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Hysteresis in organic-inorganic hybrid perovskite solar cells

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A B S T R A C T

Organic-inorganic hybrid perovskite solar cells (HPSCs) are considered to be the most rapidly developed photovoltaic technology ever till date, portraying promising potential to replace the traditional silicon photovoltaics. In spite of such impressive growth, this technology is inundated with numerous challenges impeding the progress towards commercial viability. It is mainly due to the fact that the advancements in terms of performance efficiency were not equally matched with the fundamental understanding of inherent electronic and physio-chemical properties, modulating the photovoltaic parameters of the devices. Anomalous hysteresis observed in the current-voltage response of HPSCs is one of such major elusive issues prevalent in perovskite photovoltaics. Such hysteresis phenomenon could lead to erroneous estimation of the solar cell device efficiency, thereby its reliability during actual performance becomes questionable; serving as a serious obstacle for progress from both research as well as commercialization perspective. Hence, a detailed understanding of the origin of hysteresis and its associated mechanisms are highly indispensable. Though numerous theories have been proposed to elucidate the underlying causes of hysteresis, its origin is a highly debated topic till date and the most convincing answer is yet to be unraveled. The presented review takes an opportunity to elaborate various governing mechanisms or origins affecting the hysteresis phenomenon from a comprehensive yet insightful standpoint. This report also provides a concise synthesis of intricate interdependencies among the factors influencing hysteresis and highlights potential research strategies to develop hysteresis-free devices; rendering possible pathways to facilitate the viable commercialization of perovskite solar cells.

1. Introduction

The emergence of highly efficient organic-inorganic hybrid perovskite solar cells (HPSCs) has revolutionized the photovoltaics technology and has demonstrated enormous potential to replace the traditional silicon photovoltaics [1]. Organic-inorganic hybrid perovskites can be considered as unique in terms of exhibiting numerous advantageous properties such as facile processability, low cost, tunable bandgaps and superior charge-transfer dynamics [2,3]. Furthermore, HPSCs have the lowest energy payback time (EPBT) amongst all the other photovoltaic technology [4]. The potential of organic metal halide based perovskites was initially explored as optoelectronic and transistor materials for decades [5–8] and its marvelous journey in photovoltaics began in 2009, when it was used as a photo-sensitizer on TiO_2 [9]. The working principle of perovskite solar cells (HPSCs) emerged from the field of dye-sensitized solar cells (DSSCs) [10]. In general, HPSCs consists of a light absorbing perovskite layer with electron transporting layer (n-type) and hole transporting layer (p-type) on either side forming a p-i-n like structure. Upon illumination, the perovskite layer generates both excitons and unbound electron–hole (e-h) pairs. The exciton binding energy is sufficiently low for these photogenerated excitons or e-h pairs; thereby it readily undergoes thermal dissociation resulting in free carriers. Combined with high charge carrier diffusion lengths in the μm range and charge selectivity offered by the adjacent ETL and HTL layers, the charges are extracted efficiently at the respective electrodes [10,11]. In a short span of six years, the power conversion efficiency (PCE) was improved from 3.8% to a record 22% in early 2016 [12,13]. In comparison, similar low cost PV technologies such as organic solar cells took over two decades to cross the PCE mark of over 10% [14]. Such rapid advancements in HPSCs have created a scenario in which the rate of the technological developments measured by PCE improvement have largely surpassed the learning curve with respect to understanding the basic physics, chemistry and material science of this promising organic-inorganic hybrid perovskites; from the perspective of synthesis, structure and opto-electronic properties [15]. Therefore, an in-depth comprehension of many of the electronic and physical properties of this class of eclectic materials remains elusive. Another main obstacle in the perovskite technology would be the use of toxic

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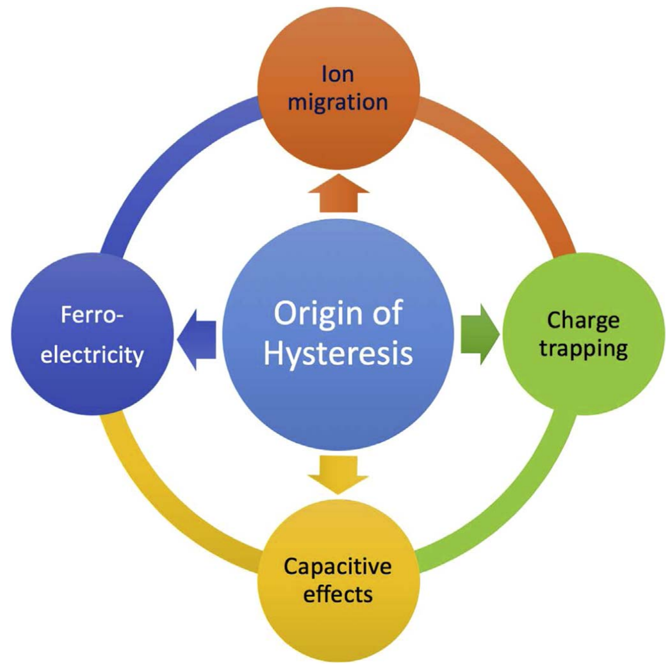
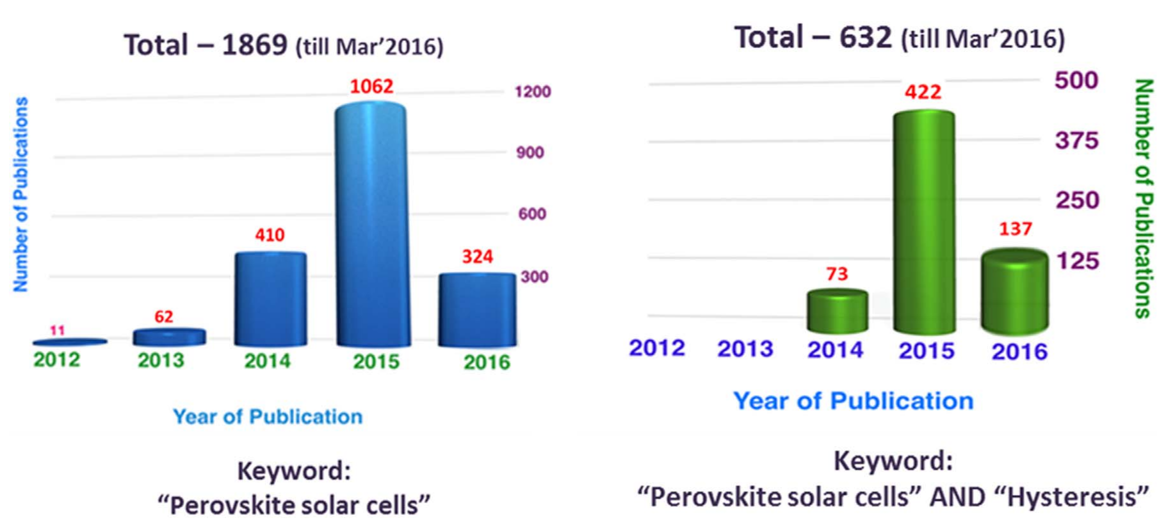
metals such as Lead (Pb) in the perovskite matrix. So far Pb^{2+} has been found to be the most suitable cation for highly efficient HPSCs, which gives rise to apprehension from an environmental standpoint [16]. However, many challenges remain; the most crucial one is the incomplete understanding of the structure–property–performance relationship, which hinders from realizing the full potential of the hybrid perovskites [17]. In specific, two of the most basic predominant issues serving as a bottle-neck for commercialization of perovskite photovoltaic technology are (i) relatively fragile stability of HPSCs which decomposes rapidly with exposure to moisture, high temperature and prolonged light illumination [18–20] and (ii) ambiguity in accurate determination of the PCE for HPSCs due to strong current–voltage (*I–V*) hysteresis, whose origin (intrinsic and/or extrinsic) is not clear [15,17,21–26]. Such hysteresis phenomenon could lead to over- or under-estimation of the solar cell device efficiency; thereby its reliability during actual performance could become aberrant and hence impeding the progress of the HPSCs research [24,26,27]. Furthermore, the hysteresis might be associated with the long-term stability of the devices [22].

Many possible theories elucidating the origin or mechanism of hysteresis in HPSCs have been proposed such as (i) trapping of electronic carriers at the perovskite interface(s) [28,29]; (ii) ionic displacement/ion migration [30–33]; (iii) ferroelectric polarization [34–36], and (iv) capacitive effects [37–39] Nevertheless, a standard acceptable framework that could convincingly explain the hysteresis phenomenon, while simultaneously considering all currently known processes governing the device operation has not been apparently unraveled; and the inference for this query remains an open question and highly debatable till date. Moreover, solving the hysteresis issue not only benefits the successful development and commercialization of the hybrid perovskite photovoltaic technology, but also culminates breakthrough advances in allied technological applications such as light emitting diodes, lasers [40,41], optoelectronics [42], spintronics [43], and thermoelectrics [44,45], among others. Therefore, prominent and rigorous research is carried out to identify the origin and related governing mechanisms of the hysteresis phenomena.

Numerous reports have been published in the last two years addressing the hysteresis issue with consistent progress/development trend as depicted in Schematic 1. It is noteworthy to mention that in the year 2015 alone, 422 documents have been published with keywords "perovskite solar cells" and "hysteresis" out of total 1062 documents published with respect to "perovskite solar cells", thereby highlighting the importance of the hysteresis research in terms of progress of the HPSCs. It also denotes that any current and future research in perovskite solar cells either aimed at improving the efficiency (PCE) or stability cannot overlook the issue of hysteresis. Hence, a detailed understanding of the origins of I-V hysteresis and the associated mechanisms is highly indispensable. (Schematic 2 and 3 shows the overview of various origins and parameters influencing the hysteresis phenomenon in HPSCs respectively.)



Schematic 2. Represents the various origins or underlying mechanism governing the hysteresis phenomenon in hybrid perovskite solar cells. Each factor modulates the hysteresis phenomenon either directly or indirectly via interrelated dependencies among them.



Schematic 1. Graph showing the number of documents published with respect to hysteresis in perovskite solar cells compared with total number of publications with respect to perovskite solar cells. (Left) Graph details obtained from scopus with search filter as "(TITLE-ABS-KEY (perovskite solar cells) AND PUBYEAR > 2011)" with a total of 1869 documents. (Right) Graph details obtained from scopus with search filter as "(TITLE-ABS-KEY (perovskite solar cells) AND PUBYEAR > 2011) AND (hysteresis)" with a total of 632 documents.