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Encapsulation for long-term stability enhancement of perovskite solar cells

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ABSTRACT

Perovskite Solar Cells (PSCs) have achieved power conversion efficiencies (PCEs) comparable to established technologies, but their stability in real-life working conditions – including exposure to moisture, heat and light - has still not been decisively demonstrated. Encapsulation of the cells is vital for increasing device lifetime, as well as shedding light on the intrinsic degradation process of the active layers. Here we compare different sealing protocols applied to large area cells (1 cm^2, average PCE 13.6%) to separate the extrinsic degradation, due to the external environment, from the intrinsic one, due to the materials themselves. Sealing methods were tested against accelerated life-time tests – damp-heating, prolonged heating and light-soaking. We thus developed and tested a novel sealing procedure that makes PSCs able to maintain a stabilized 10% PCE after heat, light and moisture stress.

1. Introduction

Together with efficiency and cost, the stability is one of the crucial factors to validate photovoltaic (PV) technologies [1,2]. Perovskite solar cells (PSCs) represent a promising PV technology due to the high power conversion efficiency (PCE) already reached in few years of intensive research [3] and the cost-effective materials and fabrication process [4–10]. Nevertheless, PSC stability is still a major issue which need to be solved for an effective industrial exploitation.

Measurement protocols focusing on the solar cell stability have been identified for conventional (IEC standards [11]) and organic (ISOS standards [12]) PV technologies. Although, there is not yet a specific stability protocol for PSCs, stability studies have been recently performed [13–16] and several key elements were identified as impacting the stability of PSCs [17–19]. The degradation mechanisms are mainly related to oxygen and moisture (environmental stability), [15,20,21] temperature and intrinsic heating under applied voltage (thermal stability) [22–24] and light (photo-stability) [25–28].

The aim of the paper is the investigation of robust and cost-effective sealing procedures to stabilize the PSC devices under several Accelerated Life Time (ALT) tests, such as damp-heat, light-soaking and temperature stress. Both intrinsic stability (related to the constituent materials and dopants) and the extrinsic stability (affected by the sealing procedure) will be discussed.

Environmental stability studies have mainly focused on the degradation of PSCs induced by moisture, which can rapidly degrade the organometal halide perovskites. In particular, methylammonium (MA) lead triiodide ($MAPbI_3$) perovskite immediately decomposes into MA, HI and PBI_2 in a wet environment due to its solubility in water [21]. The insertion of bromine atoms in the perovskite structure ($MAPbBr_xI_{3-x}$) can increase the environmental stability, as reported by Noh et al. [20]. The moisture induced degradation can be reduced by optimizing the constituent materials, [29–34], the architecture of the cell [25,35–38], the interfaces [27,39–42] and the environment conditions during the fabrication steps [43,44]. In particular, the use of carbon-based materials as Hole Transporting Layer (HTL) and back-contact can protect the perovskite layer from moisture infiltration due to its highly hydrophobic nature [13,16,45]. In the literature, moisture resistance is usually evaluated using shelf life tests of non-encapsulated cells. Sealing of the cell is, however, a requirement for the device normal operation and should be considered to assess the stability of the cell [46,47].

The thermal stability is assessed analyzing material, interfaces and sealing properties under heating and cooling cycles. Early degradation of PSCs induced by thermal cycling has been investigated by Divitini at al. [22] combining TEM and electrical characterization, finding a reversible behavior of cell performance under thermal cycles between 20 °C and 90 °C and no chemical/morphological changes of the perovskite layer until 150 °C. At higher temperature, TEM analyses shows a clear lead and iodine migration toward the device interfaces. A

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superior thermal stability was showed by Sutton et al. using fully inorganic perovskite structure ($CsPbI_2Br$) with a stabilized efficiency of 5.6%. The results show that the replacement of the organic cation (MABr) with a inorganic one (CsBr) prevents the thermal induced degradation at 85 °C for 250 h as confirmed through UV–Vis absorbance and X-Ray Diffraction (XRD) spectra [48]. The thermal stability is also influenced by the temperature dependence of the electrical properties of Spiro-OMeTAD as showed by Malinauskas et al. for solid-state dye sensitized solar cell. The results show a temperature (60 °C) induced formation of large Spiro-OMeTAD crystalline domains leading to a decrease of PV performance (−60%) after 120 h [49]. Light stability of PSCs, i.e. the effect of the light exposure on the optical/electric properties of the cell, has been investigated by several authors and has been addressed as the main stability issue of PSCs [11,12]. It is known that UV light induces the degradation of the mesoscopic TiO_2-based PSC devices due to trap-assisted recombinations. Leijtens et al. proposed that the UV-aged cells suffer from a deep trapping of injected electrons within available sites in the TiO_2 [25]. Then, a decrease in the short-circuit current J_{SC} is showed due to the charge recombination with oxidized Spiro-OMeTAD species on the μs-ms time-scale as proven using transient absorption spectroscopy. This degradation mechanism was showed for both mesoporous/planar TiO_2 devices indicating that the light induced trap sites in the TiO_2 constitute a rapid degradation pathway for photo-generated electrons, leading to lower charge collection efficiency. Although the use of UV filters could suppress the UV-induced degradation, further optimization of the ETL materials and ETL/Perovskite interface is required. Li et al. show that CsBr used as interfacial modifier on the surface of the TiO_2 ETL delays the UV-induced degradation of the TiO_2-based PSC devices due to the reduced chemical reactivity of TiO_2 and the reduced defect density at the perovskite/TiO_2 interface [50].

Organometal trihalide perovskite also shows photo-instability under light exposure in the visible wavelengths (LED lamp) when the stability test are performed in air. Bryant et al. show rapid decrease of the PV performance under continuous illumination in dry air of unsealed $MAPbI_3$-based PSC (80% relative decrease after 4 h), while a negligible PCE decrease was observed in a nitrogen-filled box (around 5% relative decrease after 4 h) [51]. The author claims that the presence of oxygen acts as main degradation factor during the light stability test: oxygen induces the formation of deep trap sites in the compact and mesoporous TiO_2 layers as previously showed for UV-induced degradation. Photo-induced degradation was also reported from Wei et al. showing the detrimental effect of the continuous light exposure using both planar and mesoscopic architectures [27]. The PCE values of planar PSCs decreased from 18% to 2.4% after 180 min of exposure time. This rapid decrease is related to the light soaking that leads to insufficient hole extraction at HTL/Au electrode interface. Interestingly, the re-deposition of the Au electrode on degraded devices causes a remarkable recovery of the PV performance, of around 80% for both PSC architectures. Sanehira et al. show that the use of MoO_x (15 nm) as interlayer between Spiro and the metal electrodes increases the light stability of PSC devices. In fact, a planar PSC device using 15 nm-thick MoO_x/Al electrode shows lower PCE decrease (−60% with respect to the initial value) with respect to an Al electrode after 120 h of light soaking [52]. Several authors also considered the combined action of light-soaking and temperature. Bush et al. show the effect of the low/high temperature (35 °C and 100 °C, respectively) on the stability of semi-transparent and opaque PSC during a light soaking test at

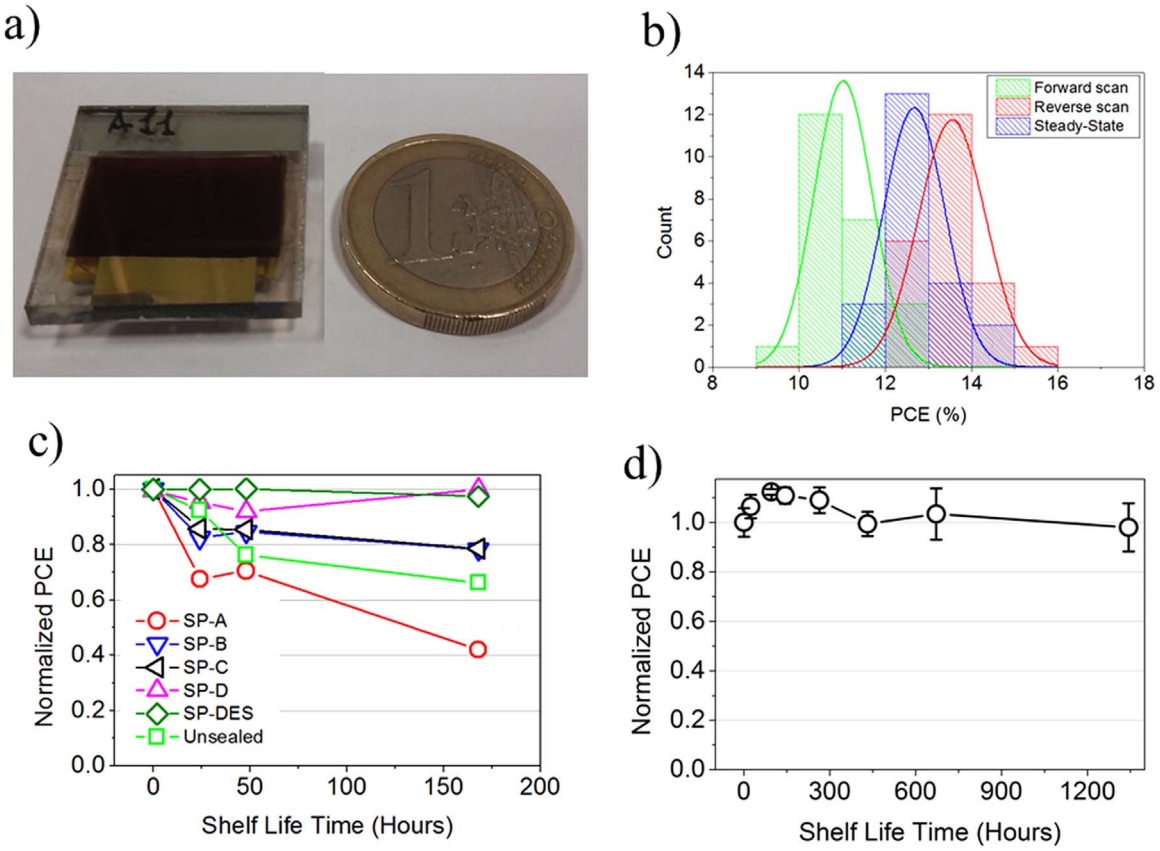

Fig. 1. (a) Image of large area PSC cell. (b) Normal dispersions of PCE obtained measuring 23 large area cells under reverse scan (red curves), forward scan (green curves) and 180 s-long MPP tracking (blue curves). (c) Short-term shelf life test varying the sealing procedure. The duration of the test was chosen in according with the T_{80} parameter defined in the introduction section. After 170 h only SP-D and SP-DES procedures showed longer T_{80} time. (d) Long-term shelf life test (more than 1300 h), using the sealing procedure SP-D. The devices were stored at low humidity (30%RH) in dark.