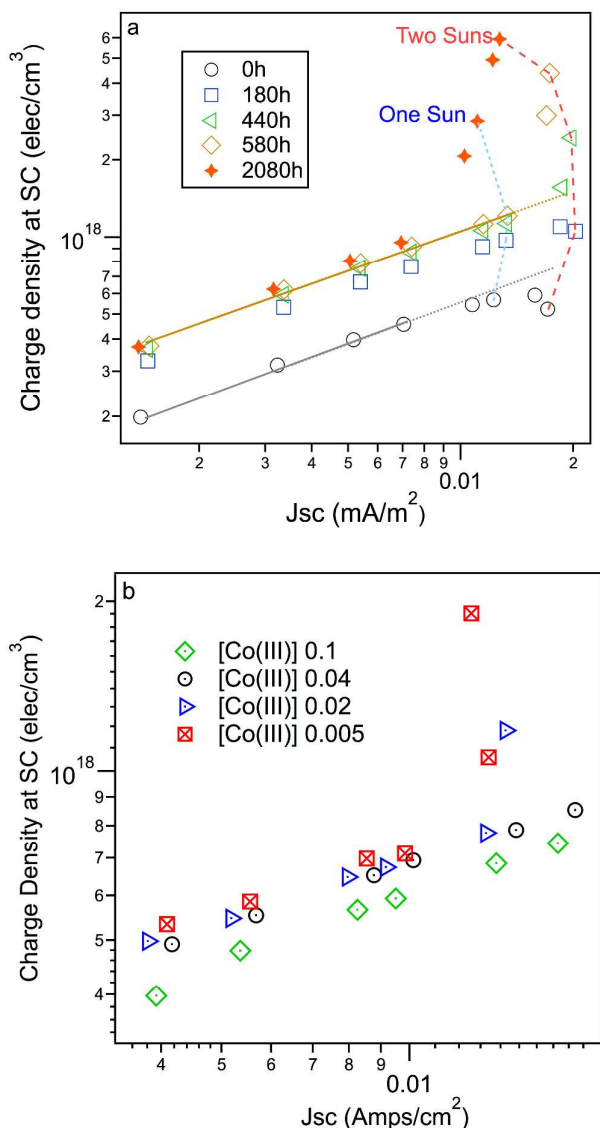
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Figure 7. a) Charge density in the TiO_2 vs. the J_{SC} for cell ACN2 during 2000h light soaking. Charge was measured by charge extraction from short circuit. J_{SC} was varied using light intensities from ~0.1 Sun to ~2 Sun.   b) Charge density in the TiO_2 vs J_{SC} for cells with varying Co(III) concentration.

We use photocurrent linearity and charge density at short circuit data to further examine the connection between the degradation of the FF and changes in the electrolyte. Figure 6a shows the J_{SC} vs light intensity data for cell ACN2. Initially the cell shows linear J_{SC} vs intensity up to one sun and sub-linear J_{SC} vs intensity above one sun. For all intensities ≤0.5 Sun equivalents the J_{SC} remained constant with light soaking.   However, at and above one sun, the J_{SC} decreased with light soaking time, becoming increasingly sub-linear. The "roll off" in photocurrent at high light, after 2000 h light soaking, is consistent with a diffusion limitation in one or more of the electrolyte species. Figure 6b shows the J_{SC} vs light intensity data for 3 cells with varying concentration of Co(III) in the electrolyte. Low concentrations of Co(III) give a sub-linear photocurrent above 1 sun, similar to the ACN2 cell after light soaking.

Figure 7a shows the density of excess electrons in the TiO_2 at short circuit vs the J_{SC}. Figure 7b shows the same data for the cells with different Co(III) concentrations. Below one sun the relationship follows a power law (straight line on log/log plot) with slope ~0.45.   This is similar to that observed in iodine/iodide cells.[28]   In figure 7b, at and above one sun there is a trend to higher charge with lower

Co(III) concentration. This trend is similar to that with exposure time in figure 7a, after 180h. The increase in charge with increasing J_{SC} in figure 7b is explained by the following logic. When the concentration of Co(III) decreases, the maximum diffusion current that can be carried across the electrolyte by Co(III) decreases. When the photocurrent produced by the TiO_2 reaches this maximum current, the concentration gradient of Co(III) to the counter electrode reaches it's maximum value. When the light level is increased further, the flux of electrons injected into the TiO_2 increases, but no more can escape through the counter electrode. Thus the concentration of electrons in the TiO_2 builds up until the resulting recombination flux balances the increased injection. The lower the concentration of Co(III) the higher the charge build up becomes, because the recombination, which goes to Co(III), is inherently slower with lower Co(III) . This causes the trend seen in figure 7b. Under this scenario, the charge vs J_{SC} trend turns vertical after a given J_{SC}, because the J_{SC} cannot increase. The data in figure 7a at long times show the same basic trend as low Co(III) concentrations in figure 7b. A similar connection between the Co(III) concentration series and the illumination time series can be seen comparing the cells current-interrupt voltages (figure S6, supporting information).

The data in figure 7 show that the "roll off" in photocurrent in figure 6a is related to a reduction in the Co(III) diffusion current after light soaking. However, the charge in figure 7a, at longer times does not turn vertical at high J_{SC} as it does for low Co(III). This implies the source of the low Co(III) diffusion current after illumination may not be simply a change in concentration but includes changes in mobility as well. For completeness, we can rule out another possibility, that the "roll off" in photocurrent in figure 6a is due to insufficient Co(II). A limitation based on low concentration of Co(II) (donor) would give a quite different pattern in charge vs J_{SC}. Low levels of donor in DSSCs cause reduction in regeneration rate constant, leading to increased electron recombination with the photooxidised dye. This recombination reduces the collection efficiency at J_{SC}, causing a charge vs J_{SC} curve that turns down at high light, rather than up as in figure 7. The trend caused by low donor concentration can be seen in iodide based cells made with intentionally low concentrations of iodide (Figure S8, Supporting information).)[31] (Surprisingly, at 0 hours illumination, the cell in figure 7a shows charge at J_{SC} that does decrease with J_{SC} above 1 sun. This trend is seen in some of our cobalt cells, before light soaking, but not others. It is presumably associated with poor regeneration that improves after light soaking, however as it is not present in all cells we will forebear any hypothesising about this issue.)

Figure 7a and b also show one other notable trend. At low J_{SC} (low light level), both the illuminated cells, after 180 hours, and cells with low Co(III) show higher charge for a given J_{SC}. At lower J_{SC}, Co(III) diffusion limitations will in principle not play a role. Part of this trend can be related to the presence of Li^+ in the electrolyte. When the cell is held at V_{OC}, Li^+ can adsorb on and/or intercalate into TiO_2 which creates additional electron traps and thus causes the higher charge density.[29,30] This trend is known to be reversible with time in the dark, and in fact does reverse during the dark storage of cells ACN3 and ACN4 (figure S7).

We have shown so far that there is a correlation between the degradation of the fill factor with illumination time, and a decreasing concentration of Co(III) or decreasing ability of Co(III) to move through the cell. It is unlikely that a simple reduction in the Co(III) concentration would cause the large loss in fill factor seen. The *JV*'s of the intentionally low cobalt cells show, on average, less than a 5% decrease in FF relative to the controls. The trends in FF, and figure 7a could be caused by a degradation in the ability of the Co(III) to diffuse out of the pores. This would increase the local concentration of Co(III) in the pores, at J_{SC}, causing increased recombination losses across the *JV* as seen. There are certainly other possible explanations, such as photochemical ligand replacement on the cobalt and the development of electrolyte concentration gradients laterally across the cell. Our most recent data indicate that the downward trends in figure 3a can be reversed by using intermittent rather than continuous illumination, supporting the hypothesis that diffusion issues are the main cause of the degradation observed in figures 1-4.

Conclusions

In summary, we have demonstrated that DSSCs using cobalt bipyridyl redox couples can show promising stability under one sun equivalent illumination at V_{OC} and MPP. It is important to note that the stability we refer to is not mechanical stability. The mechanical stability of these cells above 40 C was not good. What we have shown however, is that it is possible for cobalt electrolyte cells to show

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promising photostability under continuous illumination without UV. This has not been demonstrated previously. These stability tests have been made on "current literature" cobalt DSSCs, not yet optimised to improve the stability of the electrolyte components. Our characterisation data is consistent with a decrease in Co(III) concentration or diffusion with light soaking. Extrapolating from our current results, we predict that cobalt electrolytes can be improved to be at least as stable as iodine/iodide electrolytes and thus may be suitable for replacing iodide/iodine in commercial DSSCs in the future. A requirement for operation under 1 sun outdoor illumination will be a lower volatility electrolyte which is capable of dissolving sufficiently high concentrations of some cobalt(III) complex, and that does not sacrifice too much in viscosity.

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