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Laser sealed dye-sensitized solar cells: Efficiency and long term stability

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ABSTRACT

Long-term stability is a major issue preventing dye-sensitized solar cells (DSCs) market implementation. The DSC stability problem relates to the sealing methods which usually employ thermoplastic sealants. This communication shows for the first time that laser glass sealing originates stable and efficient DSCs. Laser sealed DSCs showed remarkable stability compared to the Surlyn® sealed devices (*ca.* 2% *vs.* 44%) after accelerated ageing during 1000 h, at 65 °C, light intensity of 765 W m^{-2} and resistive electrical load (~0.6 V). These results show that efficient encapsulation methods are crucial to DSC stability and that the developed sealing process can bring stable and efficient DSCs to the photovoltaic market.

1. Introduction

Besides offering favorable performance-to-cost ratio, emerging photovoltaic technologies must guarantee device stability. Dye sensitized solar cells (DSCs) have low manufacturing costs, use environmental friendly materials and show distinctive characteristics that make them worth to invest [1–3]. Contrary to crystalline silicon ((c-Si)) photovoltaic (PV) devices, DSCs work especially well under low light levels (0.3–0.5 sun) [4,5], such as light intensity typically available in the facades of buildings. Their ability to convert light into electricity while maintaining some transparency, unlike other PV technologies, make them particularly interesting for building integrated photovoltaics (BIPV) [6]. The operation of DSCs comprises dye excitation and electron injection into TiO_2 conduction band, charge transport through TiO_2 porous network to the SnO_2-F substrate and dye regeneration by the redox electrolyte [7]. These photo/electrochemical processes rely on the chemical compatibility of all DSC components. Gräetzel et al. [8] showed that the redox system I_3^-/I^- combined with ruthenium dyes can achieve 20 years of molecular stability [8]. However, this intrinsic stability can only be accomplished if no electrolyte leakage or external contaminants penetrate into the cell. In fact, it has been shown that DSCs durability is highly dependent on efficient cell encapsulation and it is the most common reason for long-term stability failure [9,10]. The commonly employed sealants for encapsulating DSCs are polymers, such as Surlyn® and Bynel®, which have some permeability towards oxygen and moisture [11]; their relatively low softening point makes them unreliable sealants at temperatures above 50–60 °C, which prevent their use in commercial DSC applications [6,10,12,13].

This work reports accelerated aging tests in DSCs fabricated by our previously developed laser assisted glass sealing process [14–16]. Although the laser process produces excellent glass to glass bonding, the technology is not yet fully developed for sealing the electrolyte filling holes; therefore these were sealed combining Surlyn® thermoplastic sealant and high temperature resistant resin. For comparison, Surlyn® sealed DSC devices were also tested.

The aging tests were conducted at 65 °C, under 765 W m^{-2} of continuous illumination and resistive electrical load close the maximum power point of the cells (~0.6 V). The devices were characterized every 200 h, during the aging period of 1000 h, by intensity-voltage (*I-V*) and electrochemical impedance spectroscopy (EIS) analysis. The *I-V* and EIS results were compared between Surlyn® and LAGF cells; any stability differences between both types of devices should be ascribed to their unique difference: device encapsulation method (Surlyn® and glass frit).

2. Material and methods

2.1. Laser sealed DSC fabrication

Laser sealed DSCs were prepared as described elsewhere [14–16] (Chapter 2, Section 2.4). Briefly, the photoelectrodes were prepared on 2.2 mm thick, SnO_2-F (FTO) coated glass substrates

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(7 Ω □$^{-1}$ of surface resistivity) from Solaronix®. First, the glasses were washed sequentially with a detergent solution (Alconox®, VWR) in an ultrasonic cleaner (Amsonic TTC) at 55 °C for 15 min, followed by ultrasonic cleaning in deionized water at room temperature and dried with air at 50 °C.

A TiO_2 blocking layer is deposited above the FTO layer by atomic layer deposition (ALD – Beneq Oy thin film system TFS200). Deposition of TiO_2 was carried out at 225 °C using titanium isopropoxide (TIP, feeding tank at 45 °C) and H_2O (feeding tank at 20 °C). 250 cycles (~7.5 nm) of TiO_2 were deposited under a nitrogen flow of 300 cm^3 min^{-1}, with a pulse/purge lengths of 2 s/20 s for TIP and 1 s/3 s for H_2O. Then, samples were coated with a porous TiO_2 photelectrode layer by sequentially screen-printing 3 layers of a commercial TiO_2 paste (Ti-Nanoxide T/SP from Solaronix®), followed by drying at 100 °C for 5 min, and annealing at 475 °C for 15 min in an infrared electrical oven (Nabertherm Gmbh model GF75). After firing, the samples were treated with a 40 mM $TiCl_4$ aqueous solution at 70 °C for 20 min, before being sintered at 475 °C for 30 min.

The counter electrodes, prepared on the same type of glass substrates and cleaned as described before, were drilled previously with two holes of 1 mm diameter. A commercial platinum based paste (Plastisol T/SP from Solaronix®) was applied on the glass substrate by screen-printing followed by annealing at 400 °C for 15 min. The two electrodes are then assembled and sealed using the developed laser assisted glass frit method. Dye adsorption in the porous TiO_2 photoelectrode was obtained by recirculating a dye solution (0.5 mM N719, 5 M chenodeoxycholic acid in ethanol) for 12 h using a peristaltic pump (Ismatec®, Reglo Digital MS-4/8), followed by ethanol rinsing, nitrogen drying, electrolyte filling (high stability Iodolyte Z-150 from Solaronix®) and hole sealing combining Surlyn® thermoplastic sealant (Meltonix 1170-60, Solaronix) and high temperature resistant resin (Pattex® Nural 22 from Henkel). Electrical bus bars and electrical wires were soldered to the FTO surface of photo and counter-electrodes, respectively, using an ultrasonic soldering unit (MBR electronics model USS-9210); the soldered bus bars were protected by high temperature resistant resin to prevent corrosion caused by the heat and moisture. The front glass substrate of the cells was covered with a UV cutoff filter (Solaronix® UV filter adhesive film).

Surlyn® sealed cells followed the same fabrication procedure, except for the laser assisted sealing. Commercial Surlyn® sealing film with thickness of 25 μm (Meltonix 1170-25, Solaronix) was used. Glass substrates were sealed using a hot press at 160 °C, by applying 10 bar for 20 s. No additional sealing was added (such as high temperature resins commonly employed to add robustness to Surlyn® sealed devices [12]). Fig. 1(a) and (b) illustrates a laser sealed DSC; images of the aged laser and Surlyn® sealed DSCs are presented in Supplementary information, Fig. S1.

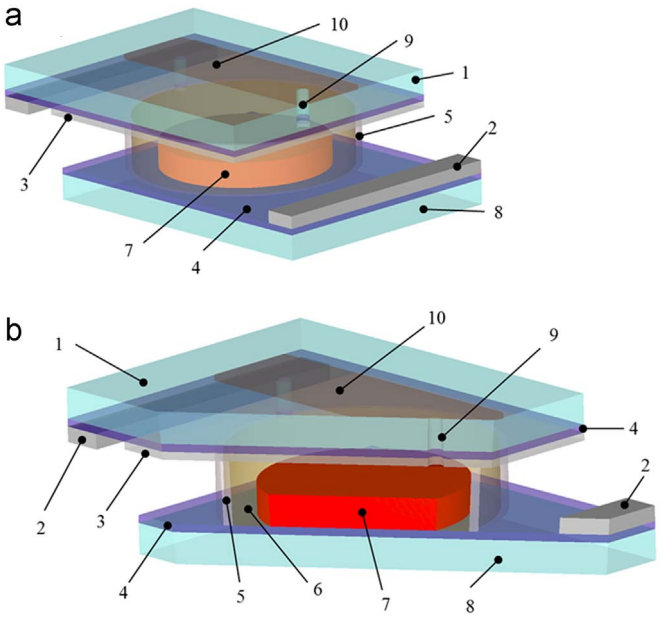

Fig. 1. Schematic of a laser sealed dye-sensitized solar cell (a) top and cross (b) sectional views: 1 – counter electrode glass; 2 – electrical contact; 3 – platinum catalyst; 4 – TCO; 5 – glass frit sealing; 6 – electrolyte; 7 – TiO_2 with adsorbed sensitizer; 8 – photoelectrode glass; 9 – filling hole; 10 – filling hole cover.

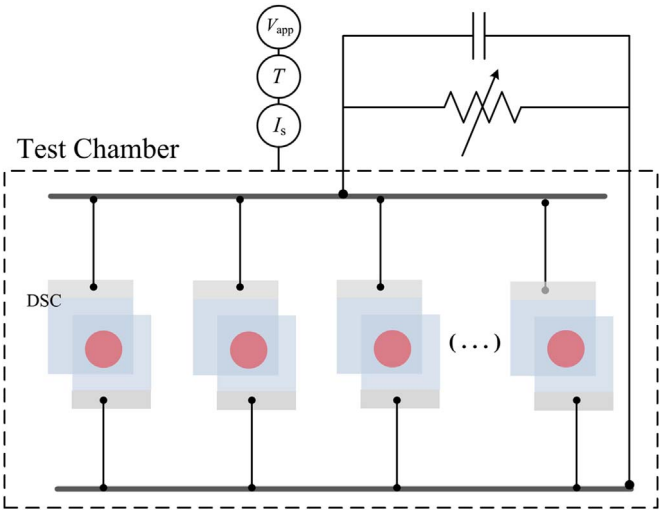

Fig. 2. Scheme of the experimental setup used for the accelerated aging tests.

2.2. I-V and EIS characterization

DSCs were characterized periodically based on recorded *I-V* curves, using a setup equipped with a 150 W xenon light source (Oriel class A solar simulator, Newport, USA) with variable light intensity, from 10 to 1000 W m^{-2} (0.1–1 sun light intensity), and using a 1.5 air mass filter (Newport, USA). The simulator was calibrated using a single crystal Si photodiode (Newport, USA). The *I-V* characteristics of the solar cells were obtained applying an external potential load and measuring the generated photocurrent using an AUTOLAB electrochemical station (PGSTAT 302N). This station was also used to characterize the cells based on electrochemical impedance spectra. The frequency range for the electrochemical impedance spectroscopy (EIS) measurements was from 100 kHz to 0.05 Hz with an AC modulation signal of 10 mV. The experimental EIS data was fitted to appropriate electrical analogues, namely a simplified transmission line model [17,18] (shown in Fig. S2, Supplementary information) using the commercial software ZView® (Scribner Associates Inc.).

2.3. Accelerated ageing tests

Accelerated ageing tests were performed with continuous light illumination, temperature control and resistive electric load, in a closed test chamber (Atlas SUNTEST XLS+, Fig. S3 in Supplementary information) during 1000 h. The ageing conditions were chosen to mimic harsh outdoor conditions: light intensity was set to 765 W m^{-2}, temperature at 65 °C and resistive electrical load close to the cells maximum power point (0.6 V). To apply a resistive electrical load to the test cells, metal bus bars and a resistor were assembled in a parallel electrical circuit, as shown in Fig. 2.