

Long-term stability of dye solar cells

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Abstract

This work provides a review of dye solar cell long-term stability under light and thermal stress factors as well as discussion on the main degradation mechanisms. Performance and EIS parameters of industrial type Z907-based cells were evaluated during the course of continuous light soaking over 25,600 h at 55–60 °C. Only minor degradation occurred under such conditions, with open circuit voltages dropping by 50–80 mV due to a shift of the conduction band towards more positive potentials and with fill factors at high light levels decreasing due to an increase of cell series resistance. There is no evidence of dye degradation, loss of iodine or decrease of Pt electrocatalytic activity. From the accelerated ageing tests, a product life time of 40 years can be extrapolated for Middle European and 25 years for South European conditions. 80 °C storage over 1000 h resulted in 10–20% decrease of performance with ionic liquid or solvent based electrolyte systems, respectively.

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1. Introduction

Dye solar cells (DSC) offer attractive performance at an affordable cost, superior performance under diffuse or otherwise non-ideal light conditions, tunable colouration and/or transparency, flexibility, low weight and low embodied energy. Since the early days of DSC (Desilvestro et al., 1985; O'Regan and Grätzel, 1991), efficiency has continually been improved for laboratory cells to presently 12.2% (Grätzel, 2009), rendering this technology increasingly competitive for practical applications. In order to be successful in the market place, any novel photovoltaic technology has to offer a favourable performance-to-cost ratio and sufficient product durability. For commercially viable building integrated applications, panel life time needs to be 20–25 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 DSC and then present some recent results with industrial type cells.

2. Review of mechanisms for loss of performance

Degradation can occur at four different levels, i.e. the molecular, cell, module/panel, and system level. Every level is characterised by higher complexity and relies on stability of the lower levels. This study will mainly deal with the molecular and cell aspects.

2.1. Molecular level

The DSC system is a chemically complex system. Hagfeldt pointed out that “the TiO₂ film, on its own, does not conduct electrical current, the dye, on its own, cannot

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be exposed to sunlight and the electrolyte is corrosive” (Hagfeldt, 2006). But, if combined all together in the correct balance, a stable and effective solar cell is obtained, thanks to a kinetically and diffusionally controlled interplay of the various components in the presence of light at electrode/solution interfaces and in the bulk of the liquid and solid phases. All photochemical and charge transfer processes such as dye excitation, electron injection into the conduction band and dye regeneration, need to occur with exceptionally high selectivity in regards to any potentially competing processes. Grätzel showed that for a 20 year life time under average solar conditions, 100 million sensitizer turnovers are required and that such a remarkable molecular reversibility can be achieved with Ru-based dyes and the I_3^-/I^- redox system (Grätzel, 2006).

More recently, some of the side reactions occurring in nitrile-based systems with N719 (Nguyen et al., 2007) and Z907 (Nguyen et al., 2009) in homogeneous solution (i.e. not adsorbed on TiO_2) had been investigated. The authors concluded that SCN^- ligands are substituted by solvent molecules at significant rates at temperatures above 80 °C. These substitution reactions were shown to be accelerated by 4-tert-butylpyridine and slowed down by guanidinium thiocyanate. Fully understanding such molecular mechanisms is important as a first step to further increase long-term stability of DSC. It has to be cautioned however that such reactions may display different kinetics for dye adsorbed on TiO_2 . There is recent evidence that Z907 and N719-based cells show excellent stability at 85 °C in the dark, even when MPN is used as a solvent (Goldstein, 2009; Duong et al., unpublished). Thus the results of Nguyen et al. may not be a direct indication of DSC high temperature stability. Superior seal integrity is of paramount importance for achieving high temperature resilience. Good DSC stability at 80 °C has been reported for K60-based cells employing MPN as the solvent (Kuang et al., 2007). Apart from ligand substitution, there are many other chemical reactions which potentially can occur within a DSC: At the TiO_2 surface ring opening and/or decarboxylation reactions can occur with solvents such as γ -butyrolactone, 3-methyl oxazolidin-2-one or cyclic carbonates at elevated positive potential (Kavan et al., 1994; Krttil et al., 1997). Such reactions may be similar to those observed on graphite surfaces (Arakawa and Yamaki, 1995). Generally, direct band gap excitation has to be avoided – valence band holes from TiO_2 have the oxidative power of fluorine – through a UV filter which cuts any light with wavelengths below around 400 nm (Pettersson and Gruszecki, 2001; Arakawa et al., 2008; Koishi et al., 2008). The many components in a typical DSC electrolyte, such as I_2 , I^- salt, guanidinium thiocyanate (Kopidakis et al., 2006), buffer and performance enhancers based on relatively small cations (Wang et al., 2007) and optional gel formers can undergo electrochemical reduction, through TiO_2 conduction band electrons, or oxidation at the counter electrode or other undesirable chemical or photochemical reactions if not selected properly. Accumula-

tion of small cations, such as H^+ or Li^+ , at the TiO_2 surface can lead to voltage loss over time. On the other hand, there is evidence that insertion of protons into titania occurring during illumination can create surface trapping states which enhance charge carrier transport within the nanocrystalline network (Wang et al., 2008a).

The presently available body of work indicates that Ru-based dyes can provide, at the molecular level, excellent long-term stability with the potential of 20 years or longer resilience of the underlying chemistry, as long as prolonged (continuous) exposure to temperatures above 80 °C can be minimised. The cell temperature of horizontally oriented DSC modules mounted outdoors in Japan (Aichi prefecture) was shown to vary between 72 °C during the hottest summer days and –10 °C during winter nights (Kato et al., 2009). Excellent stability at temperatures above 80 °C is however important in hot and very sunny climates and will require further careful adjustment of the DSC chemistry balance.

2.2. Cell level

DSC-based photovoltaic (PV) panels have, as any other PV technology, to pass stringent product and other standards such as building standards. Typical requirements for thin film PV panels (not DSC) are specified by IEC 61646 (IEC, 2008) and JIS C 8938 standards (JIS, 1995). Meeting key standard requirements at the cell level is normally a prerequisite to pass the requirements at the higher levels. In addition to purely photochemical and chemical processes at the molecular level, cell stability involves numerous further requirements to be met:

- avoid/minimise loss of solvent with consequential loss of electrolyte conductivity;
- avoid/minimise ingress of H_2O ;
- avoid/minimise chemical reactions between any electrolyte component with the primary seal structure or any other cell component;
- avoid/minimise loss of seal integrity due to differential thermal expansion.

From the above list it is apparent that many requirements at the cell level are related to seals. Seal quality/integrity is of utmost importance for DSC to pass endurance tests. Ingress of H_2O into the cell is known to lead to reduced long-term stability (Pettersson and Gruszecki, 2001). While year after year, a few hundred scientific technical publications (Kalyanasundaram) deal with DSC dyes, electrolyte components and formulations, TiO_2 and electrocatalyst film preparation and their properties or investigate physicochemical aspects in great detail, hardly any studies involve the materials science and chemistry of seals suitable for DSC. Other organic solvent based electrochemical devices, such as Li-ion batteries do not have the stringent performance criteria attached after high temperature exposure as required for PV panels. While IEC 61646 (2008) accreditation requires PV panels to provide at least

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