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From identification of electrolyte degradation rates to lifetime estimations in dye solar cells with iodine and cobalt redox couples

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ABSTRACT

Degradation of dye solar cells is a major obstacle in their commercialization. Here we look into how much information on the degradation routes and rates one can extract from accessible measurements. Specifically we focus on tracking the color of the cell since all the main components of a dye solar cell have a specific color, and their color changes with degradation. Furthermore we look into extracting the degradation coefficients based on the specific color changes. One of the most vulnerable components of a dye solar cell is the electrolyte. Here we investigate the effect of two most interesting electrolyte compositions: 1) conventional iodine based electrolyte, which to date dominates the stability records of dye solar cells, and 2) cobalt complex electrolyte, which enables record high efficiencies. UV light is known to be highly detrimental as it destroys charge carriers – typically, a UV filter is recommended, but is it enough to prevent the loss of charge carriers? Here expectedly applying a UV filter improved the performance as the cells without a filter had only 4 ± 1 % of the initial efficiency left after a 1,000 hour light soaking test, whereas those with a filter maintained 90 ± 20 % of their initial efficiency. Applying a UV filter only hindered the loss of the charge carriers, but did not eliminate their degradation. From the color changes of the electrolyte, we could identify the degradation coefficient for these electrolytes. This analysis resulted in a highly relevant discovery: the loss rate of the charge carriers in iodine electrolyte was approximately double compared to cobalt electrolyte. Furthermore we could provide indicative estimates of future lifetimes of cells, which could be highly important in improving the lifetime of dye solar cells.

I. INTRODUCTION

Third generation photovoltaics, such as dye solar cells, have a limited lifetime, and it is one of the key factors hindering their large-scale commercialization. Despite the urgency to develop this research area, the number of stability studies is marginal compared to those aiming to improve their already-high efficiency. The field of stability research is complex since the cells are composed of multiple materials, and during aging, there are often various changes overlapping, interrelated and/or masked by one another. Another problematic factor is the length of stability studies. Stability tests beyond 1,000 h (in terms of illumination this corresponds to one year outdoor light exposure in Northern Europe [1]) are rare; there is one significant report indicating over 25,000 h of stability for glass based DSC under visible light [2]. However the energy payback time (i.e., the time in which the cell has produced as much energy than was needed for its manufacturing) of these devices is about one year [3], therefore to have a positive impact on sustainable development, it is crucial to achieve lifetimes far beyond that. From a practical perspective, running

long light soaking tests is problematic – the cells cannot be stacked like in humidity or temperature tests – so one needs to carefully consider the length of the test. Many aging tests are stopped at 1,000 h – like this one – and an important question is how much longer would the cells have survived? Here we take the first step towards lifetime prediction by identifying the degradation coefficient of one component: the electrolyte. The long-term vision is that the performance of the solar cells could at least be partly predicted based on visual changes in the main components. Many components, such as electrolyte, have a distinct color so changes in that usually relate with degradation (i.e., loss of charge carriers).

The electrolyte has been identified as one of the major causes for cell degradation [4,5]. We focus on two most interesting electrolytes for dye solar cells: the conventional iodine based electrolyte and cobalt complex electrolyte. The conventional redox mediator for DSCs is triiodide/iodide, and the best lifetimes have been gained with this redox couple [4,5]. The electrolyte with tri-iodide/iodide redox couple (hereafter referred as iodine electrolyte) does

not, however, have an optimal redox potential which causes some losses in the maximum voltage and consequently in the efficiency of the cells. Furthermore iodine is highly corrosive, making the use of metallic electrodes in DSCs difficult [6]. These reasons have motivated the investigation of alternative redox mediators for DSCs. Due to their more optimal redox potential, cobalt complexes have reached high efficiencies [7] as well as being less corrosive [8,9], thus being interesting alternatives. Another advantage of the electrolytes with cobalt complexes (hereafter referred as cobalt electrolyte) is their transparency: cobalt electrolytes do not absorb much light. The stability of the cobalt complex electrolyte has traditionally been an issue [7-9], but recently the optimization of the electrolyte composition has shown some promising results [10-13]. Overall the number of studies investigating the stability of these devices is negligible compared to the amount of reports looking at initial performance.

The electrolyte is most vulnerable to UV light [4-5]. Since no UV filter is perfect, the effects of the filter must be considered. The studies reporting good stability in the case of cobalt electrolyte had light sources without UV or a UV-cutoff filter was used [10,13] or the light source or the presence of the possible UV filter has not been specified [11-12]. In studies reporting the degradation of cobalt cells, there was some UV (20 % UV compared to AM1.5G) [8-9] or the amount of UV light has not been mentioned [7]. In the case of iodine electrolytes, it has been discovered that UV light accelerates the degradation of the DSCs [14]. It is likely that UV light is detrimental to cobalt cells as well, but based on the current literature, this is unclear and is thus another interesting subtheme of this work.

Here we show that substantial indicative information can be extracted, including numerical estimations of the expected lifetime, based on accessible measurement techniques, such as photographic analysis. These estimations are not an absolute proof of the future lifetime, but they can be powerful in guiding the next steps of development. Our approach is a massive improvement on the state-of-the-art, where future predictions are just based on linear extrapolations of changes in the overall efficiency. The problem lies in that the main degradation reactions, such as the loss of charge carriers, have non-linear effects on the efficiency and hence linear extrapolations are completely inadequate. For instance, the loss of charge carriers will not reduce the performance before a certain threshold is reached, for example the limiting current density. In fact, the performance may even improve to some extent initially as with fewer charge carriers there is less current leakage from the photoelectrode to the electrolyte.

II. EXPERIMENTAL

Cell assembly.

Fluorine-doped tin oxide (FTO) glass (TEC-15,

Pilkington) was used as both the counter electrode and photoelectrode substrates. The substrates were cleaned with mild detergent, ethanol and acetone (in this order). Directly before preparation of the electrodes, the substrates were placed into a UV chamber (UV/Ozone ProCleaner™, Bioforce nanosciences) for 20 minutes. The counter electrode substrates had two small holes for electrolyte injection. The photoelectrode substrates used in the aging tests also had an atomic layer deposited (ALD) 50 nm thick layer of TiO₂. The ALD layer was used to reduce the leakage current from the substrate to the electrolyte, which is an issue particularly in cobalt cells.

A TiCl₄ treatment was given to the photoelectrode substrates: they were placed in a solution of titanium (IV) chloride tetrahydrofuran complex (1 wt-%) in distilled water and heated to 70 °C for 30 minutes [15]. The TiO₂ photoelectrodes were printed with a screen printer (AT-60PD, ATMA). For the iodine cells used in the aging tests, three layers of TiO₂ were printed: two layers with small TiO₂ particles (Dyesol DSL 18NR-T) and one mixed layer that had both small and large, light scattering particles (Dyesol 18NR-AO). The cobalt cells had only one layer of both. The layer was left thinner in the cobalt cells to avoid increased electron collection losses because the diffusion length in the photoelectrode is generally shorter in cobalt complex cells than in iodine cells [9]. The area of the printed layers was 40 mm². After all the layers were printed, the photoelectrodes were sintered at 450 °C for 30 minutes. After this, the photoelectrodes were given another TiCl₄ treatment and then sintered again. The photoelectrodes were dyed by placing them in a dye RuLL(NCS)₂ (L=2,2'-bipyridyl-4,4'-dicarboxylic acid; L'=4,4'-dinonyl-2,2'-bipyridine) (Z907, Dyesol) in a 1:1 mixture of acetonitrile (l) and tert-butanol (TBA) solution for about 12 hours.

The counter electrodes were made by spreading 4 μl of 5 mM H₂PtCl₆ in 2-propanol evenly on the substrate. After the platinum solution had dried, the counter electrodes were placed in an oven heated to 390 °C for 15 minutes.

The cobalt electrolyte was made with 0.2 M [Co(bipy)₃](PF₆)₂, 0.04 M [Co(bipy)₃](PF₆)₃, 0.5 M 4-tert-butylpyridine (TBP, Sigma-Aldrich) and 0.1 M LiClO₄ (Sigma-Aldrich) with acetonitrile (l, Sigma-Aldrich) as solvent. The cobalt complex was synthesized according to literature [16]. The iodine electrolyte used was made with 0.1 M of iodine (Merck), 0.5 M of 1-methylbenzimidazole (Sigma-Aldrich), 0.5 M 1-propyl-3-methylimidazolium iodide and 0.1 M guanidinium thiocyanate (Sigma-Aldrich) with purified 3-methoxypropionitrile as solvent. After the photoelectrodes and counter electrodes were prepared, they were attached to each other and sealed by melting Surlyn® 1702 ionomer resin film (20 μm thickness, DuPont) with a press heated to 120 °C. Next the electrolyte was added to the cooled cell through the holes in the counter electrode

with a pipette. The holes were sealed with a Surlyn® cover foil and a microscope glass. After the cell was sealed, copper tapes were added to the edges of the substrates to serve as current collectors and some silver paint (SCP, Electrolube) was spread on the copper tape and conductive side of the substrate to improve the contact. Finally some epoxy glue was added on the contacts and between the substrates to improve their mechanical durability.

The cells had a blank area next to the photoelectrode that allowed investigation of the electrolyte color. This setup is non-optimal for highest performance, but here the focus was in the understanding of the aging phenomena and particularly tracking the electrolyte color using in-situ methods, so the cell setup needed to be configured for that purpose.

Measurements

Initial and final characterization

The cells were measured thoroughly twice: once initially after the assembly and once after the 1000 hours aging. The initial and final measurements consisted of the following measurements: IV measurements were performed using a solar simulator with halogen lamps (Philips type 13117). The measurement conditions were adjusted to correspond to conditions of 1 Sun at 25 °C. The cells were covered with a black tape mask with a 1 mm larger aperture compared to the dyed TiO₂ layer. The data was collected using a Keithley 2420 3A Sourcemeter.

The IV data as a function of light intensity was measured with a Peccell PEC L-01 solar simulator, which used xenon lamps. The cells were placed on a temperature controlled plate set at 20 °C. The light intensity was varied by changing the distance between the light source and the cells, and by adding spectrally neutral filters to change the incident light intensity.

The Incident Photon to Collected Electron efficiency (IPCE) of the cells was measured with QE/IPCE Measurement system QEX7 (PV Measurement, Inc.). The studied wavelength ranged from 300 nm to 1000 nm with 2 nm intervals without a bias light.

The electrochemical impedance spectroscopy (EIS) was recorded using Zahner Zennium device. EIS measurements were made under illumination using the solar simulator at opencircuit conditions. The frequency range was from 0.1 Hz to 100 kHz and the amplitude 10 mV. The resistance of the different cell components were determined by fitting EIS data using Zview2 (Scribner Associates, Inc.) software and using equivalent circuit model presented in the literature [17].

The aging procedure and characterization during aging

The cells were aged using the same type of halogen lamps as in the solar simulator. These halogen lamps produce approximately 20 % of the UV and 100 % visible light compared to an AM1.5G spectrum. A part of the cells was equipped with a 400 nm cut-off UV filter (Asmetec GmbH) so that the effect of the

UV light could be investigated. The temperature in the aging measurement was approximately 40 °C. The performance of the cells during the aging was recorded using an in-house system, which consists of an Agilent 34980A Multifunction Switch/Measure Unit and a BioLogic SP-150 potentiostat. During the aging, IV curves and open-circuit EIS were measured repeatedly. These EIS measurements were performed with the same settings as the Zahner EIS measurements. The cells were removed from the aging unit for the weekends, during which the weekly measurements were performed. EIS in the dark over the voltage range from 0 V to 0.7 V in 0.1 V intervals were performed weekly with Zahner Zennium potentiostat. The stability test lasted for 1,000 h real-time, but the cells were in light soaking for total of 800 h because they were taken out for more detailed measurements typically once a week.

The electrolyte color was quantitatively tracked with a camera system followed by image processing [18]. The photographs were taken with Olympus E-620 camera. The basic settings in the photographing were aperture f/8.0, sensitivity ISO100, and shutter speed 1/15 s. A color checker passport was used to set the white balance for each measurement time. The color palette in the passport was used to create a color shade profile in the program Adobe Lightroom 3, where the profile was attached to the images and the format was changed from RAW to JPEG. The red, green, and blue pixels (RGB) values of the electrolyte were then analyzed and plotted with MatLab®. The pictures were taken in a dark room, and the photographing setup was covered from all sides with blackout canvas. The cells were illuminated by four LED lights equipped with light scattering films to get even lighting. The color was analyzed from a small area in the electrolyte, and for each of the individual cells, the analyzed area was approximately the same for each of the weekly measurements.

LC-MS measurements

To investigate the significance of the dye degradation versus the electrolyte degradation, we carried out liquid chromatography – mass spectrometry (LC-MS) measurements. The dye was extracted and the results analyzed from the cells according to a previously published procedure [19]. The cobalt electrolyte was rinsed from the cells using the electrolyte solvent acetonitrile. A total of nine cells were analyzed: two that contained iodine electrolyte and had not been exposed to UV light, two that contained iodine electrolyte and had been exposed to UV light, two that contained cobalt electrolyte and had not been exposed to UV light, and three that contained cobalt electrolyte and had been exposed to UV light.

III. RESULTS AND DISCUSSION

Current-voltage characteristics of the cells

The cells were exposed to a 1,000-hour aging test

under illumination (1 Sun visible light intensity and 0.2 Sun UV light intensity) with or without a UV filter. Here we start the investigation with the changes of the basic photovoltaic characteristics by looking at the average IV properties and their standard deviation for the initial and aged iodine and cobalt cells, which are listed in Table 1 and examples shown in Figure 1. Importantly, the cells were designed for stability studies, which meant leaving excess area around the cells to observe the changes in the electrolyte color – this geometry does reduce the efficiency.

The evolution of the different cell properties during aging shows that there is some oscillation in the results (Figure 1). This is caused by the weekly measurements during which the cells are mostly in dark and lower temperature (20 °C) conditions, and this appears to regenerate for instance V_{oc} by some tens of millivolts (Figure 1). In all the cells, I_{sc} improved for the first 100 hours before stabilizing. After the stabilization, I_{sc} remained constant for all the UV protected cells. In the cells without the UV filter, I_{sc} decreased soon after the stabilization in the cobalt cells and later on (around 500 h) in the iodine cells.

Table 1 Mean values and their standard deviation for basic photovoltaic characteristics of the studied cells. Mainly I_{sc} and FF result in the changes in final η . UV filter does slow down degradation, but it does not fully prevent changes in the cells.

Electrolyte	Measurement	Number of samples	I_{sc} [mA/cm ²]	V_{oc} [mV]	FF [%]	R_{cell} [Ω]	η [%]
Iodine	Initial	9	8.7 ± 1.1	692 ± 13	59 ± 6	38 ± 8	3.5 ± 0.4
	no UV filter	6	9.4 ± 1.3	634 ± 12	42 ± 7	70 ± 12	2.5 ± 0.4
	with UV filter	3	12.3 ± 1.7	664 ± 9	52 ± 8	45 ± 18	4.2 ± 0.5
Cobalt	Initial	10	6.3 ± 0.9	723 ± 12	67 ± 5	47 ± 9	3.1 ± 0.5
	no UV filter	4	1.5 ± 0.3	656 ± 16	11 ± 1	-	0.11 ± 0.03
	with UV filter	6	8.7 ± 0.5	748 ± 14	42 ± 7	104 ± 30	2.7 ± 0.5

Table 1 and Figure 1 show that while the iodine cells without the UV filter were somewhat degraded, the cells with the UV filter had even a higher efficiency after the aging than before. In the case of cobalt cells, the difference in the performance after aging is much greater: the cells with the UV blocking layer retained on 90 ± 20% of their initial efficiency (η) while the cells under UV light had only 4 ± 1% of initial performance (Table 1). Even if the overall efficiency of the UV protected cobalt cells remains quite stable, the individual photovoltaic performance components show variation: in particular there is a significant drop of fill factor (FF), on average 15 percent units, and a marked increase of short circuit current density (I_{sc}), on average 2.4 mA/cm² (Table 1).

Electrochemical impedance spectroscopy analysis of the series connected resistances

In the previous section, we observed FF to decrease significantly during aging, in particular in the cobalt cells, and for them it could be regarded as one of the main causes for degradation. To investigate the resistances contributing to the total cell resistance R_{cell} , which again affects the FF , EIS measurements were performed under illumination at V_{oc} . From the EIS response, we could analyze which of the internal resistances change during aging. A Nyquist plot showing the typical initial response for both cell types is illustrated in Supporting Information (Figure S2). The calculated average properties of the cells

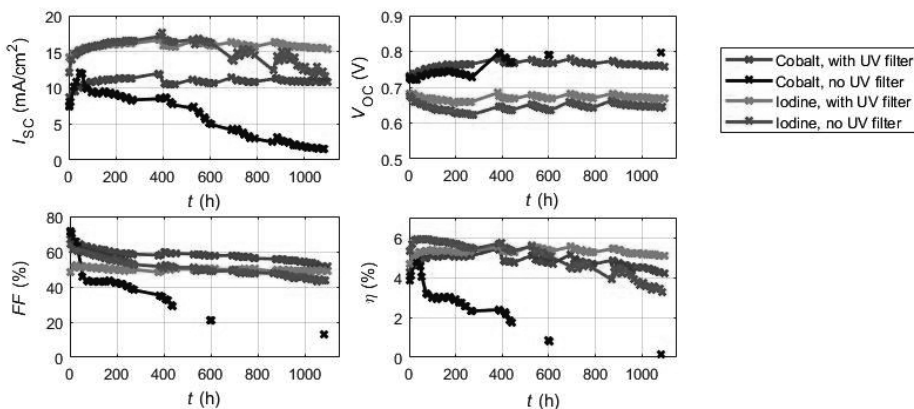


Figure 1 Example data for the development of the short circuit current, open circuit voltage, fill factor and efficiency during the aging in approximately 1 Sun and 40 °C. Data for all cells is shown in Supporting Information. The cells without UV filter experienced degradation to I_{sc} , which in the case of cobalt began after the initial stabilization (100 h) and in the case of iodine cells started later on, around 500 h.

are displayed in a bar plot showing the average and standard deviation of the cell performance (Figure 2).

the electrolyte, since it is known to degrade under illumination whereas the counter electrode catalyst

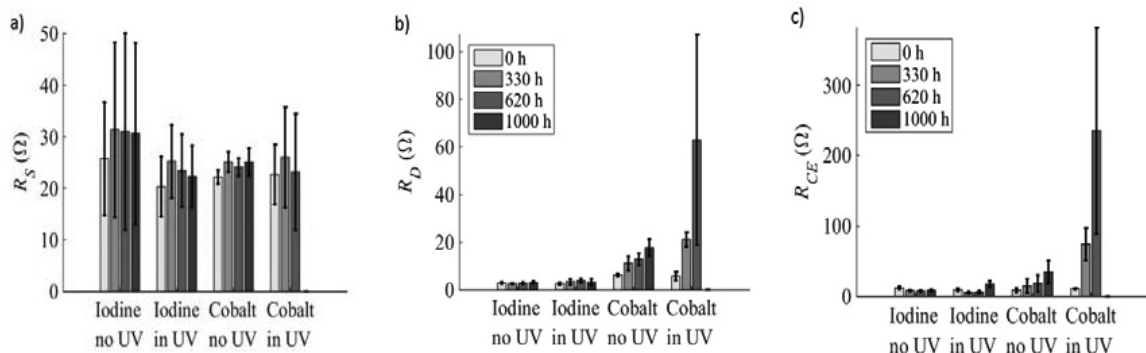


Figure 2 The average resistances and their standard deviations for the cells determined with EIS before and after the aging. a) R_s is the sum of Ohmic series resistances in the components of the cells. b) R_D is the diffusion resistance through the electrolyte. c) R_{CE} is the charge transfer resistance at the electrolyte-counter electrode interface. A dramatic increase of R_D and R_{CE} is seen in the cobalt cells exposed to UV, and the last measurement point (1000 h) is missing as the cells were too degraded to get reliable data.

Figure 2a shows that the series resistance R_s remained approximately constant during aging in all of the different cell groups. However there was some variation initially that remained approximately constant throughout the whole experiment, in particular in the UV protected iodine cells. In practice, such variation most likely originates from differences in handwork needed to make the electrical contacts, but the important result is that there was no significant change to R_s during the aging.

Significant changes can be seen in the diffusion resistance (R_D) and the resistance at the electrolyte – counter electrode interface (R_{CE}) (Figure 2b-c) in the cobalt cells during aging, whilst the iodine cells remain rather stable, in particular when accounting for the statistical variance. For cobalt cells without a UV filter, it can be seen that both R_{CE} and R_D multiplied by an order of magnitude from their initial state to 620 h. At the last measurement point, these unprotected cobalt cells were so degraded that the EIS analysis could no longer be reliably conducted (Figure 2b-c). In the case of the cobalt cells with UV protection, R_{CE} and R_D had more than doubled during the 1,000 h of aging (Figure 2b-c).

The increase of R_D directly points to degradation of the electrolyte, as it is inversely proportional to the charge carrier concentration, and the likely expected reason for the change is the decreased concentration of the redox mediator in the electrolyte (other factors affecting R_D such as cell geometries remain constant). Thus the loss of charge carriers could be evaluated based on R_D : in the cobalt cells without a UV blocking layer, the charge carrier concentration reduced by an order of magnitude, and with the UV layer, it was more than halved.

R_{CE} is affected by two materials, the electrolyte and the catalyst at the counter electrode, and a change at this interface can be caused by either one or both of them. In this case, it is likely that the main cause is

as such has been stable in previous studies [18]. It is likely that the same reason increasing R_D (e.g., loss of charge carriers) results in the degradation of R_{CE} as well.

These EIS results confirm what was seen in the IV measurements in Section 3.1: cobalt electrolyte degraded faster than the iodine electrolyte. In this case, this could mean that the chemical degradation reactions that decrease the amount of the redox mediator are more prevalent in cobalt electrolytes than in iodine electrolytes. Alternatively it is also possible that this difference in degradation rate is caused by the different initial concentration of the redox mediators in the electrolytes and the different concentration that is needed for efficient charge transfer. Also R_D is notably already higher in cobalt cells initially (Figure 2b) compared to the iodine cells, which suggests that cobalt is not as efficient as a redox mediator as iodine – this result is already known from previous literature and to be expected since cobalt complexes are physically bigger and their motion is therefore more sluggish.

EIS measurement gives us information about the possible causes of the degradation – losses are most likely related to decreased charge carrier concentration, and as to be expected, the effect is more pronounced when the UV filter is not used. To get to the most interesting part of predicting the future performance, it is imperative to look more closely at the loss of charge carriers.

Short-circuit current dependence on light intensity

The investigation of EIS results and changes in the internal resistance of the cells suggested that there are losses in the charge carrier concentration. Furthermore there were differences directly in photocurrent as shown in Section 3.1: both the cobalt and iodine cells that had been under UV had lower

I_{SC} compared to the ones protected from the UV. To determine if the photocurrent is limited by the limiting current, I_{SC} was measured as a function of the incident light intensity. The limiting current is the highest current that the cell can reach. A decrease in the limiting current typically indicates a loss of at least one of the redox mediators in the electrolyte. Basically a decrease in the amount of ions in the electrolyte slows down the rate at which electrons can be transported through the electrolyte. The reduction of charge carriers is also relevant to the resistances R_D and R_{CE} investigated in Section 3.2, since that was a likely hypothesis to their increase, particularly in the cobalt cells.

The aged UV protected iodine cells show no change in the limiting current, because the dependence of I_{SC} remains linear for the whole measured intensity region, most importantly to 1 Sun and over (Figure 3a). The aged iodine cells without a UV filter, however, display the limitation of the current: above 0.5 Sun the photocurrent remains approximately constant (Figure 3a). If the limiting current in the unprotected iodine cells is reached at intensity lower than 1 Sun, it indicates that their I_{SC} results in Section 3.1 are affected by loss of charge carriers. Below 0.5 Sun, I_{SC} is similar in both UV protected and UV exposed iodine cells which suggests that there were no other major differences affecting I_{SC} other than the loss of charge carriers in the latter cell group (Figure 3a). This type of measurement is notably good for detecting very large changes, but for more detailed analysis, other methods like IPCE measurements (Section 3.4) are called for.

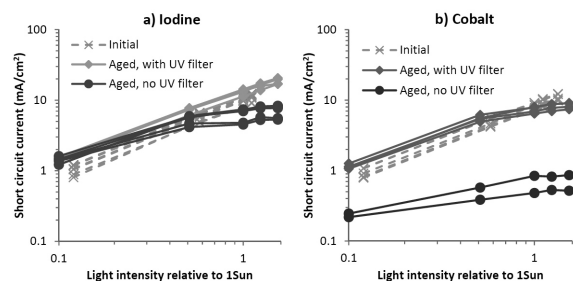


Figure 3 A log-log plot of short circuit current density as a function of the light intensity relative to 1 Sun illumination for a) iodine cells and b) cobalt cells. When I_{SC} stops increasing linearly with light intensity, the current is limited by the amount of charge carriers.

Both for UV exposed and UV protected cobalt cells, the current limitations already arise below 1 Sun light intensity. In the case of UV protected cells, I_{SC} values appeared to plateau right before 1 Sun as an indication of reaching the limiting current. Thus I_{SC} values of the aged UV protected cobalt cells (in Table 1 and Figure 1) were somewhat affected by the limiting current. For UV exposed cobalt cells, the limiting current is almost one order of magnitude lower than initially. I_{SC} of the UV protected and UV illuminated cobalt cells do not match even in the lowest measured light intensities. Therefore some additional degradation mechanisms might have activated in the UV illuminated cobalt cells,

leading us to investigate possible degradation of the photoelectrode as well.

Incident photon to collected electron efficiency

In Section 3.3, the limiting current affected I_{SC} at 1 Sun light intensity after aging in all the cells except for iodine cells protected from UV. The investigation of short circuit current as a function of light intensity clearly showed the very large changes that affect I_{SC} , but other measurements like IPCE are called for the detailed analysis. IPCE was measured at low light intensity and therefore the spectral photocurrent response does not (necessarily) correlate with the I_{SC} results obtained at 1 Sun. In fact, IPCE measurements without bias light were conducted specifically to study the photocurrent generation characteristics of the samples at conditions where I_{SC} is not limited by electrolyte diffusion and the effect of depleted charger carrier thereof. This way other factors (light harvesting, injection, regeneration, and collection efficiencies) affecting photocurrent become visible since the limitation by electrolyte diffusion is relaxed.

Interestingly the IPCE of all the cells improved during aging (Figure 4a,b). One possible reason for this is the initial measurements were performed before the cells had stabilized and reached their maximum performance. This stabilization can also be seen in the photovoltaic measurements (Figure 1) as the increase of I_{SC} during the first, approximately 100 hours, of aging. The IPCE of the UV protected cells improved the most (Figure 4a,b) – or more likely, degraded the least after the improvements during the stabilization period. If the latter is the case, the dye degrades in the cells without the UV filter: average 15 % in iodine cells and 30 % in cobalt cells compared to the cells with a UV filter. LC-MS measurements are carried out in Section 3.6 to investigate the possible changes to the dye to investigate this hypothesis more. The possible dye degradation is significant since the above-mentioned percentages indicate but it is not large enough to dominate the degradation.

In previous sections, the loss of charge carriers is a major factor, and its effects on photocurrent can be evaluated when comparing the IPCE results with the respective I_{SC} measurements (Table 1). When looking at iodine cells, Figure 5 shows that the aged cells fall on the same line with the linear extrapolation of the initial results, indicating that in these cases the charge carrier concentration was high enough that it was not (at least largely) affecting I_{SC} measurements (Table 1). In contrast, the IPCE results of the aged cobalt cells predict much higher I_{SC} (Figure 5) than the measured I_{SC} (e.g., measured I_{SC} of cobalt cells with no UV filter is 80 % smaller compared to that predicted by IPCE), which implies that the reduced I_{SC} was dominantly due to diffusion limitation. This is also supported by data shown in Section 3.3: Figure 3a shows that the UV illuminated cobalt cells suffered from a loss of charge carriers to the degree that it was affecting photocurrent under 1 Sun.

There is a significant increase in the IPCE

around 600 nm from initial to aged cells: an average 23 % in iodine cells (Figure 4c) and 36 % cobalt cells (Figure 4d). This is likely caused by an increase in electron collection efficiency, which is most affected by a short electron diffusion length at the weakly absorbed long wavelengths when the cell is illuminated from the PE side, as was the case here [17]: increase of electron diffusion length upon aging would allow more efficient collection of electrons generated by the low energy photons that penetrate deeper into the PE layer. The improvement in the collection efficiency (electron diffusion length) is possibly caused by the reduction of redox mediators in the cells, which in turn lowers the recombination at the photoelectrode/electrolyte interface. This is especially clear with cobalt electrolyte, which is understandable since the recombination is often a prominent loss mechanism in the initial state of cobalt electrolytes [22]. Additionally the IPCE of the UV illuminated iodine cells increased at 400 nm, which is most likely caused by the electrolyte becoming more transparent at this wavelength region due to the loss of charge carriers.

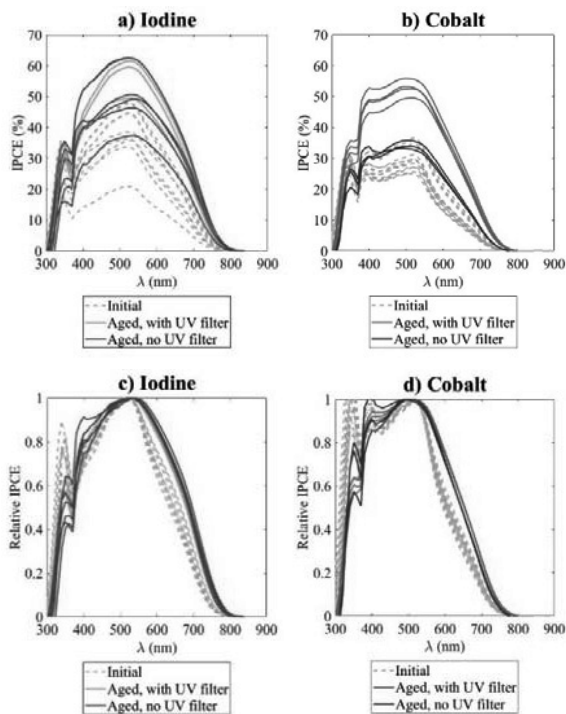


Figure 4 The IPCE curves of a) the iodine cells and b) cobalt cells. The relative IPCE curves of c) the iodine cells and d) cobalt cells. The normalization was according to the local maximum at wavelengths >450 nm. In figure parts c and d, the data presenting the aged cells is overlapping. During the aging process, the IPCE has unexpectedly increased in all the cells and therefore in the cases where there are losses to I_{SC} , they are caused by charge transfer limitation not the function of photoelectrode as such. The normalized data indicates that the cells utilize the high wavelengths (above 500 nm) more effectively after the aging than initially.

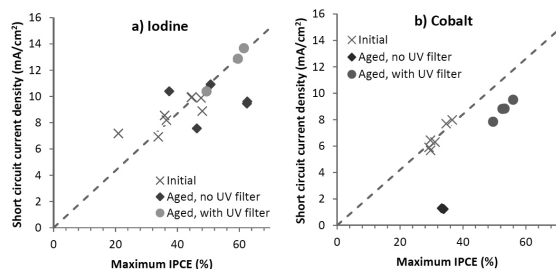


Figure 5 Short-circuit current density (the same data used in Table 1) compared to the maximum IPCE value (Figure 4). There is a linear fit made to the initial data, which is also set to go through origin; it is drawn as a guide. Based on the ideal physical models, IPCE and I_{SC} should have such linear correspondence. If after aging the data does not follow the same correspondence as initially, but falls below that line, it suggests that I_{SC} is limited by the limiting current.

LC-MS analysis

To investigate if there were changes to the dyed TiO_2 , we analyzed the aged cells using LCMS. In particular, it was seen in the IPCE measurement that the cobalt cells exposed to UV appeared to suffer from some other type of degradation in addition to the loss of charge carriers. Dye extracts from cells containing either cobalt or iodine electrolyte were analyzed by LC-MS. The dye Z907 with m/z 869.2 was found at retention time 31.0 min (Figure 6). The formula for this dye is $[RuL'(NCS)_2]$ where $L'=2,2'$ -bipyridyl-4,4'-dicarboxylic acid and $L=4,4'$ -dinonyl-2,2'-bipyridine (Supporting information, Figure S5). In addition to the main compound, three degradation products with isotope patterns corresponding to ruthenium containing compounds were found in some of the cells.

In all the cells containing cobalt electrolyte, a degradation product with m/z 778.3 was found at retention time 25.1 min (Figure 6). The formation of this ruthenium-containing degradation product was not related to the unfiltered exposure to UV light, but was present in all cells containing the cobalt electrolyte. This degradation product was not found in any of the cells containing iodine electrolyte.

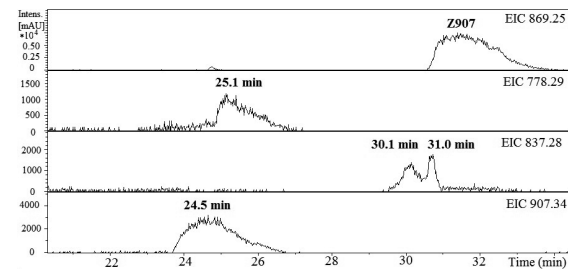


Figure 6 Extracted ion chromatograms (EIC) of dye extracted from a cell containing cobalt electrolyte that had been exposed to UV light.

At retention time 30.1 min, an ion peak with m/z 837.3 was found in all cells containing cobalt electrolyte and no UV filter, but also in about half of the cobalt cells that had a UV filter. Thus it is possible that the formation of this compound is enhanced by UV exposure. The compound at 30.1 min was tentatively identified as $[\text{RuLL}(\text{NCS})(\text{NC})]$ by high resolution mass spectrometry with m/z being within <5 ppm error margin and with an isotope pattern corresponding to that of the elementary composition of the proposed structure.

At retention time 31.0 min, another compound with m/z 837.3 is found. This compound was formed in the extraction solution and was thus present in extracts from all cells, as well as in a solution of the dye Z907. This compound was tentatively identified as $[\text{RuLL}(\text{NC})(\text{NCS})]$ by high resolution mass spectrometry with m/z being within <5 ppm error margin and with an isotope pattern corresponding to that of the elementary composition of the proposed structure. Additionally m/z 837.3 was found to be a fragment of m/z 869.2 in Z907.

A third degradation product with m/z 907.3 was found at retention time 24.5 min in 80 % of all cells without a UV filter. This degradation product was present in all cobalt cells without a UV filter, 50 % of the cobalt cells with the UV filter, 50 % of the iodine cells without a UV filter, and none of the iodine cells with the UV filter. The isotope pattern recorded by the MS shows that the compound contains ruthenium. Thus it appears that the formation of this compound is enhanced by the presence of a cobalt electrolyte and exposure to UV light. This compound is likely not a reaction product with the electrolyte components, since it is formed both in cobalt and iodine cells that have completely different electrolyte composition.

A solution of the dye Z907 in the extraction solvent and some of the dye extracts were analyzed immediately after preparation as well as hours and days later. These analyses showed that three additional degradation products with m/z 810.3, 942.3, and 945.4 are formed in the extraction solutions. All of these degradation products had isotope patterns corresponding to ruthenium containing compounds. As a conclusion, there were changes in the dye molecules, in particular when a UV filter was not employed. These changes were not the main cause of degradation as the IPCE analysis indicated.

Image processing

The majority of aging has been related to losses in the charge carriers during the aging process. These can be monitored via image processing since the changes in the electrolyte color, in particular in the case of iodine, are directly related to the changes in the charge carriers. The aim is to determine the rate of degradation for the electrolytes and based on that to estimate future lifetime for the cells. For the cobalt cells, it has not been reported what kind of color changes they might go through during degradation. Here we look into making correlations between the

color and the amount of charge carriers also for the cobalt electrolyte.

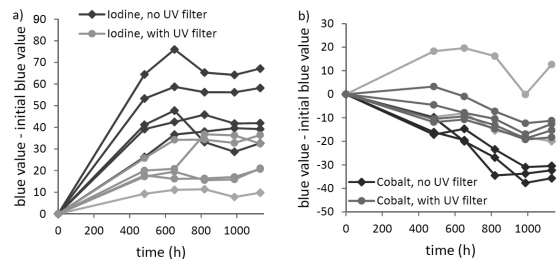


Figure 7 Normalized blue pixel values of a) the iodine cells and b) the cobalt cells. This normalization was done by deducting the initial blue pixel value of the measured blue pixel value of each cell. This allows us to present the trends in color change of the individual cells and look specifically at color change. The two cells marked by grey were discarded from further analysis (outliers): one cell due to a large air bubble leaving too little area for reliable analysis and another because the photographs of the cell were too shadowed.

Most of the color changes during aging took place in the blue pixel value of the electrolyte as shown in supporting information (Figures S3 and S4). Initially the iodine electrolyte was dark yellow due to the tri-iodide, which is the limiting charge carrier, and its yellow color is reflected as a low blue pixel value. During aging, the blue value of the iodine cells increased, which indicates that the electrolyte bleached. The iodine cells with no UV filter bleached (i.e. got to higher blue pixel values) on average faster than the iodine cells with the UV filter (Figures 7a and 8). The electrolyte of the iodine cells without the UV filter did not change much after the measurement point at 600 h (Figure 7a). The plateau comes from two factors: first, a large part of the iodine in the cells had been consumed, and second, after 600 h a very small amount of dye was desorbed, which also affected the blue pixel value by lowering it. The amount of desorbed dye was so small that it would not significantly affect the performance of the cell.

The color of the cobalt electrolyte evolved very differently from the iodine electrolyte (Figure 7b). The cobalt electrolyte is initially more transparent than the iodine electrolyte, which can be seen as higher initial values for the blue pixel (Figures S3 and S4). Here the focus was the changes of the color and those can be better detected using normalization, in particular as the color of the cobalt electrolyte was close to the background. The aging of cobalt cells caused exactly the opposite effect in the color of the electrolyte than the aging of iodine cells because the electrolyte got darker in the aging and hence the blue pixel values of the cobalt electrolyte decreased during aging (Figures 7b and 8). Like in the iodine cells, the changes were faster in the cells under UV illumination (Figures 7b and 8). The decrease of the blue values was fairly linear in both of the cobalt groups (Figure 7b).

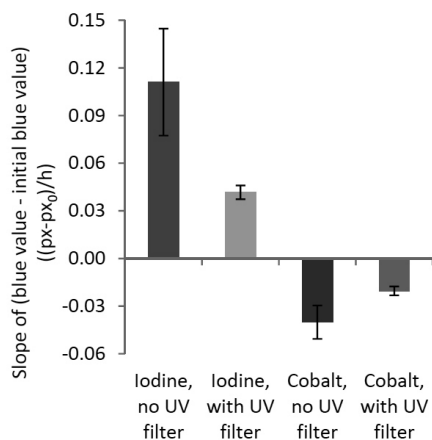


Figure 8 Mean slopes of the blue pixel values of the image processing results with standard deviations. The bigger the absolute value of the slope, the faster the degradation of the electrolyte is.

Aging causes chemical reactions in the electrolyte, and the difference in the color changes between the electrolytes is caused by different degradation processes: the degradation reaction in iodine electrolytes bleaches the electrolyte by decreasing the amount of tri-iodide (deep yellow color) [21] and the resulting degradation product is apparently colorless. The degradation reaction products in cobalt electrolyte seem to be darker in color than the original electrolyte components, which causes the darkening of the electrolyte during aging.

What does the degradation of the blue pixel value shown in Figure 8 mean in regards to the loss of charge carriers and the performance of the cell? In our previous work, we established how the blue pixel value and the amount of tri-iodide in the electrolyte correlate [18]: 7.35×10^{-4} mol/dm³ tri-iodide per blue pixel value. The loss rate of tri-iodide (Figure 9) can be calculated as the multiple of that correlation value and the rate of degradation of the blue pixel value (in Figure 8, including deviation). The photocurrent becomes diffusion limited with this type of iodine electrolyte when tri-iodide concentration of approximately 0.02 M is reached (data not shown). Based on the charge carrier loss rate (Figure 9), we can calculate when the cell performance starts to decrease. After that the photocurrent is limited by the limiting current directly proportional to the amount of limiting charge carrier (here tri-iodide). The cells will be completely dead after charge carrier concentration goes to zero since photocurrent goes to zero simultaneously (full degradation).

Lifetime prediction based on image processing

The conventional approach to lifetime analysis is to look only at the efficiency at the end of the test, which gives binary YES/NO answer on whether or not the cells retained over 90 % of the initial efficiency. By extrapolating the results shown in Figure 9, we can say

more about the lifetime of the cells. The estimated lifetimes are shown in Table 2. The rate of the charge carrier loss (purely based on color analysis) in the iodine cells without a UV filter predicts that at the end of the 1,000 hour aging test, these cells are likely to suffer from loss of charge carriers to such an extent that the limiting current may be causing losses in I_{sc} at 1 Sun (Figure 9). This estimated lifetime (Table 2) is in good correlation what the IV measurements indicated (Figure 1) since there was some degradation to the efficiency by end of the test. The charge carrier loss rates correspond to our previous studies with varying initial iodine concentrations (shown in grey in Figure 9), which demonstrates the repeatability of the method.

Figure 8 shows that the application of the UV filter on the iodine cells reduces the rate of iodine loss significantly from (0.08 ± 0.02) mM/h to (0.04 ± 0.01) mM/h. This degradation rate predicts approximately 3000 h lifetime until full degradation for the UV protected iodine cells in the given light conditions (Table 2). During the 1,000 hour aging tests, the UV protected iodine cells are, with this rate of degradation, predicted to retain their efficiency very well since the limiting current should still be well above I_{sc} at 1 Sun. This prediction is also in correlation with the measured data (Figure 1) because the cells were stable at the end of the test. Whilst this is not an absolute proof that these UV protected cells survive well over 2,000 h as suggested in Table 2, it is useful indicative information on possible future lifetime because very often (also here) the light soaking tests cannot be continued beyond 1,000 h due to practical limitations.

As said earlier, the degradation product of the cobalt cells was darker compared to the original charge carrier. This complicates relating the electrolyte color and charge carrier concentration (cf. degraded iodine turns colorless so correlation can be found simply by comparison to different initial iodine concentrations).

Hence we propose another method to estimate the degradation rates in case of cobalt cells: Figure 1 suggests that the photocurrent has reduced to almost zero during the 1,000 hour testing in the cobalt cells exposed to UV. This reduction was predominantly because of loss of charge carriers: measured I_{sc} was on average 80 % smaller than the IPCE predicts due to losses in charge carriers (Figure 5b). From this we make the approximation that the largest color change correlates with the complete loss of the limiting charge carrier $[\text{Co}(\text{bipy})_3](\text{PF}_6)_3$. This approximation may exaggerate the loss slightly, but it gives the upper limit for the rate of degradation. Based on this estimation, we get the degradation rate of (0.05 ± 0.01) mM/h for the cobalt cells without a UV filter and (0.025 ± 0.003) mM/h with UV filter (Figure 8). Based on these degradation rates, the loss rate of charge carriers would be only half of the corresponding iodine cells, and from that perspective, they could be regarded as more stable than the

iodine cells. The faster degradation in the efficiency in cobalt cells compared to iodine cells (Figure 1) would therefore relate to the low initial concentration of charge carriers in cobalt electrolyte. In the cobalt cells, the point in which I_{sc} at 1 Sun is reduced due to limiting current comes significantly earlier compared to iodine cells.

The easiest method to increase the stability of the cobalt cells would therefore be to simply increase the initial concentration of charge carriers in cobalt electrolyte – it is known that by increasing charge carrier concentration we could get a longer lifetime. What was not obvious was that based on our simple estimation, if we extend the initial concentration of cobalt charge carriers to similar level as in the iodine electrolyte, we could have lifetimes beyond 3,000 h and even 4,000 h until full degradation (Table 2). This motivates to the development of better blocking layers, so that for cobalt electrolyte, the initial concentration can be increased significantly without increased current leakage from the photoelectrode to the electrolyte. This kind of information is not solid proof of such long lifetimes, but it can point to where efforts could bear the most fruit.

Previously the lifetime predictions of dye solar cells have been merely an extrapolation of the efficiency to the future – this can be highly misleading, as major loss mechanisms may not have a linear effect on performance. Like here, the charge carrier concentration by its nature begins to degrade the photocurrent only after a certain limit has been reached. By investigating the major loss mechanism directly and not only the overall efficiency, we should be getting closer to a better quality lifetime estimations. In one sense, it is to be expected that if loss of charge carriers is the main cause of degradation, analysis looking at that would get the lifetimes right. On the other hand, it is actually amazing that the lifetime estimations based merely on photographs of the cells (with no relation to any measured performance data) can result in such good correlation with the measured efficiency data as shown here for the iodine cells. Therefore cell photographing could be used in the evaluation the electrical performance of the cells and furthermore predicting the future lifetime.

Interestingly, the UV filter should reduce the amount of UV light to 1 %. Both iodine and cobalt cells with the UV filter have, however, only about 50 % reduction in the degradation rate (Figure 8); not 99 % which should be the case if only the amount of UV would be affecting the degradation. Hence it appears evident that other factors contribute to the degradation processes in addition to exposure to UV or the effects are stronger at low light intensities. To confirm these results, it would be interesting to compare the degradation results when no UV light (e.g., white LED illumination) is used in aging to the case where there is UV light and a UV filter. This type of investigation is, however, out of the scope of this study.

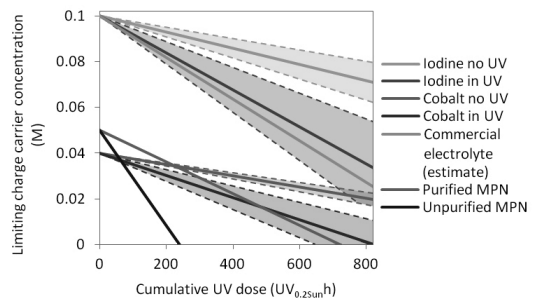


Figure 9 The estimated decrease of the limiting charge carrier concentration as a function of the cumulative UV dose (vs. Figure 1 shows the real time including intervals during which the cells have been taken for external measurements). The estimates were made on the basis of the image processing and IV results. The colored series are from this study and the grey series are from literature: cells containing purified or unpurified MPN as the solvent of the iodine-based electrolyte are from [20] and the cells containing iodine-based commercial electrolyte from [18]. The degradation begins to affect performance when the limiting charge carrier concentration goes below 0.02 M. The cobalt cells degrade at a lower rate than iodine cells, but due to the low initial concentration of charge carriers, their degradation affects the efficiency at an earlier stage.

Table 2 Comparison of the conventional analysis of the aging, i.e., efficiency after the test, compared to the lifetime estimations of when the efficiency begins to degrade (0.02 M charge carrier concentration has been reached) and when full degradation is reached. While conventional analysis gives only a binary YES/NO answer, looking at the charge carrier concentration with color analysis we can estimate future lifetimes.

	Is efficiency stable (above 90 % of initial) after the test?	Lifetime until efficiency begins to degrade	Lifetime until full degradation
Iodine, with UV filter	YES (120 %)	2200 ± 400 h	2800 ± 600 h
Iodine, no UV filter	NO (70 %)	1000 ± 200 h	1300 ± 400 h
Cobalt, with UV filter	YES (90 %)	800 ± 100 h	1600 ± 200 h
Cobalt, no UV filter	NO (4 %)	400 ± 100 h	800 ± 200 h

IV. CONCLUSIONS

The focus of this study was to investigate how much information can be harvested from a typical 1,000 h light soaking test of dye solar cells. We had selected the electrolyte as the main focus of investigation since it is one of the most sensitive components regarding aging. And we had selected the effect of UV light as the stress factor because it is one of the most detrimental conditions, in particular for the electrolyte. We looked at how much information we can harvest regarding degradation routes and rates, and moreover if we can say anything about the future performance – as most tests are kept due to practical limitations within 1,000 h.

In this test, the cells degraded mainly due to the losses in the charge carrier concentration. The biggest losses were seen in the cobalt complex cells without a UV filter, which degraded quickly: after 1,000 h under 1 Sun illumination, the efficiency had dropped to 4 % of their initial value. The vast majority of this efficiency drop was due to the loss of charge carriers: the photocurrent had dropped by 80 % due to losses in limiting current, and a ten-fold increase was seen in both diffusion resistance and charge transfer resistance at the counter electrode/ electrolyte interface resulting in major decreases in the fill factor. There were other minor losses – most likely dye degradation, but based on IPCE results its contribution was at maximum 30 % (i.e., much smaller compared to charge carrier related losses). LC-MS measurements confirm that there was some dye degradation, and it was the most significant in the case of cobalt cells without a UV filter.

The color analysis of the electrolyte was instrumental in identifying the degradation rates of charge carrier losses. The most surprising finding was that the degradation rate of the charge carriers in the cobalt cells was only about half of the corresponding iodine cells. This shows that the cobalt redox pair was actually more stable than the iodine redox pair. The reason why the iodine cells had better efficiency at the end of the experiment was apparently because they had initially larger excess of redox pair compared to what was required to sustain the initial I_{sc} . This caused the performance of cobalt cells to start degrading sooner, even if the rate of degradation of the cobalt electrolyte was slower than that of iodine electrolyte. Therefore instead of developing a more stable cobalt complex to carry the charge, it could be actually easier to develop a better blocking layer on the TiO_2 / electrolyte interface and merely increase the charge carrier concentration to reach longer lifetimes. The novelty of this work is that we can give quantitative estimations on how much longer lifetime could be reached if the blocking layer was improved.

The degradation rate of the charge carriers was used for lifetime estimation of the cells. Both the color analysis based lifetime estimation as well as the

actually measured lifetime of the iodine cells without the UV filter were similar. As long as the charge carrier loss is the main degradation mechanism of the cell type, it could work as a good lifetime estimator for the whole lifetime. Though the degradation did not yet affect the measured electrochemical performance characteristics, based on the color changes in the cell, we were also able to estimate the full degradation time of the UV protected iodine cells, which would take nearly 3,000 h. This means that having photographs of light soaking tested dye solar cells after 1,000 h and still stable, we could give indicative estimation of the whole lifetime, at least in terms of charge carrier degradation.

V. ACKNOWLEDGEMENTS

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VII. SUPPORTING INFORMATION

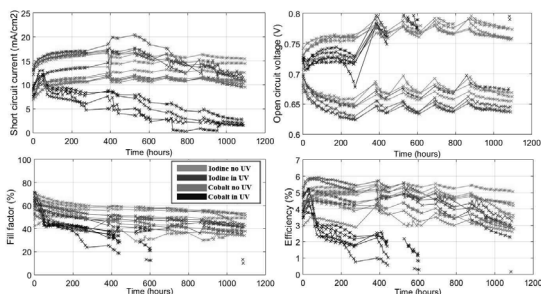


Figure S1 The development of the short circuit current, open circuit voltage, fill factor and efficiency of all the measured cells during the aging in approximately 1 Sun and 40 °C.

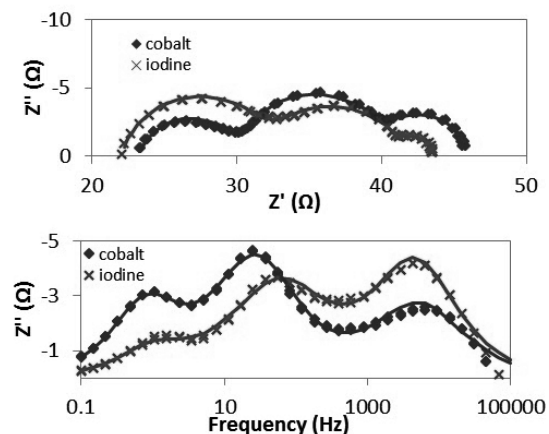


Figure S2 Example Nyquist plots of both cell types in the initial state under 1 Sun illumination at OC state. The markers represent measured data and the solid lines the fit.

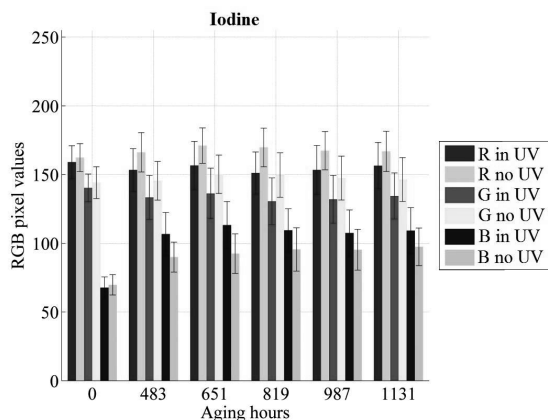


Figure S3 The average RGB values and their standard deviation as a function of time for iodine cells. Red, green and blue bars indicate red, green, and blue pixels correspondingly. The bars with the light colors refer to the cells protected from UV and the ones with dark color to the cells exposed to UV. Red and green pixel values remain constant throughout the measurement and therefore it is important to focus on the blue pixel value, which shows the bleaching of the yellow color of the electrolyte.

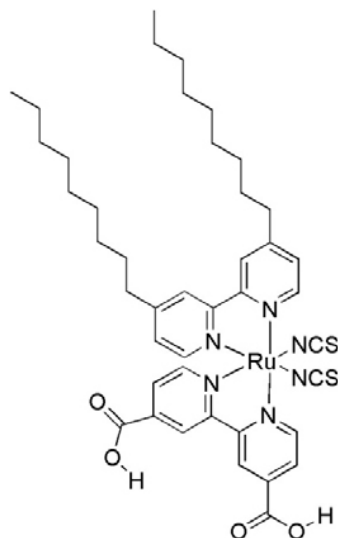


Figure S5 The structure of the dye Z907.

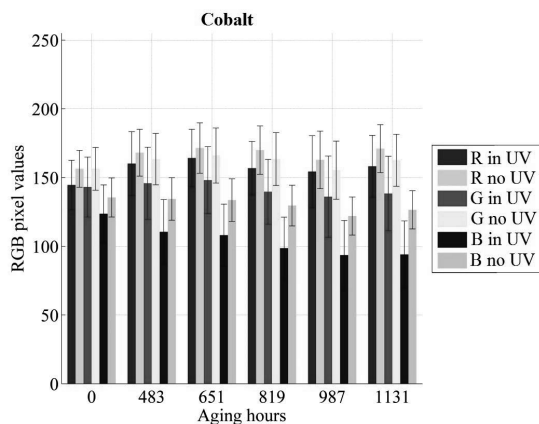


Figure S4 The average RGB values and their standard deviation as a function of time for cobalt cells. Red, green and blue bars indicate red, green, and blue pixels correspondingly. The bars with the light colors refer to the cells protected from UV and the ones with dark color to the cells exposed to UV. Red and green pixel values remain constant throughout the measurement and therefore the focus is the blue pixel value, which here indicates the cobalt electrolyte getting darker during the aging process.