Review of stability for advanced dye solar cells

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Received 30th October 2009, Accepted 10th December 2009
First published as an Advance Article on the web 4th February 2010
DOI: 10.1039/b922801b

The current status of the long-term stability of dye solar cells (DSCs) and factors affecting it is reviewed. The purpose is to clarify present knowledge of degradation phenomena and factors in these cells by critically separating the assumptions from the solid experimental evidence reported in the literature. Important degradation processes such as dye desorption, decrease in the tri-iodide concentration, degradation at the photoelectrode and counter electrode, affect of ultraviolet light and moisture, and issues related to the sealing, are covered. It is concluded that techniques giving chemical information are needed for the stability investigations of DSCs to reveal possible ways to improve their lifetime. In this regard, experimental methods suitable for separating degradation mechanisms in complete cells during long-term testing are proposed employing specifically designed sealed cell structures, called segmented cells, that provide windows to measure specific cell components without being obscured by the others.

1. Introduction

With the dawn of the 21st century, the world's increasing energy demand and rising environmental pollution have made it extremely important to search for clean, carbon-emission-free energy sources. Among other renewable energy sources, photovoltaic cells are being investigated as a solution to this situation. Different kinds of solar cells have been developed and explored so far. In this regard, dye solar cells (DSCs) are seen as a possible alternative to the conventional crystalline silicon and thin-film solar cells. The prominent features of DSCs include usage of cheap and easily available materials and efficiency around 11.1%.[1] With suitable selection of materials, characteristics such as flexibility of cells, feasibility for large scale roll-to-roll production on flexible substrates, and semi-transparency of cells can be reached.

The stability of DSCs like other kinds of solar cells is an important aspect for their commercialization. However, the evaluation of the lifetime of solar cells is a difficult task as it depends on the specific degradation mechanisms.[2] As different types of solar cells involve different kinds of degradation mechanisms, the accelerated stress tests suitable for one type of solar cell may not be fruitful to study the degradation of another type of solar cell. Establishing standard stability testing protocols for a solar cell requires the knowledge of degradation modes in the cells. Thus the understanding of degradation mechanisms is essential. Furthermore, it will help to develop better materials for the cells.

For establishing standard stability tests for DSCs, its stability goals need to be defined. For instance how much decrease or increase in the performance of a DSC can be tolerated in order to consider the cell stable. Another important question is whether

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efficiency (η) alone can be set as a criterion to evaluate the performance of a DSC or should all current–voltage (I–V) parameters including short-circuit current (I_{sc}), open-circuit voltage (V_{oc}), and fill factor FF be examined. Finally, ultimate applications of DSCs should be considered as well, for instance many indoor applications such as toys do not have to be stable at high temperatures, such as 80 °C.

Although there are no standards defined, there are several commonly used tests to evaluate the stability of DSCs under different stress factors such as 60 °C and 80 °C dark tests, light-soaking tests at 1 Sun at 60 °C or 80 °C, heat-cycle durability test, ultraviolet (UV) test, and humidity test. Usually these accelerated ageing tests run for 1000 h. Furthermore, these tests are usually carried out by doing intermediate measurements at 100 h intervals. Some research groups perform light-soaking before the measurements and others do not. This can create a completely different or even misleading picture of the stability. There is no exact figure mentioned in the literature, but usually the DSCs are declared to pass a certain test provided η does not change more than 10% of its initial value.[3–8]

The stability of DSCs at room temperature has already been reported under continuous illumination for 12 000 h[9] and at 2.5 Sun for 8000 h.[10] This shows that light soaking alone is not a major reason for degradation. An amazing long-term stability of DSCs for 20 000 h at 55 °C under 0.8 Sun illumination has also been achieved.[11] The light-soaking tests become, however, more demanding as the temperature is increased. In fact, DSCs have not yet passed light soaking at 80 °C for 1000 h. The high-temperature (80 °C) dark test is also quite challenging for DSCs, but some DSCs based on ionic liquid electrolytes and polymer gel electrolytes have been reported to pass this test.[3,6] It was also found that at high temperatures *i.e.* above 60 °C, the degradation of the cell performance is much faster in light-soaking tests than in dark tests.[12]

It is clear that at high temperatures *i.e.* above 60 °C, either certain degradation mechanisms are accelerated or new degradation reactions are generated, which result in faster degradation of the DSCs. In addition to the problems occurring in demanding conditions, introducing non-conventional materials for instance flexible substrates often bring out degradation problems. Understanding the degradation mechanisms is the key to achieve long term stable DSCs. Knowledge of degradation mechanisms also gives insight for the design of standard test for this type of cells.

In literature, degradation is associated with various hypotheses about the degradation mechanisms and their relation to external degradation factors such as temperature, visible and UV light, intrusion of water into the cell, leakage of electrolyte, *etc.* The aim of this work is to critically study these hypotheses and separate them from the solid evidence. The objective is to provide background information for more systematic study of degradation phenomena in DSCs.

2. Degradation phenomena in DSCs

2.1. Current status of performance and stability of DSCs

The most discussed DSC components regarding stability are the dye and the electrolyte. The most frequently used ruthenium dyes are the red dyes N3 and N719, the black dye N749 and the hydrophobic dye Z907. Other dyes, such as N845, Z955, Z910, K77, and organic dyes, have also been employed in DSCs.[13] The molar extinction coefficient and spectral broadness of a dye affect its performance, but at the same time the dye needs to be stable for long-term operation at high temperatures. A list of important dyes with their molar extinction coefficients values and their stability status is given in Table 1.

The stability of DSCs depends on a suitable dye/electrolyte combination. With the hydrophilic dyes N719 and N749, a stable combination of the dye and electrolyte to pass a 80 °C dark test has not been achieved.[6,17] However, DSCs have been reported to pass 80 °C dark tests using the hydrophobic dyes K19,[16,19] K77[3,7] and Z907[6] with certain types of liquid electrolyte, ionic liquid electrolyte and polymer gel electrolyte as shown in the Table 1. A high molar extinction coefficient ruthenium dye, C104, is

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Table 1 List of important dyes with their molar extinction coefficients and their stability status at 80 °C. Note that for instance the selection of the electrolyte affects the stability of the cell as well

Dye	Peak molar extinction coefficient/M^{-1} cm^{-1}	Reference	Stability at 80 °C for 1000 h	Reference
N749	7.8×10^3	14	Unstable	17
N719	14×10^3	15	Unstable	6, 16
Z907	12.2×10^3	16	Stable	6
K19	18.2×10^3	16	Stable	16, 19
K77	19.4×10^3	7	Stable	3,7
C103	18.8×10^3	5	Not known	—
C104	20.5×10^3	17	Not known	—
TH304	41×10^3	18	Not known	—

reported to yield 10.53% efficiency at 1 Sun, however, stability at 80 °C has not been addressed.[17] Recently, amphiphilic dye C103 belonging to the same family as C104 recorded a new bench mark for the efficiency of stable liquid electrolyte and solvent-free ionic liquids after passing a light soaking test at 60 °C under 1 Sun for 1000 h.[5] The metal-free 'black dye' TH304 has a very high molar extinction coefficient (Table 1). However, the stability of this dye has not been reported yet.

The current state-of-the-art in the stability of ionic liquid electrolytes, low-volatility liquid electrolytes and polymer gel electrolytes is presented in Table 2 where the results are selected according to the maximum efficiency achieved for the respective electrolytes. The current status of stability of the electrolytes is presented according to two extreme tests, light soaking at 60 °C and thermal stress at 80 °C (Table 2), both run for 1000 h. All three electrolyte types have passed both tests with satisfactory efficiency. Usually further increase of the temperature above 60 °C brings up problems: Electrolytes based on acetonitrile and other organic solvents were found to degrade during a 85 °C dark test.[12] Interestingly, in a thermal cycling test *i.e.* 85 °C dark annealing and 45 °C light soaking, a recovery occurs during the light soaking at 45 °C.[12] The degradation recovery behavior in the thermal cyclic test is dependent on the composition of the electrolyte.[12] A comparative study on the degradation behavior of molten salt electrolytes, gelled molten salt electrolytes, liquid solvent electrolytes, and gelled organic solvent electrolytes revealed that only gelled molten salts electrolytes are stable at 85 °C for 1000 h.[4]

Table 2 The current state-of-the-art of DSCs using different kinds of electrolyte with respect to their stability at extreme conditions *i.e.* Test No. 1 (light soaking at 60 °C run for 1000 h) and Test No. 2 (thermal stress at 80 °C run for 1000 h)

Electrolyte type	Dye	Stability status	Efficiency (%)
Liquid electrolyte	C103[5]	Passed Test No. 1	9.6
	K77[7]	Passed both Test No. 1 & 2	9
Polymer gel electrolyte	Z907[6]	Passed Test No. 1 at 55 °C & 2	6
Ionic liquid electrolyte	C103[5]	Passed Test No. 1	8.5
	K77[3]	Passed both Test No. 1 & 2	7.6
	Z907Na[20]	Passed Test No. 1	8.2

Iodide/tri-iodide (I^-/I_3^-) is the most common redox couple used in DSC electrolytes. However, this redox couple has some drawbacks: the open circuit voltage is limited due to the low redox potential, tri-iodide absorbs visible light, and it is aggressive towards metals like silver, which is used in the current collector grid[21] that thus needs to be sealed to prevent contact with the electrolyte. These disadvantages of I^-/I_3^- led to the study of alternative redox couples such as Co^{II}/Co^{III} and $SeSC^-/(SeCN)_3^-$. Co^{II}/Co^{III} showed promising results at low light intensity but were found to be inefficient at 1 Sun light intensity. This was due to the mass transport limitation of the photocurrent, as with Co^{II}/Co^{III} both oxidized and reduced complexes are subject to mass transport limitation.[21] $SeSC^-/(SeCN)_3^-$ gave promising results as well at room temperature[22] but stability at higher temperatures for long-term operation has not been reported yet.

The stability of other components than electrolyte and the dye is important as well. The performance of counter electrodes (CEs) is characterized by the catalytic activity *i.e.* charge transfer resistance. The highest performances have been reached with platinum and carbon. Stable DSCs performing at record efficiencies for liquid electrolytes and ionic liquids utilize Pt as a catalyst at the CE.[3,6,7] Pt is good for semi-transparent applications such as facades since efficient catalyst performance can be reached with only a few nanometres thick layer.

The main advantage of carbon compared to Pt is that it is cheaper, for instance a composite of nanocarbon (catalyst) and TiO_2 (binder) showed potential as a low-cost CE material.[23] However, a thick layer of carbon (up to a thickness of 10 μm) is needed to gain low enough charge transfer resistance resulting in complete opaqueness of the CE. To gain high performance, a high surface area is needed: nanocarbon (average diameter 30 nm) is almost 4 times more efficient than microcarbon (2–12 μm) showing the effect of particle size and surface area on the material's catalytic activity.[24] Stability studies of carbon (nanosized) as CEs show that DSCs retain 84% of their initial efficiency (7.56%) after 60 days in the dark at room temperature.[25]

Carbon nanotubes have also been suggested as a CE material. In a 30-day stability test in the dark at room temperature for multiwall CNTs, a continuous decrease in I_{sc} was observed due to detachment of weakly adhered CNTs from the FTO glass and deposition on the photoanode side.[26] The larger diameter CNTs show better performance.[27] A short-term stability of single wall carbon nanotube (SWNT) has been reported for 12 days at room temperature.[28]

All the high stability records of DSCs have been reached using glass substrates. To reduce the cost,[29–31] improve the suitability for mass production, and increase the variety of possible applications, flexible metal and plastic substrates have been introduced. However, the greatest problem with these alternative substrates is stability, as for them the 60 °C light-soaking test is still a challenge. Most of the metals such as copper corrode in the iodine-containing electrolyte.[32–34] Stainless steel has passed electrolyte soaking tests,[32–34] which are used for studying corrosion. However, complete stainless-steel-based DSCs have not been stable.[33,35,36] Our previous studies reveal that the short lifetime of DSCs with stainless steel photoelectrode substrates does not seem to be apparently due to corrosion or contamination[36,37] and more work is needed to reveal the underlying causes for the instability. On the other hand, corrosion was seen in the case of stainless steel counter electrode cells.[35]

2.2. Experimental methods to study degradation

Conventional accelerated ageing tests monitor the photovoltaic performance of solar cells over time but give very limited information about the origin of instability. Thus, conventional stability tests have to be coupled with other techniques to trace the cause of degradation mechanisms. Measurement methods to study the ageing of DSCs can be grouped into *in situ* and *ex situ* techniques. *In situ* techniques do not require cell disassembly whereas *ex situ* techniques do. Basically, *in situ* techniques allow continuous examination during the ageing test whereas *ex situ* techniques are useful for the post-mortem analysis of the degradation effects. *In situ* techniques are based on optical and electrical measurements, or their combinations and include electrochemical impedance spectroscopy (EIS),[38–40] the incident-photon-to-current conversion efficiency (IPCE) technique,[41] intensity modulated photocurrent spectroscopy (IMPS),[42] intensity modulated photovoltage spectroscopy (IMVS),[43] optical infrared (IR) spectroscopy,[44,45] Raman spectroscopy,[46,47] and spatially-resolved photocurrent imaging techniques.[48,49] The *ex situ* techniques include microscopic techniques such as scanning electron microscopy (SEM),[47,50] transmission electron microscopy (TEM),[51,52] scanning tunneling microscopy (STM),[52] atomic force microscopy (AFM),[53] energy dispersive X-ray spectroscopy (EDS),[54] and electron energy loss spectroscopy (EELS).[55]

Recently, a segmented cell method was introduced to factor the different causes that lead to cell degradation.[36] In this method two or more cells share the same electrolyte as shown in Fig. 1. Any degradation in one cell related to electrolyte can be seen in other cells as well. The method can be employed in different combinations to study various degradation phenomena that will be discussed in the next section. The use of segmented cell configuration has already been applied to study the stability of stainless steel substrates, namely the participation of the electrolyte in the ageing process.[36]

2.3. Hypotheses and their analyses

There are several hypotheses reported in the literature affecting the lifetime of DSCs. To study these hypotheses, stability of the DSCs can be categorized into extrinsic stability and intrinsic stability. The extrinsic stability deals with the sealing failures which make it possible for harmful contaminants to enter into the cell or for the useful contents to escape from the cell. In order to study the intrinsic stability of DSCs, it is critical to make sure that a sealing failure does not dictate changes in the cell performance. Usually the degradation mechanisms are triggered or accelerated under certain conditions such as temperature, light intensity, amount of impurities or water present in the cell. Here, we will discuss some of the important hypotheses and try to comprehend the degradation mechanism. Suggestions are given to experimentally study these hypotheses utilizing the advantages of the segmented cell configuration when feasible.

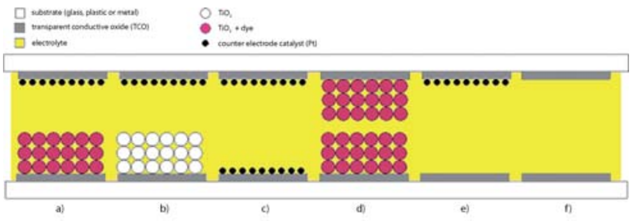

Fig. 1 The segmented cell configuration. a) PE-CE, b) dye-free PE-CE, c) CE-CE, d) PE-PE, e) TCO-CE, f) TCO-TCO (photoelectrode = PE, counter electrode = CE, transparent conducting oxide = TCO).

Dye desorption. Desorption of dye can be regarded as one of the most critical reasons for the instability of DSCs for long-term operation. Dye desorption was suggested to explain the dramatic decrease in I_{sc} under dark test at 85 °C.[10,12] In another study a DSC containing the hydrophilic dye N719 decreased its performance whereas a DSC containing the hydrophobic dye Z907 was stable demonstrating the effect of the molecular structure of the dye on the DSC stability.[6] In another study, dye desorption was estimated by measuring the amount of dye left in the photoelectrode as a function of time.[56] The absorption of dye on the TiO_2 was measured from the disassembled photoelectrodes desorbing the dye to a basic solution and measuring the absorption spectra of the solution,[56,57] hence confirming the occurrence of dye desorption in DSCs.

Several hypotheses have been given in the literature to explain the degradation due to dye desorption. One hypothesis explained it with the help of equilibrium between the dye adsorbed onto the surface of TiO_2 and the dye dissolved in the electrolyte.[12] A change in temperature shifts the equilibrium and this may explain the lower performance of the DSCs at high temperatures *i.e.* around 80 °C triggered by dye desorption. The cell performance was found to recover under illumination at lower temperature *i.e.* less than 45 °C, which was attributed to dye re-adsorption.[12] However, this hypothesis needs more elaboration regarding the equilibrium kinetics and temperatures. So far there is no direct evidence presented, other than DSC performance related, supporting or opposing this hypothesis.

According to another hypothesis, decomposition products in the electrolyte co-adsorbing to the TiO_2 surface can cause desorption of the dye at high temperatures.[58] Yet, another hypothesis explained the dye desorption as a result of side reactions between the oxidized dye and radicals, *e.g.* iodine radicals, in the electrolyte.[58] For stable functioning of the dye, the electron injection and the recovery of the oxidized dye by the redox couple should be fast enough to suppress these side reactions but may fail to do so in practice. Nevertheless, both the co-adsorption and the side reaction hypotheses are thus far based merely on speculations. Finally, it has been suggested that the hydrophilic nature of TiO_2 can cause dye desorption even at only a small amount of moisture present in the cell.[38] It is supported by the fact that hydrophobic dyes have shown stability at a 80 °C thermal test run for 1000 h[3,6,16] whereas no hydrophilic dye has ever passed this test.

It has also been suggested that dye desorption is the reason for DSCs' failure to pass the 80 °C thermal test,[6] but this can be overcome by using amphiphilic dyes, consisting of molecules having a hydrophobic group attached to hydrophilic group with the advantage that the hydrophilic part strongly attaches to the

TiO_2 and the hydrophobic part resists penetration of water molecules. For instance DSCs using the amphiphilic dyes Z907,[6] K77[3] and K19[16,19] have passed the 80 °C dark test. However, light soaking at high temperatures *i.e.* 80 °C or above, which is a more demanding condition compared to a 80 °C dark test, has not been reported yet for DSCs.

The dye desorption can be observed continuously using a three-segment configuration PE-CE/dye free PE-CE/TCO-TCO shown in Fig. 1. Any dye desorbed in the segment 'PE-CE' can flow to segments 'dye free PE-CE' and 'TCO-TCO' *via* the electrolyte. In the 'TCO-TCO' segment the relative concentration of the desorbed dye can be measured using optical techniques. In the 'dye-free PE-CE' segment a small amount of dye re-adsorbing on the bare TiO_2 is expected to be measurable as an increase of I_{sc} or V_{oc} of that segment. Hence these are two complementary ways to estimate the extent of dye desorption in the segment 'PE-CE'. It should however be noted that based on our initial tests, inhomogeneous distribution of desorbed dye in the electrolyte and irregular adsorption of dye on TiO_2 in 'dye-free PE-CE' segment may limit the quantitativeness of this method. The segment 'PE-PE' can be added to the segmented cell configuration with the advantage that it would increase the concentration of desorbed dye in the electrolyte which may be needed due to limited sensitivity of the measurement techniques. The behavior of the dye desorption can be studied in more detail by carrying out the measurements at various temperatures under different light intensities and humidity conditions.

Electron collection at the photoelectrode. The degradation of DSCs is often associated with changes in the electron transport in the TiO_2 and interfacial transfer of electrons at the TiO_2–electrolyte interface measured with EIS.[10,38,39] Electron transport depends on the electrical contact between the TiO_2 particles and between the TiO_2 layer and the TCO layer. The TiO_2 particles may lose contact with each other or with the TCO, thereby increasing the transport resistance or contact resistance of the film respectively. More often however, the degradation of DSC performance is accompanied by a decrease of electron lifetime and recombination resistance.[36] This decreases the photovoltaic performance, in particular V_{oc}. The suggested reasons for the increase in recombination are formation of side products in the electrolyte[10,59] and detachment of catalyst particles at the counter electrode, which can then diffuse to the photoelectrode and act as recombination centers there.[26] Surface contamination of TiO_2 layers by harmful metal oxides has been suggested to lower the performance of DSCs.[60,61] Indeed, mixing iron oxide with the TiO_2 layer decreased the cell performance.[60] However, getting the harmful metal oxides into the TiO_2 by surface contamination was very difficult according to our previous study.[37]

The electrical quality of the photoelectrode layer depends on the deposition method and it might also affect the stability. Screen printing and doctor blading are the most common methods for deposition of the photoelectrode. The layer is usually sintered at around 450 °C to get a good connection between the TiO_2 particles and to burn off organic residues. In the case of plastic substrates, the heating temperature is limited to below *ca.* 150 °C and the quality of the TiO_2 film is typically not as good. The stability of low-temperature-treated plastic DSCs has not been as good as that of the high-temperature-treated glass cells.[38] This feature is typically attributed to the permeability of plastic[38] which may enable the intrusion of water or contaminants to the cell or leakage of the electrolyte. However, the lower quality of the TiO_2 layer might also affect its stability. Therefore, it would be interesting to perform a comparative stability study of glass and plastic DSCs having identical low-temperature TiO_2 layers. Such a study could reveal to what extent the degradation is caused by the low-temperature treatment of the TiO_2 film and how much by the plastic substrate. Another interesting test would be to seal plastic cells with glass to check whether the stability problem is related to the permeability or the plastic substrate as often assumed. Surprisingly, these simple tests have not been reported yet.

It has also been put forward that it would be interesting to study whether there is a difference between having contamination on the TiO_2 layer or on the TCO layer as both cause recombination of the charge carriers.[10] This can be examined by applying a compact TiO_2 layer to the TCO layer for instance with atomic layer deposition (ALD).[62] On the other hand if the recombination from TiO_2 to the electrolyte is more affected by contamination, applying insulating layers such as Al_2O_3[63,64] or MgO[54,64] to cover the whole photoelectrode might be advantageous. Moreover, the temperature effects on the TCO–electrolyte or TiO_2–electrolyte interface might also be different as suggested previously.[10] These temperature effects could be studied together with different blocking layers to observe how they affect the ageing of the whole photoelectrode.

The stability of the TCO–electrolyte interface could be studied with the two segmented cell configuration TCO-CE/PE-CE shown in Fig. 1. The change in performance of both segments could be monitored simultaneously. This would help to understand the effects on the TCO interface over time with the presence of a photoelectrode in the cell. However, the actual degradation mechanism leading to that effect would require chemical analysis.

Degradation of the counter electrode. The catalytic performance at the counter electrolyte is described by the charge transfer resistance R_{ct} at the counter electrode/electrolyte interface. An increase in R_{ct} as a function of time can be attributed to the degradation of the counter electrode in EIS measurements.[24,25,65,66] In order to separate the degradation at the counter electrode from the effect at photoelectrode, the CE-CE configuration is used.[67,68]

The degradation of the counter electrode may be due to a poor contact or impurities between the catalyst layer and the TCO, leading to detachment of the catalyst particles. The conventional tape tests can be applied to study the adherence of the catalyst layer which can give an idea of the counter electrode stability. The contact between TCO and catalyst layer and between the catalyst particles themselves depends on the preparation method.[67,69] Papageorgiou *et al.* introduced a method to observe the flux of catalyst material from the counter electrode to the other electrode employing a cell with a counter electrode on the other side and bare TCO glass on the other side,[67] identically to the 'TCO-CE' segment in Fig. 1. As the charge transfer at the bare TCO is very poor, even a small amount of catalyst material ending up there significantly affects its electrochemical properties.

Also, other reasons for counter electrode performance degradation have been speculated: chemical reactions such as corrosion between the electrolyte and the catalyst[67,70] or deposition of by-products in the electrolyte onto the counter electrode surface.[58] If the degradation involves chemical reaction between the catalyst and the iodine in the electrolyte, it would affect also the charge transport in the electrolyte due to decreased concentration of I_3^-. The presence of corrosion can be confirmed with chemical analysis of the electrolyte. The deposition of by-products onto the counter electrode could be analyzed with microscopy techniques such as TEM or SEM combined with EDS or EELS analysis giving information about the material composition.

Decrease in tri-iodide concentration. Another important factor associated with the stability of DSCs is the decrease in tri-iodide concentration. Using EIS, a decrease in the tri-iodide concentration was confirmed, as the Nernst diffusion impedance of tri-iodide was found to increase under an outdoor exposure test.[71] This confirmation was further supported by Raman spectroscopy measurements of the electrolyte.[71] The diffusion impedance acts as an internal resistance of the cell and thus its increase results in a decrease of *FF*, and, in the extreme case, depletion of tri-iodide may decrease I_{sc} by decreasing the diffusion-limited current density.[68] In another study, a decrease in tri-iodide concentration over time was determined by the decrease in absorbance of the electrolyte.[56]

There are two probable ways that can lead to a decrease in the tri-iodide concentration. Firstly, some studies explained it with the help of sublimation of iodine.[45,72,73] In a long-term durability test at high temperature, gelation of the ionic liquid electrolyte depressed the decrease in tri-iodide caused by sublimation of iodine.[72] In another study, higher performance was gained using an additive, phenothiazine, in the electrolyte; again proposed due to reduced sublimation.[45]

Secondly, the decrease in tri-iodide concentration has been proposed to be due to the irreversible reaction of tri-iodide with an impurity like water forming iodate. However, direct detection of iodate was not obtained using FTIR spectra of the electrolyte.[48] Thus detailed chemical analysis of the electrolyte is needed before and after the ageing of the cell to determine whether such an irreversible reaction exists or not.

Bleaching of electrolytes was observed at elevated temperatures, *i.e.* 50 °C, under 1 Sun illumination and was associated with the loss of tri-iodide.[48] In another study almost the whole electrolyte was bleached at 85 °C under 1 Sun light intensity due to the loss of iodine whereas at 85 °C dark test bleaching of electrolytes was not observed.[12] It would be interesting to perform a thermal cyclic test involving light soaking test at 85 °C to observe if there is any recovery of performance. If there would be no recovery, it would indicate a permanent loss in performance due to an irreversible photochemical reaction at high temperature. In the case of recovery in the dark, the decrease in performance would be due to a shift in equilibrium between the reactants and products of the bleaching reaction.

To study the decrease in tri-iodide concentration, there is no need for the *ex situ* techniques such as chemical analysis of electrolyte as it can be studied with *in situ* techniques as well, such as optical measurements. Besides using absorption techniques, it may be difficult to study the decrease in the tri-iodide concentration as tri-iodide's absorption spectra is quite similar to other polyiodides.[56,74] Raman or IR spectroscopic techniques may be needed to differentiate tri-iodide from other polyiodides.[75–77] The two segmented cell configuration PE-CE/CE-CE or PE-CE/TCO-TCO provides the larger viable aperture needed for the optical measurements as shown in Fig. 1. As the electrolyte is shared by both segments, optical measurements can be done in the 'CE-CE' or 'TCO-TCO' segment to detect the loss of tri-iodide in the 'PE-CE' segment of the cell. Since a decrease in tri-iodide concentration involves a change of color,[78] a color-sensitive camera can be used to study the loss of tri-iodide as a function of time without dismantling of the cells. Moreover, this should be useful for detecting inhomogeneous distribution of the electrolyte species in the cell, which according to our experience, does occur.

Water and oxygen inside DSCs. Water and oxygen inside the DSCs have been reported to be harmful in regard to long-term stability of the cell performance.[29,44,58,79] However, water has also been reported to improve the performance of DSCs containing ionic liquid electrolytes.[80] Also, it was found that the amount of water in the cell can significantly change the concentration of protons which later on can affect the conduction band position of TiO_2 by adsorbing to the TiO_2 surface or by intercalation into TiO_2.[59] Keeping in mind the contradictory effect of water on DSC stability, it would be important to know exactly how much water in DSCs is critical for their stability. The amount of water inside DSCs should be restricted below the critical value where it starts affecting the cell performance. This critical value of water may depend on several factors such as the type of dye, electrolyte, and substrates as well as the quality of the photoelectrode. The ambient air humidity is an important factor which can alter the water content in DSCs.

One of the speculations regarding the oxygen present inside the DSCs, is that it can oxidize the organic components of the DSCs with the passage of time.[58,81] Another hypothesis is that I_2 can be irreversibly oxidized to IO_3^- due to oxidative surface states.[58] However, no proof has been given regarding these speculations. Many hypotheses regarding degradation of DSCs involve the presence of water or oxygen in the DSC, for instance in the case of dye desorption. Thus the role of water and oxygen in DSCs needs to be investigated in more detail to obtain the long-term stability of DSCs.

UV. The exposure of DSCs to UV light can degrade their performance during long-term operation as it can generate a number of degradation mechanisms. For instance, UV light can cause TiO_2 direct band excitation which may lead to oxidation of the dye or electrolyte components.[10,12] Using optical spectroscopy, it was found that UV light can cause irreversible reaction of iodine leading to the bleaching of the electrolyte.[10]

It was found in a UV test that adding MgI_2 and CaI_2 to the electrolyte increases the tolerance towards UV illumination.[10] However, despite the solid evidence, no explanation has been given yet. UV filters *e.g.* polyester films, have been successfully employed in the cell to remove the degradation caused by UV light.[7,82–84] The use of higher band gap materials such as SnO_2 with a thin MgO coating to replace TiO_2 showed better resistance to UV light.[81] It was suggested that TiO_2 is more photocatalytically active than SnO_2/MgO.[81] However, SnO_2-based DSCs have not been tested at severe conditions such as a light-soaking test at 60 °C and thermal stress at 80 °C whereas TiO_2-based DSCs have passed both of those tests.[3,5–7,20]

On the other hand, UV light can also be used to improve the cell performance. Irradiating the TiO_2 film with UV light has been found to increase the efficiency either by improving the necking between TiO_2 particles,[85] by increasing the adherence of TiO_2 to the substrate,[86] by affecting the dye adsorption,[86] or possibly by removing organic residuals.[87] Also other mechanisms have been suggested.[88,89] UV irradiation could be used for instance in the low-temperature fabrication of TiO_2 films on plastic substrates.[90,91]

The same experimental methods can be applied to study the degradation by UV as were proposed to study degradation by a decrease in tri-iodide concentration as both involve similar degradation processes. In addition selective-area UV light, exposure or gradient exposure, coupled to spatially-resolved photocurrent imaging using a scanning laser could be fruitful for studying the degradation of compounds fixed locally in the cell such as dye, TiO_2, and substrate contacts.

Sealing of the DSCs. The leakage of electrolyte and evaporation of solvents out of DSCs can be detrimental for their stability. Similarly the penetration of impurities like water and oxygen into DSCs may be harmful. The DSCs deposited on plastic are believed to be prone to these kinds of leakage and penetration problems.

In general, good sealing of DSCs is essential for long-term operation of the DSCs. The sealing should be mechanically stable to avoid any damage to the DSCs as it has to withstand both external factors such as hail storms and internal factors such as gas bubbles inside the DSCs.[58] Moreover, the sealing has to be flexible enough so that it does not break due to thermal expansion and increase of vapor pressure of the electrolyte.[73]

The commonly used sealing material, Surlyn 1702, cannot be used in the cells that are subjected to high temperature *i.e.* above 60 °C since it has quite a low softening temperature.[10] Proper sealing with suitable materials such as Bynel and glass frit have been successfully employed to avoid solvent leakage and evaporation at high temperature *i.e.* 80 °C.[29] In one example, a double sealing package using hotmelt adhesive sheet (DuPont-Mitsui Polychemicals, HIMILAN) was introduced: it consisted of a primary seal, preventing the sublimation of iodide and intrusion of moisture, and a secondary seal preventing exposure of moisture to the cell's parts.[73]

The electrolyte leakage or evaporation can also be prevented by altering the electrolyte. Instead of using volatile liquid electrolytes, the use of ionic liquid electrolytes,[92–95] p-type semiconductors,[96,97] inorganic hole transport materials,[98] organic hole transport materials,[99,100] nanocomposites,[101–103] and polymer gels[104–106] has been introduced in the literature.

The current collectors of the DSCs can degrade, if they are exposed to moisture long-term or are subject to mechanical stress. The degradation of the current collectors can be studied by measuring their resistance as a function of time. More importantly, the sealing needs to protect the current collectors from the electrolyte which is highly corroding towards, for instance, silver and copper.[34] Contact between the electrolyte and the current collector destroys both since the corrosion reaction consumes quickly both the current collector metal and tri-iodide of the electrolyte. The mechanical stability of sealing can be studied by standard test used for testing integrated circuits, where the samples are exposed to periodic external forces.

Cross-line between performance and stability limiting factors. Finally we would like to point out that although in this study different degradation mechanisms were discussed separately, they may not be generally independent of each other when it comes to their effect on the cell performance. Hence, evaluation of performance-limiting factors simultaneously with stability investigations is necessary. As an example, consider a hypothetical case where degradation of I_{sc} is suspected to be either due to dye degradation which diminishes the photocurrent generation or due to loss of tri-iodide in the electrolyte, which put the cell current to diffusion limited condition. If the photocurrent is limited by mass transport in the electrolyte instead of the absorption and injection by the dye, the achieved stability is not a sufficient proof to conclude that the dye was stable as well. For instance suppose that a poorly performing electrolyte suppresses the I_{sc} to 50% of the value obtained with a higher performance electrolyte, due to diffusion limitation. Then, 50% of the dye may degrade while I_{sc} stays constant. In general, this is just an example of the fact that investigation of stability in terms of η, I_{sc}, FF, V_{oc}, is sensitive to changes in only those properties that in the practical case affect these parameters. In this case I_{sc} was not sensitive to the dye. However, this limitation can be removed by using lower light intensities to reveal the degradation.

3. Conclusions

The stability of DSCs is reported in hundreds of publications, yet very little is known as a whole about the chemical reactions responsible for cell degradation and their relation to stress factors, such as visible and UV light, and elevated temperatures. In practice, stability investigation papers mainly report the time evolution of I–V parameters and the effect of different material components on these. Only a small proportion of these papers report investigations using chemical analysis or spectroscopic techniques giving direct evidence on the material changes behind the degradation. Quite often only positive stability results are reported whereas negative ones are seldom published. There is a great need to establish a set of procedures by which degradation can be quantified and data can be more reliably compared.

Conventional DSCs have been shown to be stable at 80 °C in the dark and at 55–60 °C light soaking at 1 Sun using hydrophobic dyes with liquid electrolyte, ionic liquid and polymer gel electrolytes. However, stability has not been obtained for light soaking at 80 °C yet. Some alternative materials such as flexible substrates have shown stability problems even under milder conditions.

To improve the stability of DSCs, it is imperative to take all proposed degradation mechanisms which lack reliable experimental evidence as hypotheses and investigate them further. It becomes evident that techniques giving chemical information need to be used in the stability investigations of DSCs. In this regard, segmented cell configurations are very useful as they open up the possibility to examine different degradation mechanisms in isolation and provide increased measurement aperture required for the spectroscopic techniques.

Acknowledgements

The study was funded by the Academy of Finland. K. Miettunen is grateful for the scholarships of the Graduate School of Energy Technology.

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