ABSTRACT: Perovskite light-emitting diodes (PeLEDs) have drawn considerable attention for their favorable optoelectronic properties. Perovskite light-emitting electrochemical cells (PeLECs)—devices that utilize mobile ions—have recently been reported but have yet to reach the performance of the best PeLEDs. We leveraged a poly(ethylene oxide) electrolyte and a lithium salt in CsPbBr₃ thin films to produce PeLECs of improved brightness and efficiency. In particular, we found that a single-layer PeLEC from CsPbBr₃:PEO:LiPF₆ with 0.5 wt % LiPF₆ produced bright (∼15000 cd/m²) electroluminescence of improved efficiency (3.0 Lm/W). To understand this improved performance among PeLECs, we characterized these perovskite thin films with photoluminescence (PL) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD). These studies revealed that this optimal LiPF₆ concentration improves electrical double-layer formation, reduces the occurrence of voids, charge traps, and pinholes, and increases grain size and packing density.

Perovskite light-emitting diodes (PeLEDs) based on inorganic—organometallic halide perovskites, such as CH₃NH₃PbX₃ and CsPbX₃ (X = Cl, Br, or I), have attracted much attention due to their low-temperature solution processability, high color purity with narrow spectral width (full width at half maximum (FWHM) of 20 nm), band gap tunability, and large charge carrier mobility.¹–⁴ To date, devices based on these perovskites have achieved high luminance in excess of 10000 cd/m² with high efficiencies (EQE ≈ 10%), comparable to organic LEDs and quantum dot (QD) LEDs.¹–¹⁰

Interestingly, effects such as hysteresis and high capacitance in perovskite semiconductor devices suggest that ion motion can largely influence device operation. In this vein, researchers have recently been investigating perovskite materials in light-emitting electrochemical cell (LEC) architectures instead of traditional LEDs.¹¹–¹⁵ These LEC devices (PeLECs) leverage ion redistribution to achieve balanced and high carrier injection, resulting in high electroluminescence efficiency. Due to this mechanism, LEC devices can be prepared from a simple architecture consisting of a single semiconducting composite layer sandwiched between two electrodes. In addition, they can operate at low voltages below the band gap, yielding highly efficient devices. Recently, perovskite LECs (PeLECs) have been reported and show promise as electroluminescent devices.¹¹–¹⁵ However, these PeLECs are generally limited to luminance maxima of 1000 cd/m² or lower, below what has been typically observed in PeLEDs. This disparity suggests that further understanding and refinement of...
PeLEC materials and devices could produce significant improvements of brightness, efficiency, and other performance metrics. To this end, we fabricated a bright (\(\sim 15000 \text{ cd/m}^2\)) single-layer LEC of improved efficiency (3.0 Lm/W) based on a cesium lead halide perovskite, CsPbBr\(_3\). To achieve high performance, a polyelectrolyte and additive mobile ions were carefully selected to achieve optimal ionic redistribution and doping effects. To understand the nature of this performance and its correlation with materials properties, we characterize these perovskite thin films and devices with photoluminescence (PL) spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction (XRD).

We first consider the distinct stages of LEC device operation, which are illustrated in Figure 1a–c. Initially, ions are uniformly distributed in the film (Figure 1a). In response to an applied bias, cations drift toward and accumulate near the cathode, and anions likewise move toward and pack near the anode (Figure 1b). This leads to electric double layer (EDL) formation at each electrode that induces higher electric fields, decreased width of the potential barriers (doping), and enhanced injection of electrons and holes that is insensitive to the work function of the electrodes (Figure 1c).\(^{16–19}\) These injected carriers are transported through the bulk and radiatively recombine in the center of the device. The key features needed for successful LEC operation are therefore (1) a sufficient concentration of mobile anions and cations; (2) efficient transport of ions through the bulk for balanced EDL formation at the anode and cathode, leading to efficient charge injection; (3) facile transport of electrons and holes through the semiconductor (which, for our system, requires a percolating network of the perovskite); and (4) efficient light emission upon recombination of the electrons and holes in the bulk, typically supported by a high quantum yield of the film. In our specific case, high luminescence efficiency is supported by the spectral properties of the CsPbBr\(_3\) perovskite. To satisfy the other requirements, we introduce LiPF\(_6\) salt, a salt that we have previously used to attain high performance in LECs utilizing ionic transition metal complexes.\(^{20–22}\) (We have previously found that the lithium cation\(^{20}\) and hexafluorophosphate anion\(^{23}\) optimize device parameters.) We prepare films with an optimal concentration of the polymer electrolyte poly(ethylene oxide) (PEO) and systematically study the effect of LiPF\(_6\) salt addition.

The LECs were constructed with a single layer of spin-cast perovskite film using an ITO anode, a CsPbBr\(_3\):PEO:LiPF\(_6\) perovskite composite (1:0.8 weight ratio of CsPbBr\(_3\):PEO, various LiPF\(_6\) weight fractions), and an In–Ga eutectic cathode, as illustrated in the inset of Figure 1d (see Supporting Information Figure S1 and the text for details of fabrication and testing). Also in Figure 1d, the current density versus voltage (\(J\) vs \(V\)) and luminance versus voltage (\(L\) vs \(V\)) graph of our devices with different ratios of LiPF\(_6\) is shown. Figure 1e presents the maximum luminance and power efficiency from the data of Figure 1d. All of the devices showed green electroluminescence centered near 528 nm with a fwhm of 20 nm (see Supporting Information Figure S2). The reference device (CsPbBr\(_3\):PEO with no LiPF\(_6\)) showed a turn-on voltage (\(V_{\text{on}}\)) of 2.5 V and a substantial maximum luminance of 8175 cd/m\(^2\) at 5.5 V, with a maximum power efficiency of 1.6 Lm/W. This substantial luminance for a PeLEC accounts for the optimized PEO electrolyte concentration within the film. As LiPF\(_6\) was added into the CsPbBr\(_3\):PEO film, the luminance and efficiency maxima increased gradually, peaked at an optimal concentration, and then decreased. The best performance was achieved with a 0.5% LiPF\(_6\) weight percentage, which...
that competing processes a diminished by higher concentrations (Figure 1d), suggesting 1e) was enhanced density.28 In the absence of lithium salts, un
S4), consistent with faster ionic redistribution. We also measured the stability of devices under constant voltage operation and found that 0.5% LiPF6 can improve the stability of onset of emission (Supporting Information Figure S4), a favorable result in view of previous observations.

Further investigation of the devices reveals other key features. The turn-on voltage is generally lowered by LiPF6 addition, denoting its ability to assist in bipolar injection. Luminance is enhanced by adding 0.2 or 0.5% LiPF6 but diminished by higher concentrations (Figure 1d), suggesting that competing processes affect device performance. We also observe that the optimal 0.5% LiPF6 concentration considerably reduces the hysteresis in current density curves from voltage cycling (Supporting Information Figure S3) and lowers the time for onset of emission (Supporting Information Figure S4), consistent with faster ionic redistribution. We also measured the stability of devices under constant voltage operation and found that 0.5% LiPF6 can improve the stability 3-fold in comparison with control devices (Supporting Information Figure S4), a favorable result in view of previous reports.24 We performed additional study to gain further mechanistic and phenomenological understanding of these observations.

For further investigations of the optical, electronic, and morphological states of our perovskite films, we prepared CsPbBr3:PEO:LiPF6 thin films through an optimized one-stage spin-coating process and vacuum treatment before annealing (Supporting Information Figure S3 and text). We subsequently measured the PL intensity versus time of these films (Figure 2a) in air. For CsPbBr3 and CsPbBr3:PEO films, the PL intensity dramatically increased with time. These PL dynamics have been observed in perovskite thin films and are associated with a carrier-assisted, oxygen-dependent trap deactivation reaction.25−27 As LiPF6 is added to CsPbBr3:PEO films, the PL dynamics trends toward constant intensity. This PL trend with lithium addition can be understood from a reduced trap density.28 In the absence of lithium salts, unfilled trap states are present, potentially due to grain boundaries, vacancies, and other imperfections that create nonradiative decay states in the middle of the optical gap. In air, these trap states must be deactivated before steady PL can be achieved. Lithium salt addition lowers the concentration of these traps, leading to more stable PL. The oxygen dependence of this effect is confirmed by the lowering of the PL in nitrogen in Supporting Information Figure S6a. The morphological studies described below can further clarify the nature of trap suppression.

Time-resolved PL is also beneficial for observing the effects of lithium salts on trap suppression (Supporting Information Figure S6b). A CsPbBr3:PEO film follows bieponential fluorescence decay with a significant fast (8.6 ns decay) and a smaller-amplitude slower (36 ns) decay component. This fast component is likely associated with trapping states. Once LiPF6 is added, the lifetimes follow a monoexponential decay with time scales of 20−30 ns. The suppression of the faster component is consistent with a reduced trap concentration.

To understand the influence of LiPF6 addition on steady-state quantum yield, we measured the absolute photoluminescence quantum efficiency (PLQE) in air for CsPbBr3:PEO:LiPF6 films with an integrating sphere according to the methods described by de Mello et al. and Porre et al. Figure 2b reveals that the PLQE increases from 29% for a CsPbBr3:PEO film to a maximum of 49% for a 0.5% LiPF6 film of CsPbBr3:PEO:LiPF6 and then is lowered as the LiPF6 concentration is further increased. This PLQE concentration trend of CsPbBr3:PEO:LiPF6 films qualitatively follows the concentration dependences of luminance and current efficiency for PeLEC devices (Figure 1e). Also, in Supporting Information Figure S6a, the PLQE is improved by over 6-fold between 0 and 0.5% LiPF6 films when measured under nitrogen, where traps are not suppressed by oxygen. Furthermore, the relative change (∆PLQE/PLQEair) between air (trap suppressing) and nitrogen (trap permitting) is lowered with LiPF6 addition, correlating with lower trap concentration. This reinforces our assertion that LiPF6 suppresses nonradiative trapping states to improve emission yield in thin films and devices.

PL spectra were also measured to ascertain the impact of lithium doping on optical emission from CsPbBr3:PEO:LiPF6 thin films (Figure 2c). The PL spectra show a gradual blue shift from λmax = 522 nm for the pure CsPbBr3 thin film to λmax = 516 nm for the CsPbBr3:PEO:LiPF6 (5%) thin film. Similar blue shifts and other spectral changes have been reported for Li, K, Sb, and Bi addition in perovskites and have been attributed to the Burstein−Moss effect and trap passivation.14−33

To further understand the morphological influence of the beneficial electrical and optical properties afforded by electrolyte and lithium addition, we studied thin perovskite films by

Figure 2. PL properties of thin films of CsPbBr3 and CsPbBr3:PEO:LiPF6 in air. (a) PL intensity as a function of time (λex= 405 nm). (b) photoluminescence quantum efficiency (PLQE) versus LiPF6 concentration for CsPbBr3:PEO:LiPF6 films in air. (c) PL spectra of CsPbBr3 and CsPbBr3:PEO:LiPF6.
Figure 3. Morphological study of CsPbBr₃:PEO:LiPF₆ thin films by SEM and AFM. (a) SEM for thin films of (I) CsPbBr₃, (II) CsPbBr₃:PEO, (III) CsPbBr₃:PEO:LiPF₆ (0.2%), (IV) CsPbBr₃:PEO:LiPF₆ (0.5%), (V) CsPbBr₃:PEO:LiPF₆ (1%), and (VI) CsPbBr₃:PEO:LiPF₆ (2%). (b) Surface roughness of CsPbBr₃:PEO:LiPF₆ thin films versus LiPF₆ concentration as measured by AFM. The horizontal dotted line denotes the surface roughness of the pristine CsPbBr₃ film.

Figure 4. High-resolution XPS and XRD of CsPbBr₃:PEO:LiPF₆ films, as well as a conceptual illustration of Li⁺-induced performance enhancement. High-resolution XPS spectral regions for (a) Pb (4f½, 4f¾) and (b) Br (3d½, 3d¾) peaks from CsPbBr₃ and CsPbBr₃:PEO:LiPF₆ thin films of various LiPF₆ weight ratios. (c) XRD pattern of CsPbBr₃ and CsPbBr₃:PEO:LiPF₆ thin films of various LiPF₆ weight ratios. (d) Conceptual illustration of the benefits afforded by LiPF₆ doping in PeLECs.

SEM and AFM. The SEM image of the pristine CsPbBr₃ film (Figure 3a,I) reveals randomly oriented grains and substantial pinholes in the film. Addition of PEO (Figure 3a,II) reduces the average grain and pinhole sizes, but significant pinholes still remain. Subsequent addition of low concentrations (≤2%) of LiPF₆ in CsPbBr₃:PEO increases the average grain size (Supporting Information Table S2) and decreases the number and size of pinholes (Figure 3a,III–VI; Supporting Information Figure S7). The largest and most monodispersed grain sizes are observed for 0.5 and 1.0% LiPF₆ concentrations. Also, the 0.5% LiPF₆ dopant film (Figure 3a,IV) provides the most continuous network of perovskite crystals with the lowest amount of pinholes. This correlates well with the high luminescence and efficiency of the 0.5% LiPF₆-doped LEC device (Figure 1e): reducing the number of pinholes limits detrimental leakage current, and the interpenetrating network of perovskite crystals supports facile transport of electrons and holes for efficient electroluminescence. On the other hand, excess LiPF₆ (5%) was detrimental to the quality of the thin film, leading to discontinuous films (Supporting Information Table S2).
Figure S8). This is likely due to the formation of lithium dendrites and subsequent phase separation.34

In Figure 3b, we relate the average surface roughness of the CsPbBr3:PEO:LiPF6 films with various percentages of LiPF6 as measured by AFM (Supporting Information Figure S9). We observe a reduction in the root-mean-square roughness from 15.7 nm for the pristine CsPbBr3:PEO film to 11.9 nm for the 0.5% LiPF6-doped film and an increase in surface roughness for higher concentrations. Again, this correlates with the optimal LiPF6 device concentration as low surface roughness improves the spatial uniformity of the electroluminescence and limits pinhole formation. Hence, the overall interpretation from SEM and AFM analysis indicates that 0.5% LiPF6 corresponds to the optimal concentration for smooth films with large, percolating perovskite grains and minimal pinholes, all beneficial for superior device performance.

XPS analysis of the high-resolution spectra involving Pb 4f, Br 3d, C 1s, and F 1s (Figure 4a,b and Supporting Information Figure S10) was conducted to further understand the effect of the LiPF6 dopant in CsPbBr3:PEO films. As shown in Figure 4a, the Pb 4f spectrum for the pristine CsPbBr3 film has two peaks associated with 4f5/2 and 4f7/2 orbitals located at 138.40 and 143.20 eV, respectively, which correspond to Pb2+ cations. The two Br 3d signals, corresponding to 3d3/2 and 3d5/2 peaks, are also clearly seen at 68.4 and 69.2 eV (Figure 4b). Addition of PEO to the CsPbBr3 film shifts all of these peaks to higher binding energies, which is attributed to the interaction between PEO and metallic/ion Pb reported previously.35 Furthermore, we also observe that adding LiPF6 dopant to the CsPbBr3:PEO film further shifts these peaks. These spectral shifts are a clear indication of a lattice contraction of perovskite after Li+ incorporation, shorter Pb–Br bonds, and higher binding energy for Pb 4f and Br 3d.28,36 The presence of PEO and LiPF6 in films has been further confirmed from the C 1s and F 1s XPS spectra (Supporting Information Figure S10a,b). The adventitious C 1s signal is obvious at 285.2 eV for the pristine CsPbBr3 thin film. However, after PEO addition, a new C 1s peak appears at 287 eV, which corresponds to the C−O−C groups of the PEO.37 An F 1s spectral peak at 686.6 eV appears after adding LiPF6 to CsPbBr3:PEO, confirming the presence of the fluoride ion in the film. Also, we note that the photoemission of Li 1s could not be detected due to the very low sensitivity factor of Li. The detailed chemical bonding of the composite perovskite films was analyzed by deconvoluting the XPS peaks (Supporting Information Figure S10).

Figure 4c illustrates the XRD spectra of CsPbBr3, CsPbBr3:PEO, and CsPbBr3:PEO:LiPF6. The thin film XRD spectra indicate the primary diffraction peaks at 15.21, 21.46, and 30.70° that correspond to diffraction planes of (110), (112), and (220), respectively, in agreement with previous reports for an orthorhombic (Pnma) crystal structure.38,39 The peaks at 12.7 and 22.41° indicate the presence of a trigonal phase of Cs4PbBr6 with diffraction planes of (102) and (213), respectively, as seen in the literature, indicating a mixed phase of CsPbBr3 and Cs4PbBr6.40−42 In addition, we analyzed the peak widths, finding successive contraction of the perovskite crystallite size from 16.5–17.0 nm to 13.0–13.2 nm with increasing amounts of LiPF6 (see Supporting Information Table S2). This is consistent with experimental and computational observations that lithium ions occupy interstitial sites and stabilize the lattice.43

Overall, these observations suggest several benefits of lithium salt addition that led to high luminance (14730 cd/m²) among single-layer PeLECs that is comparable to that of high-performance PeLEDs, which are typically multilayer devices (Supporting Information Table S3). These benefits are summarized in Figure 4d. First, an overall consideration of the system and a detailed view of the device performance suggest that an optimal concentration of LiPF6 facilitates double-layer formation, thus improving charge carrier injection. Second, SEM and AFM studies demonstrated that an optimal lithium concentration reduces the spacing between grain boundaries, leading to smooth, pinhole-free films. This limits leakage current and enables high electron and hole conductivities for enhanced carrier transport. PL study correlated with XPS and XRD studies shows that lithium reduces the crystallite size through filling traps and voids, reducing sources of nonradiative losses for highly efficient light emission in thin films and devices. A detailed balance of all of these features thus leads to high-performance LECs of simple, single-layer architectures for next-generation optoelectronic applications.

**ASSOCIATED CONTENT**

 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenergylett.9b01925.

Experimental methods, electroluminescence spectra, current and luminance versus voltage and time, efficiency metrics, capacitance versus frequency, time-resolved PL measurements, photoluminescence quantum efficiency in air and nitrogen, SEM and AFM images, XPS spectra, XRD data, illustrations of film formation and ion accumulation, and discussion of ionic redistribution (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*E-mail: slinker@utdallas.edu.
*E-mail: zakhidov@utdallas.edu.

**ORCID**

Qing Gu: 0000-0003-3855-3690
Jason D. Slinker: 0000-0001-7338-586X
Anvar A. Zakhidov: 0000-0003-3983-2229

**Notes**

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