

Can understanding ion migration in halide perovskite be the key for high efficiency and stability?

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Ion migration in halide perovskites leads to device degradation and changes the properties of the device during operation, both undesirable for applications. The understanding of ion migration is therefore crucial for the fabrication of stable and efficient perovskite devices. However, measurements and theoretical predictions of the activation energy, diffusion coefficient, and concentration for mobile ions vary widely in the literature. [1] There is not even a consensus yet on which ions migrate.

To quantify ion migration in halide perovskites we measure capacitance transients at various temperatures which we then describe using the theory of transient ion-drift (see Figure 1). [2, 3] By studying methylammonium lead triiodide (MAPbI₃) we found that both MA⁺ and I⁻ ions migrate at room temperature, but with very different diffusion coefficients (10⁻⁹ and 10⁻¹² cm²s⁻¹ respectively), in agreement with diffusion coefficients obtained by NMR measurements. [4]

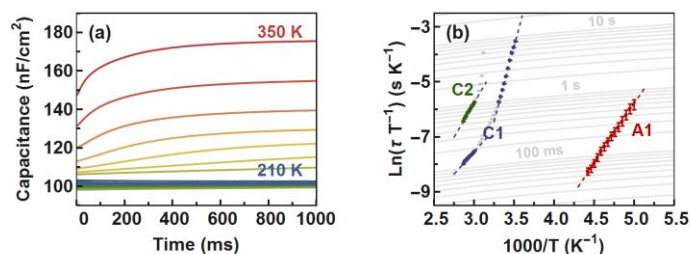


Figure 1. (a) Capacitance transient measurements of a MAPbI₃ solar cell between 180 and 350 K measured at 0 V after a voltage pulse of 0.4 V. **(b)** Arrhenius plot of the observed transient decay times of (a) as a function of temperature. The linear fit reveals the activation energy and the diffusion coefficient of the mobile ion species. We attribute A1 to the migration of I⁻ ions and C1 and C2 to the migration of MA⁺ ions.

Compared to mixed-cation mixed-halide perovskites, MAPbI₃ perovskites are rather unstable because the MA⁺ cations can be easily dissociated from MAPbI₃. [5] As a consequence, we find that the migration of MA⁺ ions depends strongly on device fabrication, while the migration of mobile I⁻ ions is highly reproducible for different devices (see Figure 2). Interestingly, we observe that the cation migration is impeded in mixed-cation mixed-halide perovskites and that the diffusion coefficient of mobile halide ions is two orders of magnitude lower than in MAPbI₃

perovskites. This reduction in ion migration could be the reason for the increased stability compared to MAPbI_3 .

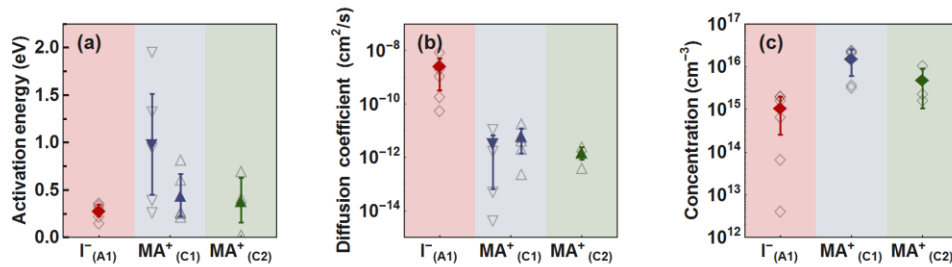


Figure 2. (a) Activation energy, (b) diffusion coefficient, (c) and concentration of mobile ions in MAPbI_3 perovskites obtained by transient ion-drift. The downward and the upward triangle represents measurements below and above the tetragonal-to-cubic phase-transition temperature.

Recently it was shown that introducing additives such as potassium into triple-cation mixed-halide perovskites can increase the stability even further without compromising charge transport or extraction. [6] We find that the activation energy of mobile halides in these triple-cation mixed-halide perovskites is not influenced by potassium passivation, but that the concentration decreases and the diffusion coefficient increases with increasing potassium passivation, showing the inhibition of ion migration upon potassium passivation. These findings indicate that fewer and faster mobile ions make the device more efficient.

So far, we consistently find that fewer mobile ions seem to improve device stability and performance. However, the influence of the diffusion coefficient of these mobile ions is still unclear, and the connection to the material, morphology and devices is missing. What is the effect of additives and composition, how does the lattice parameter influence the migration of ions, how do the mobile ions change the electric field distribution across the device, and how fundamental is the existence of ion migration in an ionic semiconductor such as halide perovskites? Answering these questions are important to fully understand the effects of ion migration and its role in the operation and degradation of perovskite solar cells.

References

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