Supporting Information

Thermal Degradation of the Bulk and Interfacial Traps at 85°C in Perovskite Photovoltaics

*Alan Jiwan Yun,[a] Seokjoo Ryu,[a] Jiheon Lim,[a] Jinhyun Kim,[b] and Byungwoo Park[a,]**

[a]Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul 08826, Korea

[b]Department of Chemical and Materials Engineering, The University of Suwon, Hwaseong 18323, Korea

Keywords: Perovskite Solar Cell, Thermal Degradation, Trap Density of States, Depth-Profile Defect Analysis, Evolution of Traps.

* E-mail: byungwoo@snu.ac.kr; Phone: +82-2-880-8319; Fax: +82-2-885-9671.

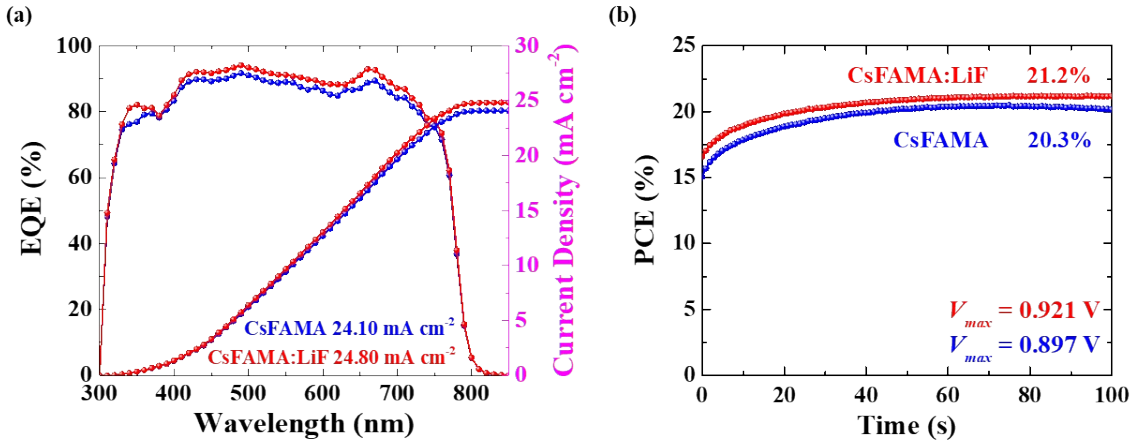


Figure S1. Properties of the solar cells without/with LiF. (a) Incident photon-to-electron conversion efficiency (IPCE) measurement with the integrated current density. (b) Steady-state currents measured under the maximum power voltages.

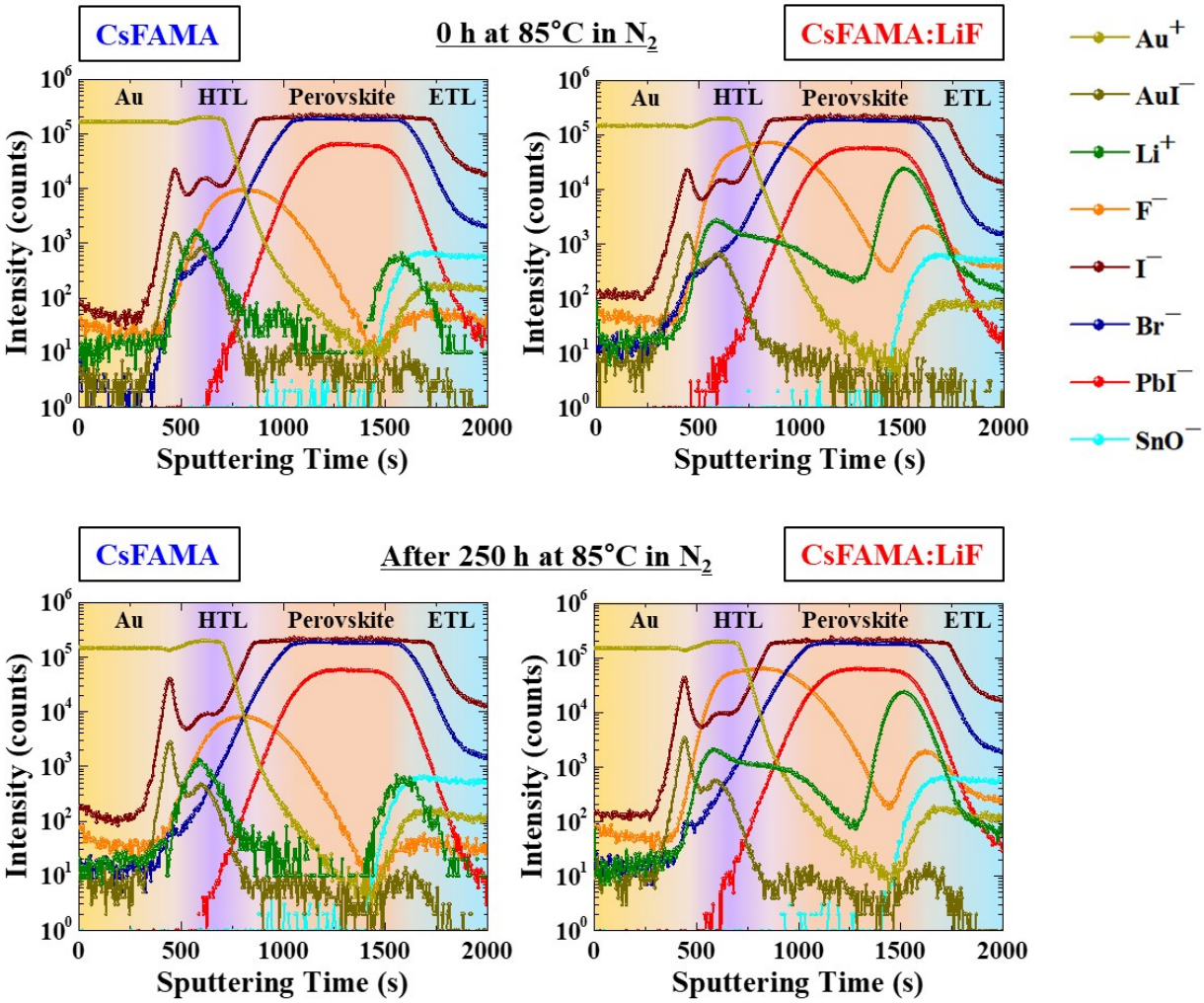


Figure S2. Time-of-flight secondary ion mass spectroscopy (TOF-SIMS) of the perovskite solar cells. Depth profiling of the elemental distributions in CsFAMA and CsFAMA:LiF before/after the 250 h storage at 85°C in N_2.

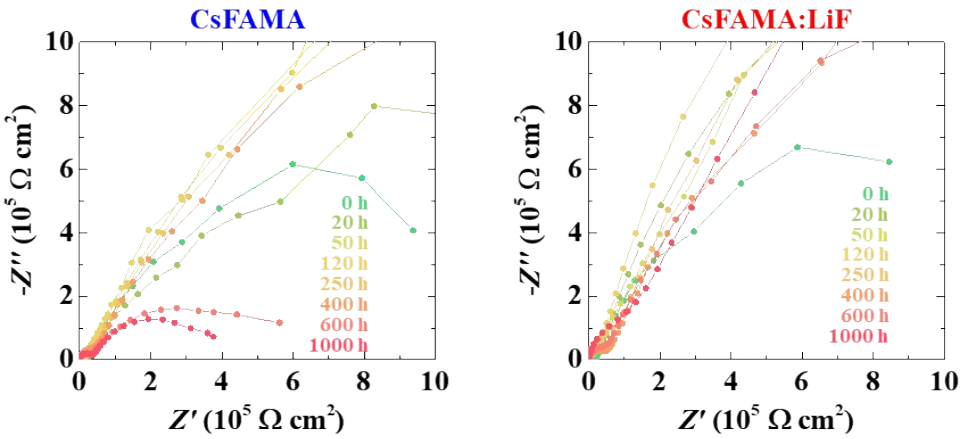
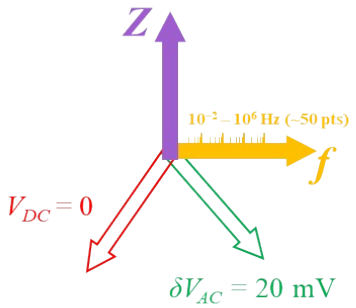


Figure S3. Nyquist plots of the PSCs without/with LiF as a function of time at 85°C.

Impedance Spectroscopy for tDOS = N_t^Z vs. E_ω



$$V_{DC} + \delta V_{AC} = I \cdot Z$$
$$= 0$$

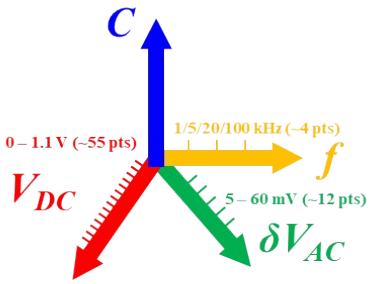
Capacitance $C^Z \equiv \left[\frac{1}{i\omega Z}\right]_{real}$

Trap Density $N_t^Z(\omega) = \frac{V_{bi}}{qW}\left(\frac{\partial C^Z}{\partial \omega}\right)\frac{\omega}{k_B T}$

Trap Level $E_\omega = k_B T \, ln\left(\frac{\omega_0}{\omega}\right) = E - E_{bandedge}$

Z	measured impedance of PSC
V_{bi}	built-in potential measured by C-V (≅ 1.1 V)
$\omega = 2\pi f$	angular frequency of the AC perturbation
ω_0	attempts of escape (~10^{10} s^{-1} at 300 K)
$N_t^Z(\omega)$	trap density [= $N_t^Z(E_\omega)$]
W	depletion width (≅ 500 nm)

Drive-Level Capacitance Profiling (DLCP) = N_t^C vs. $<x>$, ω



Capacitance

$$C(V_{AC}, V_{DC}, \omega) = \left[\frac{dQ}{d(\delta V_{AC})}\bigg|_{V_{DC}}\right]_{real} = C_0(V_{DC}, \omega) + C_1(V_{DC}, \omega)\,\delta V_{AC} + \cdots$$

Carrier Concentration

$$N^C(x, \omega) = N_0^C(x, \omega) + N_t^C(x, \omega) = -\frac{[C_0(V_{DC}, \omega)]^3}{q\varepsilon A^2 C_1}$$

Trap Density

$$N_t^C(x, \omega) \approx N^C(x, \omega) - N_0^C(x, MHz)$$

Apparent Profiling Distance $< x > = \frac{\varepsilon A}{C_0(V_{DC}, \omega)}$

V_{DC}	DC bias voltage
δV_{AC}	AC amplitude
$N_0^C(x, \omega)$	free-carrier concentration
$N_t^C(x, \omega)$	trap density
A	area of device (≅ 0.4 cm^2)
ε	dielectric constant (≅ 23)

Figure S4. Differences between the impedance analysis and drive-level capacitance profiling analysis.

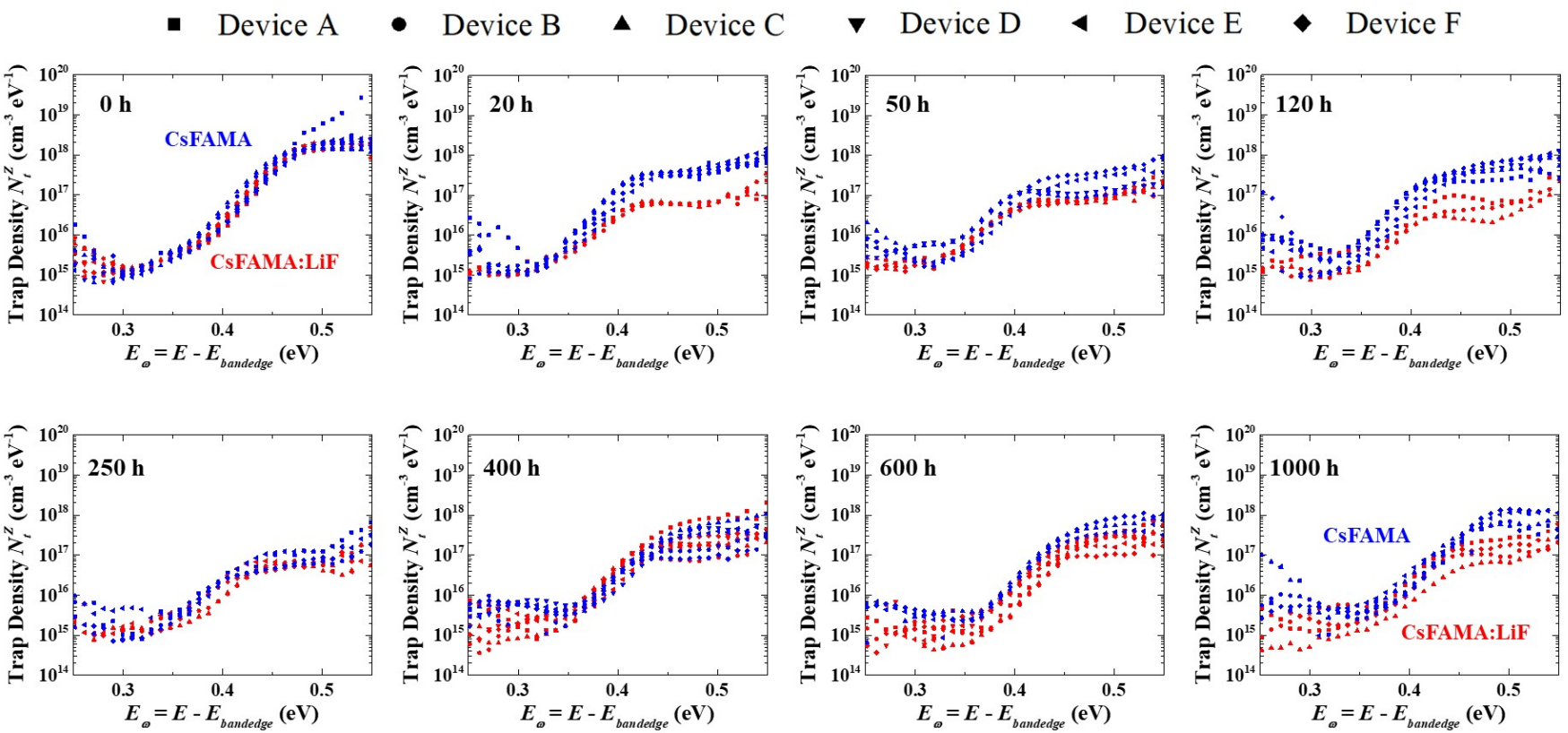


Figure S5. tDOS $N_t^Z(\omega)$ of the PSCs without/with LiF as a function of time at 85°C.

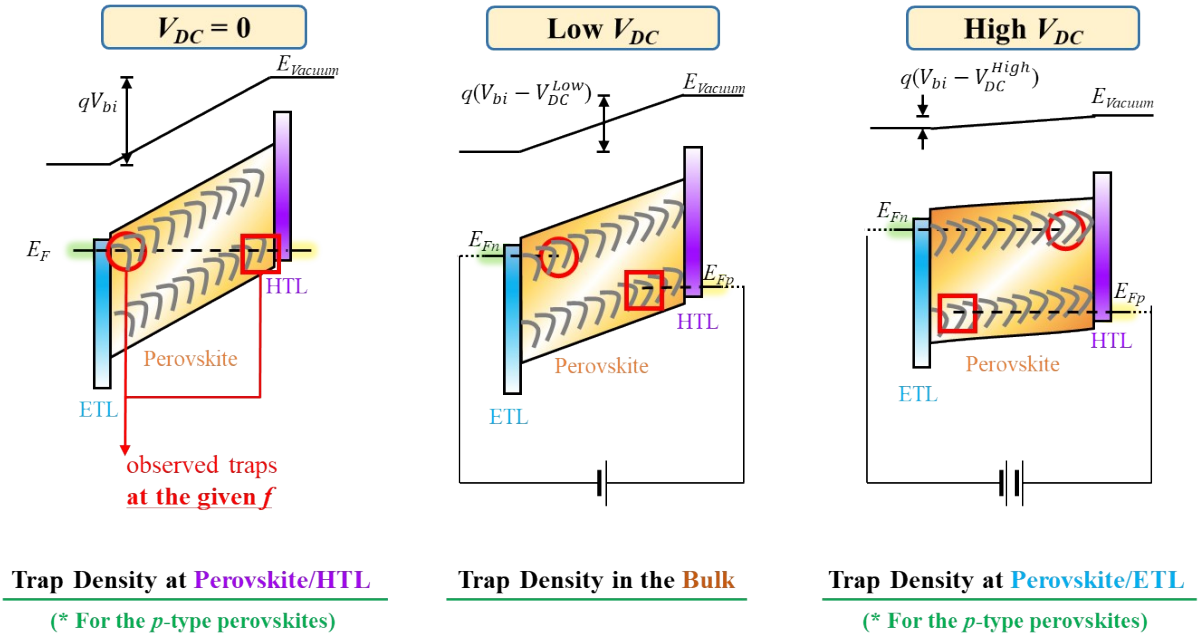


Figure S6. Schematic band diagrams of PSC during the capacitance measurement.

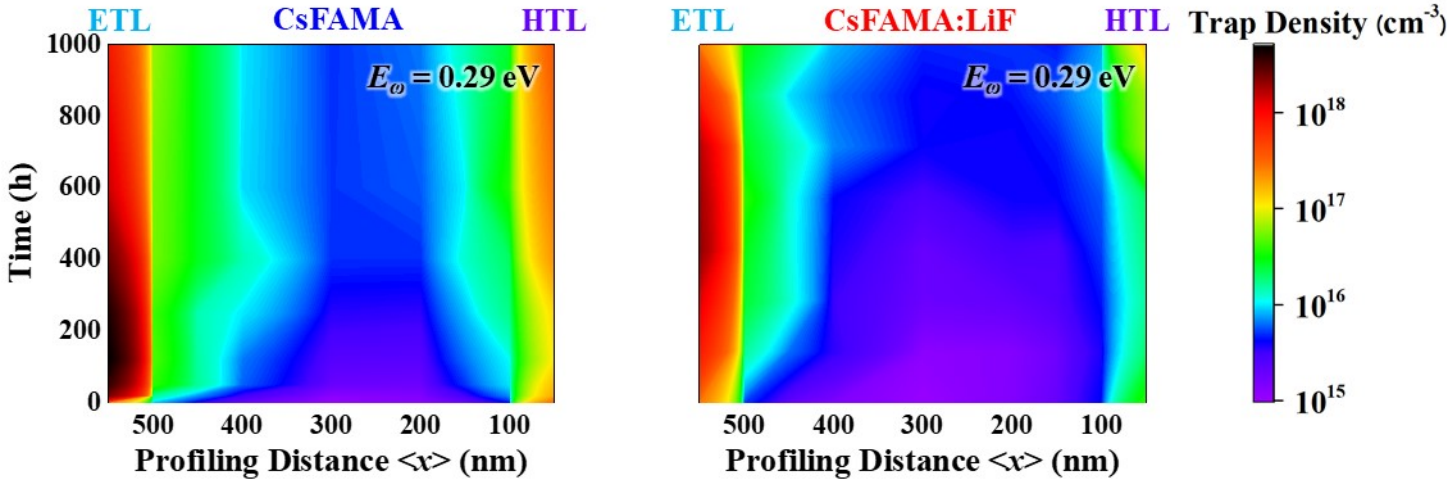


Figure S7. 2D maps of the trap densities $N_t^C(x,\omega)$ at 20 kHz (E_ω = 0.29 eV) measured by drive-level capacitance profiling (DLCP) analysis.

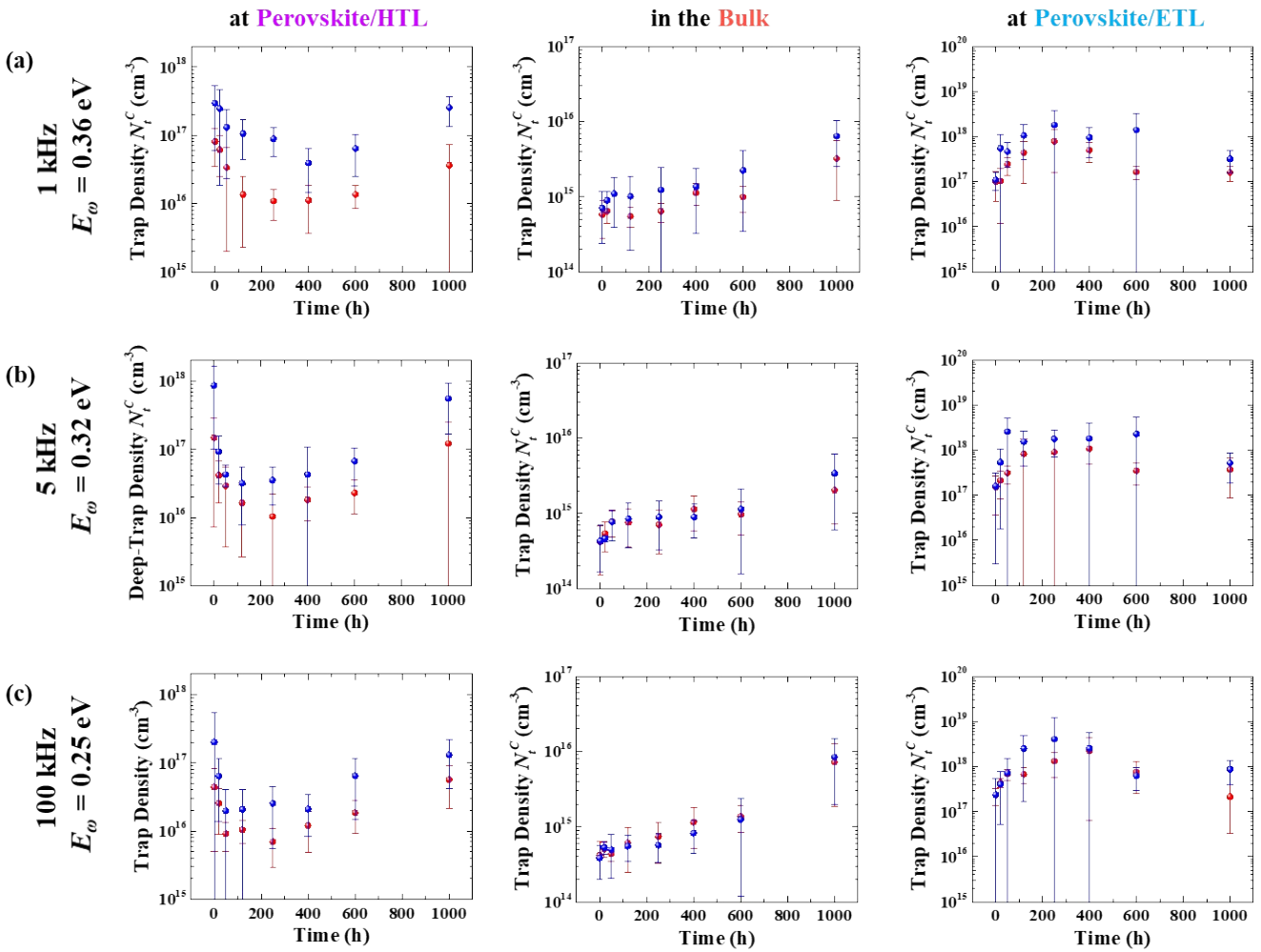


Figure S8. Evolution of the trap densities by positions obtained from the drive-level capacitance profiling (DLCP) analysis. Trap densities $N_t^C(x,\omega)$ at the perovskite/HTL interface, in the bulk, and at the perovskite/ETL interface are shown for (a) 1 kHz (E_ω = 0.36 eV), (b) 5 kHz (= 0.32 eV), and (c) 100 kHz (= 0.25 eV).