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Research Highlight

A redox shuttle imparts operational durability to perovskite solar cells

Yabing Qi *

Energy Materials and Surface Sciences Unit (EMSSU), Okinawa Institute of Science and Technology Graduate University (OIST), 1919-1 Tancha, Onna-son, Kunigami-gun, Okinawa 904-0495, Japan

The family of perovskite materials are described by the formula ABX_3, where A are monovalent cations, B are divalent cations, and X are anions. The associated crystallographic structure can be stabilized by considering a tolerance factor t ($0.81 < t < 1.11$), and t is defined as the ratio of the distance A-X to the distance B-X in an ideal solid-sphere model, i.e., $t = (R_A + R_X)/\{\sqrt{2}(R_B + R_X)\}$, where R_A, R_B and R_X are the ionic radii of the corresponding ions. Since the first discovery of perovskite materials in 1839, these materials have been intensively studied and developed with demonstrated properties such as ferroelectricity, photoconductivity, superconductivity, and optoelectronic properties. The perovskite materials used in solar cells and other optoelectronic devices usually employ the following compositions: A are $CH_3NH_3^+$ (MA), Cs^+, $HC(NH_2)_2^+$ (FA), or a combination of two or more of these cations. B are Pb^{2+}, Sn^{2+}, or a combination of Pb^{2+} and Sn^{2+}. X are the halide anions such as Cl^-, Br^-, I^-, or their combinations.

The application of perovskite optoelectronic devices can be dated back to the early 1990s, where Mitzi and co-workers [1] studied some fundamental properties of organic/inorganic hybrids perovskite materials as well as device architecture designs. In 2009, Kojima and co-workers [2] demonstrated the first perovskite solar cell with an efficiency of 3.81%, by using the perovskite nanocrystals (NCs) as sensitizers in the dye-sensitized solar cells. In 2012, Park and co-workers [3] developed all-solid-state perovskite solar cells using the hole transport material spiro-OMeTAD. Thanks to these pioneering works, the research on organic-inorganic hybrid lead halide perovskites have been rapidly developing. These materials were found to possess excellent properties particularly attractive for solar cell applications, e.g., high optical absorption coefficient, tunable optical bandgap, low exciton binding energy, long free carrier diffusion length, and high defect tolerance. The fundamental understanding further stimulated enormous research efforts on the device fabrication. Up to now, the power conversion efficiencies (PCEs) of perovskite solar cells (PSCs) based on low temperature solution-process have achieved over 23% (National Renewable Energy Laboratory (NREL), https://www.nrel.gov/pv/assets/pdfs/pv-efficiency-chart.20190103.pdf. (Accessed January 2019)), which is comparable to or has surpassed other thin film photovoltaic technologies.

Despite the unprecedented development in achieving high PCEs, attaining of long-term stability is the key to the commercialization of perovskite solar cells. Perovskite based devices often suffer from instability issues, and the device lifetime is still far behind the requirements for field deployment impeding further development of perovskite solar cells. In the past few years, we have witnessed great progress with the major focus on blocking the external aging factors, such as oxygen, moisture, etc. However, some other stress conditions are inevitable during solar cell device operation, such as light, built-in electrical field and thermal stress. This requires further improvement from the material intrinsic stability point of view, which is still not fully explored.

With respect to the intrinsic stability of PSCs, degradation of perovskite materials accompanied by the generation of metallic Pb^0, I^0 defects and a wide variety of other volatile by-products have been reported by several studies [4–7], and are expected to have a profound impact on perovskite device stability. Such degradation is rooted in the low formation energy and relatively weak bonding strength (in other words the "soft" nature) of these metal halide perovskite materials, of which the constituent components are mostly large and polarized, such as I^-, MA^+, and Pb^{2+}. It has also been found that in perovskite based optoelectronic devices such as solar cells, LEDs, photodetectors, both Pb^0 and I^0 defects are detrimental to device performance and long term stability. I^- can be easily oxidized to I^0, which serves as carrier recombination centers, and initiates chemical chain reactions to accelerate the degradation in perovskite layers [4]. Pb^0 is a primary deep defect state that severely degrades the performance of perovskite optoelectronic devices [8]. Several attempts have been reported to eliminate either Pb^0 or I^0 defects, such as optimizing film processing, additive engineering, etc. Most of these additives passivate specifically one type of defects (i.e., either Pb^0 or I^0) at the inital application, but lose their efficacy at the later stage (i.e., not replenishable). But long-term operational durability requires the simultaneous elimination of both Pb^0 and I^0 defects in perovskite materials in a sustainable manner. This remains as an urgent task for PSCs in order to achieve a stable operation lifetime of over 5 years.

Elimination of intrinsic defects of both Pb^0 and I^0 can indeed enhance the long-term stability of the device significantly, which is demostrated by the research work published on January 18, 2019 in *Science*, by Zhou, Sun, Yan and co-workers [9], entitled

* Corresponding author.
E-mail address: Yabing.Qi@OIST.jp

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"A Eu^{3+}-Eu^{2+} ion redox shuttle imparts operational durability to Pb-I perovskite solar cells".

In this work, the authors employed the "redox shuttle" to oxidize Pb^0 and reduce I^0 simultaneously. Among many candidates that can potentially serve as redox shuttles, the rare earth ion pair of Eu^{3+}-Eu^{2+} was identified as the most suitable one. Eu^{3+} can be reduced to Eu^{2+} with the stable half-filled f^7 electron configuration to form the naturally associated ion pair. The redox shuttle can transfer electrons from Pb^0 to I^0 defects in a cyclical manner, wherein Eu^{3+} oxidizes Pb^0 to Pb^{2+} and simultaneously reduces I^0 to I^- (Fig. 1a). Each type of the ions in the ion couple are mutually replenished during the entire defect elimination process. The underlying mechanism for the redox shuttle to eliminate Pb^0 to I^0 defects is illustrated by the following two chemical reactions (Fig. 1a):

$$2Eu^{3+} + Pb^0 \rightarrow 2Eu^{2+} + Pb^{2+}$$

$$Eu^{2+} + I^0 \rightarrow Eu^{3+} + I^-$$

The authors calculated the intensity ratio of $Pb^0/(Pb^0 + Pb^{2+})$ in the Eu^{3+}-incorporated sample and the reference sample. As compared to the reference (5.4%), this ratio in the Eu^{3+}-incorporated perovskite sample was reduced to nearly 1.0%. This result indicates that the metallic Pb^0 species resulted from degradation of perovskite films can be effectively transformed back to Pb^{2+}. In addition, Eu^{2+} was 36% of the total Eu content based on the XPS results, which is the further confirmation of the Eu^{3+}-Eu^{2+} ion pair working as a redox shuttle.

With respect to the I^0 species, the authors examined the ratio of I/Pb and binding energy (BE) shift to monitor the iodine evolution indirectly. A higher I/Pb ratio was observed in the Eu^{3+}-incorporated sample compared with the reference sample, indicating a smaller amount of volatile I^0 species produced in the Eu^{3+}-incorporated perovskite thin film sample. This result is further corroborated by the lower BE of I $3d_{3/2}$ as observed in the Eu^{3+}-incorporated sample as compared with the reference sample.

The authors performed aging tests to further examine the effectiveness of the Eu^{3+}-Eu^{2+} redox shuttle in improving perovskite film stability. Perovskite films were subjected to 1 sun illumination (or 85 °C) for aging tests. After more than 1,000 h, the $Pb^0/(Pb^0 + Pb^{2+})$ ratio in the Eu^{3+}-incorporated sample was 2.5% (or 2.7%), compared with 7.4% (or 11.3%) in the reference sample, respectively. It clearly shows that the redox shuttle effectively preserves the element ratio in the film. Meanwhile, the corresponding I/Pb ratio in the Eu^{3+}-incorporated sample was 2.68 (or 2.57) while the ratio in the reference sample was 2.30 (or 2.13), once again indicating that the I/Pb element ratio was well preserved.

The authors incorporated the perovskite absorbers with the redox shuttle in two device configurations. Configuration-1 is ITO/TiO_2/perovskite/spiro-OMeTAD/Au, with $MAPbI_3$(Cl), and Configuration-2 is ITO/SnO_2/perovskite/spiro-OMeTAD (modified)/Au, with the perovskite absorber layer to be (FA, MA, Cs)Pb(I, $Br)_3$(Cl) for higher PCE and stability. The two devices showed similar trends upon Eu incorporation. The Eu^{3+}-incorporated devices exhibited the best PCE, and the average PCE increased from 18.5% to 20.7%, which is attributed to the effective elimination of defects. This result is further confirmed by the measurements of space charge limited current. One of the optimized devices achieved the PCE of 21.52% (21.89% for reverse scan and 21.15% for forward scan) (Fig. 1b) with negligible hysteresis (certified PCE of 20.73% for

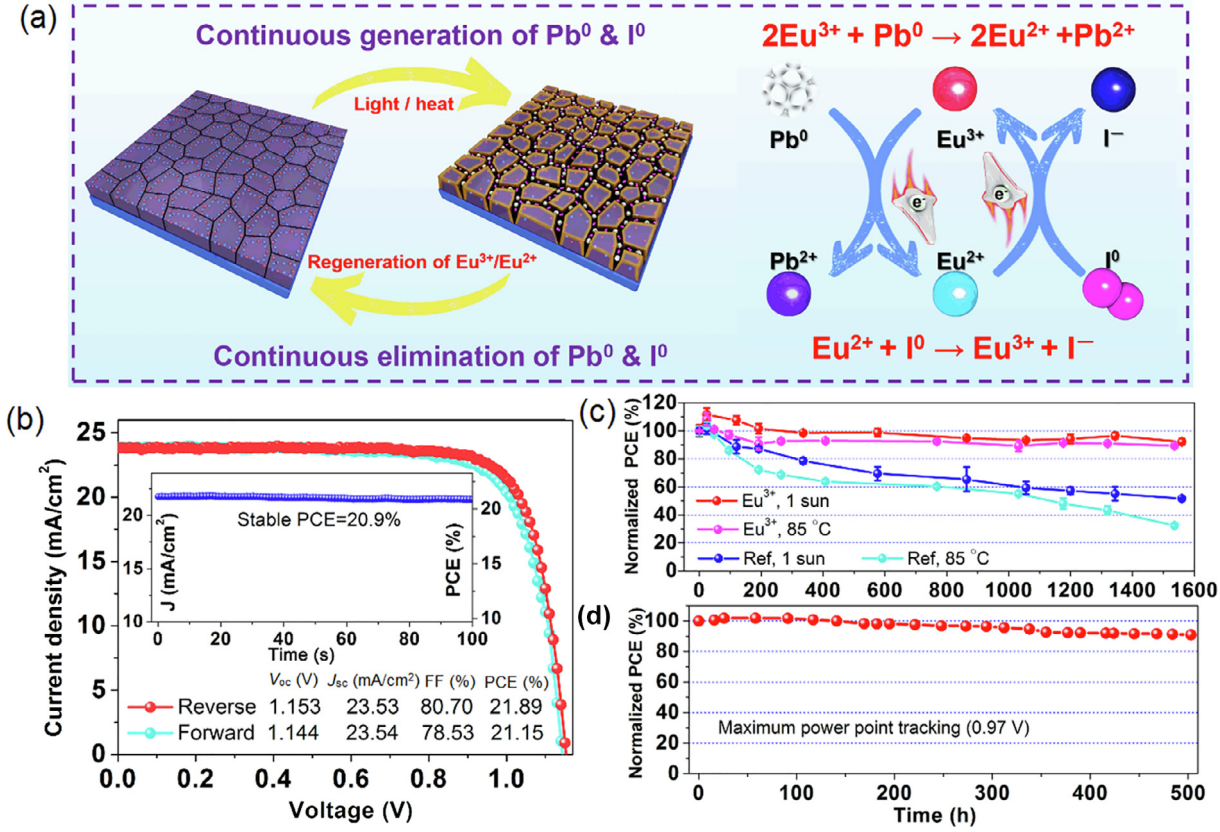

Fig. 1. (Color online) (a) Schematic drawing showing the proposed mechanism of cyclical elimination of Pb^0 and I^0 defects and regeneration of Eu^{3+}-Eu^{2+} metal ion pair. (b) *J-V* curve, stable output (measured at 0.97 V), and parameters of 0.15% Eu^{3+}-incorporated champion device. (c) The PCE evolution of Eu^{3+}-Eu^{2+}-incorporated device and reference devices under 1 sun illumination or 85 °C aging condition. Scanning speed is 20 mV/s. (d) The MPP tracking of the 0.15% Eu^{3+}-incorporated device, measured at 0.97 V and 1 sun illumination. Reprinted with permission from Ref. [9], Copyright 2019 Science.

reverse scan and 20.30% for forward scan; average 20.52%). The measured stable output at the maximum power point (0.97 V) was 20.9%. The devices with the Eu^{3+}-Eu^{2+} ion pair exhibited excellent shelf lifetime, thermal and light stability. Devices were aged under either continuous 1 sun illumination or 85 °C aging condition, respectively. In addition, the devices based on Configuration-2 maintained 92% and 89% of the original PCE, showing long-term stability improvement in V_{OC} and FF under the same light or thermal stress for 1500 h (Fig. 1c). Furthermore, the Eu^{3+}-incorporated device maintained 91% of its original stable PCE after operation under the maximum power point (MPP) for 500 h (Fig. 1d).

The new strategy developed in this work provides a promising solution to addressing the perovskite material degradation issues during device operation. Further investigations on identification of other intrinsic instability issues of perovskite materials and development of appropriate solutions for these issues are expected to speed up stability improvement of perovskite solar cells and eventual commercialization of this technology.

Conflict of interest

The author declares that he has no conflict of interest.

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Yabing Qi is the Director of Energy Materials and Surface Sciences Unit at Okinawa Institute of Science and Technology Graduate University. He received his B.S., M.Phil., and Ph.D. from Nanjing University, Hong Kong University of Science and Technology, and University of California Berkeley, respectively. His research interests include perovskite solar cells, surface/interface sciences, lithium ion batteries, organic electronics, energy materials and devices.