Transient Phenomena and Ion Kinetics in Lead-Halide Perovskites

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Charge carrier dynamics, for example their scattering in lead halide perovskites, remains a topic of considerable research interest due to their important role in photovoltaics and optoelectronics. In addition to free carrier dynamics, soft perovskite materials are known to be strongly affected by the displacement of lattice vacancies, charged atoms or even entire molecules. Also, extrinsic ion additives attracted much attention recently, as they tend to improve the device stability. It is therefore essential to understand the temporal and spatial dependence of different types of charge carriers in films and devices. The motion of charge carriers in perovskites occurs on very different time scales and cannot usually be easily captured in a single transient experiment. In a first example, I will illustrate the so-called open-circuit voltage decay (OCVD) technique. In our early work, we applied it to $CH_3NH_3PbI_3$ solar cells and observed unexpectedly slow recombination dynamics persisting over long timescales, exhibiting a plateau (shoulder) that we tentatively attributed to mobile ionic species. [1] More specifically, we observed several time domains in the voltage transient. On a short timescale, a voltage drop is observed, which is most likely due to free carrier kinetics (e.g., surface recombination). The transients are qualitatively similar in organic and perovskite solar cells when the excess charge densities are present under sufficiently strong illumination. On much longer times, a rapid voltage drop is often observed, however, these losses are not associated with the absorber material itself, but rather due to shunts, which act as additional recombination pathway. Most intriguingly, something distinctly different occurs in the perovskite devices in between. On this timescale, the OCVD shoulder of the ion-containing device is clearly distinguishable from the rest of the voltage drop. Combining transient drift–diffusion simulations and experimentally measured OCVD transients, we assigned the omnipresent shoulder in perovskite devices to ionic redistribution. By introducing a simple expression allowing calculating the differential capacitance from the OCVD and a simultaneously measured current–voltage relationship, we provide a method enabling the determination of both concentration as well as diffusion coefficients for the slowly moving ionic species in fully operational perovskite solar cells. [2] The presence of mobile ions is often associated with accelerated degradation of solar cell devices. To demonstrate application relevance, we also performed OCVD measurements to gain insight into the possible mechanism responsible for thermal stress-induced degradation of solar cells. [3]

To investigate the charge carrier mobility and the recombination behavior, time-resolved microwave conductivity (TRMC) is applied. TRMC allows for the investigation of the intrinsic mobility of photo-generated charge carriers in a contactless manner, avoiding the impact of superimposed extrinsic effects related to additional layers and their interfaces. [3,4] In a second part of my contribution, I'll give an overview of the experimental techniques used to study transport phenomena in semiconducting perovskites and show some examples. More specifically, we investigated temperature-dependent charge carrier dynamics in various types of lead-halide perovskites, to determine the prevalent scattering mechanisms. Dynamic disorder is proposed to be the predominant scattering mechanism at room temperature and above, as evidenced by the exponent of the power-law mobility dependence. [4]

References:

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