Electrochimica Acta 115 (2014) 478–486

Contents lists available at ScienceDirect

Electrochimica Acta

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

Stability of templated and nanoparticles dye-sensitized solar cells: photovoltaic and electrochemical investigation of degradation mechanisms at the photoelectrode interface

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ARTICLE INFO

Article history:
Received 25 March 2013
Received in revised form
20 September 2013
Accepted 3 November 2013
Available online 15 November 2013

Keywords:
Dye sensitized solar cells
Electrochemical impedance spectroscopy
Light soaking
Templated mesoporous films
Thermal stress
UV degradation

ABSTRACT

A key issue in the commercialization of dye-sensitized solar cells is to maintain high efficiency and long lifetime. As reported in the literature, dye-sensitized solar cells are stable under visible light soaking but thermal stress and UV exposure lead to efficiency degradation. However, all the stability studies published so far have been performed on cells whose TiO_2 electrodes were prepared by tape casting or screen printing of nanoparticle pastes/inks. The present study concerns cells based on highly porous templated TiO_2 electrodes, whose larger surface area could enhance the negative effects of thermal stress, light soaking and UV exposure. The long-term stability of these cells is compared with a classical nanoparticle-based cell using current-voltage measurements (I-V curves) and electrochemical impedance spectroscopy. Due to their higher active interface, templated cells are more sensitive than nanoparticle cells to UV illumination, although this can be easily solved in both cases by the use of a UV filter. The templated cells are as stable as the nanoparticle cells under visible light soaking (UV filtered). However, we showed that templated cells are more stable under thermal stress. Moreover, as evidenced by electrochemical impedance spectroscopy, templated cells show lower transfer resistance, as well as lower recombination resistance compared to nanoparticle cells. The crystallite connectivity promoted by the templating route seems to favor the electron transfers inside the porous layer. Using templated films in dye-sensitized solar cells is therefore really promising because higher conversion efficiencies are reached without promoting cell degradation.

1. Introduction

Due to their low cost and their mild-temperature manufacturing process, dye-sensitized solar cells (DSSCs) have been identified as promising alternatives to the conventional silicon solar cell technology. However, industrialization and commercialization require long-term stability of the solar cells under prolonged operation.

Many research groups have studied how the long-term stability of DSSCs is influenced by various factors. Based on the dye regeneration ability, lifetimes of at least 20 years have been predicted for DSSCs working with N-3 and N-719 dyes under normal outdoor conditions [1]. Harikisun and Desilvestro even extrapolated DSSC lifetimes up to 25 years and 40 years for Southern and Middle Europe respectively, when Z-907 dye is used [2]. Moreover, DSSCs based on Z-907 dye are more heat-resistant than with N-719 dye [2,3]. In addition, cells working with propionitrile as electrolyte solvent exhibit slower degradation than with acetonitrile or methoxyacetonitrile and stability is highly improved when gellators are added to the electrolyte solution [2,4,5]. The presence of impurities, especially water, also strongly influences cell stability. Finally, as processing conditions differ from one laboratory to the other, it is quite difficult to compare the contributions of different research groups [2–5].

Numerous pathways can lead to the DSSCs degradation over extended periods of operation. To ensure long-term stability, perfect sealing of the cells is a key point. Indeed, in liquid electrolyte DSSCs, the sealing has to prevent electrolyte leakage and penetration of water and oxygen pollutants. As temperatures above 70 °C can be reached under outdoor operation, sealing material must be heat resistant [2,5]. The most commonly used Surlyn® thermoplastic films do not withstand such high temperatures, therefore other

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http://dx.doi.org/10.1016/j.electacta.2013.11.009

sealing materials must be considered, such as frit glass, hotmelt resins or UV curing resins [3,6].

So far, no specific ageing tests have been established for DSSCs and most of the accelerated tests reported are closely related with the standard tests IEC:1646:1996[7] defined for the Si, CdTe and CI(G)S thin films technologies. These tests are not tailored for solar cells containing a liquid or a solid electrolyte.

Even if cells are perfectly sealed, they can suffer from prolonged heating. High temperatures (up to 70 °C) have been proved to be detrimental to the cell stability. Sommeling *et al.* reported a performance drop when cells using the N-719 dye and an acetonitrile-based liquid electrolyte were heated for 1000 h at 85 °C in the dark [3]. Hinsch *et al.* obtained promising results at 60 °C with N-3 or N-719 dyes and purified propionitrile as electrolyte solvent but observed a performance drop of 30% for cells heated at 85 °C for 900 h in the dark [6]. Arakawa *et al.* and Pettersson *et al.* defined respectively the upper limit of thermal stability around 60 °C and 50 °C [5,8].

Although thermal stability tests are mostly performed in the dark, DSSCs have also to be stable under prolonged illumination periods. However, visible light soaking is reported to be an insignificant stress factor compared to thermal stress [1,3,6]. Cells studied by Hinsch *et al.* showed good stability over light soaking test (1 SUN illumination, 45 °C), with a decrease in performance by less than 15% after 3400 h of ageing.

However, as TiO_2 is known as a good photocatalyst, UV illumination can lead to electrolyte and dye degradation. Dye photodegradation is controversial[4,6,9,10], while the I^-/I_3^- redox couple generally used in liquid electrolyte DSSCs is reported to be very sensitive to the TiO_2 photoexcitation. Carnie *et al.* as well as Hinsch *et al.* reported the irreversible consumption of iodine leading to the bleaching of the electrolyte solution under prolonged UV irradiation of DSSCs. [6,9,11] UV filters are often used to solve this problem. MgI_2 or CaI_2 can also be added to the electrolyte solution [6].

To our knowledge, all the stability studies concern cells based on TiO_2 nanoparticle films prepared by doctor-blade or screen-printing. We have recently reported that templated films improve the photovoltaic efficiency [12]. However, templated layers could lead to a faster degradation of the cell performances due to their increased surface area. Therefore the present study focuses on the comparison of the long-term stability between DSSCs made from a TiO_2 nanoparticle layer or from a TiO_2 templated mesoporous film. Stability under UV exposure was studied. In accordance with IEC:1646:1996 standard tests, light soaking tests at 45 °C under open circuit conditions were used to determine the cell stability under prolonged illumination. To be closer to real working conditions, the light soaking test was also performed under resistive load [3,9]. In parallel, we investigated the influence of thermal stress in the dark. In IEC:1646:1996 standard tests, experimental conditions are defined to be 85 °C in 85% relative humidity atmosphere. However, under prolonged illumination, spontaneous heating of the DSSC cells studied here led to a temperature of only 35-40 °C. Therefore, the thermal stress tests were performed at 45 °C as for light soaking experiments. In addition to the photovoltaic efficiency measurements, electrochemical impedance spectroscopy (EIS) was used in order to investigate the degradation mechanisms occurring at the different interfaces over time.

2. Experimental

2.1. Mesoporous thin films synthesis

The precursor solution was prepared by mixing 22.4 mL of 1-butanol (Acros Organics), 2 g of surfactant (Pluronic P123, Sigma Aldrich), 7.9 g of titanium tetraisopropoxide (Acros Organics) and 4.1 mL of concentrated hydrochloric acid (Merck, 36 wt%), as reported in reference [12]. FTO conducting glass substrates (15 Ω/sq) were purchased from Dyesol. 3 μm-thick mesoporous films were prepared according to the procedure reported in reference [12], with a calcination step at 400 °C for 2 h. Commercial 3 μm-thick nanoparticles TiO_2 photoanodes were purchased from Dyesol as reference nanoparticle electrodes. The active areas were 0.95 cm^2 and 0.81 cm^2 for the templated and nanoparticle photoelectrodes, respectively.

2.2. Solar cell assembly

All TiO_2 photoelectrodes were sensitized by a ruthenium complex-based dye (N-719 dye, Solaronix), in ethanolic solution (2.7×10^{-4} mol dm^{-3}). The electrodes were immersed in dye solution during one night at room temperature.

Counter electrodes consisted of a FTO conducting glass substrate (Dyesol, 15 Ω/sq) coated with a platinum layer to catalyze electron transfer. The Pt coating was obtained by sputtering performed at 30 mA intensity during 80 seconds, at a working distance of 3 centimeters. The thickness of the platinum layer was of approximately 29 nm, determined by spectroscopic ellipsometry.

The electrodes were separated by a polymer spacer SX-1170-25 (25 μm-thick, purchased from Dyesol) applied under spring pressure and heating. An iodine-based electrolyte solution[13] composed of 0.6 mol dm^{-3} 1-butyl-3-methylimidazolium iodide (Aldrich Chemistry), 0.03 mol dm^{-3} iodine (Sigma-Aldrich), 0.1 mol dm^{-3} guanidine thiocyanate (Sigma-Aldrich) and 0.5 mol dm^{-3} 4-tert-butylpyridine (Aldrich Chemistry) in acetonitrile (ABCR GmbH and Co.)/valeronitrile (Aldrich Chemistry) (85/15, vol/vol) was prepared and introduced via vacuum backfilling in a hole drilled in the Pt-coated FTO electrode. The hole was sealed with SX-1170-25 polymer and a cover-glass.

2.3. Accelerated ageing tests

Light soaking tests under open circuit conditions and under resistive load were performed at 45 °C under continuous illumination (0.7 SUN, filter AM 1.5) for 6 days. As UV exposure leads to the cell degradation[1–3,6,8,9,11], a UV blocking filter (transmission 50% at 410 nm, purchased from UQG Optics) was applied to the cells during the light soaking tests. Efficiencies of the cells were measured every 2 days. For the test under resistive load, electrodes were connected and electrons could flow into the external circuit. A resistance of 270 Ω was added in series to avoid short-circuit.

Thermal stress tests were performed at 45 °C in dark conditions for 1000 h (~41 days). The relative humidity in the ageing chamber was set at 85% by using a saturated salt solution. Efficiencies of the cells were periodically measured (every 7 to 10 days).

2.4. Characterization techniques

Photovoltaic performances were measured by a class A solar simulator purchased from Newport Spectra Physics, coupled with a Keithley 2400 SourceMeter. Photocurrent versus applied potential curves (I-V curves) were measured under simulated 0.77 SUN illumination (filter AM 1.5) at 25 °C. The electrode active area was set to 0.2064 cm^2 with a mask.

Electrochemical impedance spectroscopy was performed using a BioLogic SP-200 potentiostat (Science Instrument) and data were analyzed with the EC-Lab software. A sinusoidal potential perturbation was applied to the cell and the current variation response was recorded. EIS spectra were recorded over a frequency range of 10^{-1} to 10^6 Hz, with 10 mV sinusoidal modulation signal. Measurements