

# Towards Long-Term Photostability of Solid-State Dye Sensitized Solar Cells

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The solid-state dye-sensitized solar cell (DSSC) was introduced to overcome inherent manufacturing and instability issues of the electrolyte-based DSSC and progress has been made to deliver high photovoltaic efficiencies at low cost. However, despite 15 years research and development, there still remains no clear demonstration of long-term stability. Here, solid-state DSSCs are subjected to the severe aging conditions of continuous illumination at an elevated temperature. A fast deterioration in performance is observed for devices encapsulated in the absence of oxygen. The photovoltaic performance recovers when reexposed to air. This reversible behavior is attributed to three related processes: i) the creation of light and oxygen sensitive electronic shunting paths between  $TiO_2$  and the top metal electrode, ii) increased recombination at the  $TiO_2/$ organic interface, and iii) the creation of deep electron traps that reduce the photocurrent. The device deterioration is remedied by the formation of an insulating alumino-silicate shell around the TiO2 nanocrystals, which reduces interfacial recombination, and the introduction of an insulating mesoporous SiO<sub>2</sub> buffer layer between the top electrode and TiO<sub>2</sub>, which acts as a permanent insulating barrier between the TiO<sub>2</sub> and the metal electrode, preventing shunting.

# 1. Introduction

In terms of research trends in photovoltaic, the main direction in emerging PV has been towards the achievement of high power conversion efficiency under simulated sunlight. However, with increased pressure for emerging PV technologies to deliver a product due to efficiencies approaching commercially realistic values for certain applications, long term operation and the understanding of any critical instability issues has become increasingly topical.<sup>[1–8]</sup> Dye-sensitized solar cells (DSSCs) have

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generated immense drive in the scientific community since their inception owing to their low cost processing and close to commercially realistic power conversion efficiency from early in their development.<sup>[9–11]</sup> In DSSCs, current is generated when a dye molecule, which is adsorbed on a mesostructured n-type semiconductor metal oxide, absorbs a photon, giving rise to electron injection into the conduction band (CB) of a metal oxide. Further to complete

In DSSCs, current is generated when a dye molecule, which is adsorbed on a mesostructured n-type semiconductor metal oxide, absorbs a photon, giving rise to electron injection into the conduction band (CB) of a metal oxide. Further, to complete the circuit the dye must be regenerated by electron transfer from a redox species in solution, which is then reduced at the counter electrode.<sup>[11]</sup> Even though DSSCs are composed of a preformed mesoporous metal oxide electrode, which should not be susceptible to structural degradation, long-term stability has remained a challenge owing to the liquid form of the most high performance redox electrolyte (iodide/ triiodide). This can be substituted however, by a solid-state hole transporting material,

giving rise to a complete solid-state dye-sensitized solar cell with a respectable performance.<sup>[12]</sup>

Solid-state dye sensitized solar cells (ssDSSCs) have good potential in terms of performance, cost, and stability. In ssDSSCs, the dve is regenerated from its oxidized state within a few hundred picoseconds, orders of magnitude faster than in the iodide/triiodide-based liquid electrolyte cells, where dye regeneration occurs on the microsecond time scale.<sup>[13]</sup> These extremely rapid regeneration dynamics should play a role in improved long-term stability of the dye in the DSSC because the dye is most likely to degrade in its charged oxidized state.<sup>[14]</sup> Despite these apparent advantages over the electrolyte DSSC and other competing organic photovoltaic concepts, the solidstate DSSC has yet to deliver on its promise of enhanced stability. Encapsulation of these devices is required to predominantly exclude oxygen and moisture because the organic components in the solar cell suffer from photodegradation in the presence of oxygen.<sup>[5,14–16]</sup> Nevertheless, to the best of our knowledge, there are no thorough long-term aging analyses of ssDSSCs where they have been aged and tested under homogeneously sealed conditions and measured in real time while the devices are being stressed at high temperature and continuous illumination. Usually stressing is conducted in an unspecified atmosphere, and the cells are removed from the stressing chamber and tested for an unspecified time.<sup>[17-19]</sup> Although

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these previous methods of stressing may indicate that the material system is fundamentally stable, it does not guarantee that the solar cell can operate and deliver power for a prolonged period of time under sunlight.

Here, we demonstrate that there is a reversible deterioration in performance of solid-state DSSCs, which occurs when the solar cells are exposed to sunlight in an inert atmosphere. This has been observed before and has previously been assigned to de-doping of the hole transporter.<sup>[20,21]</sup> Here, we observe that light soaking in an inert atmosphere induces a rapid drop in both photovoltage and short-circuit current, but the cells return close to original operation after relaxation in ambient conditions. We identify that this deterioration is primarily caused by a change to the nature of the TiO<sub>2</sub> surface and we postulate that it is driven by photoinduced desorption of adsorbed oxygen. We inhibit this deterioration by i) including an insulating mesoporous buffer layer separating the mesopourous TiO<sub>2</sub> from the metal cathode, which markedly stabilizes the open-circuit voltage,<sup>[22]</sup> and ii) by depositing an insulating shell around the TiO<sub>2</sub> nanoparticles, which substantially stabilizes the photocurrent.

## 2. Experimental Section

ssDSSCs were prepared according to a standard procedure. Briefly, fluorine-doped tin oxide (FTO) substrates (8  $\Omega/\Box$ , Pilkington) were etched with zinc powder and HCl (2 M) to give the desired electrode pattern. The substrates were cleaned with Hellmanex soap (2% in deionized water), deionized water, acetone, and ethanol. The last traces of organic residues were removed by a 10 min oxygen plasma-cleaning step. The FTO sheets were subsequently coated with a compact layer of TiO<sub>2</sub> (100 nm) by aerosol spray pyrolysis at 300 °C, using air as the gas carrier. 1 µm thick TiO<sub>2</sub> (Dyesol 18NR-T) films were then deposited by screen-printing. The TiO<sub>2</sub> films were slowly heated to 500 °C and allowed to sinter for 30 min in air. The samples were immersed in a 0.015 M TiCl<sub>4</sub> water solution for 45 minutes at 70 °C, and then reheated to 500 °C for another sintering step of 45 min.

For an alumina-silicate shell treatment, a sol of 3-(glycidyloxypropyl)trimethoxysilane (GLYMO) and aluminum secbutoxide (mole ratio of 8:2) was prepared following a two-step acid-catalyzed hydrolysis procedure described previously.<sup>[23]</sup> The synthesized sol was diluted to 20 mm. After TiCl<sub>4</sub> treatment, the TiO<sub>2</sub> substrate was dried at 80–100 °C before immersion into the alumino-silicate precursor solution for 1 min, 5 min, and 20 min in a closed chamber at room temperature (RT). The resulting samples were abbreviated as 1AS, 5AS, and 20AS. The substrates were then rinsed with anhydrous ethanol and dried in N<sub>2</sub> before sintering at 500 °C in air. It is unclear whether this process formed conformal coatings on the TiO<sub>2</sub> nanocrystals or adsorbed in the form of clusters, as is often observed in the chemical bath deposition method. In addition to the formation of an alumino-silicate shell, this process may dope the TiCl4 surface layer of the crystallites. During TiCl<sub>4</sub> treatment, TiCl<sub>4</sub> hydrolyzes to the Ti(OH)<sub>4</sub>, which can form a covalent bond with a hydroxyl group on the surface of TiO<sub>2</sub>. The attached  $Ti(OH)_x$  is then sintered in to crystalline  $TiO_2$ .

If however the hydrolyzed  $\text{TiO}_2$  mesoporous material containing  $\text{Ti}(OH)_x$  is dipped into an alumino-silicate bath to form an AlSiO shell, the hydrolyzed alumino-silicate precursor can form a covalent bond with the hydroxyl group of  $\text{Ti}(OH)_x$ . The following sintering step then possibly dopes the outer layer of  $\text{TiO}_2$  with the high bandgap metal oxide.<sup>[24]</sup>

The buffer layer was synthesized from a 30% colloidal solution of SiO<sub>2</sub> in ethylene glycol (Alfa Aeser). Appropriate amounts of ethyl cellulose and terpeniol were added to the colloidal solution before mixing thoroughly, similarly to a conventional TiO<sub>2</sub> paste made from TiO<sub>2</sub> nanoparticles.<sup>[25]</sup> Depending upon the required thickness, the resulting paste was diluted with ethanol. For buffer layer deposition, the SiO<sub>2</sub> paste was spin-coated onto the TiO<sub>2</sub> mesoporous layer and sintered at 400 °C.

After the shell and/or buffer treatment, the substrates were immersed in a 0.5 mM C106 dye solution (in a 1:1 mixture of acetonitrile and tert-butyl alcohol) for 12 h. The dye-adsorbed films were then rinsed with acetonitrile before spinning-on spiro-OMeTAD (LUMTECH) hole conductor at 1000 rmp for 60 s in air. The solutions for spin coating consisted of spiro-OMeTAD dissolved in anhydrous chlorobenzene (reagent grade) at 10 vol%, assuming a density of spiro-OMeTAD of 1 g cm<sup>-3</sup>. Tert-butyl pyridine (tbp) was added to the solution at a concentration of 1.26  $\mu$ L mg<sup>-1</sup> (tbp: spiro-OMeTAD). Lithium bis(trifluoromethyl sulfonyl)imide salt (Li-TFSI) (170 mg mL<sup>-1</sup> in acetonitrile) was added. After drying overnight, back contacts were applied by thermal evaporation of 150 nm of silver.

The devices were sealed in a glove box in inert atmosphere. Surlyn (DuPont Surlyn packaging resins) film was cut to form a gasket, placed on the devices and covered by a glass slide. The assembly was then placed onto a hot plate at 130  $^\circ\text{C}$ with the glass slide facing down and a uniform pressure was applied while the gasket melted, sealing the device. Commercially available two-part epoxy resin mixed with an appropriate hardener was then applied around the edges to further protect the device. For device measurements, solar-simulated AM 1.5 sunlight was generated by an ABET solar simulator calibrated to give 100 mW cm<sup>2</sup> using an NREL-calibrated KG5 filtered silicon reference cell, and the current density-voltage (I-V) curves were recorded with a Keithley 2400 source meter. The solar cells were masked with a metal aperture defining an active photovoltaic area of 0.09 cm<sup>-2</sup>. Photovoltage and photocurrent decay measurements were performed by a similar method as described elsewhere.<sup>[26-28]</sup> Transient absorption spectroscopy (TAS) measurements were performed by a similar method as previously reported.<sup>[29]</sup> Absorbance measurements of the films were taken in air (about 1 min air exposure) using a commercial spectrophotometer (Varian Cary 300 UV- Vis, USA).

Aging measurements were performed in a SUNTEST CPS+ (Atlas material testing solution) aging chamber equipped with a 1500 W air-cooled xenon lamp, which was calibrated to 0.76 suns for our measurements. There was an additional home-made UV filter in place above the cells, fabricated from  $\approx$ 200 nm thick compact ZnO coated FTO glass. The spectrum for the UV filter is shown in the Supporting Information (Figure S1). Its role was to reduce, though not entirely prevent UV absorption directly in the TiO<sub>2</sub>. Inside the chamber, the temperature was regulated by a direct setting and control of



**Figure 1.** a) Normalized solar cell performance during continuous aging at 85 °C under simulated AM1.5 sun light of 76 mW cm<sup>-2</sup> irradiance, for encapsulated and non-encapsulated ssDSSCs. Devices were encapsulated in an inert atmosphere. Non-encapsulated devices show gradual performance degradation whereas encapsulated device deteriorate rapidly within 5 h, mainly due to losses in photocurrent and photovoltage. b,c) UV-Vis absorption spectra for before and after aging of sealed and unsealed TiO<sub>2</sub> films with adsorbed C106 dye (b) and with added spiro-OmeTAD film (c). Samples were aged at RT under 1.5AM light for 48 h.

black standard temperature (BST) system. An electrically connected device holder was placed inside the chamber, which was then connected to a PC interfaced source-meter to directly measure current voltage curves while the solar cells were being aged. The equivalent irradiance within the aging box was estimated with a KG5 filtered silicon reference cell to be approximately 76 mW cm<sup>-2</sup>.

### 3. Results and Discussion

Aging tests were performed in an aging box under continuous illumination at 85 °C and open-circuit conditions. Current voltage curves were measured every 30 min. Prior to testing; the devices were encapsulated as described in the Experimental Section. We show the temporal evolution of solar cell performance parameters for encapsulated and non-encapsulated devices in Figure 1a. Surprisingly, the encapsulated devices deteriorated rapidly during 5 to 10 h of testing, entirely losing their photovoltaic efficiency. In contrast the non-encapsulated devices lost only approximately 50% of their power conversion efficiency over 70 h of testing. This may be useful for products which require only a short lifetime, for instance on a flexible platform where minimal atmospheric sealing is feasible. However, in Figure 1b,c, we show UV stability of C106 dye film adsorbed on TiO2. UV-Vis absorption spectra were collected for encapsulated and non-encapsulated TiO<sub>2</sub> films adsorbed with C106 dye (b) and a similar film with an additional spiro-OMeTAD. The absorbance was re-measured of the respective films after aging for 48 h under full sun light. This indicates that stability targets of many years will require encapsulation of the materials. These data show that the absorption spectrum of the encapsulated dye coated TiO<sub>2</sub> film does not noticeably change with aging, but the unsealed film deteriorates considerably. Hence, the drop in photocurrent of the unsealed device is consistent with dye degradation, but the rapid drop in photocurrent in the sealed device originates from different electronic processes in the device.

Interestingly, the non-functional sealed devices fully recuperate performance once the seals are broken and the photoactive layer is exposed to air, as we show in Figure 2, the respective device parameters are presented in the Supporting Information (Table S1). The reversible deterioration of encapsulated devices or devices operating in an inert atmosphere indicate that a reversible change in the electronic properties of the device is occurring and not the commonly observed irreversible photodegradation of the dye or the hole conductor. Irreversible photodegradation, as determined from the UV-vis measurements, is observed only when device is exposed to light in the presence of air.<sup>[5,14]</sup> The reversible deterioration observed here is not widely reported for electrolyte based DSSCs, and hence the obvious culprit for this should be the hole transporter because it is the only key difference between the two technologies. However, we believe that it is unlikely that the hole transporting material (HTM) plays a critical role in the fast deterioration of device performance. In a recent publication we have shown that in the presence of oxygen and light, Li-TFSI acts as a p-dopant and shifts the reaction equilibrium completely towards oxidized Spiro-OMeTAD, forming Spiro-OMeTAD+ TFSI-.<sup>[30,31]</sup> In our experiments here, Spiro-OMeTAD is already oxidized before encapsulation and its return to the neutral state is unlikely during the aging process since the oxidization with Li-TFSI is irreversible.<sup>[32]</sup> To corroborate that the degradation of the encapsulated device performance does not arise from the HTM de-doping, we replaced Spiro-OMeTAD with P3HT. P3HT is a much higher mobility HTM, and in principle does not require p-doping to operate effectively in a DSSC.<sup>[6,33,34]</sup> The resulting DSSCs follow a similar trend as Spiro-OMeTAD

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**Figure 2.** Current–voltage curves measured under simulated AM1.5 sunlight at 100 mW cm<sup>-2</sup> during various stages of aging, showing quick deterioration of device performance and recuperation when re-exposed to air. a) Aging of encapsulated devices at 85 °C under 100 mW cm<sup>-2</sup> illumination with subsequent breaking of the seals. b) Aging at RT in a vacuum chamber at 70 mW cm<sup>-2</sup> illumination and subsequent re-exposure to O<sub>2</sub>.

based devices when aged under similar conditions (Supporting Information Figure S2). In addition, the fill factor is the only parameter that does not rapidly degrade during the aging process. If reduced doping of the hole conductor was responsible for the degradation, then one would expect to see a drop in fill factor before observing a drop in short-circuit current.<sup>[34]</sup>

Since neither dye degradation nor changes in the HTM appear to be responsible for the marked loss in device performance upon sealing, it is necessary to investigate the electronic properties of the mesoporous TiO<sub>2</sub> during illumination in an inert atmosphere at 85 °C. The drop in short-circuit photocurrent and open-circuit voltage of the sealed devices could be consistent with: i) the formation of low-resistance shunting paths, leading to a rapid drop in the open-circuit voltage, as we have previously assigned for SnO2<sup>[22]</sup> and ii) the rapid drop in shortcircuit current may either be caused by a rapid acceleration of electron hole-recombination (which would also contribute to the voltage loss),<sup>[35,36]</sup> or the introduction of deep electron traps, from which the electrons cannot escape, leading to a direct recombination with holes. The generation of deep electron traps has been previously reported for TiO<sub>2</sub>, where UV lightinduced formation of energetically deep traps in TiO<sub>2</sub> nanocrystals can occur.[37]

Assuming that the reduction in photocurrent is in part a result of increased recombination rate at the TiO<sub>2</sub> surface, the formation of an insulating dielectric shell (such as alumino-silicate) on the TiO<sub>2</sub> nanocrystal surface should prevent direct contact between TiO<sub>2</sub> and the HTM, thereby inhibiting charge recombination. Such a surface treatment may also passivate defect sites, which could be responsible for electron trapping. We therefore coated the TiO<sub>2</sub> with differing amounts of alumino-silicate by immersing the mesoporous TiO<sub>2</sub> in solutions of alumino-silicate salt precursor for varying times (1, 5, and 20 min). The respective samples are referred to as 1AS, 5AS and 20AS (see Experimental Section for details).

The J-V curves of the corresponding devices are shown in the **Figure 3**a. The device based on the 1AS sample exhibited higher short-circuit photocurrent density compared with the control device, i.e., without passivation layer, but a further increase in thickness of the passivation layer (i.e., 5AS



and 20AS) had lower  $J_{sc}$  values compared to 1AS, albeit higher than the control device. All devices with alumino-silicate shell delivered lower Voc values compared to the control device tested initially in air. The fill factors (FF) of all samples ware comparable, irrespective of the alumino-silicate shell. The lowering of  $V_{oc}$  for the alumino-silicate coated devices is readily rationalized in terms of the acidic nature of the shell, quantified by its lower point of zero charge (PZC). The CB energetics of nano-crystalline TiO<sub>2</sub> has been shown to exhibit a Nernstein dependence on the pH of its surrounding medium.<sup>[38-40]</sup> An increase in surface pH (lowering of the PZC) of TiO<sub>2</sub> can lower its CB edge resulting in a lowering of  $V_{oc}$  and an increase in  $J_{sc}$  by enhancing charge injection.<sup>[40-43]</sup>

We performed transient absorption (TA)

spectroscopy to probe whether the interfacial recombination dynamics between electrons in the  $TiO_2$  and holes in the spiro-OMeTAD or dye are influenced by the AS shells. In the absence of the hole acceptor, we can observe the ground-state bleaching of C106 dye at 520 nm.

Figure 3b shows transient absorption decay profile for dye C106 adsorbed on a bare TiO<sub>2</sub> films and TiO<sub>2</sub> with different thickness of shell (i.e., 1AS, 5AS, and 20AS) but with no spiro-OMeTAD, whereas Figure 3c shows the similar films with spiro-OMeTAD infiltrated into the porous dye-sensitzied TiO<sub>2</sub> and therefore reflect the transient absorbance of the spiro-OMeTAD cation. While the back electron transfer is not significantly affected by the AS shell, oxidized spiro-OMeTAD lifetime is significantly longer in the presence of an aluminum-silicate shell. It is apparent in this latter case that the insulating metal oxide barrier retards the charge transfer compared with the bare TiO<sub>2</sub> control films. This is consistent with the expected blocking layer function of the insulating oxide, although this effect may also arise from the passivation of surface states responsible for accelerated recombination.<sup>[39,44,45]</sup>

This is also consistent with the increased photocurrents measured in the solar cells compared to the control device, and suggests that the chemical bath method for growing aluminasilicate may not necessarily grow a thick shell, but rather a surface passivation layer. Shells thicker than 1 nm are expected to reduce injection yield and hence photocurrent.<sup>[46]</sup>

No clear difference in recombination dynamics between 1AS, 5AS, and 20AS films was observed, indicating that most of the inhibition of recombination arises from the first shell layer.<sup>[46,47]</sup> Despite the inhibition of recombination with the alumina-silicate shells, solar cells fabricated from such films still exhibited a similar deterioration in performance when exposed to simulated sun light in an inert atmosphere, as we shown in **Figure 4**.

As we have discussed previously, a further basis for the rapid deterioration of encapsulated device performance may arise from the existence of a light and oxygen sensitive Schottky barrier at the  $TiO_2$  and metal electrode interface, which disappears when the device is exposed to light in an inert atmosphere and which is restored upon oxygen exposure.<sup>[48]</sup> This interface

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**Figure 3.** a) J-V curves for 1AS, 5AS, and 20AS devices. Device parameters  $J_{sc}$  (mA cm<sup>-2</sup>), PCE (%),  $V_{oc}$  (V) and FF of these devices are as mentioned. b) TA decay profile for C106 sensitized TiO<sub>2</sub> films for control and with 1AS, 5AS, and 20AS shells, without Spiro OMeTAD, probing the bleaching of the dye ground state absorption at 520 nm. c) TA decay profile of C106 sensitized TiO<sub>2</sub> films infiltrated with Spiro-OMeTAD, probing the absorption of the oxidized spiro-OMeTAD at 520 nm.

should not be present in a perfectly manufactured cell. However, in reality there is a good likelihood for significant contact to occur through pin-holes, thin regions of the spiro-OMeTAD capping layer, and through metal filaments or regions where the metal has migrated through the spiro-OMeTAD capping layer.<sup>[22,49–52]</sup> To avoid such a direct contacts here, we deposited an insulating mesoporous buffer layer, fabricated from sintered SiO<sub>2</sub> nanoparticles, between the TiO<sub>2</sub> and the metal electrode. We chose mesoporous SiO<sub>2</sub> for this purpose because of its transparency, high band gap, and low PZC value. The low PZC value of SiO<sub>2</sub> significantly reduces the amount of dye that adsorbs to this non-photoactive layer, and it is hence less likely to increase the parasitic absorption (absorption that does not lead to charge generation) compared to other dielectrics, such as Al<sub>2</sub>O<sub>3</sub> or ZrO<sub>2</sub>.<sup>[38–40]</sup>

We fabricated devices with two different thickness of  $SiO_2$  buffer layer (about 50 and 300 nm). We observed that encapsulated devices with 300 nm buffer layer show a marked stabilization of overall device performance during aging as we have shown in Figure 4 and Supporting Information Figure S3. However, this layer alone also failed to entirely prevent the rapid drop in photocurrent.

The two separate results described above led us to adopt a two-pronged strategy to simultaneously inhibit interfacial recombination at the  $\text{TiO}_2$  interface by an alumino-silicate shell and shunting between metal electrode and  $\text{TiO}_2$  using a mesoporous  $\text{SiO}_2$  buffer layer. The *J*–*V* curves of these devices before aging are shown in the Supporting Information (Figure S4).

Figure 4 shows the performance data for devices containing a 20AS shell, a 300 nm thick  $SiO_2$  buffer layer and combination of the two, compared with a control device that contains neither, over a period of 100 h light exposure at 85 °C. All devices were encapsulated in a nitrogen atmosphere. Clearly, neither the shell nor the buffer layer alone are able to remedy the early time deterioration in device performance while a combination of the two resulted in excellent device stability for up to 110 h.

The above results are very encouraging, and clearly identify that manipulating the nature of the mesoporous TiO<sub>2</sub> can have a strong impact on this degradation phenomena. However, longer term stressing beyond 100 h still results in deterioration of the photocurrent and solar cell efficiency. In the following section we therefore look to further understand the system, in order to enable further improvements moving forward. We have performed transient photocurrent and photovoltage decay measurements on control and device containing shell (20AS) and buffer (300 nm) before and after aging, as we show in Figure 5. At the same charge density, corresponding to the same number of mobile electrons in the TiO<sub>2</sub> CB, the recombination in the 20AS device is approximately two times slower initially than in the control device. Upon aging however, the recombination in the control cell speeds up by more than an order of magnitude, whereas the recombination with the alumino silicate shell and buffer layer is only marginally accelerated. Demonstrating that the insulating metal oxide shell and buffer layer increases the lifetime of the photogenerated charges more significantly for the aged devices. This justifies the predominantly sustained open-circuit voltage for the aged devices incorporating the shell treatment and buffer layers.

The reduced ability for the aged control device to sustain a large charge density is visualized in Figure 5b. Here we show the the differential capacitance plotted against the open-circuit VERG



Figure 4. Solar cell performance vs aging time of encapsulated devices under continuous simulated AM1.5 76 mW cm<sup>-2</sup> illumination at 85 °C for devices with a 20AS shell, a 300 nm thick SiO<sub>2</sub> buffer layer and a combination of the two, compared with a control device. The combined effect of shell and buffer layer appears to be most effective in suppressing quick device deterioration during aging.

voltage, which qualitatively draws the density of state (DOS) distribution for the electron in the TiO<sub>2</sub>.<sup>[38,53,54]</sup> A shift in the relative position of the differential capacitance-voltage curve, with respect to voltage, is consistent with a shift in the surface potential at the dye-sensitized heterojunction. For both the control device and that comprising the shell and buffer layer, there is a positive shift of around 100 mV after ageing. However, the absolute capacitance at the highest voltages (generated under the highest background light intensities) of the treated device, is much larger after aging, than that of the aged control device.

This indicates that the shell treatment and buffer layer has enabled the cell to sustain a much higher charge density under operating conditions. We do note however, that after aging both devices show a positive shift and a drop in capacitance for any given background light intensity, illustrating that these solutions have only partially resolved the deterioration.

It is hence consistent that the predominant stabilization of the solid-state DSSCs with the shell and buffer treatment occurs due to the inhibition of recombination at both the dye-sensitized heterojunction and at the mesoporous TiO<sub>2</sub>



Figure 5. Photovoltage-current decay measurements for control and a device containing both shell (20AS) and buffer (300 nm). The data have been collected for devices sealed in inert atmosphere, before and after the aging to extract: a) recombination lifetimes plotted against charge density at open circuit condition and b) open-circuit voltage ( $V_{oc}$ ) plotted against the capacitance.



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silver electrode contact. However, the mechanism leading to the enhanced recombination and loss of photocurrent in the untreated cells is not clear. The unusual behavior of rapid device deterioration and regeneration is likely to arise from the defect chemistry of the n-type semiconducting oxide, mainly introduced by oxygen vacancies and interstitial defects, giving rise to a non-stoichiometry composition (TiO2-x). Thermal annealing often removes bridging oxygen atoms from the lattice, creating two under-coordinated Ti(III) and one oxygen vacancy. Due to their unsaturated co-ordination they are reactive and adsorb  $O_2$  molecules forming a Ti(IV)<sup>+</sup> -  $O_2^-$  complex.<sup>[55]</sup> Among various forms of adsorbed oxygen (O<sup>+</sup>, O<sub>2</sub><sup>-</sup>, O<sup>-</sup>), O<sub>2</sub><sup>-</sup> superoxide has been identified as the most thermodynamically stable, in which the electron is transferred from the  $TiO_{2-x}$ surface to the adsorbed oxygen molecule.[56] Simultaneously, in the case where excess electrons are available in the conduction or sub-bandgap states, superoxide radical  $(O_2^{-})$  formation may also occur via the additional reaction<sup>[55]</sup> as Ti(IV) +  $e_{CB}$  +  $O_2 \rightarrow$  $Ti(IV)^+O_2^-$ .

To avoid confusion between these two types of super oxide complexes we refer to oxygen vacancy induced superoxide  $Ti(IV)^+O_2^-$  as  $\alpha$  and the other one  $\beta$  superoxide. The reversible nature of the superoxide complex at the  $TiO_2$  surface and its consequences on the electronic and photocatalytic behavior of  $TiO_2$  is a plausible premise to explore the deterioration and recovery of  $TiO_2$  based DSSCs. In our recent article we have shown that by blocking UV light completely can resolve such a quick deterioration to an extent.<sup>[58]</sup>

We suggest the following mechanism as illustrated in Figure 6. In DSSCs, a dye molecule transfers one electron to the Ti(IV) (3d0) of  $TiO_2$  and as a result of which one Ti(III) (3d1)

is generated. The energy gap between the Ti(IV) and Ti(III) is rather small so that the electron is easily transferred from Ti(III) to a neighboring Ti(IV) instead of remaining trapped as a space charge in the TiO<sub>2</sub> lattice as discussed by Dupuis et al.<sup>[57,59]</sup> Oxygen-defect-induced under-coordinated Ti(III) may however act as deep trap sites since they occupy much deeper energy levels in the band gap.<sup>[57,60]</sup> In ambient conditions (air), these under-coordinated Ti(III) trap states attract molecular oxygen with the subsequent formation of Ti(IV)<sup>+</sup>O<sub>2</sub><sup>-</sup> ( $\alpha$ ).<sup>[35,55,61]</sup> Similarly, electrons in sub-bandgap states may induce Ti(IV)<sup>+</sup>O<sub>2</sub><sup>-</sup> ( $\beta$ ) as mentioned above. Both modified states do not interfere with the device performance when illuminated.

These adsorbed negative oxygen molecules (superoxide radical  $O_2^-$ ) induce a positive potential at the TiO<sub>2</sub> surface, and hence establish a depletion layer (increase in the work function), which results in an upward bend in the CB.<sup>[62,63]</sup> Oxygen adsorption in the form of superoxide radical ( $O_2^-$ ) at the TiO<sub>2</sub> surface therefore not only reduces the density of deep traps but also subsequently generate a Schottky potential barrier, inhibiting interfacial charge recombination,<sup>[63,64]</sup> which could also aid in the rapid separation of charge following photo-induced electron transfer.

When devices are stressed by continuous illumination and high temperatures in an inert atmosphere they become nonfunctional within a few hours. In the above scenario, photoexcitation of the mesoporous TiO<sub>2</sub> causes the formation of electron hole-pairs. The hole in the valance band can recombine with the unpaired electron of O<sub>2</sub><sup>-</sup> in the  $\alpha$  superoxide complex, releasing an O<sub>2</sub> molecule,<sup>[37,65]</sup> converting the Ti(IV)<sup>+</sup>O<sub>2</sub><sup>-</sup> complex to a Ti(III) electron trap site. The corresponding free electron in the CB<sup>[21,32]</sup> is subsequently trapped at the reappearing



**Figure 6.** Suggested mechanism of oxygen adsorption and desorption at the TiO<sub>2</sub> interface. a) The formation of two different types of superoxide,  $\alpha$  and  $\beta$  (Ti(IV)<sup>+</sup> - O<sub>2</sub><sup>-</sup>) are shown.  $\alpha$  (Ti(IV)<sup>+</sup>O<sub>2</sub><sup>-</sup>) can be desorbed by the UV excitation but  $\beta$  (Ti(IV)<sup>+</sup>O<sub>2</sub><sup>-</sup>) is affected only by high temperatures. b) The desorption of negatively charged superoxide molecules and their effect on the depth on depletion zone (gray shaded area) is indicated. Adsorbed negative charge induce an increase in the depletion area and induce an upward bend in the CB that reduces interfacial charge carrier recombination. O<sub>2</sub> desorption upon illumination reduces this upward band bending and hence causes the disappearance of the Schottky barrier and the lowering of the Fermi level, increasing interfacial recombination.





deep trap site and will eventually recombine with an excess hole in spiro-OMeTAD.<sup>[21,32]</sup>

The continual emptying of a large number of deep trap sites through recombination with holes in spiro-OMeOTAD will result in a steady-state population of vacant deep trap sites and in the subsequent consumption of a large number of injected electrons in the TiO2. Additionally, the O2 desorption will lead to the disappearance of the depletion layer, a flattening of the CB-edge and a lowering of the Fermi level.<sup>[62,63]</sup> This would enhance interfacial recombination with excess holes in the spiro-OMeTAD by increasing the average electron density near the interface, and also be consistent with positive shift in the surface potential and lowering of the open-circuit voltage seen in Figure 5. Re-exposure of the device to oxygen reforms the  $\alpha$  superoxide complexes, re-establishing deep traps passivation<sup>[55]</sup> as well restoring the interfacial Schottky barrier by band bending.<sup>[62,63]</sup> This leads to recuperation of device performance.<sup>[37]</sup>

It is instructive to revisit the device performance deterioration of Figure 2 in the light of the above argument. We observe higher values of  $J_{sc}$  after recuperation for devices illuminated at RT and 85 °C, indicating a higher rate of charge injection, faster charge transport, inhibited recombination, or all three after aging.  $V_{oc}$  values of devices stressed at RT remain constant, but we observe a substantial decrease in  $V_{oc}$  for devices stressed at 85 °C. This irreversible lowering of  $V_{oc}$  is possibly associated with the permanently healing of oxygen defects and the resulting flattening of band edge bending.

Previous studies of the SnO<sub>2</sub>/Pt interface have established that interfacial oxidization and reduction can modify the electronic barrier height at this metal-semiconductor junction.<sup>[49,66-69]</sup> The metal surface was shown to be unaffected and the metal oxide surface alone was responsible for this effect.<sup>[49,69]</sup> This is in agreement with our observations here, where the transformation from rectifying to Ohmic behavior may be correlated with the lowering of a Schottky potential barrier at the TiO<sub>2</sub> surface. Physical separation of the electrodes by placing a buffer layer of optimal thickness onto the top electrode avoids a direct contact between TiO<sub>2</sub> and the metal electrode, preventing the formation of shunting paths during continuous aging in the absence of oxygen. But contact between the hole transporter and the TiO<sub>2</sub> throughout the bulk of the photoactive layer requires more subtle modifications, only in part resolved by our alumina-silicate shell treatment.

#### 4. Conclusion

In this work we have emulated realistic conditions for durability testing of ss-DSSCs to evaluate their long-term stability. Unlike previous studies, we performed aging tests under continuous illumination at 85 °C while recording the device performance in situ every 30 min, simulating a high stress situation. When encapsulating devices in an inert atmosphere to enable long-term stability of the organic components, a fast deterioration in device performance occurred. Re-exposing the stressed devices to air led to a full recovery of their initial performance. Through a detailed study, we show strong evidence that changes to the defects states in the mesoporous TiO<sub>2</sub> are primarily responsible

excess for this performance deterioration. This short term deterioration was substantially inhibited by both the introduction of a mesoporous insulating buffer layer on top of the mesoporous TiO<sub>2</sub> electrode, and the use of an alumino silicate shell coating upon the internal surface of the mesoporous TiO<sub>2</sub>. As of yet however, further aging beyond 100 h resulted in substantial device deterioration and further work stabilizing the electronic nature of the TiO<sub>2</sub> is required for ultimately stable solid-state DSSCs. This work highlights a very important route forward with respect to this goal. In addition, significant enhancement of the peak performance is also likely, once a better understanding and control over the subtleties of the TiO<sub>2</sub> defect chemistry is and the precise energetics at the dye-sensitized

solid-state heterojunction is achieved.

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