Recovery of dye-sensitized solar cell’s performance by heat treatment†

Marko Berginc,* Marko Topič and Urša Opara Krašovec

The formation of iodine containing crystals with ageing in ionic liquid based dye-sensitized solar cells (DSSCs) containing an \( \text{I}_3^-/\text{I}^- \) redox couple has already been confirmed. In this report we show how the size of these crystals can reversibly change during operation and the effects this has on cell performance. We also show how heat treatment and applied forward and reverse current treatment influence crystal growth in the cell. Crystal growth was tracked using electroluminescence and transmittance imaging, while current–voltage characterization and electrical impedance spectroscopy were used to measure cell performance and follow the changes in \( \text{I}_3^- \) diffusion, charge transfer resistance, and recombinations occurring in the DSSCs. Results reveal that applying a reverse current to the DSSC leads to the rapid formation of \( \text{H}_2 \) bubbles while crystals grow rapidly when a forward current is applied. Additionally heat treatment at 80 °C can completely recover performance of a degraded cell showing visible defects and a large inhomogeneous active area.

1 Introduction

Dye-sensitized solar cells (DSSCs) have been extensively studied as low-cost alternatives to silicon solar cells.\(^1\,^2\) Over the last two decades various materials including dyes and electrolyte components have been developed with the aim of improving conversion efficiency and cell stability. Despite this cell stability remains an issue.\(^5\,\,^9\,\,^11\) Photovoltaic cells/modules must pass tests related to stability as specified in the IEC 61646 or IEC 61215 standards to qualify for the market. In addition solar cells are expected to pass specific industry-driven tests of which the most challenging for DSSC technology remains the light soaking test at 85 °C,\(^5\) while the thermal test at 85 °C in the dark and the light soaking test under full sunlight at 60 °C\(^6\,\,^12\) are slightly less demanding.

Cell or PV module aging can be done both indoors starting with temporal stability testing in the dark at room temperature, albeit more usually under continuous accelerated conditions, or outdoors under location-specific and field-specific

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In our previous studies we examined such crystals using the light-beam-induced current technique, transmittance imaging (TI) and electroluminescence (EL).\textsuperscript{11,24,25} These methods allowed us to study local defects.\textsuperscript{24} Electroluminescence imaging demonstrated that short term ageing (irradiation \(\leq 30\;\text{kw h m}^{-2}\)) is associated with crystal growth in the electrolyte.\textsuperscript{25} Under an open-circuit condition crystal growth increased both \(V_{OC}\) and \(\eta\), while under a short-circuit condition crystal growth was more pronounced and a decrease in \(J_{SC}\), \(V_{OC}\) and \(\eta\) was observed.\textsuperscript{25} More recently we revealed that the dark crystals are introduced into the cells along with the electrolyte.\textsuperscript{14} We also found that these crystals continued to grow when the cells were stored in the dark causing an increase in \(V_{OC}\) and a decrease in \(J_{SC}\), but dissolved during the first 2 months of a 7 month outdoor ageing study (irradiation \(\leq 909\;\text{kw h m}^{-2}\)) regardless of the operating condition.\textsuperscript{11} Interestingly, one large crystal typically grew during the final stage of ageing under open-circuit conditions.\textsuperscript{11}

Because the formation/growth/dissolution of iodine based crystals in the electrolyte significantly influences the performance of DSSCs we believe that it is important to understand the correlation between crystal development and cell performance. For this reason we have studied the effect of crystal development in cells that were (i) kept in the dark at standard room temperature (25 °C), (ii) exposed to heat, and (iii) subjected to either a forward or reverse current. Temperatures of 60 °C and 80 °C were chosen for heat treatment since cell temperature when outdoors can exceed 60 °C.\textsuperscript{8,26} Reverse or forward currents proportional to the \(J_{SC}\) were also applied to non-illuminated cells to simulate shade conditions for cells connected in either series or parallel in a PV module. The EL and TI were used to track crystal development while current-voltage characterization (I-V) and electrical impedance spectroscopy (EIS) were used to correlate cell performance with processes occurring in the cells such as \(I_3^-\) diffusion, charge transfer resistance, and recombinations.

2 Experimental

2.1 Cell preparation

A fluorine-doped SnO\textsubscript{2} coated glass (TCO) with a sheet resistance of 8 \(\Omega\cdot\square\) was used for the front and back cell substrate. An optimized Pechini sol-gel TiO\textsubscript{2} paste (based on P25,Degussa, Germany)\textsuperscript{27} was then applied to the surface of the front TCO glass substrate using the “doctor blading” technique. The TiO\textsubscript{2} layer was then sintered at 450 °C for 1 h before being immersed for 12 h in an ethanol solution of a Ruthenium complex based dye N719 (Ru(2,2′-bipyridyl-4,4′-dicarboxylate)\textsubscript{2} (NCS))\textsubscript{2}, Solaronix, Switzerland). For a counter electrode, platinum (thickness \(\sim 5\;\text{nm}\)) was sputtered on a TCO glass substrate. The active and counter electrodes were then sealed using a 25 \(\mu\text{m}\) thick polymer foil frame (Surlyn, DuPont, USA). This also acts as a spacer between the two electrodes. As an electrolyte we used a binary ionic-liquid mixture of 1-propyl-3-methyl-imidazolium iodide (Iolitec) and 1-ethyl-3-methyl-imidazolium tetracyanoborate in a volume ratio of 13:7 (Merck), with the addition of

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0.5 M \textit{N}-methylbenzimidazole, 0.1 M guanidinium thiocyanate and 0.2 M of I$_2$. This composition is considered the best binary ionic liquid electrolyte for DSSCs.\textsuperscript{28} After injecting the electrolyte through two pre-drilled holes in the counter electrode the cells were sealed and stored in the dark for 24 h to allow for complete penetration of electrolyte into the pores of the TiO$_2$ layer. The size of the active area was 0.63 ± 0.05 cm$^2$.

2.2 Characterization

Cells under test were routinely characterized at different times according to Table 1. The \textit{I–V} scan under STC, the electroluminescent image (EL) and the transmission image (TI) were always used for characterization. After initial characterization (phase a) the cells were stored in the dark at room temperature (RT, 25 °C) under an open-circuit condition for an initial resting period of 11 months (1st resting period). The cells were then treated as described in Table 1 (phase b). After each heat treatment (each time period and temperature) the cells were cooled down prior to taking the \textit{I–V} scan under STC. After phase b the cells were rested for a second time (2nd resting period) in the dark at RT under an open-circuit condition. A series of reference cells were also stored in the dark at RT.

\textbf{I–V scan.} \textit{I–V} characterization was performed using an Oriel Class ABA solar simulator (Newport, USA) equipped with a 1.5G air mass filter, the spectrum of which closely matches the required AM1.5 spectrum. In accordance with the IEC60904-3 standard the short-circuit current mismatch parameter was calculated and in conjunction with a calibrated c-Si reference solar cell covered with a KG5 glass filter, the level of standard illumination (1 sun, 1000 W m$^{-2}$) was determined. The cells were also masked to leave only the active area of the cell exposed. This is considered the most rigorous condition regarding cell efficiency. \textit{I–V} characteristics of the cells were then measured using a Keithley 238 source meter by applying a voltage and measuring the current. The cells were scanned stepwise (10 mV) from 0 V (short-circuit condition) to 0.9 V (beyond \textit{V}_{OC}). During the measurement the cell temperature was always stabilized to 25 °C using the cooling/heating setup based on the Peltier element.

\textbf{EL.} The electroluminescence measurement (EL) is a powerful method to observe spatial defects in solar cells. When a current (usually equal to short-circuit current) is applied to the solar cell in the dark the cell radiates the IR photons which are detected using an imaging device. In our setup we used a CCD camera (FLI, MLx285, USA), which utilizes a low noise monochromatic 1.5 megapixel CCD sensor with improved EQE in the NIR region and a cooling system to minimize background noise. The camera was equipped with a 12 mm colour corrected Vis-NIR lens with a wide focus range. During measurements the camera, the camera lens and the cell were housed in a custom-built dark enclosure. The working electrode was oriented towards the camera. A laboratory power supply was then used to forward bias the cells with a short-circuit current previously measured under STC. The CCD array

<table>
<thead>
<tr>
<th>Phase</th>
<th>Heat treatment</th>
<th>Reverse bias current</th>
<th>Forward bias current</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>\textit{I–V}, EL, TI</td>
<td>11 months/dark, RT</td>
<td>11 months/dark, RT</td>
</tr>
<tr>
<td>b</td>
<td>\textit{I–V}, EL, TI</td>
<td>5 min at RT/60 °C/80 °C</td>
<td>\textit{I–V}, EL, TI</td>
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<tr>
<td></td>
<td>\textit{I–V}, EL, TI</td>
<td>10 min at RT/60 °C/80 °C</td>
<td>6 min 30 s at 0.2 \times J_{SC}, TI</td>
</tr>
<tr>
<td></td>
<td>\textit{I–V}, EL, TI</td>
<td>15 min at RT/60 °C/80 °C</td>
<td>18 h at 2 \times J_{SC}, TI</td>
</tr>
<tr>
<td></td>
<td>\textit{I–V}, EL, TI</td>
<td>30 min at RT/60 °C/80 °C</td>
<td>1 h at 80 °C</td>
</tr>
<tr>
<td></td>
<td>\textit{I–V}, EL, TI</td>
<td>60 min at RT/60 °C/80 °C</td>
<td>1 h at 80 °C</td>
</tr>
<tr>
<td></td>
<td>\textit{I–V}, EL, TI</td>
<td>2 h at RT/60 °C/80 °C</td>
<td>1 h at 80 °C</td>
</tr>
<tr>
<td></td>
<td>\textit{I–V}, EL, TI</td>
<td>2 h at RT/60 °C/80 °C</td>
<td>1 h at 80 °C</td>
</tr>
<tr>
<td>c1</td>
<td>\textit{I–V}, EL, TI</td>
<td>9 months/dark, RT</td>
<td>6 h 40 min at 0.2 \times J_{SC}, TI</td>
</tr>
<tr>
<td>c2</td>
<td>\textit{I–V}, EL, TI</td>
<td>8 h at 80 °C</td>
<td>6 h 40 min at 0.2 \times J_{SC}, TI</td>
</tr>
</tbody>
</table>

* Not shown.
was kept at 0 °C and an exposure time set to 300 s. Optical and spatial constraints meant that only 600 × 600 pixels were effectively used for image acquisition.

**TI.** The transmittance image (TI) is a method to observe visual spatial defects. The semi-transparent DSSC is backlit using a diffused white light emitting diode and the photograph of the cell is then acquired using a 2-mega pixel digital microscope camera DigiMicro 2.0 Scale (DNT, Germany).

**EIS.** Electrical impedance spectroscopy (EIS) was performed using a potentiostat (Zahner Elektrik IM6e, Germany) with Thales software in a 10 mHz-1 MHz frequency range with an AC amplitude of 5 mV. The illuminated cells (1000 W m⁻²) were kept under open-circuit conditions. The EIS spectra were analysed according to the procedure described in the literature.²⁹ More information about the analysis and a typical Nyquist plot with denoted parameters can be found in the ESI† (Fig. S4).

### 3 Results and discussion

#### 3.1 Heat treatment

Electroluminescent images and performance parameters (*J*ₘ, *V*ₘ, FF and η) of the reference cell (cell 1) and the cells heat treated at 60 °C (cell 2) and 80 °C (cell 3) are presented in Fig. 1 and 2, respectively. For the reference cell the same measurement protocol and timeline as for the heat treated cells were applied (see Experimental). This means that any changes observed in cell performance and crystal development in the reference cell are results of repeated *I*-*V* scans and EL image acquisitions. Herein, only the progress of a typical DSSC for each temperature is presented. The performance parameters of these cells and an additional cell at each temperature together with TI and EL images with additional intermediate snapshots are given in the ESI† (Table S1 and Fig. S2 and S3, respectively).

**Phase a → phase b.** The results show that after cell fabrication (phase a) all the cells had small inactive spots comprised of iodine containing crystals (Fig. 1). These crystals were already formed in the electrolyte and were introduced into the cells along with the electrolyte during cell fabrication.¹¹,²⁴,²⁵ During the 1st resting period the crystals continued to grow (Fig. 1) resulting in a reduction in the concentration of tri-iodine, [I₃⁻], in the electrolyte. This is reflected by a decrease in *J*scc (approx. 1 mA cm⁻²) and an increase in the *V*ₘ (approx. 40 mV) after the 1st resting period (Fig. 2) and agreeing with Kim et al. They also observed a small increase in the FF, which is probably associated with reduced serial resistance losses due to a reduced *J*scc. In all three cases, the increase in *V*ₘ and FF overcomes the decrease in *J*scc resulting in an increase in η after the first resting period.

**Phase b.** Our results show that the crystals in the reference cell (cell 1) were not affected by either continuous *I*-*V* characterization or EL imaging (phase b in Fig. 1). Continuous measurements did observably cause the *J*scc to initially increase, but after a few measurements it remained unchanged. This is thought to be related to the reactivation of the counter electrode by repeated *I*-*V* measurements after a long resting period. There was also a negligible increase in *V*ₘ while the FF initially decreased but then remained constant. This decrease in FF is associated with the increase in the *J*scc. As a result, η remained stable. Taking into account all our observations we find that repeated *I*-*V* measurements and EL imaging do not significantly affect either cell performance or the size of the crystals in cell 1.

Heat treatment at 60 °C (cell 2) and 80 °C (cell 3) affects both cell performance and crystal size. The crystals in cells 2 and 3 gradually dissolve during heat treatment (Fig. 1) with dissolution being significantly faster at 80 °C compared to 60 °C. Our EL measurements show that the crystals completely disappeared in the cells exposed to 80 °C for 4 h (ESI†, Fig. S2). When exposed to 60 °C for 6 h the crystals did not disappear but were significantly reduced in size (Fig. 1). The dissolution of the crystals also affects cell performance. The *J*scc of the cell exposed to 60 °C and the cell exposed to 80 °C logarithmically increased with time. This initial increase in the *J*scc may, in part, be related to the reactivation of the DSSC due to repeated *I*-*V* measurements as observed for the reference cell. Nevertheless, a more intense and rapid increase in *J*scc is observed when the cells were heated at 80 °C (cell 3) and is related to the rapid evaporation of the electrolyte.
dissolution of the crystals. The $J_{SC}$ of cell 3 after being heated for 6 h (phase b) exceeds the initial $J_{SC}$ (phase a), while remaining below the initial $J_{SC}$ in the case of cell 2. The $J_{SC}$ of cell 2 (treated at 60 °C) monotonically increased with time, whereas $J_{SC}$ decreases during the final 2 h of heat treatment at 80 °C (cell 3). Similar observations were found for the equally treated cell 3a (Table S1 in the ESI†). We believe that this decrease in $J_{SC}$ is probably related to a degradation of the electrolyte, an observation affirmed by electrical impedance spectroscopy (see below).

The dissolution of the iodine containing crystals in cells 2 and 3 also leads to an increase $J_{SC}$ in the electrolyte, which shifted the redox potential of the electrolyte upward and stimulated recombinations. Both mechanisms decrease the $V_{OC}$, which is confirmed by the exponential decrease in $V_{OC}$ with time (Fig. 2). According to expectations the observed reduction in $V_{OC}$ is faster and more intensive in the case of cell 3. The FF sharply decreases during the first 30 min but then remains unaffected. This is a probable result of serial resistance losses due to the sudden initial increase in the $J_{SC}$. With the exception of a minor initial fluctuation, $\eta$ remained stable during heat treatment at both 60 °C and 80 °C, although significant variations in $J_{SC}$ and $V_{OC}$ were observed (Fig. 2).

**Phase b → phase c.** After heat treatment the cells were rested in the dark for a further 9 months at 25 °C. During this 2nd resting period, the crystals that were present after heat treatment continued to grow (cell 1 and cell 2), whereas in cell 3, where the crystals had completely disappeared, EL measurements revealed the active area to have remained unchanged. Previously, crystal growth had resulted in an increased $V_{OC}$ and decreased $J_{SC}$ (cell 2) but in this case the $J_{SC}$ and $V_{OC}$ of the reference (cell 1) decreased slightly albeit an increase in $V_{OC}$ would have been expected due to crystal growth. The reason for this remains unknown. The FF of all the cells increased and is probably related to a decrease in the $J_{SC}$. A small decrease in $\eta$ was also observed. Cell 3 followed the same trend although no crystal formation was observed during this period. This behaviour is difficult to explain but could be related to either cell degradation that occurred during the final 2 h of heat treatment at 80 °C or that any crystals present were too small to be detected with EL imaging. Interestingly, for any individual cell, $J_{SC}$ remained constant after the 1st and 2nd resting period while in between, due to the different heat treatments, large variations were observed.

**Phase c.** Finally, all the cells were exposed to 80 °C for 8 h. The resultant EL images revealed that during heat treatment the crystals had almost completely dissolved in cell 1 and cell 2 leaving only negligible residues. Cell 3 had remained homogeneous. According to expectations all cells showed an increase in $J_{SC}$, a decrease in $V_{OC}$ and a decrease in FF. Unexpectedly, the performance of the cell 3 had changed in a similar manner to cells 1 and 2 but the magnitude of change was smaller. The opposite behaviour was observed for $\eta$, which increased slightly for the reference cells (cell 1 and 1a; see Table S1 in the ESI†), increased or decreased for cells 2 and 2a, and decreased for the cells 3 and 3a.

The electrolyte used in our study contained both guanidinium thiocyanate and the N-methylbenzimidazole which means that the crystals could originate from either dye desorption as proposed by Kim et al.**22** or are crystals of...
(MBI)₆(MBI-H⁺)₂(Γ)(I₃⁻) as proposed by Fischer et al. In our case, crystallization is best explained by the formation of an iodine containing crystal such as an (MBI)₆(MBI-H⁺)₂(Γ)(I₃⁻) complex. First, the crystals were introduced into the cells along with the electrolyte (phase a) and second, the Jₛₑ increased and the Vₒc increased as the crystals grew. This can be explained by dye desorption, since the presence of an undyed TiO₂ surface acting as a strong recombination centre would cause a decrease in Vₒc. Finally, heat treatment demonstrated the reversibility of the process, which is related to crystal growth/dissolution – a fact that supports the presence of iodine containing crystals. After heat treatment the Vₒc decreased while Jₛₑ increased possibly to its highest recorded value (cell 3, Fig. 2). Such an increase would be unlikely if crystal formation was a result of dye desorption.

EIS. Fig. 3 shows the EIS spectra of a typical illuminated cell under an open-circuit condition measured before and after being heated to 80 °C for 4, 12 and 20 h. The procedure on how to extract parameters from the EIS scans²⁹ together with the obtained values for this cell and two additional identical cells are given in Table S2 in the ESL.²⁹

A typical Nyquist plot of the EIS spectrum consists of three semicircles each measured in a different frequency range; a high frequency semicircle describes the processes at the counter electrode (CE), a central semicircle for the working electrode (WE), while a semicircle measured at a low frequency range shows the diffusion of I₃⁻ in the electrolyte (EL). The results show that the series resistance Rₛ remained unaffected by heat treatment, whereas there is an initial sharp decrease followed by a gradual decrease in the charge transfer resistance Rₜₑ. Two mechanisms can explain this decrease: (1) crystal dissolution and (2) a cleaning of the Pt layer on the counter electrode. Initially, it appears that not only the Pt but mostly a too low initial [I₃⁻] in the electrolyte determine the Rₜₑ. After 4 h of heat treatment the [I₃⁻] increases sharply reducing the Rₜₑ to that extent that only the Pt layer limits the charge transfer at the counter electrode. Presumably, prolonged heat treatment causes a continuous increase in the [I₃⁻]. Because there is a sufficient amount of I₃⁻ for the charge transfer to occur at the counter electrode the Rₛ does not further decrease. A cleaning of the Pt layer on the counter electrode during heat treatment is also possible causing Rₛ to gradually decrease.¹¹ The effective recombination constant for the electrons kₑff is proportional to the angular frequency ωₑ = 2πkₑff where the central semicircle of the impedance spectra (Fig. 3) reaches its lowest imaginary part. The kₑff linearly increases with time until 12 h, where after prolonged treatment up to 20 h reduced the kₑff by 4.35%. This initial linear increase in the kₑff supports our hypothesis that the [I₃⁻] increases when the iodine containing crystals are dissolved. Alternatively, cell degradation might be responsible for the decrease in the kₑff after prolonged heat treatment. This is in accordance with our previous findings where an irreversible loss of [I₃⁻] was observed after ageing.¹¹ The diffusion coefficient of the I₃⁻ ions in the electrolyte Dᵢ decreases with heat treatment up to 12 h and although Dᵢ would be expected to be independent of the [I₃⁻], the higher [I₃⁻] in the electrolyte hampers the [I₃⁻] transport from the working to the counter electrode. Additionally, higher [I₃⁻] promotes the recombinations of electrons with I₃⁻ ions and both effects will reduce Dᵢ upon prolongation of heat treatment. After 12 h the Dᵢ increased which is potentially another consequence of the irreversible loss of the [I₃⁻] due to cell degradation.

The charge transfer resistance related to the recombination of the electrons Rₜₑ, resistance of diffusion of the I₃⁻ ions in the electrolyte Rₑᵣ and, the peak frequency of the semicircle in a high frequency range (ωₑ) that is related to capacitance at the counter electrode are difficult to explain since they do not give direct insight into the processes taking place in the cells and do not have a significant effect on the performance.

3.2 Reverse and forward current treatment

Cells 4 and 5 were connected to a reverse and forward bias current, respectively, in the dark. The flows of the electrons and I₃⁻/I⁻ ions are presented in Fig. 4 (left). The values of the reverse and forward bias currents (in relation to the Jₛₑ measured under STC) are illustrated as dots on a typical dark I–V characteristic curve of a DSSC (Fig. 4, right).
The reverse bias was applied to cell 4. In this case the flow of the electrons and ions is the same as under normal operation under illumination, i.e., the applied current is positive. Since the current was applied in the dark, the voltage on the cell was negative. This condition would generally occur in a shaded cell that is connected in series with others in a PV module. Alternatively, the electrons and ions flow in the opposite direction when a forward bias current was applied, i.e., the applied current is negative, while the voltage on the cell becomes positive (Fig. 4). A similar situation will occur in a shaded cell connected in parallel with the others in a PV module, i.e., the shaded cell would perceive a fixed voltage from the illuminated cells.

Fig. 5 shows EL images of cells 4 and 5 measured after the following: fabrication (phase a), after 1st resting period, after applying reverse or forward current treatment, and after heat treatment at 80 °C for 1 h. Table 2 gathers the performance parameters: $J_{SC}$, $V_{OC}$, FF and $\eta$, measured under STC at equivalent stages. All stages of ageing including the more frequent TI snapshots during reverse or forward current treatment are shown in Fig. S6 in the ESI†. Additionally, a movie is given in the ESI† which demonstrates the accelerated evolution of spatial defects (formation of bubbles and crystal growth) under reverse and forward current treatment.

**Phase a → phase b.** Keeping these cells in the dark at 25 °C leads to the same conclusions as already observed for the cells examined in Section 3.1 (Fig. 1 and 2) i.e., crystal growth during the resting period decreases the $[I_3^-]$ in the electrolyte therefore $J_{SC}$ decreased significantly while $V_{OC}$, FF and $\eta$ increased.

**Phase b**

Reverse current treatment. After the 1st resting period a reverse current (Fig. 4) was applied to the non-illuminated cell 4. After applying a constant current equal to $0.2 \times J_{SC}$ for 5.5 min bubbles appeared after only a few seconds (Fig. 6; for more details see the movie and Fig. S6 in the ESI†). These small bubbles then combined to form a few large bubbles. Applying a reverse current equal to $2 \times J_{SC}$ for 6.66 h resulted in a gradual decrease in bubble size and dye molecules to become detached from the TiO$_2$ surface. Finally, a current equal to $2 \times J_{SC}$ was applied for a further 18 h. Initially a few large bubbles appeared, but soon after the cell became severely damaged. The active area became very inhomogeneous and covered with bright and dark spots moving in the active area/electrolyte. During all three stages when a reverse current was applied the absolute value of the reverse bias voltage increased, i.e., the voltage across the cell became more negative, indicating a likely decrease in the $[I_3^-]$, which is in agreement with Mastroianni et al.30,31

The formation of bubbles and/or detachment of the dye molecules under reverse bias have already been observed.30-32 Figgemeier et al.12 observed the formation of oxygen and/or hydrogen bubbles when water entered a cell while Mastroianni et al.30,31 observed a rapid degradation of DSSCs accompanied by dye detachment, evolution of gas inside the cell, and cell breakdown after applying voltages more negative than $-1.65 $ V. They found that the bubbles have an electrolysis-dependent origin and form at the Pt/electrolyte interface where I$_2$ reacts with residual H$_2$O, which in turn creates hydrogen bubbles.30 They also observed that long bias stresses retain the dye in its oxidized state for a prolonged period of time making it more probable that it can suffer destructive reactions and irreversible degradations involving ligand oxidation, thiocyanate (SCN$^-$) detachment, and binding between SCN$^-$ and impurities (such as H$_2$O/OH$^-$) or $\Gamma$/I$_3^-$ ions.30

Our results show that an applied reverse current significantly reduces cell performance. All performance parameters of cell 4 became virtually zero (Table 2). Such severe damage was also observed using EL which revealed that cell 4 was inactive (Fig. 5). After the reverse bias current treatment, cell 4 was then heated at 80 °C for 1 h. The virtual TI homogeneity of the cell (Fig. 6 and Fig. S6, ESI†), the intensity of the EL response (Fig. 5), and the performance parameters (Table 2) improved

<table>
<thead>
<tr>
<th>Cell</th>
<th>Time</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell 4 (reverse)</td>
<td>Fresh</td>
<td>9.74</td>
<td>0.664</td>
<td>56.2</td>
<td>3.63</td>
</tr>
<tr>
<td></td>
<td>1st resting period</td>
<td>7.52</td>
<td>0.758</td>
<td>70.7</td>
<td>4.03</td>
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<tr>
<td></td>
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<td>0.007</td>
<td>0.0</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>1 h at 80 °C</td>
<td>0.08</td>
<td>0.254</td>
<td>21.2</td>
<td>0.01</td>
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<tr>
<td>Cell 5 (forward)</td>
<td>Fresh</td>
<td>10.17</td>
<td>0.658</td>
<td>62.4</td>
<td>4.18</td>
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<tr>
<td></td>
<td>1st resting period</td>
<td>9.37</td>
<td>0.695</td>
<td>65.8</td>
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<td>0.605</td>
<td>45.3</td>
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<td>Forward current treat. (12th meas.)</td>
<td>6.95</td>
<td>0.628</td>
<td>54.7</td>
<td>2.39</td>
</tr>
<tr>
<td></td>
<td>1 h at 80 °C</td>
<td>10.64</td>
<td>0.630</td>
<td>62.1</td>
<td>4.16</td>
</tr>
</tbody>
</table>
but major defects remained such that heat treatment did not have a restorative effect. The cell was then rested for a 2nd resting period. Measurements were taken before and after an additional heat treatment at 80 °C for 8 h. Results show that cell performance parameters had improved during the 2nd resting period and partly during a further heat treatment but overall cell performance remained low ($J_{SC} = 0.11$ mA cm$^{-2}$, $V_{OC} = 0.434$ V, FF = 33.7% and $\eta = 0.02\%$). Both defects and inhomogeneities were clearly observable by TI and EL (not shown here).

**Forward current treatment.** A forward bias current treatment was applied to the non-illuminated cell 5 after the 1st resting period (Fig. 5 and 6). First, a current equal to $-J_{SC}$ was applied to the cell for 6.66 h. During this period crystal growth was extremely fast when the current was applied and the area covered by the crystals almost doubled in size after the first 6.66 h (Fig. 6; see also movie and Fig. S6 in the ESI†). We then applied a current equal to $-2 \times J_{SC}$ for 17.5 h. The crystals rapidly grew out in all directions in a dendritic pattern. The colour of the crystals also became brighter. Finally the same current was applied for a further 66 h during which a similar phenomenon, albeit more gradual one, was observed. Then at the 59th h a strong collapse of the electrolyte occurred introducing a major inhomogeneity in the cell. During all stages the value of the forward bias voltage also increased, indicative of a reduction in the $[I_3^-]$. The breakdown of the cell that occurred after the forward bias current treatment was also observed by EL (Fig. 5). The active area of the cell also became inhomogeneous and covered with large inactive dark spots. In addition, performance parameters and especially the $J_{SC}$ decreased significantly (Table 2), i.e., $\eta$ was reduced from 4.29% to 0.52% (88% relatively). Repeating $I$-$V$ measurements gradually increased cell performance, which stabilized after 12 measurements. The value of $\eta$ (2.39%) remained below 4.29% measured before applying a forward bias current.

After heating cell 5 at 80 °C for 1 h the cell’s active area became homogeneous (Fig. 5), which implies an extensive restoration of cell performance. The $J_{SC}$ reached its highest value while $V_{OC}$ remained below its initial value (Table 2). Interestingly FF and $\eta$ were practically the same as initially measured, which demonstrates the restorative effect of heat treatment on the performance of the DSSCs. After the 2nd resting period (not shown here) several small crystals had  reappeared, which was also observed with TI and EL. The $I$-$V$ measurements reveal a decrease in $J_{SC}$ while FF and $V_{OC}$ increased ($J_{SC} = 9.87$ mA cm$^{-2}$, $V_{OC} = 0.655$ V, FF = 66.0%). Surprisingly, $\eta$ reached 4.27% equalling the maximal value measured prior to applying a forward bias current. After heating cell 5 at 80 °C for a further 8 h (not shown here) the crystals dissolved and $J_{SC}$ increased and $V_{OC}$ decreased due to the higher $[I_3^-]$. In addition, FF decreased due to increasing serial resistance losses while $\eta$ remained the same ($J_{SC} = 10.33$ mA cm$^{-2}$, $V_{OC} = 0.630$ V, FF = 65.6%, $\eta = 4.27\%$).

4 Conclusions

Electroluminescent imaging and TI were successfully used to track the development of iodide containing crystals in ionic liquid based DSSCs with a $I_3^-/I^-$ redox couple that had been (i) stored in the dark, (ii) heat treated at 60 °C or 80 °C since cell temperature outdoors could easily exceed 60 °C, and (iii) exposed to reverse and forward current treatment in the dark to simulate a shaded cell connected in either series or parallel in a PV module. This study confirms that crystal growth occurs in cells stored in the dark for a significant period of time (9–11 months) and that heat treatment at both 60 °C and 80 °C leads to their dissolution.

$I$-$V$ characterization confirmed that the presence of these crystals significantly influences the performance of the DSSCs. The formation/growth of the crystals is associated with a decrease in $[I_3^-]$ in the electrolyte which causes a decrease in $J_{SC}$ and an increase in $V_{OC}$, while the opposite behaviour is observed when the crystals dissolved. Interestingly, the crystals do not reappear even after a resting period of 9 months if they had been completely removed by heat treatment. Our observations support the theory that in the electrolyte the additive N-methylbenzimidazole reacts with iodine forming iodine containing crystals such as the ([MBI]$_2$([MBI-H$^+$_])$_2$I$)(I$)$I_3^-$ complex.

In general, repeated $I$-$V$ measurements under standard test conditions do not influence crystal growth. Applying a reverse current to the DSSC leads to the rapid formation of H$_2$ bubbles and detachment of the dye molecules from the TiO$_2$ surface which results in the irreversible breakdown of the cell. When a forward current is applied crystal growth is rapid and cell performance decreases by 88%. In this case repeated $I$-$V$ measurements and especially a heat treatment at 80 °C for 1 h can restore cell performance showing a strong restorative effect of the heat treatment although the visible defects and strongly inhomogeneous active area caused a significant loss of the cell’s performance in first place. From the findings of our study heat treating DSSCs at 80 °C should be used to either initially stabilize or restore an $I_3^-/I^-$ redox couple based electrolyte and in turn cell performance.

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