



Studying the Role of Ion Migration on Perovskite Light-Emitting Diodes by Steady-State Approach

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ABSTRACT: Despite the rapid development of Perovskite-based Light-Emitting Diodes (PeLEDs) within the last decade, the role of ion migration on the operation of the devices has not been completely understood. Affecting PeLED's operation is considered as the most complicated and mysterious process. It is widely accepted that the ion migration, as an intrinsic phenomenon, is one of the main origins for low stability of PeLEDs. On the other hand, the defect passivation caused by mobile ions gives rise to enhanced charge injection from the electron and hole transporting layers, leading to more efficient light-emitting diodes. Therefore, it is critical to have a comprehensive insight to the underlying principles of ion migration and its contributing factors. In this paper, the ion migration phenomenon and its influence on the operation of a PeLED are surveyed using the Finite Element Method (FEM) simulation. The accumulation of anions and cations at the hole and electron transporting layer's interface with the perovskite facilitates hole and electron injection, which result in more carrier density favoring the radiative recombination. Therefore, ion migration is a phenomenon that is closely related to the operation and stability of the device by controlling which more stable PeLED is attainable. Our results provide a better understanding of the physics behind the ion migration, which is the first step to design more efficient devices.

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1- Introduction

Metal Halide Perovskites (MHPs) have attracted a great deal of attention as a new class of materials for next-generation optoelectronic low-cost, solution-based [1-3] devices. The success of perovskites is due to their fascinating electronic and optical properties such as bandgap tunability [4-7], intense absorption of light [8], long carrier diffusion length [9], and low frequency of deep trap states [10, 11]. Owing to these unique properties, Perovskite-based Solar Cells (PSCs) have achieved up to 25% power conversion efficiencies [12]. In addition to PSCs, the great potential of MHPs in light-emitting diodes has also been recognized. The first Perovskite-based light-emitting diode (PeLED) with high brightness was prepared by Tan et al. in 2014 with External Quantum Efficiency (EQE) of 0.76% and 0.1% for the infrared and green light, respectively [13]. Thus far, external quantum efficiencies exceeding 20% for PeLEDs have been reported. This brisk rise in EQE is mainly achieved through perovskite compositional engineering [14-16].

However, nowadays the worldwide LED market is dominated by conventional semiconductors, such as gallium arsenide. Similar to the photovoltaic market, the "golden triangle" which includes cost, efficiency, and acceptable stability should be considered in designing PeLEDs before presenting them into the global market [17] (fig.1 (a)). Despite the signifi-

cant enhancement in efficiencies reported by different groups for PeLEDs, short stability hinders their commercialization [18]. They cannot be regarded as new exploitable materials for optoelectronic applications unless reasonable stability of the perovskite-based devices is attained. There are many factors contributing to the operational lifetime of PeLEDs which can be classified into intrinsic and extrinsic groups. In addition to the sensitivity of organic elements in the perovskite structure, these materials have hygroscopic nature, meaning they interact with moisture and oxygen in the ambient air [19, 20]. This extrinsic degradation can effectively be suppressed by encapsulation techniques [21]. On the other hand, the degradation of perovskite while applying the electric bias during the device operation is considered as an intrinsic factor affecting its performance. MHP thin films are considered as soft-lattice [22, 23] ionic semiconductors [24] with dynamic disorders [25] resulting from the fabrication techniques. Recent studies have shown that ion migration is one of the main origins for the intrinsic degradation of perovskite-based devices and their resultant short operational lifetime [26].

The ion migration phenomenon was first discovered in the 1980s in perovskite oxides followed by theoretical computer-modeling studies to investigate ionic transportation [27-29]. MHPs with ABX₃ structures constitute of multiple cations and anions. Several experimental and theoretical studies have shown ion migration in the perovskites. Yuan et al. used

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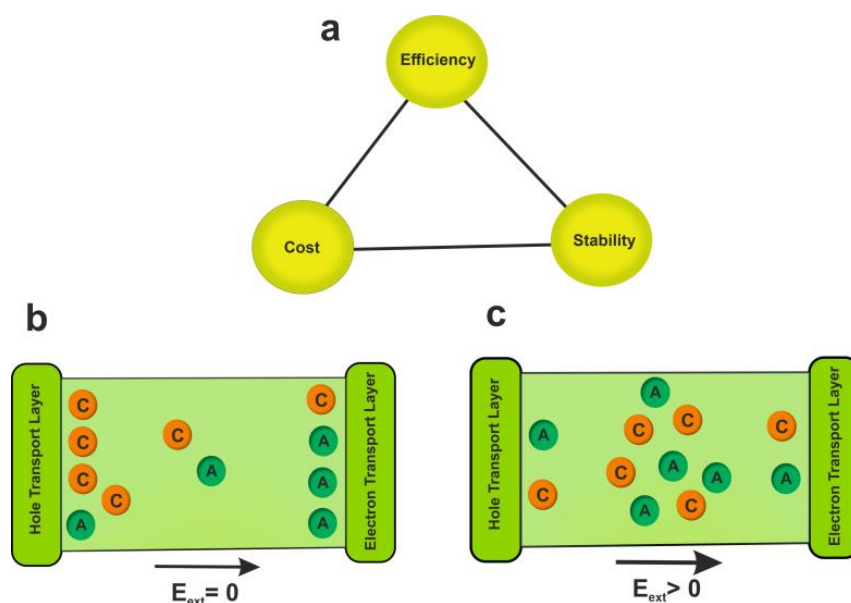


Fig. 1. a) The golden triangle of LED including efficiency, cost, and stability [17]. Schematic of ions drift in the perovskite b) at zero bias and c) under forward bias.

Energy-Dispersive X-ray spectroscopy (EDX) and X-ray Diffraction analysis (XRD) measurements and presented a microscopic vision that shows the migration of I^- and MA^+ ions, and the formation of PbI_2 at anode site, transporting to cathode site under the applied electric field that proves ion migration in MAPbI_3 [30]. Fig.1 (b) and (c) show the schematic of ion migration under an external electric field. Increasing applied voltage leads to migration of cations and anions to the perovskite bulk, and then to the Electron Transport Layer (ETL) and Hole Transport Layer (HTL) interfaces, respectively, creating a new equilibrium that results in a space-charge accumulation zone there. Accumulation of these ions is equivalent to n-dope and p-dope zones at interfaces called “self-doping”, which gives rise to band bending at ETL/perovskite and HTL/perovskite interfaces [31].

Both cations and anions in the perovskite structure can respond to the applied electric field, migrate through the active layer, and accumulate at the ETL and HTL interfaces. It should be noted that the activation energies (E_a) for distinct ions are different. Azpiroz et al. and Eames et al. calculated the activation energies for vacancy migration of Br and MA^+ , 0.09 eV and 0.56 eV, and between 0.8 and 2.31 eV for Pb [32-34]. Thus, considering activation energies for ion migration, cations show a slower response to external stimulations such as electric field [35] and radiation [36].

Migration and the resultant redistribution of ions in the PeLEDs are responsible for their stationary and transient behavior, and are determinants of the operation of the device.

Due to the ionic nature of perovskites, the characterization of PeLEDs is sensitive to measurement protocols. It has been reported by several groups that ion migration is the origin of hysteresis in the current density-voltage (J-V) characteristics [32, 35, 37]. Unfortunately, there are a few studies that investigated ion migration in PeLEDs. Bermudez et al. used a combined computational and experimental study to investigate the benefits of LiF interlayer on PeLED mechanism. They showed that migration of Li to cathode and F to anode results in enhanced electron injection and improved current density [38]. Dong et al. studied the slow response of current and electroluminescence of PeLED, which they attributed to Br migration to anode. Accumulation of halide at anode interface gives rise to charge imbalance due to facilitated hole injection [39]. Wang et al. indicated that dynamic redistribution of ions affects charge injection and transport, thus hysteresis in EQE curve appears [37]. Although some efforts have been made to understand the ion migration mechanism and its impacts on PeLED's operation, there is no comprehensive device modeling to study this phenomenon in PeLEDs. Therefore, it is critical to have a real insight into the underlying principle of ion migration and its impacts on PeLEDs characteristics. In our work, we simulate ion migration in a planar PeLED with steady state approach using the Finite Element Method (FEM). Our model incorporates two distinct mobile species (positive and negative) of the same density but different mobility, which are allowed to move within the perovskite layer according to ionic transport equations.

2- Theoretical Modeling

In this work, a 1-dimensional PeLED is resembled by COMSOL, using FEM. The device consists of Ag/ZnO/ MAPbBr₃/PEDOT: PSS/ITO, where Ag and ITO are cathode and anode contacts, ZnO (90 nm) is the Electron Transport Layer, and PEDOT: PSS (90 nm) is the hole transport layer. A 150 nm layer of MAPbBr₃ is considered to be the active layer of the LED. The device structure and energy level diagram are shown in Fig. 2 (a) and (b). PeLED's operation was

simulated by solving continuity and drift-diffusion equations for electrons and holes within three layers. Ion migration as a general form Partial Differential Equation (PDE) was introduced to the model. We consider two mobile species as cations and anions with the same density in the PDE calculations. Moreover, anions are assumed to be ion species with lower activation energy and higher mobility. Parameters used in the FEM simulation are listed in Table 1.

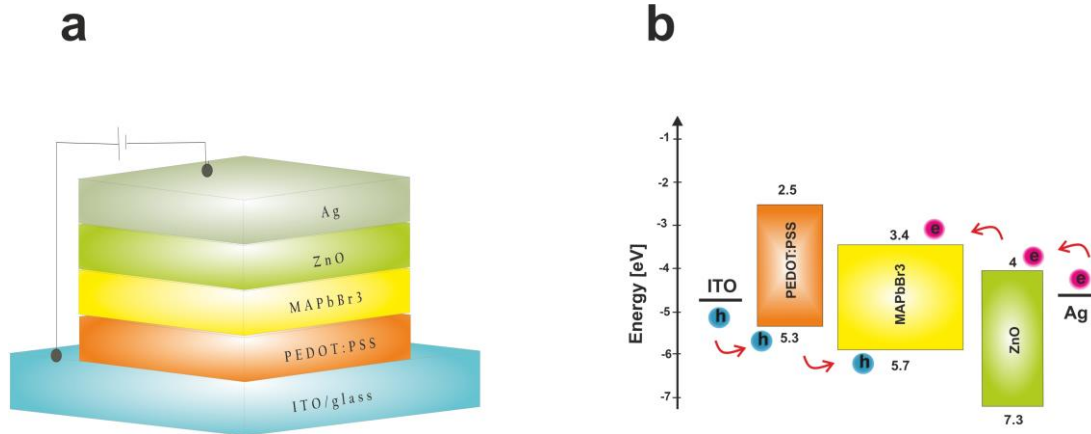


Fig. 2. a) PeLED structure, and its b) Energy diagram.

Table 1. List of the parameters used in PeLED simulation

Parameter	HTL	Perovskite	ETL	Unit
Thickness	90	150	90	nm
Bandgap	2.8	2.29	3.3	eV
Relative permittivity	5	28	9	1
Affinity	2.5	3.4	4	eV
Electron mobility	0.01	10	100	cm ² V ⁻¹ s ⁻¹
Hole mobility	0.1	10	25	cm ² V ⁻¹ s ⁻¹
Conduction band effective density of states	10 ¹⁸	10 ¹⁸	10 ¹⁸	cm ⁻³
Valance band effective density of states	10 ¹⁸	10 ¹⁸	10 ¹⁸	cm ⁻³
Doping concentration	10 ¹⁸	-	10 ¹⁸	cm ⁻³
Auger recombination factor for electron and hole	1.7×10 ⁻²⁸	10 ⁻²⁹	1.7×10 ⁻²⁸	cm ⁶ s ⁻¹
SRH recombination lifetime	5×10 ⁻⁷	5×10 ⁻⁷	5×10 ⁻⁷	s
Spontaneous lifetime	-	2×10 ⁻⁹	-	s
Ion density	-	10 ¹⁵ -10 ¹⁷	-	cm ⁻³
Cation mobility	-	10 ⁻⁹	-	cm ² V ⁻¹ s ⁻¹
Anion mobility	-	10 ⁻⁷	-	cm ² V ⁻¹ s ⁻¹

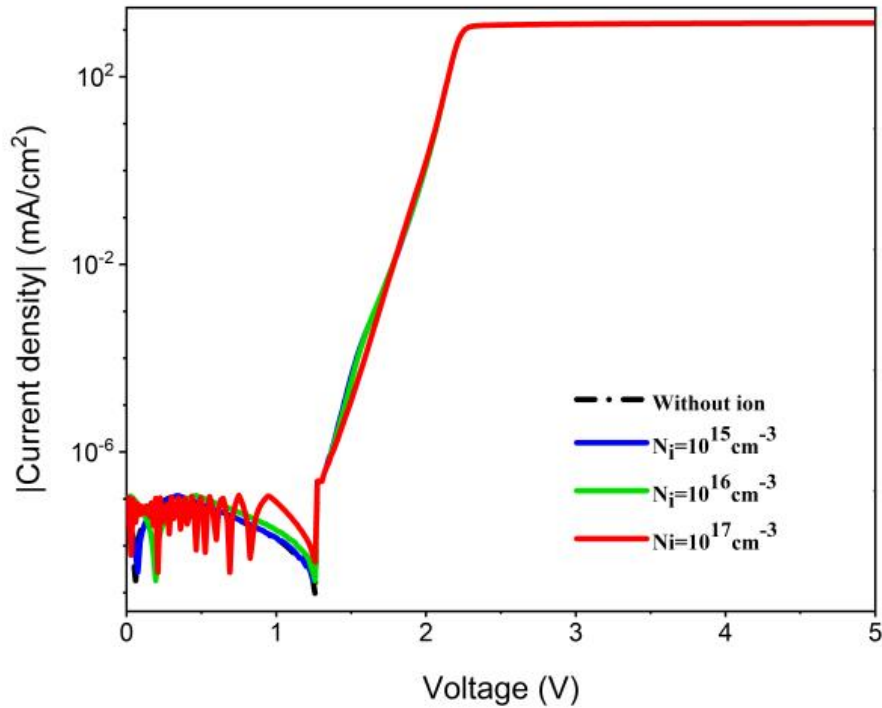


Fig. 3. J-V curves of PeLED in the absence and presence of different ionic densities

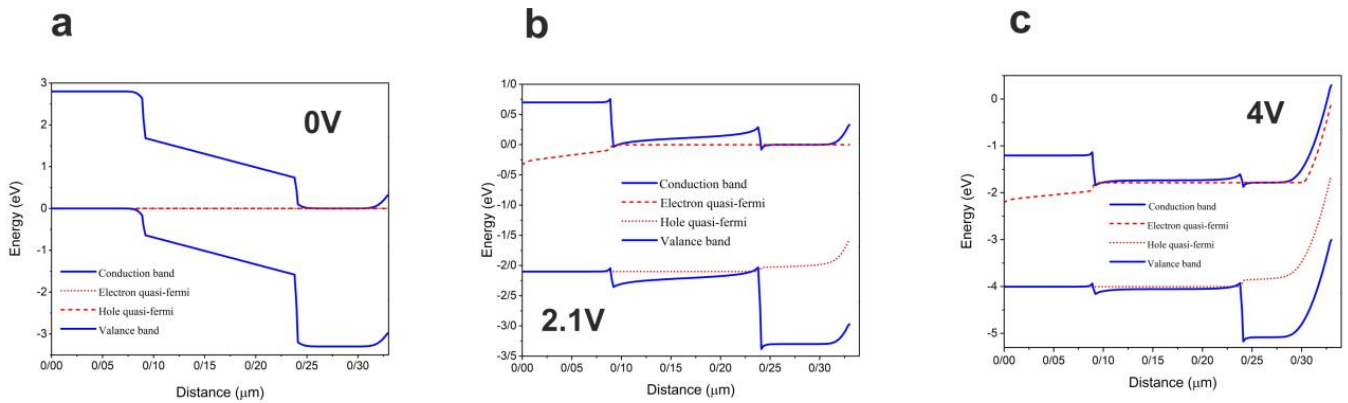


Fig. 4 Band alignment of PeLED in the absence of mobile ions at different applied voltages: a) 0V, b) 2.1V, and c) 4V

3- The Results and Discussion

In order to study the mechanism of the operation of the device and the influence of ion migration on PeLED, equations governing the ionic motion as a set of PDE were introduced to the model. Fig.3 compares the J-V curves of PeLED in the absence and presence of mobile ions with different densities, varying from 10^{15} to 10^{17} cm^{-3} . An Increase in the bias voltage from zero to 5 V results in rapid current growth at the threshold (i.e., 2.1V). In the absence ($N_i=0$) and low densities of migrating ions ($N_i = 10^{15}$ cm^{-3}), the J-V curves are almost

identical. As ion density increases, the current improves at the threshold. The reason behind this incident lies in the energy band diagram of the device and ion migration mechanism.

Fig.4 shows the band alignment of PeLED in the absence of ionic charges at equilibrium (Fig. 4(a)), threshold (Fig. 4(b)), and saturation (Fig. 4(c)) in the distance (position) from ITO to Ag contact across the PeLED layers. Electron and hole quasi-fermi levels splitting and band bending at ETL and HTL interfaces by increasing voltage can be observed, as expected.

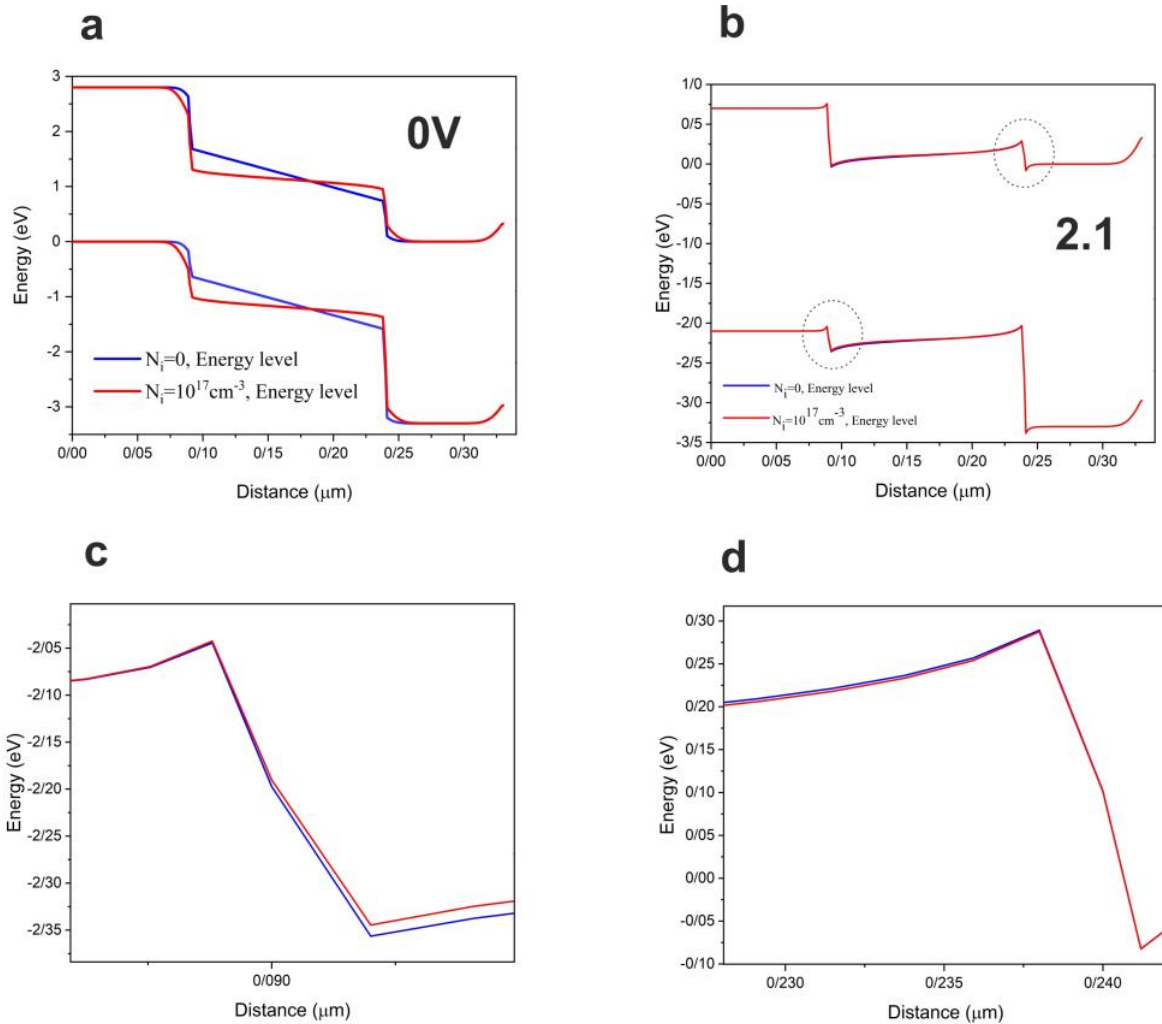


Fig. 5. Band alignment of PeLED in the absence and presence of mobile ion density of 10^{17} cm^{-3} at the applied voltage of a) 0V and b) 2.1V. And the zoomed in specified region at c) HTL/perovskite interface d) at ETL/perovskite interface

Fig. 5 illustrates the band alignment in the absence vs. the presence of mobile ion density of 10^{17} cm^{-3} . As mentioned earlier, cations and anions are initially assumed to be at HTL and ETL interfaces at 0V, respectively. As the applied voltage increases, ions start migrating through different channels towards perovskite bulk and opposite contacts (i.e., anions to the anode and cations to the cathode), creating a new equilibrium (Fig. 6(a) and b). The presence of anions at HTL and cations at ETL interfaces reduce the hole and electron injection barrier, respectively (Fig. 5(c) and (d)). Charge carrier concentration in the distance from ITO to Ag contact across

the PeLED layers in the presence and absence of ions at the applied voltage of 2.1V, as shown in Fig. 7. The effect of anions accumulation at HTL interface on hole injection is more distinct due to this species smaller mobility. This accumulation also gives rise to the confinement of carriers inside the perovskite. Accumulation of ions at ETL and HTL interfaces with perovskite facilitates charge injection, enhancing the radiative recombination [39]. Hence the emitted power per unit volume and unit energy (Fig. 8), and internal quantum efficiency (IQE) of the PeLED increase about 2% in the presence of mobile ions.

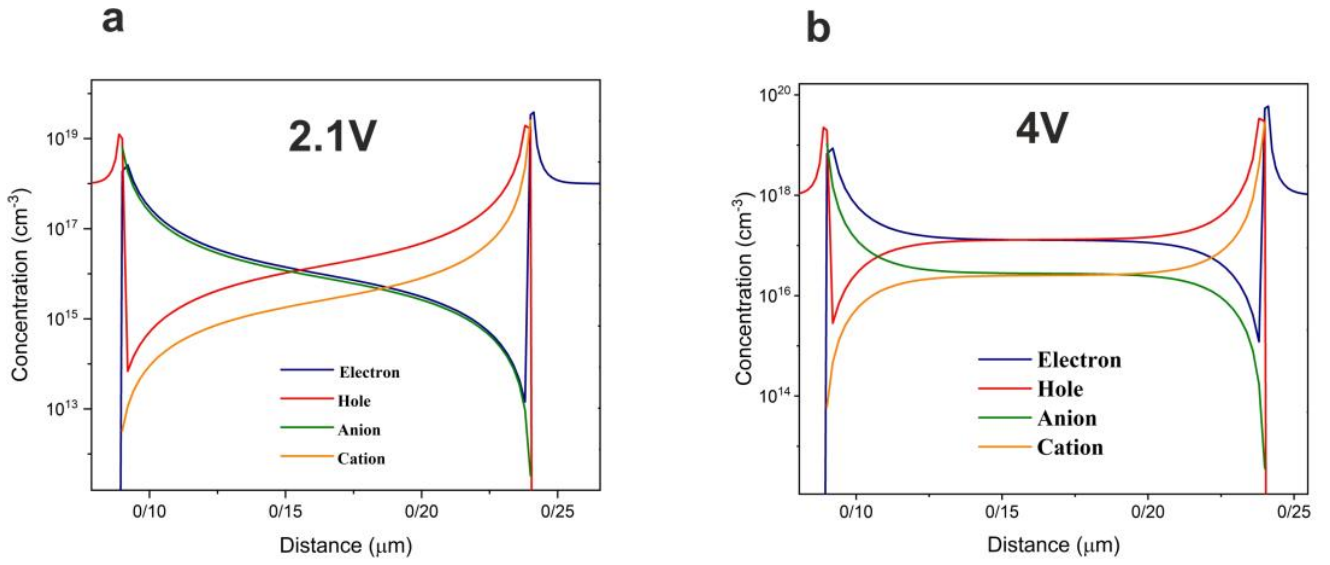


Fig. 6. Concentration profile of electrons, holes, anions, and cations at two different applied voltages: a) 2.1V and b) 4V

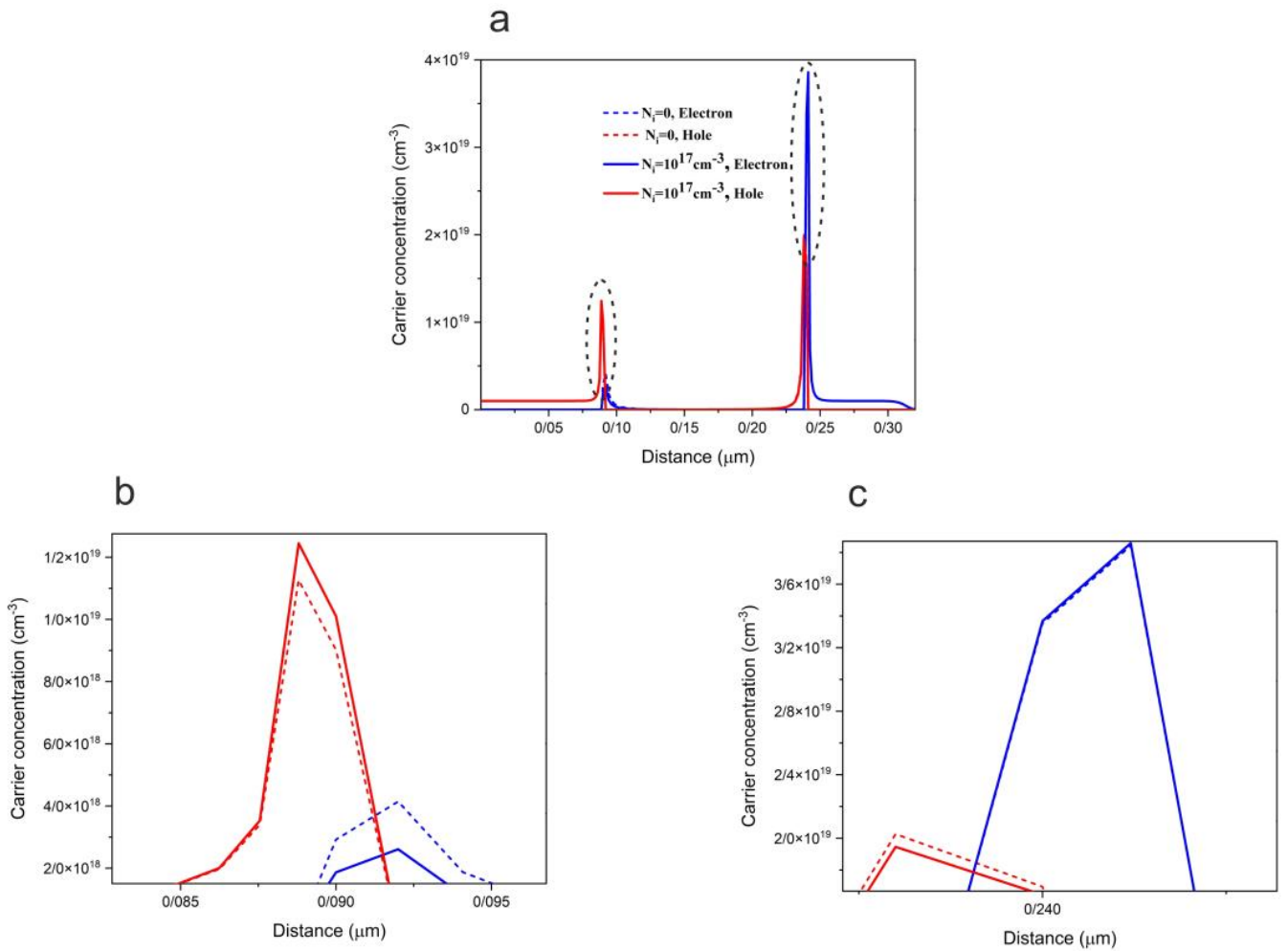


Fig. 7. a) Carrier density of PeLED in the absence (dashed lines) and presence of mobile ion density of 10^{17} cm^{-3} (solid lines) at applied voltage of 2.1V. The zoomed in specified region at b) HTL/perovskite interface c) at ETL/perovskite interface

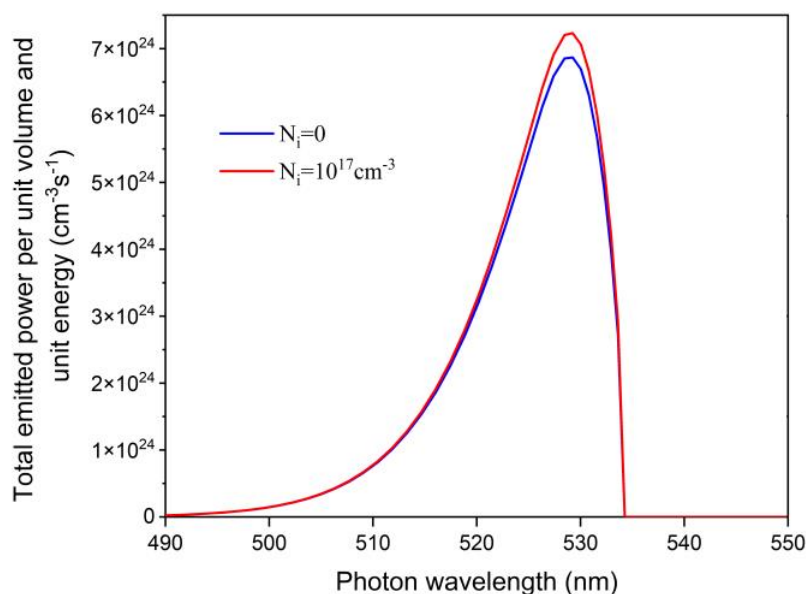


Fig. 8. Total emitted power per unit volume and unit energy of the PeLED in the absence and presence of the mobile ion density of 10^{17} cm^{-3}

4- Conclusion

In this work, the operation of a PeLED in the presence of ion migration was simulated to investigate the role of cations and anions migration on charge injection from ETL and HTL layers. By interpreting the energy level diagram, carrier and ion concentrations, and the field profiles, the effect of the ion migration on charge injection was observed. In summary, the accumulation of the anions and cations at the HTL and ETL interfaces with the perovskite facilitates hole and electron injection, respectively, which results in more carriers favoring radiative recombination and hence, enhanced IQE. Our results give rise to a better understanding of the physics behind the ion migration and designing more efficient PeLEDs. Since ion migration is a time-dependent phenomenon, much more information is expected to achieve by studying its transient effect.

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