Solar Energy Materials & Solar Cells 144 (2016) 457–466

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

High boiling point solvent-based dye solar cells pass a harsh thermal ageing test

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ARTICLE INFO

Article history:
Received 21 July 2015
Received in revised form
17 September 2015
Accepted 25 September 2015

Keywords:
Dye solar cells
Ageing
Thermal stability
High boiling solvent
Redox electrolyte

ABSTRACT

Dye solar cells (DSCs) have emerged as one of the most efficient third-generation photovoltaic (PV) technologies, whose commercialization is mainly hampered by the lack of sufficient long-term stability compared to conventional PV devices. In this work, it is demonstrated that solvent based DSCs using tetraglyme as a non-nitrile, high boiling point, organic solvent for the iodide/triiodide redox shuttle, can pass a harsh accelerated thermal ageing test of 3000 h light soaking followed by additional 2000 h thermal ageing at 85 °C. Electrochemical and spectroscopic analysis on thermal degradation effects revealed that a conduction band edge shift towards more negative potentials for tetraglyme-DSCs underlies the enhanced photopotential of aged cells, compensating for the thermally induced photocurrent reduction due to slight triiodide loss. The tetraglyme-based solar cells (in contrast to cells based on methoxypropionitrile-MPN) showed exceptional stability, compatible with the established IEC61646 protocol for thin film PVs, keeping ca. 90% of their initial performance under 1 sun illumination. Quite notably, the cells even increased their initial efficiency by 4% when illuminated under 0.1 sun. This is the first time in literature that such a stability record is accomplished for solvent based DSCs utilizing commercially available and cost-effective materials.

1. Introduction

Although the sensitization of semiconductors by organic dyes dates back to the pioneer work of Prof. Heinz Gerischer in the late 1960s [1], it was only 20 years later when a breakthrough in the development of nanocrystalline solar cells was achieved by Brian O'Regan and Michael Grätzel using mesoporous, high surface area TiO_2 film electrodes sensitized by a panchromatic dye in conjunction with the I^-/I_3^- redox couple [2]. Since then, the power conversion efficiency of dye solar cells (DSCs) consolidated at the level of 10–12% (with certified efficiencies of 11.9% under standard 1 sun AM1.5 G illumination conditions) [3] and quite surprisingly major advances came up (with efficiencies higher than 13%) again after about 20 years of stillness, when cobalt-based electrolytes [4] or organometal halide perovskite sensitizers [5,6] were employed.

In addition to existing data confirming high power conversion efficiencies, the characterization of DSCs in terms of life time and stability lays the basis for further industrial developments and practical applications. In fact, despite the great perspectives for further efficiency enhancement in the very near future of either liquid DSCs based on the Co^{2+}/Co^{3+} redox mediator [7] or solid-state perovskite solar cells [8–10], long-term stability remains the key challenge for DSC's commercialization. Although no formal figure of merit for qualifying the DSCs lifetime is currently available, 10% loss in efficiency is considered acceptable [11], perhaps up to 20% [12]. That can be evaluated by established accelerated ageing tests for photovoltaic (PV) devices, simulating a lifetime of 20 years outdoor operation [13]. It should be noted that stability has been scarcely addressed for the newly developed DSC systems [14–16], whereas, conventional DSCs employing the "old-fashioned" iodide/triiodide redox shuttle seem most efficient in terms of achieving long operating lifetime [17].

The stability of DSCs depends critically on the interplay of diverse degradation processes that may occur in each of the different cell components, i.e. dye (desorption, ligands substitution, isomerisation) [18,19], electrolyte (decomposition, solvent leakage,

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http://dx.doi.org/10.1016/j.solmat.2015.09.052
0927-0248/

additives evaporation, triiodide loss) [20,21], cathode (desorption of electrocatalyst, inactivation due to poisoning effects) [22,23] and current collecting grids (corrosion) [24]. The occurrence or not of these detrimental reactions on stressed DSCs depends on the ageing conditions and certainly the underlying degradation effects can be accelerated in the presence of UV light as well as the ingress of O_2 and/or H_2O into the cell due to imperfect sealing [11]; more details on the existing degradation mechanisms identified up to now can be found in our recent paper [25]. All the degradation routes lead to significant performance losses due to severe reduction of distinct electrical parameters (photopotential, photocurrent and fill factor), or a combination of them, defining the overall conversion efficiency.

Even though certified ageing tests exist for the PV industry according to international standards such as IEC 61646 [26], currently, there are no corresponding established tests for DSCs. However, three stress tests can be applied for the evaluation of DSC stability, i.e. a) light soaking for 1000 h at ~60 °C under 0.8–1 sun illumination, b) thermal ageing at temperatures between 55 and 95 °C for 1000 h in the dark and c) thermal cycling from −40 °C to +85 °C [27]. It should be noted that the latter thermal cycle test is not common for DSCs; the authors are only aware of two literature reports, which however showed excellent stability for both solvent and ionic liquid based DSCs, indicating the robustness of the cell chemistry and seals to temperature extremes [28,29]. Thus, prolonged light soaking and/or thermal ageing in the dark have been the most prominent stress tests thus far used for the assessment of DSC long term lifetime/stability.

In particular, DSCs employing various robust dyes combined with non-volatile electrolytes readily sustained their performance after 1000 h continuous solar light (1 sun) illumination [30,31]. Extensive tests, carried out at Dyesol, demonstrated an impressive stability of DSCs under even more prolonged light soaking; i.e. over 6450 h [32] or even 25,600 h of continuous light soaking at 55–60 °C under resistive load [29].

On the other hand, long-term thermal stability of DSCs remains a highly challenging task at elevated temperatures (> 80 °C), where thermal stress can accelerate degradation reactions or even create new degradation pathways [33]. Promising thermal stability has been reported at 85 °C for DSCs employing ionic liquid based [34] or gelled electrolytes [35]. Ionic liquid electrolytes, employed in industrial DSCs at Dyesol and stored in the dark under open-circuit conditions for over 1000 h at 80 °C, resulted in a 22% decrease of cell performance [29]. However, ionic liquids are quite expensive (when compared with usual molecular solvents) and rather difficult to synthesize and purify [35], compromising to some extent the inherent advantage of DSC as a low cost PV technology.

Significant stability under thermal stress has been also observed in DSCs utilizing electrolytes with typical low-cost organic solvents (such as methoxypropionitrile, MPN) [36], especially when the cells were frit sealed [37]. However, considerable deterioration of the cell performance was evidenced in many cases [18,20], implying that the integrity of the MPN-based solar cells under ageing seems more susceptible to the quality of the sealing. For instance, a 31% performance loss was observed in MPN-cells upon thermal stress at 80 °C for 1000 h [29], while much higher degradation (more than 70% power conversion efficiency loss) was reported for similar DSCs subjected to ageing at 80 °C for 2000 h in the dark (after a successful light soaking test under 0.8 sun for 2000 h) mainly due to substantial triiodide loss [38].

To mitigate the ensuing DSC degradation, a non-nitrile high boiling point organic solvent, tetraglyme (TGL) (Fig. S1 and Table S1), was originally applied to dissolve the iodide/triiodide redox shuttle, resulting in significantly improved durability of the cells at high temperatures; the efficiency of the TGL-cells was reduced by only 20% after a harsh ageing test of 2000 (light)+2000 (dark at 80 °C) hours [38]. In this work, we extended the life-time ageing tests to a total of 5000 h (3000 h light soaking followed by 2000 h thermal ageing), at a temperature as high as 85 °C (such temperatures could be frequently met in tropical or desert locations) [27]. This is in agreement with current IEC protocols for thin film PVs [26] that adopt testing at 85 °C as the most reasonable temperature for accelerated lifetime experiments. By improving the sealing of the devices and protecting the cells from electrolyte leakage and/or triiodide loss, we achieved a nearly 90% stability of the initial performance at 1 sun, meeting the stability standards of conventional PVs [11]. Quite notably, the efficiency of TGL-cells increased by 4% (in comparison with their initial performance) after thermal ageing when the solar cells were illuminated at 0.1 sun. This could be a significant advantage for DSCs' performance in hot climates, as recently demonstrated in systematic studies of their long term stability under high temperatures and low irradiance levels pertinent at real outdoor conditions [39]. A combination of experimental techniques including linear sweep voltammetry, UV–vis absorption, electrochemical impedance, and micro-Raman spectroscopy were applied to identify the underlying degradation mechanisms, unveiling that a favorable conduction band edge shift for the TGL-cells effectively compensated for the diffusion limitations of the cell photocurrent induced by a moderate triiodide loss at high temperatures. This is the first time that such a harsh thermal test has been successfully passed by DSCs employing low-cost conventional organic solvents, which are readily accessible for evaluation to the whole research community of dye solar cells.

2. Materials and methods

2.1. Solar cell devices assembly

DSCs of 0.88 cm^2 active area were manufactured by Dyesol using standard Dyesol materials. The photoelectrode consisted of DSL 18NR-AO titania paste printed on TEC-15 glass, with both $TiCl_4$ underlayer and overlayer, further sensitized with the N719 ruthenium dye. The cathode was composed of PT1 platinum paste, also printed on conductive glass [32]. I^-/I_3^--based electrolytes were prepared with 1-propyl-3-methylimidazolium iodide (PMII, > 99%, Merck), iodine (I_2, 99.8%, Aldrich), guanidinium thiocyanate (99.9%, Fluka) and an imidazole derivative stabiliser. The solvent was tetraglyme (TGL, 99%, Sigma-Aldrich), while methoxypropionitrile (MPN, 99%, Fluka) was used as a reference. The devices were assembled with thermoplastic primary and hermetic secondary seals.

2.2. Ageing conditions

Cells were initially illuminated using high pressure sodium lamps corresponding to a light intensity of > 0.8 sun and a cell temperature of close to 55 °C for 3000 h with resistors applied to maintain near MPP conditions. These cells, denoted as TGL-ref and MPN-ref cells, respectively, did not present any deterioration in their electrical parameters, having virtually the same efficiency as fresh cells. Then, the above cells were further thermally aged at 85 °C for an additional 2000 h in the dark under open-circuit conditions, denoted as TGL-aged and MPN-aged cells, respectively.

2.3. Characterization

Current–voltage (I–V) measurements were performed by illuminating the DSCs from the photoelectrode side; a Xe lamp in combination with AM 1.5 G and 400 nm (UV) cut-off optical filters (Oriel) was employed in order to provide solar simulated light