

# ADVANCED FUNCTIONAL MATERIALS

## Supporting Information

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Time Transients with Inductive Loop Traces in Metal Halide Perovskites

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## *Supporting Information*

### **Time Transients with Inductive Loop Traces in Metal Halide Perovskites**

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#### **Theoretical Analysis**

The structure of Equation (2) exhibits the general form of a conduction/polarization system,  $j(t) = C_g \frac{dV(t)}{dt} + 1/R_1 f(V(t), X_1(t)) + C_x \frac{dX_2(t)}{dt}$ ,<sup>[1,2]</sup> with the following small perturbation amplitude approximation:

$$\begin{aligned} \Delta j(t) = & C_g \frac{d(\Delta V(t))}{dt} + \frac{1}{R_1} \left( \frac{\partial f}{\partial V} \right)_{X_1} \Delta V(t) + \frac{1}{R_1} \left( \frac{\partial f}{\partial X_1} \right)_{\bar{V}} \Delta X_1(t) \\ & + C_m \frac{d(\Delta X_2(t))}{dt} \end{aligned} \quad (S1)$$

where we will consider from now on that  $\left( \frac{\partial f}{\partial V} \right)_{X_1} = f'_V$  and  $\left( \frac{\partial f}{\partial X_1} \right)_{\bar{V}} = f'_{X_1}$ . The current is therefore composed of several terms: (i) a static capacitive charging, (ii) a conduction current described through a resistance scale parameter  $R_1$  and the internal current variable denoted as  $X_1(t)$ , and (iii) a second internal voltage variable  $X_2(t)$  that introduces a dynamical capacitance  $C_m$ . In terms of a physical explanation, we can additionally specify that Equation (3) represents a migration time of ions that introduces a delay of  $\Delta j_L(t)$  with respect to the external stimulus by the characteristic time constant  $\tau_L$ . Equation (4), on the other hand, describes the voltage-controlled activation of the interfacial charging configuration,  $\Delta V_s(t)$ .  $\tau_C$  is the relaxation time associated to the charge accumulation process. As one commonly obtains the remarkable property of  $\tau_L = \tau_C$  which specify that the slow modes in metal halide perovskite devices exhibit the same characteristic times,<sup>[3-5]</sup> it can be easily deduced that, stating adequate initial conditions, the transient response to a voltage step stimulation,  $\Delta V(t) = V_{app}$ , of both internal state variables are governed by the same rate change under small-signal conditions.

Let us consider the general nonlinear differential equation for internal state functions,  $\tau_{\text{kin},i} \frac{dX_i(t)}{dt} = g_i(X_i(t), V(t))$ ,  $i = 1, 2, \dots, M$ , and the respective small signal expression:

$$\tau_{\text{kin},i} \frac{d(\Delta X_i(t))}{dt} = \left( \frac{\partial g_i}{\partial X_i} \right)_{\bar{V}} \Delta X_i(t) + \left( \frac{\partial g_i}{\partial V} \right)_{\bar{X}_i} \Delta V(t), \quad i = 1, 2, \dots, M \quad (\text{S2})$$

derived from the first-order Taylor expansion around a steady-state value. Note that  $\Delta X_i(t)$  represents the dominant internal variable of the perovskite (with an initial state of  $\Delta X_{0,i}$ ),  $\tau_{\text{kin},i}$  is the associated relaxation time, and  $g_i(\Delta X_i(t), \Delta V(t))$  is the slow recovery function expressed in Equation (S3) by using partial derivatives (small perturbation methods). Note that we will henceforth consider  $g'_{x,i} = \left( \frac{\partial g_i}{\partial X_i} \right)_{\bar{V}}$  and  $g'_{v,i} = \left( \frac{\partial g_i}{\partial V} \right)_{\bar{X}_i}$ . Thus, the analytical solution of Equation (S3) may be generalized as:

$$\Delta X_i(t) = -\frac{g'_{v,i}}{g'_{x,i}} V_{\text{app}} + \left( \Delta X_{0,i} + \frac{g'_{v,i}}{g'_{x,i}} V_{\text{app}} \right) \exp \left[ \frac{g'_{x,i}}{\tau_{\text{kin},i}} t \right], \quad i = 1, 2, \dots, M \quad (\text{S3})$$

Here,  $M = 2$  and thus, the memory variables  $\Delta X_1(t) = \Delta j_L(t)$  or  $\Delta X_2(t) = \Delta V_s(t)$  are delayed by characteristic times  $\tau_L$  or  $\tau_C$  ( $\tau_{\text{kin},1}$  and  $\tau_{\text{kin},2}$ ) owing to slow coupling ionic-electronic effects in organic-inorganic perovskites. The adaptation functions,  $g_1(\Delta V(t), j_L(t))$  or  $g_2(\Delta V(t), \Delta V_s(t))$ , are also separated to additive components, where  $g'_{x,1} = -1$  and  $g'_{v,1} = 1/R_a$  or  $g'_{x,2} = -1$  and  $g'_{v,2} = 1$  for Equations (3) or (4), respectively. As indicated Equation (S3), the metal halide perovskite device importantly operates under stable conditions because  $g'_{x,i} < 0$  and logically  $\tau_{\text{kin},i} > 0$  (decreasing exponentials). In the steady-state situation, the slow memory variables indeed take the generalized value of  $-\frac{g'_{v,i} V_{\text{app}}}{g'_{x,i}}$ . The values of the equivalent circuit elements, in terms of the model parameters, have the following expressions:  $R_b = R_I / f'_V$ ,  $R_a = -\frac{R_I g'_{x,1}}{f'_X g'_{v,1}}$ ,  $L_a = \frac{R_I \tau_{\text{kin},1}}{f'_X g'_{v,1}}$ ,  $R_x = -\frac{\tau_{\text{kin},2}}{C_m g'_{v,2}}$ , and  $C_x = -\frac{C_m g'_{v,2}}{g'_{x,2}}$ . This theory allows to consider the general electrical charge coupling or further scenarios ( $\tau_{\text{kin},1} \neq \tau_{\text{kin},2}$ ) in perovskite semiconductors.

## Experimental

*Fabrication.* Fluorine-doped tin oxide (FTO) glass sheets were etched with Zn powder and diluted HCl. Then, the etched substrates were cleaned in an ultrasonic bath with Hellmanex®, acetone, and ethanol for 15 min and finally were immediately dried with dry air. Compact TiO<sub>2</sub> (c-TiO<sub>2</sub>) solution was prepared with titanium diisopropoxide bis(acetylacetonate):acetylacetonate:ethanol=0.6:0.4:9 (v:v) and then were sprayed onto FTO substrates at 450 °C. Mesoporous TiO<sub>2</sub> (m-TiO<sub>2</sub>) paste was prepared with titanium paste:ethanol=1:6 (w:w), and was spin coated to c-TiO<sub>2</sub> substrates at 5000 rpm for 20 s and then annealed at 450 °C for 30 min. After that, the as-prepared FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub> substrates were quickly transferred to a N<sub>2</sub> filled glove box for perovskite and spiro-OMeTAD deposition. The triple-cation halide perovskite Cs<sub>0.05</sub>MA<sub>0.15</sub>FA<sub>0.80</sub>Pb<sub>1.05</sub>(Br<sub>0.15</sub>I<sub>0.85</sub>)<sub>3</sub> was prepared as follows. Briefly, first 1.5 M stock solution of (1) CsI (DMSO), (2) PbBr<sub>2</sub> (DMSO:DMF=1:4), and (3) PbI<sub>2</sub> (DMSO:DMF=1:4) were prepared, respectively. Then, 1.5 M (4) (MABr)(PbBr<sub>2</sub>) (DMSO:DMF=1:4) and (5) (FAI)(PbI<sub>2</sub>) (DMSO:DMF=1:4) were freshly prepared by dissolving MABr or FAI powder in solution (2) and (3), respectively. After that, the solutions were mixed at a ratio of (4):(5):(1):(3)=150:800:50:100 (v:v) in sequence. The perovskite spin coating process was carried out at 2000 rpm for 10 s, and then 6000 rpm for 30 s. Initially, 50 μL perovskite solution was dropped on a 1.5×2.5 cm<sup>2</sup> FTO/c-TiO<sub>2</sub>/m-TiO<sub>2</sub> substrate. During the second step of spin coating, 100 μL chlorobenzene was dropped at 15 s before ending. The samples were annealed at 100 °C for 1 h on a hot plate for crystallization. Hole transporting layer was prepared by dissolving 0.12 g spiro-OMeTAD in 1130 μL chlorobenzene and then doped with 47.3 μL TBP and 23.5 μL Li-TFSI (1.8 M in acetonitrile). The spin coating was conducted at 4000 rpm for 20 s with 50 μL solution. The finished devices were placed inside a dry air box for 12 h to fully oxidize the spiro-OMeTAD. Finally, 80 nm Au was deposited as the front electrode by thermal evaporation. The evaporation rate was controlled in different stages to limit the damage to the spiro-OMeTAD layer.

*Characterization.* Electrical measurements were carried out with a PGSTAT302N Potentiostat/galvanostat, equipped with an impedance and ultra-fast sampling module, FRA32M and ADC10M, respectively, from Metrohm AutoLab. Impedance measurements were carried out by configuring the AutoLab to apply sinusoidal signals of 10 mV amplitude from 1 MHz to 1 Hz at 1 V. On the other hand, chronoamperometric

experiments were developed, immediately after frequency resolved measurements, by applying a constant signal of 1 V and, after a long time, a voltage-excited step of 10 mV. A sampling rate of 1 MHz was used to record the current responses of CsMAFAPbIBr-based perovskite solar cells. All the experiments at room temperature were carried out under ambient atmosphere with the dry-air flow.

## References

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