

Potential-Induced Degradation and Recovery of Perovskite Solar Cells

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In recent years, metal halide perovskite solar cells have become a major competitor in the run to lower the levelized cost of electricity (LCOE) of photovoltaic (PV) systems. Commercialization of this new technology mainly depends on the long-term stability of such devices, for which potential-induced degradation (PID) may represent a factor of detrimental impact. As PID can trigger rapid and significant losses in PV systems, it is generally considered among the most critical failure modes with a high financial repercussion. Herein, the results of PID tests on perovskite solar cells are reported for the very first time. The solar cells are found to be extremely susceptible to PID: 18 h of high-voltage stress, according to the PID test standard IEC 62804-1 TS (foil method at 60 °C), shows a performance degradation of up to 95%, which mainly results from a decrease in the short-circuit current. These results also uncover near full PID recoverability and pave the way toward further research into its mechanisms, kinetics, and mitigation.

In the course of the last decade, metal halide perovskites have revolutionized the field of photovoltaics (PV).^[1] Their bandgap tunability, defect tolerance, and ease of fabrication render them ideal candidates to further lower the levelized cost of electricity (LCOE), where particular appeal lies in multi-junction devices to overcome the single-junction Shockley–Queisser limit.^[2] To achieve this at a commercial level, long-term stability is a key prerequisite. Notably, potential-induced degradation (PID) is a branch of this aspect that has been identified as a major reliability issue for PV plants using established technologies, but is yet to be addressed for perovskite solar cells.^[3] For both crystalline silicon (c-Si) and thin-film PV (TFPV) technologies, such as Cu(In,Ga)Se₂ (CIGS) solar cells, extensive research has identified the root

cause of PID mainly as the migration of alkaline metal ions, such as sodium ions (Na⁺), migrating toward the solar cell under the influence of the electric field arising between the PV modules' frame and the solar cells when multiple PV modules are connected in a series.^[3–5] In contrast, and to the best of our knowledge, no reports are available on the susceptibility of perovskite solar cells to PID. Although it has been hypothesized that migrated Na⁺ ions originating from the soda-lime glass (SLG) substrate can impact the efficiency of organic–inorganic hybrid perovskite (OIHP) p-i-n solar cells, these tests, in fact, yielded an efficiency improvement through passivation at grain boundaries but were conducted in the absence of an external electric field.^[6] With this work, we aim to address the impact of such an


external electric field (PID stress) on the perovskite solar cells.

This was achieved using encapsulated perovskite n-i-p solar cells of 2 × 0.5 cm² active area on a 3 × 3 cm² SLG substrate. The perovskite solar cell stack consisted of an SLG substrate, an indium tin oxide (ITO) front contact, a tin oxide (SnO₂) electron transport layer, a cesium/formamidinium double-cation (Cs_{0.1}FA_{0.9}PbI_{2.775}Br_{0.225}) perovskite absorber, a 2,2',7,7'-tetrakis(*N,N*-di-4-methoxyphenylamino)-9,9'-spirobifluorene (spiro-OMeTAD) hole-transport layer, and a gold (Au) back contact.^[7] Prior to the experiment, all solar cells were encapsulated inside a nitrogen glove box by gluing a glass cover at the rear side of the cells with an epoxy resin. Note that there was no physical contact between the solar cell and the resin, nor the rear glass. The PID experiment itself was conducted according to the foil method as described in IEC62804-1, whereas the perovskite devices resided in an environmental chamber at 60 °C and less than 60% relative humidity (RH).^[8] During 18 h of PID stress, a 1000 V potential difference was applied between the aluminum (Al) foil attached to the front glass (i.e., the SLG substrate) and the perovskite solar cell (the solar cell being at a negative potential with respect to the Al foil, causing, for example, positive charges to be driven toward the solar cell). It is to be noted that the solar cell under PID stress was short-circuited to avoid an external electric field across the device stack. **Figure 1** shows such an encapsulated perovskite solar cell together with the foil method, including the electric field as applied during PID stress. Following PID stress, the perovskite solar cell was subjected to a PID recovery test by reversing the polarity of

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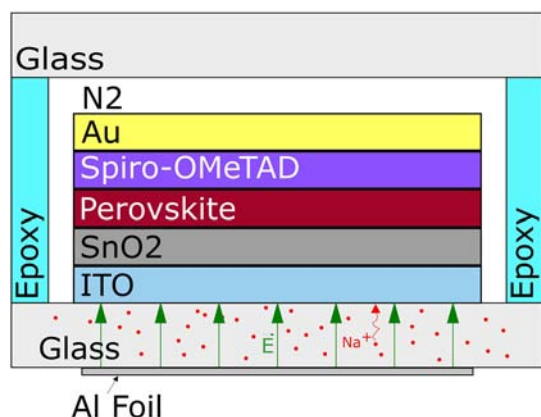


Figure 1. An encapsulated n-i-p perovskite solar cell as used in this PID experiment (not drawn to scale). The high voltage was applied between the short-circuited solar cell and the Al foil attached to the SLG substrate.

the high-voltage source for 72 h in the same environmental conditions. Previous studies have shown that an increased temperature of 60 °C accelerates the PID mechanism.^[3–5] However, an increased temperature can also affect the properties of the spiro-OMeTAD hole-transport layer capped under an Au film, which, in fact, yields an additional efficiency decrease during the PID experiment.^[9] Therefore, one identical encapsulated perovskite solar cell was used as a reference to account for the impact of the applied thermal stress during the PID experiment. This reference sample was inside the environmental chamber together with the PID sample (thus receiving an equal amount of thermal stress), but no high-voltage stress was applied. The performance of both the reference sample and the PID sample under test was quantified by light J - V measurements under standard test conditions (STC, 25 °C, 1000 W m⁻², AM1.5G).

Figure 2a shows the J - V curves of the reference sample during thermal stress. After 18 h of thermal stress, we observed a P_{MAX} degradation of 26% with losses originating from fill factor (FF) (–18%), J_{SC} (–6%), and V_{OC} (–4%). After 90 h of thermal stress, a P_{MAX} degradation of 42% was recorded, with losses originating from FF (–24%), J_{SC} (–14%), and V_{OC} (–11%). This degradation was anticipated and mainly caused by the well-documented

morphological deformation of the spiro-OMeTAD hole-transport layer capped under the Au rear contact due to the increased temperature.^[9] Figure 2b shows the J - V curves of the PID sample before and after PID stress and after subsequent PID recovery. It is abundantly clear that the perovskite solar cell is very prone to PID, with degradation levels significantly higher than the reference sample. Only after 18 h of PID stress in aforementioned conditions, a P_{MAX} degradation of 95% was observed, predominantly resulting from a J_{SC} decrease of 94%. Next to the J_{SC} , the P_{MAX} was also affected by a decrease in FF of 14%, whereas the V_{OC} remained quasi unchanged (+4%). In the interpretation of these figures, it is important to realize that a potential difference of 1000 V (which is representative for the typical accumulated voltage on module strings in a PV system)^[10] is capable of inducing large diffusive fluxes of Na⁺ ions.^[11] It is hypothesized that this results in a twofold effect. 1) The perovskite layer becomes oversaturated with mobile species, which is well known to alter bulk perovskite properties^[12] and block charge transport at its grain boundaries,^[13–15] with a lower device efficiency as a result (as opposed to the beneficial effect of grain boundary passivation for spontaneous Na⁺ diffusion in mild conditions).^[6] 2) In addition, an excess of positive Na⁺ ions can then readily build up inside and/or at the interface with the electron transport layer, preventing its proper operation in the solar cell by creating recombination centers, as evidenced by the markedly reduced J_{SC} observed in our experiment. Based on this, we infer that any beneficial effect resulting from Na⁺ ion diffusion in perovskite modules (such as grain boundary passivation, as reported by Bi et al.^[6]) is at risk of being dramatically overshadowed by PID. On the other hand, with the nature of ionic conduction in mind, it is perfectly plausible that the opposite effect would be equally valid. Indeed, Figure 2b shows that the perovskite solar cell in our experiment exhibits a reversible form of PID. By reversing the polarity of the high-voltage source, a P_{MAX} recovery of 80 percentage point was observed after 72 h while the sample remained subjected to the same environmental conditions. The P_{MAX} recovery mainly originated from an 86 percentage point recovery in J_{SC} , whereas the FF showed an increase of 4 percentage point and the V_{OC} remained quasi unchanged (–1 percentage point). Altogether, the PID stress and recovery experiments resulted in a non-recovered P_{MAX} degradation of

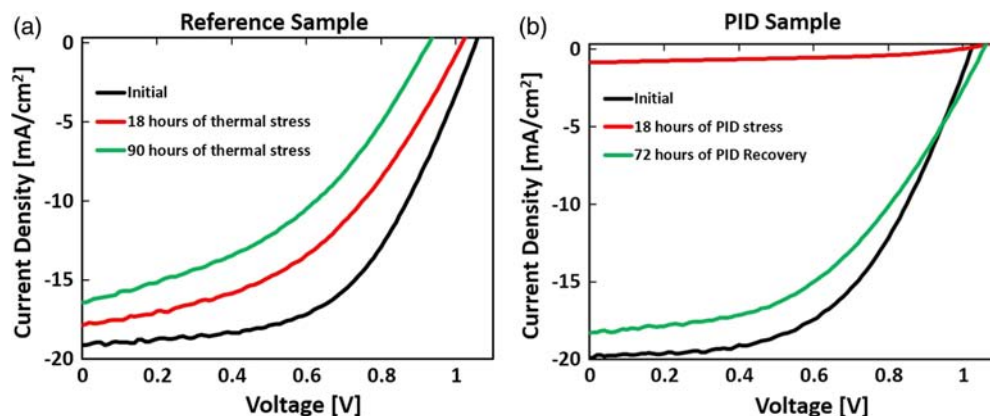


Figure 2. a) The J - V curves of the reference sample during PID stress; note that no external electric field was applied to this sample, and the observed degradation is solely due to thermal stress. b) The J - V curves of the PID sample before and after PID stress and after subsequent PID recovery.

15%. The remaining losses mainly originate from FF (−10%) and J_{SC} (−8%), whereas the V_{OC} showed a negligible change of +3%. Notably, the degradation due to thermal stress by morphological deformation of the spiro-OMeTAD hole-transport layer, as observed from the degradation of the reference sample,^[9] is much more limited for the PID sample. This points to an additional regenerative capability due to the reversed polarity that is unrelated to PID and also indirectly suggests that the PID could potentially be fully reversible by tuning the device stack. Both of these aspects offer excellent prospects for future investigations. Although the stability of perovskite solar cells has been investigated in terms of various phenomena that occur on the film or cell level primarily, in this work, we have uncovered PID as a stability concern that can have a dominant effect on full-scale installations. Our results do uncover its fortuitous reversibility and pave the way toward further research into its mechanisms, kinetics, and mitigation, which is of consequential importance for the perovskite PV technology to operate successfully on the large scale and the long term.

Experimental Section

For the 1 cm² perovskite solar cells, we applied 3 × 3 cm² glass substrates coated with 150 nm ITO with low sheet resistance ($R_{sh} \approx 10 \Omega/\square$). A 2 × 0.5 cm² cell was obtained by laser patterning of the ITO (P1), followed by layer depositions and a second patterning step (P3) done with a mechanical scribe (Figure S1, Supporting Information).

Perovskite Film Preparation: A detailed description has been reported earlier.^[7] The perovskite films were fabricated with a two-step interdiffusion method. CsI (0.031 g) and PbI₂ (0.553 g) were dissolved in 0.876 mL dimethylformamide (DMF) and 86.4 μ L dimethylsulfoxide (DMSO). This solution was spin-coated onto the substrate at 3000 rpm for 30 s. Then, a mixture of 0.1634 g formamidinium iodide (FAI) and 0.0369 g formamidinium bromide (FABr) in 3 mL isopropyl alcohol (IPA) was spin-coated at 3000 rpm for 60 s. After that, the substrate was annealed on the hotplate at 100 °C for 30 min.

Device Fabrication: The ITO-coated glass was cleaned with ultrasonic baths of detergent, deionized water, acetone, and isopropanol for 10 min each. The SnO₂ was spin-coated onto the substrate at 2800 rpm for 60 s. After that, the substrate was annealed on the hotplate at 150 °C for 10 min. Then, the perovskite film was deposited as described earlier. After this, an 80 mg mL^{−1} Spiro-OMeTAD solution doped with 17.5 μ mol L^{−1} lithium bis(trifluoromethanesulfonyl) imide (520 mg mL^{−1} in acetonitrile) and 28.5 μ mol L^{−1} 4-*tert*-butylpyridine was spin-coated onto the perovskite film. The perovskite films coated with Spiro-OMeTAD were exposed to air with 30% RH overnight for Spiro-OMeTAD oxygen doping. The devices were completed by depositing an 80 nm Au layer. The devices were later encapsulated (glass–glass encapsulation) by edge sealing with a UV-curable epoxy glue.

Device Characterization: The PV characteristics of the devices were measured under a nitrogen atmosphere using a Keithley 2602A Source–Measure Unit and an Abet solar simulator with simulated AM1.5G illumination. The light irradiance was calibrated by a KG5 band-pass equipped with ISE Fraunhofer–certified Si photodiode. The devices were measured from forward to reverse bias with a scan speed of 1 V s^{−1}.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

high-voltage stress, perovskite solar cells, photovoltaic modules, potential-induced degradation, sodium

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