

In-Situ Observation of Moisture-Induced Degradation of Perovskite Solar Cells Using Laser-Beam Induced Current

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Abstract — Solar cells based on organic-inorganic metal halide perovskites have been the focus of photovoltaic research over the past few years due to high power conversion efficiencies up to 22.1% and inexpensive manufacturing costs. However, commercialization of perovskite PV technology is hindered by lack of long-term stability. To elucidate the degradation mechanisms in the state of the art perovskite solar cells, we used laser beam induced current (LBIC) mapping to spatially resolve the device degradation during aging under high humidity conditions. We confirm that perovskites are prone to decomposition in the presence of water. By varying the absorber and hole-transport materials of the devices, we are able to compare performance and identify the water ingress and degradation mechanisms. These results provide insight into the design of materials and device architectures that may improve operational stability of perovskite solar cells.

Index Terms — perovskite solar cells, stability, LBIC, degradation, humidity.

I. INTRODUCTION

Solar cells based on organic-inorganic metal halide perovskites (e.g., methylammonium lead halides, MAPbX_3 , where $X = \text{I, Br, or Cl}$) have emerged as a cheaper alternative to conventional photovoltaic (PV) technologies such as crystalline silicon and thin-film solar cells over the past few years [1]. Within 6 years, the power conversion efficiencies of perovskite cells have rapidly surged from 3.8% to 22.1% [2, 3]. In addition to excellent PV performance, the perovskite materials possess several competitive advantages, including abundant and inexpensive source materials, simple and easy to adopt fabrication techniques, benign nature of intrinsic defects [4], and tolerance for stoichiometric variation [5]. Life cycle assessments show that the energy payback times of perovskite PV technologies are 1 to 1.5 years [6] and the cost of manufacturing perovskite module could be as low as \$0.20 per watt [7], making perovskite solar cells competitive with mainstream electricity generating technologies in the foreseeable future [8].

Despite the potential to generate solar electricity at a low levelized cost of energy (LCOE), commercialization of perovskite-based PV technology is limited by several critical

issues such as materials instability [9], J-V hysteresis [10], and lack of long term stability [11]. Among them, the most significant challenge is to extend the lifespan of perovskite solar cells. Although device stability up to 3000 h (~4 months) has been demonstrated when high quality encapsulation was applied [9, 12], it is still far away from the 30 year lifetime of commercially available PV modules. The performance of perovskite devices often dramatically degrades when exposed to intensive light or moisture due to thermal instability of the materials and water catalyzed decomposition [11].

To further improve the stability of perovskite devices, the underlying physical processes associated with perovskite device degradation need to be explored, understood, and controlled. Here we use a laser beam induced current (LBIC) mapping technique to probe *in-situ* degradation of perovskite solar cells under high humidity conditions. By comparing the devices with different perovskite absorbers and hole transport materials (HTMs), we are able to identify different degradation mechanisms and suggest possible routes to improve device stability.

II. EXPERIMENTAL DETAILS

A. Perovskite Solar Cells

Fig. 1a shows the schematic of the device structure. Perovskite solar cells were fabricated on fluorine doped tin oxide (FTO) coated glass substrates. A ~30 nm thick TiO_2 compact layer was sprayed on FTO at 450 °C from a titanium diisopropoxide bis(acetylacetonate) solution. A ~150 nm thick mesoporous TiO_2 layer was then deposited by spin coating at 4000 rpm for 10 s using 30 nm particle paste (Dyesol) diluted in ethanol. The mesoporous TiO_2 was doped with lithium by spin coating a 0.1 M solution of Li-TFSI in acetonitrile at 3000 rpm for 30 s [13] and sintered at 450 °C for 30 min.

The perovskite films were deposited from a precursor solution containing 1.1 M methylammonium iodide (or bromide) and 1.2 M lead iodide (or bromide) in anhydrous DMF:DMSO 4:1 (v:v). The precursor solution was spin coated at 4000 rpm for 30 s. During the end of spin, 100 μL of

chlorobenzene was poured on the spinning substrate. The substrates were then annealed at 100 °C for 1 h in the nitrogen filled glove box.

After the deposition of the perovskite layer, 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) or poly triarylamine (PTAA) was deposited as the HTM. Details on HTM preparation can be found in the literature [14, 15]. Finally, 80 nm of gold was deposited by thermal evaporation using a shadow masking to pattern the electrodes. The active area of the device is 5 mm by 5 mm.

Here, we investigated the devices with MAPbI₃ or MAPbBr₃ absorber material and Spiro-OMeTAD and PTAA HTMs. Samples were labeled as I/Spiro, I/PTAA, Br/Spiro, and Br/PTAA, respectively.

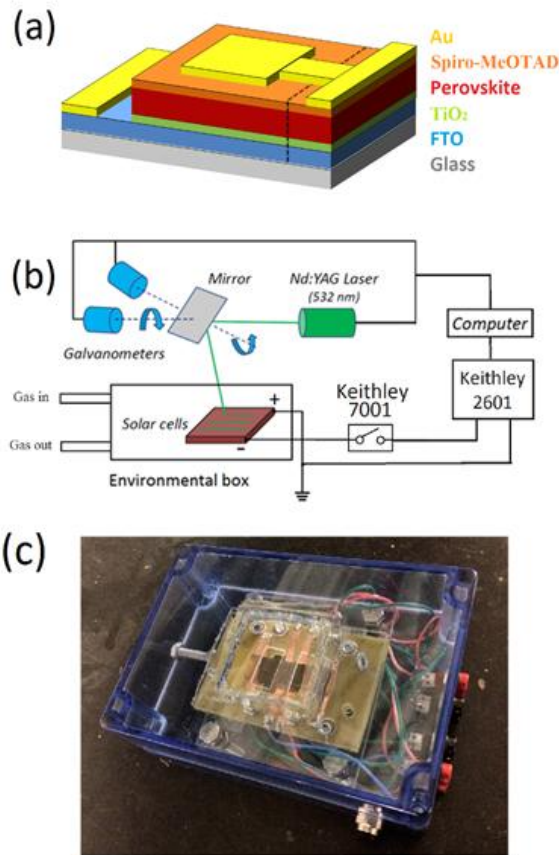


Fig. 1. (a) Schematic of perovskite solar cell structure. (b) Schematic of LBIC measurement system. (c) Photo of homemade environmental chamber.

B. LBIC Setup

LBIC measurement was performed using a laser system developed in-house (Fig. 1b) [16, 17]. A Nd:YAG laser operating at a repetition rate of 600 kHz was used to generate a 532 nm light beam with an average power of 0.01 mW and a

40 μm diameter. Computer controlled over-head mirrors and lens were used to scan the laser beam across the solar cells at a constant speed of 1 mm/s with a 30 μm spacing between two lateral scans. A LabVIEW program was developed to collect the current signal at a data acquisition rate of 5 kHz as the laser beam was rastered across the area of the device at a speed of 10 mm/s.

C. Environmental Control

A chamber with an optical window (Fig. 1c) was designed to hold 2 samples under constant environmental conditions. Copper tape was used to connect the Au/FTO electrodes to a source meter (Keithley 2601). After loading the samples, the environmental chamber was purged with dry air flowing at 3 SCFH (0.083 m³/min) through a gas bubbler. The gas bubbler was kept at 60 °C to maintain an 80 ± 5% relative humidity (RH).

III. RESULTS AND DISCUSSION

A. Iodine-Based Devices

To probe the origin of degradation and failure of the perovskite devices under high humidity condition, spatial photocurrent collection was mapped *in-situ* using LBIC. Fig. 2 shows the evolution of the LBIC map of two I-based perovskite devices with different HTMs. It is clear that the I/Spiro device degraded much more rapidly than the I/PTAA device.

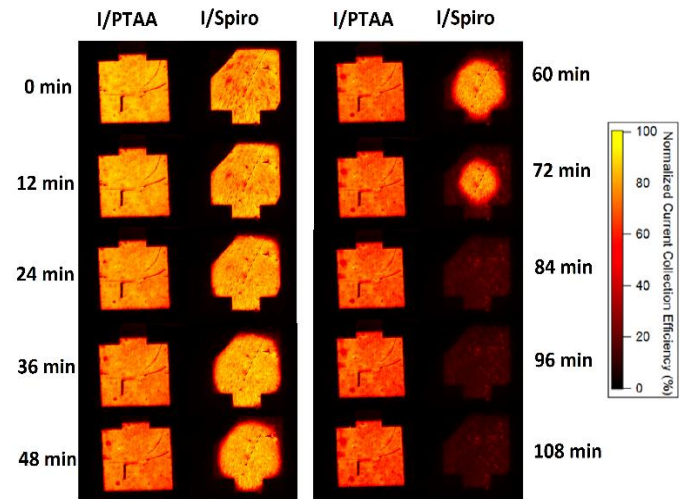


Fig. 2. Evolution of LBIC maps of I/PTAA and I/Spiro devices after exposure to 80% RH. The time span between each frame is 12 min.

The rapid degradation of the I/Spiro device is due to the hydration of the perovskite materials [18]. As previously reported [19], the water induced degradation in the I/Spiro devices consist of four stages, the two of which are caused by

carrier extraction and transport changes in the spiro-OMeTAD layer and the other two are due to phase transformation in the perovskite material. Due to the high RH, the features of the first two stages are eclipsed by the rapid photocurrent drop in the accelerated Stage 3 [19]. During this stage, the water ingress started on the edge of the device where the spiro-OMeTAD is exposed to the ambient, and rapidly propagated inward to the center of the device. The formation of monohydrate perovskite ($\text{CH}_3\text{NH}_3\text{PbI}_3 \cdot \text{H}_2\text{O}$) as a result of the interaction with water dramatically changed the optoelectronic properties of the perovskite materials, leading to the decrease in current collection efficiency.

In contrast, the photocurrent generation in I/PTAA device decreased gradually and uniformly across the whole device area, indicating a different degradation. Unlike the hydroscopic spiro-OMeTAD, the hydrophobic PTAA polymer chains can impede water ingress. The slow degradation rate is likely due to water permeation through pinholes in the thin (~ 20 nm) PTAA film. This result indicates that water resistive HTMs can improve the stability of perovskite solar cells under high humidity, showing great potential for long-term stability when the perovskite/PTAA device structure is optimized.

B. Bromine-Based Devices

To assess the role of the perovskite composition on device stability we measured the temporal evolution of the LBIC maps of Br-based perovskite devices (Fig. 3). Compared with the I-based devices, the Br-based devices exhibited improved stability under the high humidity condition due to higher resistance to water [20].

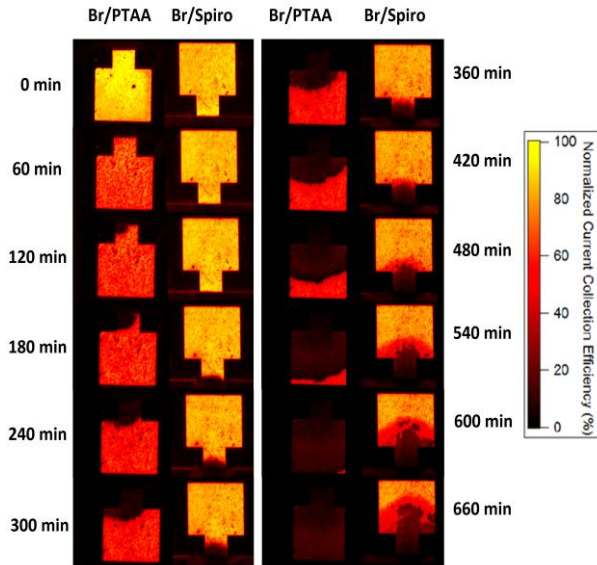


Fig. 3. Evolution of LBIC maps of Br/PTAA and Br/Spiro devices after exposure to 80% RH. The time span of each frame is 60 min.

The Br/PTAA device degraded earlier and faster than the Br/Spiro device, likely due to pin-hole formation on the Au back contact of the Br/PTAA sample (Fig. 4). Although the dynamics of water ingress through the HTMs should be the same, the reaction between water and Br-based perovskite occurs at a much slower rate. This indicates a different degradation mechanism for the Br-based devices.

For both Br-based devices, degradation first occurred at the neck region (anode) and propagated toward the back of the devices. This may be related to accumulation of negative ionic defects (Br_i^- , V_{MA^-} and $\text{V}_{\text{Pb}^{2+}}$) close to the anode. These defects favor the formation of a volatile organic halide and may stimulate the decomposition of the perovskite. It is also possible that Cu diffused from the external contact into the device and deteriorated the perovskite materials.

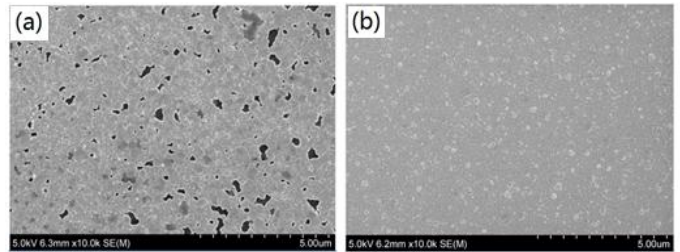


Fig. 4. SEM image of aged (a) Br/PTAA and (b) Br/Spiro devices.

C. Insights on the Degradation Mechanisms

Fig. 5 summarizes the evolution of integrated LBIC of the perovskite devices. Based on the results, we hypothesize 3 mechanisms underlying the perovskite device degradation. (1) Rapid water ingress through the Spiro-MeOTAD accelerates the degradation of I-based perovskite. (2) Deformation of a thin PTAA film leads to pin-hole formation and opens pathways for water to enter. (3) Ionic defect (both intrinsic and extrinsic) accumulation on the anode side causes the decomposition of the perovskite materials, especially the Br-based perovskites. Thus, to enhance water resistance and improve stability of perovskite devices, a hydrophobic HTM with good electrical and mechanical properties is needed.

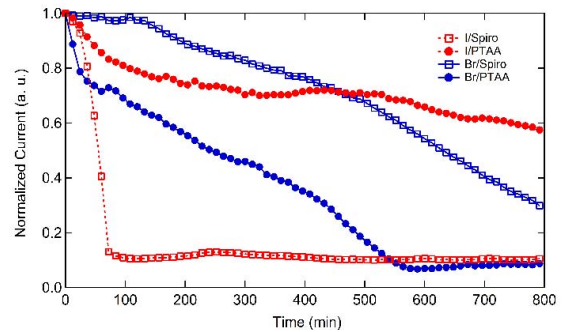


Fig. 5. Degradation of integrated LBIC signal of the perovskite devices as a function of exposure time.

IV. CONCLUSION

We investigated the device stability of perovskite solar cells under the high humidity condition using the LBIC mapping technique. Different degradation behaviors were observed in the devices with different perovskites and HTMs. Spiro-MeOTAD was found to allow rapid water ingress in the I-based device, while the defects in the thin PTAA film also lead to water ingress and degradation. We observed that degradation of the Br-based devices originated from the anode side which may be due to accumulation of ionic defects. We propose that a thicker and optimized PTAA may greatly enhance the stability of perovskite solar cells.

V. ACKNOWLEDGEMENTS

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