Supporting Information

for Adv. Optical Mater., DOI: 10.1002/adom.202000226

Enhanced Operational Stability of Perovskite Light-Emitting Electrochemical Cells Leveraging Ionic Additives

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Enhanced Operational Stability and Efficiency of Perovskite Light Emitting Electrochemical Cells Using Ionic Additives

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Table S1 Comparative performances of the best-in-class perovskite-based LEDs and LECs.

| Device structure | Device Stability with operation condition | Ref |
|------------------|-----------------------------------------|-----|
| ITO / Pero-PEO-composite /In (Ga,Au) | 1hr (L30) at constant 2.7 V | [1] |
| ITO/ZnO/PVP/perovskite/CBP/MoOx/Al | 0.01 h (L50) at constant 5V driving | [2] |
| ITO/PEDOT: PSS/perovskite/SPW111/LiF/Ag | 2.4 @ 0.1 cd/m² 3.9 h (L70) | [3] |
| ITO/PolyTPD/FAPbBr₃/TpBi/LiF/Al | 0.1 h (EQE50) at constant 10 mA/cm² | [4] |
| Au/p-MgNiO/CsPbBr₃/PMMMA/n-MgZnO/n'-GaN | 0.1 h (L80) | [5] |
| ITO/PEDOT: PSS/ MAPbBr₃/B₃PYMPM:Tp Bi/B₃PYMPM: Cs₂CO₃/Al | 0.1 h (L50) | [6] |
| ITO/PEDOT: PSS/CsPbBr₃:MABr/B₃PYMPM M/LiF/Al | 100 h @100 cd/m² (L50) with constant 5mA | [7] |
| ITO/NiOₓ+PVK+TFB/ CsPbBr₃+LiBr/TpBi/LiF/Al | 108 h @100 cd/m² (L50) | [8] |
| **Our Work** | **6700 h @100 cd/m² (L50) with constant 1.5mA** | |

*References are listed at the end of this file.
Table S2 Summarized ionic parameters relevant to PeLECs from literature.

| Ion type and ionic process | Activation Energy (eV) | Diffusion coefficient (cm² s⁻¹) | Mobile ions concentration (cm⁻³) | Characteristic Times | Ref* |
|----------------------------|------------------------|---------------------------------|---------------------------------|----------------------|------|
| MA⁺, FA⁺                   | Theory: 0.46-1.12       | (3.4±3.3)×10⁻¹²                 | (1.3±0.8)×10¹⁶                  | τ=12±0.4 min (EDL by drift of MA⁺) | [9]  |
|                            | Experimental: Depends on device fabrication |                           |                                 |                      |      |
| Cs⁺ (EDL by cations)       | 0.8-2.31                | (3.1±2.8)×10⁻⁹                  | (1.1±0.9)×10¹⁵                  | τ=30±1.5 s (EDL by halide drift) | [10] |
| I⁻, Br⁻ (EDL by halides)   | 0.08-0.58               | 0.29±0.06                       |                                 |                      |      |
| Li⁺                        | 0.24                   | 10⁻⁷                            | Varies                          |                      | [11,12] |
| PF₆⁻                       | 0.366                  | 1.18 × 10⁻¹³⁻¹³                 | Varies                          |                      | [13] |
| P-doped layer formation    |                        |                                 |                                 | τ=1.6±0.1 h (growth of charge carriers via ions) | [14] |
| n-doped layer formation    |                        |                                 |                                 |                      |      |

*References are listed at the end of this file.
Figure S1 Luminance versus time for PeLEC devices with 0.5% and 0% LiPF$_6$ concentrations under 1.5 mA constant current driving. Exponential fits are made in the regions indicated by thicker data points and contrasted fit lines.
Figure S2 Power efficiency vs time of PeLEC devices with various LiPF$_6$ concentrations under constant current driving (0.050 A/cm$^2$).
Figure S3 Luminance versus time for a PeLEC devices with 0.5% LiPF$_6$ under 3.0 mA constant current driving. The device was turned off after approximately 30 h of driving and stored in a nitrogen glove box for 24 hours. The device was subsequently turned on and returned to a maximum level near where the luminance had decayed before pausing operation, indicating irreversible degradation.
Figure S4 Performance of PeLEC devices with various LiPF$_6$ concentrations under constant voltage driving (3.5V) (a) Current density (left axis) and luminance (right axis) versus LiPF$_6$ concentration (wt%) in PeLEC. (b) Maximum current efficiency and maximum external quantum efficiency obtained during constant voltage driving (3.5V) versus LiPF$_6$ concentration (wt%) in PeLEC.
Figure S5 Current density (J) versus voltage (V) of PeLEC devices with 0% and 0.5% of LiPF₆. The cyclic J-V curve clearly shows that in the optimized ratio of Li (0.5%), the hysteresis state decreases significantly.
Figure S6 Nyquist plots of imaginary versus real components of impedance for PeLEC devices with various LiPF₆ concentrations. Solid lines represent fitting according to the equivalent circuit model discussed in the main text.
Figure S7 Real and imaginary components of impedance vs frequency plots of PeLEC devices with various LiPF$_6$ concentration.
Figure S8 (a) Impedance versus voltage (V) of PeLEC devices with various LiPF$_6$ concentrations. (b) Capacitance versus voltage (V) of PeLEC devices with various LiPF$_6$ concentrations.
Table S3 Parameters extracted from the impedance spectra of devices with different concentration of LiPF$_6$ concentration.

| Sample (%LiPF$_6$) | $C_{GEO}$ (nF) | $R_E$ (MΩ) | $R_{ion}$ (KΩ) | $R_{EDLA}$ (MΩ) | $R_{EDLC}$ (MΩ) | $R_{INT}$ (MΩ) | $Q_{INT}$ (Cx10$^9$) | $α_{INT}$ |
|-------------------|----------------|-------------|-----------------|-----------------|-----------------|-----------------|---------------------|-----------|
| 0%                | 1.90           | 4.62        | 8.50            | 9.39            | 15.9            | 0.729           | 8.67                | 0.757     |
| 0.5               | 3.40           | 0.0309      | 4.08            | 106             | 91.3            | 0.0801          | 14.2                | 0.793     |
| 1                 | 4.46           | 0.120       | 5.05            | 67.7            | 56.9            | 0.150           | 24.6                | 0.707     |
| 2                 | 2.53           | 5.62        | 8.56            | 0.542           | 0.0489          | 0.160           | 37.3                | 0.731     |
| 5                 | 1.70           | 95.3        | 18.3            | 0.00244         | 0.000128        | 18.8            | 9.11                | 0.749     |
Discussion of inductance effect on impedance

Our system can be modeled most simply in terms of a parallel resistor and capacitor in series with an inductor, with the inductance originating from the leads leading to the device:

\[ Z = \frac{Z_R Z_C}{Z_R + Z_C} + Z_L \]  
\[ \text{Im}(Z) = \frac{\omega R^2 C}{1 + (\omega R C)^2} + \omega L \approx \frac{1}{\omega C} + \omega L \]  
\[ \text{Im}(Z) \approx \frac{1}{\omega C}. \]

For our data, the minimum value of \(1/\omega C\) is on the order of 100 \(\Omega\), and the maximum value of \(\omega L\) is on the order of 0.01 to 1 \(\Omega\) (at the high frequency limit of \(10^6\) s\(^{-1}\)). Therefore,

\[ \text{Im}(Z) \approx \frac{1}{\omega C}. \]  

Thus, the impedance of our LRC system is approximated as a simple RC parallel circuit. (This is supported by the lack of inductance loops in the Nyquist plots in Figure S6.) In this case:

\[ Z \approx \frac{Z_R Z_C}{Z_R + Z_C} \]  
\[ \frac{1}{Z} = \frac{1}{Z_R} + \frac{1}{Z_C} = \frac{1}{R} + i \omega C = G(\omega) + i \omega C(\omega) \]
References

[1] J. Q. Li, S. G. R. Bade, X. Shan, Z. B. Yu, *Adv. Mater.* **2015**, *27*, 5196-5202.

[2] L. Q. Zhang, X. L. Yang, Q. Jiang, P. Y. Wang, Z. G. Yin, X. W. Zhang, H. R. Tan, Y. Yang, M. Y. Wei, B. R. Sutherland, E. H. Sargent, J. B. You, *Nat. Commun.* **2017**, *8*, 15640.

[3] S. J. Lee, J. H. Park, B. R. Lee, E. D. Jung, J. C. Yu, D. Di Nuzzo, R. H. Friend, M. H. Song, *J. Phys. Chem. Lett.* **2017**, *8*, 1784-1792.

[4] L. F. Zhao, K. M. Lee, K. Roh, S. U. Z. Khan, B. P. Rand, *Adv. Mater.* **2019**, *31*, 805836.

[5] Z. F. Shi, Y. Li, Y. T. Zhang, Y. S. Chen, X. J. Li, D. Wu, T. T. Xu, C. X. Shan, G. T. Du, *Nano Lett.* **2017**, *17*, 313-321.

[6] F. Yan, J. Xing, G. C. Xing, L. Quan, S. T. Tan, J. X. Zhao, R. Su, L. L. Zhang, S. Chen, Y. W. Zhao, A. Huan, E. H. Sargent, Q. H. Xiong, H. V. Demir, *Nano Lett.* **2018**, *18*, 3157-3164.

[7] K. B. Lin, J. Xing, L. N. Quan, F. P. G. de Arquer, X. W. Gong, J. X. Lu, L. Q. Xie, W. J. Zhao, D. Zhang, C. Z. Yan, W. Q. Li, X. Y. Liu, Y. Lu, J. Kirman, E. H. Sargent, Q. H. Xiong, Z. H. Wei, *Nature* **2018**, *562*, 245-248.

[8] T. Wu, J. Li, Y. Zou, H. Xu, K. Wen, S. Wan, S. Bai, T. Song, J. A. McLeod, S. Duhm, F. Gao, B. Sun, *Angew. Chem.-Int. Ed.*, **2020**, *59*, 4099-4105.

[9] M. H. Futscher, J. M. Lee, L. McGovern, L. A. Muscarella, T. Y. Wang, M. I. Haider, A. Fakharuddin, L. Schmidt-Mende, B. Ehrler, *Mater. Horizons* **2019**, *6*, 1497-1503.

[10] B. M. D. Puscher, M. F. Ayguler, P. Docampo, R. D. Costa, *Adv. Energy Mater.* **2017**, *7*, 1602283.

[11] N. Vicente, G. Garcia-Belmonte, *Adv. Energy Mater.* **2017**, *7*, 51700710.

[12] Y. F. Sun, M. Kotiuga, D. Lim, B. Narayanan, M. Cherukara, Z. Zhang, Y. Q. Dong, R. H. Kou, C. J. Sun, Q. Y. Lu, I. Waluyoe, A. Hunt, H. Tanaka, A. N. Hattori, S. Gamage, Y. Abate, V. G. Pol, H. Zhou, S. Sankaranarayanan, B. Yildiz, K. M. Rabe, S. Ramanathan, *Proc. Natl. Acad. Sci. U. S. A.* **2018**, *115*, 9672-9677.

[13] S. Miyoshi, T. Akbay, T. Kurihara, T. Fukuda, A. T. Staykov, S. Ida, T. Ishihara, *J. Phys. Chem. C* **2016**, *120*, 22887-22894.

[14] C. Aranda, A. Guerrero, J. Bisquert, *ACS Energy Lett.* **2019**, *4*, 741-746.