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High temperature stability of dye solar cells ☆

Nancy Jiang, Taro Sumitomo, Timothy Lee, Alba Pellaroque, Olivier Bellon, Damion Milliken, Hans Desilvestro *

Dyesol Limited, 3 Dominion Place, Queanbeyan, NSW 2620, Australia

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ABSTRACT

This work provides the state-of-the-art of dye solar cell chemical stability, assessed through accelerated ageing at temperatures up to 95 °C and shows that solvent-based dye solar cells (DSCs) can pass 1000 h/85 °C tests with less than 10% loss of performance. Prior work is reviewed and compared with recent in-house results from DSCs based on three different solvents and two representative Ru dyes as well as the organic dye Y123. An "industrial DSC toolbox" of analysis methods, including IV testing at various light levels and in the dark, IPCE, EIS (at a single or at multiple cell voltages) and post mortem analysis, is used to better understand degradation mechanisms. For highly stable Z907-based cells, loss of performance due to high temperature ageing is dominated by loss of V_{oc}, rather than J_{sc} or *ff*. Based on literature and this work, loss of I_3^-, resulting in partial bleaching of the electrolyte, appears to be strongly correlated with loss of performance upon high temperature storage, with the most stable systems investigated in this work displaying only marginal bleaching at temperatures above 80 °C. Two in situ methods, EIS under light at zero DC current and IPCE in the sub 450 nm region were used to quantitatively or semi-quantitatively gauge electrolyte I_2 concentration within the active area. The nature of I_3^- degradation products still remains unknown. A lower limit of 68 kJ/mol was estimated for the activation energy of the rate determining step, which leads to increased dark currents and thus lowered V_{oc} upon high temperature storage. In addition there is evidence from IPCE of some changes to the dye structure, especially in MPN and GBL-based electrolyte systems. Dye desorption and degradation of platinum catalytic activity was shown to occur to some degree at the highest temperatures, but the impact on cell performance from these two mechanisms upon high temperature stress testing is only minor. Y123 showed particularly good stability at elevated temperature, surpassing even Z907 in terms of durability. Further improved device seals may lead to continued improvement of DSC stability under the harshest environmental conditions even for materials with a better performance-to-cost ratio than Z907 or Y123.

1. Introduction

Since the early days of dye solar cells (DSCs) [1,2], efficiency has continually been improved. Laboratory cells featuring Zn porphyrin and Y123 co-sensitisation in combination with a Co-based redox couple presently achieve 12.3% under 995 and 13.15% under 501 W/m^2 illumination [3], rendering this technology increasingly competitive for practical applications. DSCs offer attractive performance, particularly for applications in the built environment as Building Integrated Photovoltaics (BIPV) products, where panel orientation in regards to the North–South direction and the angle from horizontal direction is often far from optimum and where more traditional PV panels such as crystalline silicon significantly lose efficiency due to increased electron–hole recombination at lower light levels. DSCs in contrast, work especially well under light levels corresponding to around 0.3–0.5 sun, such as typically available on building façades during the course of an 'average' day. In addition, the unique attribute of DSC in the built environment is its ability to capture and convert light into electricity while maintaining a level of transparency unattainable for other PV technologies. The value of capturing and converting the sun's energy into electricity at the site of consumption cannot be stressed enough since the built environment consumes approximately 50% of the world's energy production, half of which is consumed as electricity. Distributed power, in the form of BIPV products such as roofs and exterior walls, offer other advantages, including low to no transmission costs and significantly reduced overall costs. This is in contrast with the case of electricity production by wind farms in the US, for which the costs for electricity transmission have been estimated on average at $300/kW and can extend to over $1500/kW [4]. Thus technologies, which enable the electricity producer to be the consumer at the same time, i.e. to become an energy "prosumer" [5], can profit from

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* Corresponding author. Tel.: +61 2 6299 1592.
E-mail address: hansd@dyesol.com (H. Desilvestro).

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an often very significant bonus due to relief of electricity grids, which frequently have to run close to the limits of their design capacity. Distributed power generation at the site of consumption competes with electricity costs at the retail price level, whereas power from solar farms has to be competitive at the much lower electricity wholesale price. DSC based BIPV products leverage many of the costs previously burdened into the cost of construction. Using BIPV windows as an example, the costs associated with transporting the windows to the site remain the same, the cost difference in installation between ordinary glass windows and a BIPV window is similar and often, the cost of the BIPV substrates, in the case with a glass based device, are already "paid" for as ordinary windows. DSC devices, glass-based panels in particular, can be tuned to a considerable extent in terms of colouration and transparency and can become part of a building such as cladding or semi-transparent windows. Similarly, DSCs on steel, manufactured in a roll-to-roll process, can become an electricity-producing roofing material [6] without the additionally required expense for PV-specific mounting fixtures and labour-intensive installation of PV panels. In summary, the added cost for PV functionality of a building material can be lower than the full cost of traditional building applied PV products, which are generally added to a building's roof. Considering the billions of square meters of glass and metal used in the built environment today, DSC based technologies offer a bridge between the current "add on" modality of traditional PV to the future of "built in", i.e. BIPV, where the technology enables buildings to become stand alone energy producers. Combined with improvements in energy efficiency, in which DSC can play a major role, future buildings will be ever closer to becoming energy neutral, or even new energy producers in the case of very large warehouses.

Even with AM1.5 G DSC efficiency considerably lower compared to crystalline silicon, DSC levelised cost of energy can be comparable or even lower than for traditional PV panels offering much higher peak efficiencies, especially on façades in areas with relatively high levels of diffuse radiation. Further advantages of DSC [7] compared to other PV technologies [8,9] include particularly low embodied energy, even when compared to OPV (see "Polymer" solar cells in [9]). DSCs do not depend on rapidly dwindling resources such as In or Te and do not employ highly toxic materials such as Cd, as required for CIGS and CdTe. While Ru-based dyes and Pt electrocatalysts are expected to be used in early-stage DSC products, quantities employed are very low (~100 mg/m^2 Ru, ~20 mg/m^2 Pt), which would not strain natural resources for DSC production levels up to tens of millions of m^2 per year [7], corresponding to >1 GW$_p$ p.a. Around the world, Ru-free dyes [10] and Pt-free electrocatalysts [11] are under development and rapid progress is being made in both areas.

In addition to niche applications such as battery chargers, solar bags and backpacks [12], DSC technology is, thanks to its numerous advantages, becoming an increasingly credible contender for BIPV with the prospect of meeting grid parity once mass manufacture has started. One of the main remaining challenges is to validate that DSC products can last more than 20 years as part of the building structure. Therefore, a better understanding of the dominant failure modes is required as well as deep insight into how accelerated testing under laboratory conditions relates to conditions experienced in the field. Conditions in practical applications can vary widely and generally depend on the annual temperature profile, visible light and UV conditions, wind (which contributes to cooling of panels under high light levels), panel orientation and type of mounting on a building. Tests according to international standards such as IEC 61646 [13] are regarded as a reasonable guideline. Some of the tests may however not be harsh enough to provide certainty of product life times of at least 20 years.

As with any PV technology, a variety of mechanisms can lead to loss of performance over extended periods of time. In the case of DSC, where the principle of operation is based on molecular processes, similar to photosynthesis, some of the mechanisms for loss of performance are fundamentally different from those occurring in other solid-state devices based on p-/n-junctions. This paper will review the main degradation mechanisms in DSCs and then present some recent results with industrial type cells based on three different solvents.

Some time ago, Hagfeldt et al. [14] proposed a set of measurement techniques as a "toolbox" to study DSC internal processes under practically relevant conditions. Their toolbox included photocurrent and photovoltage transients, EIS, IMPS and IMPV as well as photoinduced absorption. While the combination of these techniques is very powerful to unravel mechanistic details of DSC chemistry and some of the degradation processes, industrial R&D involves testing and assessing a large number of cells with high statistical relevance and is driven by the goal to achieve commercial objectives rather than to create academic knowledge. Therefore, an "industrial DSC toolbox" has been devised for the analysis of cell characteristics, which offers a good compromise between depth of analysis and provision of adequate information to aid with improvement of materials and cell chemistry to meet commercial goals. As shown in Fig. 1, Dyesol's industrial DSC toolbox includes *JV*-testing (at three light levels and in the dark), IPCE, EIS (either at one single standard cell voltage in the dark or under light at multiple cell voltages as multi potential EIS, i.e.MP-EIS) and post mortem analysis, which includes visual and microscopic inspection and dye desorption after opening cells.

2. DSC thermal stability—Review of prior investigations

As discussed in our previous work [15], DSC performance loss can occur at four different levels, i.e. the molecular, cell, module/panel, and system level. In the following discussion, we will mainly concentrate on the cell level. Most PV technologies require stringent encapsulation since the combination of heat and moisture can have serious negative impacts not only on the PV-active materials but also on the conductivity of substrates such as Al-doped ZnO [16] or ITO, on solder bonds [17] and cause corrosion of metallic current collectors and bus bars. This work will however not deal with device encapsulation nor with damp heat testing [18], but will primarily focus on how high temperatures (up to 95 °C) affect cell performance. Since DSC long term stability is, like other PV technologies, negatively impacted by H_2O contamination [19], which potentially leads to dye desorption [20,21], dye NCS^- to OH^- substitution [22], chemical and/or photochemical side reactions with electrolyte constituents such as possible formation of IO_3^- [23], and/or Pt dissolution and precipitation on TiO_2 [24], any thermal stability investigation needs to be scrutinised in terms of seal quality in order to exclude overriding effects of H_2O ingress.

Based on in-house [15] and literature data [25], light soaking of DSCs employing dyes such as N719 or Z907 is not a significant stress factor as long as cells are sealed properly to prevent any evaporation of solvent or leakage and/or major ingress of H_2O and as long as temperatures are not much higher than 60 °C. Temperatures of 85 °C often lead to rather severe degradation of cell performance. 85 °C thermal stress testing, performed as required by the IEC 61646 standard [13] in the dark and under open circuit, has been reported for acetonitrile or propionitrile as the solvent [25,26]. Sommeling et al. [25] found partial recovery of performance under illumination at 45 °C but virtually no recovery in the dark at ambient temperature. Their results indicate that electrolytes using 4-*tert*-butyl pyridine (4-TBP) and LiI are less stable than those containing *N*-methylbenzimidazole and no LiI. The same

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