



# Unraveling the hysteretic behavior at double cations-double halides perovskite - electrode interfaces

Dohyung Kim<sup>a</sup>, Yongtao Liu<sup>a,b</sup>, Anton V. Ievlev<sup>b</sup>, Kate Higgins<sup>a</sup>, Olga S. Ovchinnikova<sup>c</sup>,  
Jae Sung Yun<sup>d</sup>, Jan Seidel<sup>e</sup>, Sergei V. Kalinin<sup>b</sup>, Mahshid Ahmadi<sup>a,\*</sup>

<sup>a</sup> Joint Institute for Advanced Materials, Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA

<sup>b</sup> The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

<sup>c</sup> Computational Sciences and Engineering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

<sup>d</sup> Australian Centre for Advanced Photovoltaics (ACAP), School of Photovoltaic and Renewable and Engineering, University of New South Wales, Sydney, NSW 2052, Australia

<sup>e</sup> School of Materials Science and Engineering, University of New South Wales, NSW 2052, Australia

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## ABSTRACT

Despite over a decade of research on metal halide perovskites (MHPs) in the context of photovoltaic applications, understanding the nature of electronic and ionic processes associated with current-voltage (*I*-*V*) hysteretic behavior has been limited. Here, we explore the hysteretic behavior in (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> perovskite devices with lateral Cr electrodes by applying first order reversal curve (FORC) bias waveform in *I*-*V*, Kelvin probe force microscopy (KPFM) measurements, and in-situ chemical imaging by time-resolved time-of-flight secondary ion mass spectrometry (tr-ToF-SIMS). In dark, we reveal pronounced hysteretic behaviors of charge dynamics in the off-field by probing time-dependent current and contact potential difference (CPD). Under illumination, transient and hysteretic behaviors are significantly reduced. The tr-ToF-SIMS results reveal that the hysteretic behaviors are strongly associated with accumulation of Br<sup>-</sup> ions at the interfaces. In addition, the low mobility MA<sup>+</sup> ions result in transient behavior and contribute to the hysteretic phenomena. It was shown that Pb<sup>2+</sup> ions can be reduced at the interfaces due to electrochemical reactions with the electrode in the presence of charge injection and photogenerated charges. These hysteretic behaviors associated with charge dynamics, ion migration, and interfacial electrochemical reaction are critical to further improve the performance and stability of MHPs photovoltaics and optoelectronics.

## 1. Introduction

In recent years, the power conversion efficiency (PCE) of metal halide perovskite (MHP) solar cells have been rapidly improved with PCEs exceeding 25.5% for a single junction solar cell [1]. Beyond photovoltaic applications, the development of these materials for other applications such as light-emitting diode [2], photodetectors [3], ionizing radiation sensors [4] has been remarkable due to their interesting optoelectronic properties. Besides, these materials are now being explored for information technology applications such as memristors [5]. It was recognized that many intriguing properties of MHPs including giant dielectric polarization [6], phase segregation [7], lattice expansion [8], photovoltaic switching [9], anomalous photovoltaic effect [10], and structural variations [11] are inherently linked to ionic

behaviors. MHPs are mixed ionic and electronic conductors and the ion migration in these materials generally result from high mobility of ion species especially halides [12–15]. These ionic motions lead to the electrode polarization where the ions with opposite sign to the electrode polarity are accumulated at blocking electrodes [16], or result in electrochemical reactions and charge injections where ions of the same sign as the electrode polarity are generated and injected [11].

In addition to internal electrochemistry of MHPs, the biased electrodes in MHPs can participate in electrochemical processes and ion injections simultaneously [11,17]. Indeed, the metal migration-induced degradation is a critical issue in MHP devices [18]. The common metal electrodes in MHP devices such as Au and Ag can diffuse into the perovskite layer, and result in the escape of volatile species from perovskites [19]. It was observed by us [17] and others [18,20] that not

\* Corresponding author.

E-mail address: [mahmadi3@utk.edu](mailto:mahmadi3@utk.edu) (M. Ahmadi).

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