

Numerical analysis of a hysteresis model in perovskite solar cells



Yecheng Zhou^{a,*}, Fuzhi Huang^b, Yi-Bing Cheng^c, Angus Gray-Weale^a

^aSchool of Chemistry, The University of Melbourne, Parkville, VIC 3010, Australia

^bMaterials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

^cDepartment of Materials Science and Engineering, Monash University, Victoria 3800, Australia

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ABSTRACT

Previously, we proposed that the polarization and capacitive charge in $\text{CH}_3\text{NH}_3\text{PbI}_3$ screens the external electric field that hinders charge transport. We argue here that this screening effect is in significant part responsible for the power conversion characteristics and hysteresis in $\text{CH}_3\text{NH}_3\text{PbI}_3$ photovoltaic cells. In this paper, we implement capacitive charge and polarization charge into the numerical model that we have developed for perovskite solar cells. Fields induced by these two charges screen the applied hindering field, promote charge transport, and improve solar cell's performance, especially in solar cells with short diffusion lengths. This is the reason why perovskite solar cells made from simple fabrication methods can achieve high performance. More importantly, with relaxations of capacitive charge and polarization charge, we quantitatively reproduce experimental "anomalous" hysteresis J-V curves. This reveals that both polarization relaxation and ions relaxation could contribute to anomalous hysteresis in perovskite solar cells.

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1. Introduction

Perovskite solar cells have achieved power conversion efficiencies (PCEs) up to 22% in just five years [1,2]. They attract great attention due to their high performance and anomalous hysteresis. It is believed that the large charge carrier diffusion lengths and the compensated field are two key factors for high performances of hybrid perovskite solar cells. In experiment it was observed that the slowly built compensated field contributes to the anomalous hysteresis [3,4]. It is believed that the compensated field is induced by ion migration and electronic charge traps [3–5]. The compensated field works as a screening effect resulting in a high dielectric constant, which has been observed up to 1000 for $\text{CH}_3\text{NH}_3\text{PbI}_3$ [6,7].

At high frequencies only electronic orbitals are able to respond and become polarized, whereas at low frequencies all of the electronic orbitals, defect charges and ions are able to respond. As a result, at high frequencies low dielectric constants of 6–7 are observed [6,8], compared to dielectric constants approximately 100 times higher at low frequencies [6]. This frequency dependent dielectric constant behavior is consistent with the compensated field and the extremely slow photo-conductivity response in

$\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells [9]. We argue that both compensated field and slow photo-conductivity come from certain slow relaxations. This relaxation screens external fields and increases the dielectric constant. It is widely believed that ion migration is one possible reason for this slow relaxation [3–5,10–12]. But the slow response experiment carried out by Gottesman et al. shows two opposite behaviors of decreased/increased photo-conductivity in identically constructed devices. This cannot be explained by ion migration [9]. It needs to be revised that ion migration is not the only origin of hysteresis. VanReenen et al. modeled this hysteresis and found the combination of ion migration and electronic traps brings about hysteresis [5].

Besides ion migration, polarization is another possible reason for hysteresis. Beilsten-Edmands et al. claimed that there is no ferroelectric nature contribution to hysteresis due to the intrinsic polarization being too small [10]. They treated the polarization at very high frequency ($f \rightarrow \infty$) as its intrinsic polarization, however this is incorrect. For any ferroelectric polarizations under a very high frequency it should be zero as the electronic orbitals and ions are unable to respond. There is no direct evidence to deny ferroelectric polarization in perovskite solar cells. Additionally, Kutes et al. showed a direct observation of ferroelectric polarizations [13]. Debate of polarization in hysteresis continues.

From a theoretical standpoint most research supports the existence of polarization. First-principles studies have shown that the energy barriers for defect migrations are from 0.08 eV to 0.40 eV

* Corresponding author.

E-mail addresses: yecheng.zhou@unimelb.edu.au (Y. Zhou), angusg@unimelb.edu.au (A. Gray-Weale).

depending on ion types [14,15]. This energy barrier is low enough to be crossable at room temperature. We also reported the energy barrier for methylammonium ions (MA^+) reorientation is about 0.01 eV to 0.098 eV, which depends on the initial and final MA^+ orientations and neighbor MA^+ orientations [8]. From the base of their energy landscapes, polarization is easier to respond and screen external fields. MA^+ ions are able to be rotated collectively under an applied external field, which then polarizes the $\text{CH}_3\text{NH}_3\text{PbI}_3$ crystal or thin film. This collective reorientation and polarization combined with capacitive charges screen external hindering field and promote power conversion efficiency. Hence, another slow relaxation should be polarization relaxation. Our argument is in good agreement with Sanchez's experiment that the slow dynamic process depends strongly on the organic cation, MA^+ or FA^+ [16]. The rotation of MA^+ ions and migration of I^- ions are systemically discussed by Frost et al. [17–19]. They argued that the internal electrical fields associated with polarization contribute to hysteresis in J-V curves [17]. They also observed that a single cation rotation and anion migration take several picoseconds [18,19]. Hence, we argue here that polarization and ion migration are both possible to induce screening fields and contribute to hysteresis.

We propose that the screening charge contains two components: one is the polarization charge resulted from MA^+ reorientation and inorganic frame, which we name the polarization charge; another is capacitive charges from defects and trapped charges including ions. For normal perovskite solar cells without polarization, photon generated charge carriers accumulate in defects near interfaces, shown as blue¹ charge in Fig. 1. These accumulated charges induce a field that counteracts the applied hindering field. We name the applied field the hindering field because it is opposite to the work current vector. For perovskite solar cells, polarization charges can further counteract the hindering field and promote charge carrier transport. Due to these capacitive and polarization screening effects, high PCEs are expected for hybrid perovskite solar cells. This is the first hypothesis we are going to test.

The second hypothesis we are going to test is that hysteresis in J-V curves come from these two kinds of slow relaxations. As their relaxations are slow, screening fields fall behind the applied hindering field if the measurement scanning is fast enough. This delay induces hysteresis. We apply numerical simulations to reproduce and explain the anomalous hysteresis effect in perovskite solar cells. Our results show both capacitive charge and polarization charge could contribute to hysteresis effects. Relaxation times of these two charges determine the overall behavior of scan rate dependent hysteresis.

2. Methods

Our model is based on the continuity equations and Poisson's equation in one dimension, adapted for perovskite solar cells [20]:

$$\begin{aligned} J_n &= eD_n \frac{\partial n}{\partial x} + n\mu_n F \\ J_p &= -eD_p \frac{\partial p}{\partial x} + p\mu_p F \\ \frac{\partial J_n}{\partial x} &= -eG + eR \\ \frac{\partial J_p}{\partial x} &= eG - eR \\ \frac{\partial F}{\partial x} &= \frac{p - n}{\epsilon\epsilon_0} \end{aligned} \quad (1)$$

¹ For interpretation of color in Figs. 1–4, the reader is referred to the web version of this article.

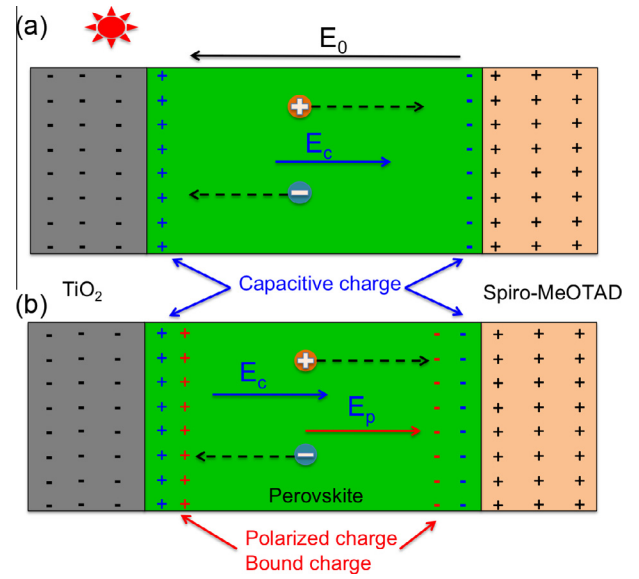


Fig. 1. Our proposed mechanism of perovskite solar cells.

where J_n and J_p are electron current and hole current respectively; n is electron density and p is hole density; μ and D are charge carriers mobility and diffusion coefficient respectively; footnote symbols $_n$ and $_p$ mean they belong to electron and hole respectively; G and R are generation rate and recombination rate; F is the external applied electric field. Boundary conditions and parameters are shown in Ref. [20].

Light harvest and charge generation are expressed as $G = IPCE \times N$, where $IPCE$ is Incident Photon-to-Current Efficiency. N is the incident photon density calculated by $\int \frac{I(\lambda)}{hc/\lambda} d\lambda$, where $I(\lambda)$ is incident light density, h is the Planck constant, c is the speed of light and λ is the photon's wavelength. According to the Beer–Lambert law, light intensity inside a material decays exponentially from the surface as: $I(\lambda, x) = I(\lambda, 0)e^{-\alpha(\lambda)x}$, where x is the incident depth from the surface and $\alpha(\lambda)$ is the absorption coefficient. Therefore, the charge generation rate becomes:

$$G(x) = \int_0^{\lambda_0} G(\lambda, x) d\lambda = \int_0^{\lambda_0} IPCE(\lambda) \times \frac{I(\lambda, 0) \times \alpha(\lambda) \times e^{-\alpha(\lambda)x}}{hc/\lambda} d\lambda \quad (2)$$

λ_0 is the absorption edge, corresponding to the bandgap. After a photon is absorbed, an exciton formed by a separated hole and electron pair is generated. The hole and electron attract each other and try to combine. We assume all excitons separate to pairs of free holes and electrons, which means $IPCE(\lambda) = 100\%$ [20]. Then the charge generation rate becomes:

$$G(x) = \int_0^{\lambda_0} IPCE(\lambda) \times \frac{I(\lambda, 0) \times \alpha(\lambda) \times e^{-\alpha(\lambda)x}}{hc/\lambda} d\lambda = \alpha N_0 e^{-\alpha x} \quad (3)$$

where $N_0 = \int_0^{\lambda_0} \frac{I(\lambda, 0)}{hc/\lambda} d\lambda$; $I(\lambda, 0)$ is the AM1.5 Standard Solar Spectra. The experiment band gap of MAPbI_3 is in the region from 1.45–1.70 eV [21–26]. In our simulations, we use a linear fitting to estimate incident photon density near 1.55 eV. $N_0 = -2.20 \times 10^{17} \times E_{bgap} \text{ (eV)} + 5.12 \times 10^{17} \text{ (cm}^{-2}\text{)}$, where E_{bgap} is the band gap of the perovskite thin film. As shown in Fig. 2, for the band gap in the range of 1.45–1.62 eV, the accurate integral density and fitted density are almost the same. The incident photon density is calculated to be $1.59 \times 10^{17} \text{ cm}^{-2}$, if the band gap is 1.60 eV.

A planar perovskite solar cell has a sandwich structure. Two electrodes clip a compact (TiO_2) layer, a perovskite layer and a hole

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