

Predicting long-term stability from short-term measurement: insights from modelling degradation in perovskite solar cells during voltage scans and impedance spectroscopy

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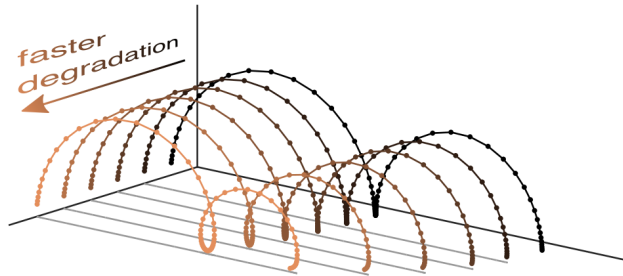
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Abstract

A drift-diffusion model is used to investigate the effect of device degradation on current-voltage and impedance measurements of perovskite solar cells (PSCs). Modifications are made to the open-source drift-diffusion software IonMonger to model degradation via an increasing recombination rate during the course of characterisation experiments. Impedance spectroscopy is shown to be a significantly more sensitive measure of degradation than current-voltage curves, reliably detecting a power conversion efficiency drop of as little as 0.06% over a four hour measurement. Furthermore, we find that fast degradation occurring during impedance spectroscopy can induce loops lying above the axis in the Nyquist plot, the first time this experimentally observed phenomenon has been replicated in a physics-based model.



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Over the last decade, perovskites have established themselves as one of the most exciting and promising photovoltaic materials [7, 10, 18, 22]. Power conversion efficiencies (PCEs) for perovskite solar cells (PSCs) have recently surpassed those of silicon cells, with a current record NREL certified PCE of 26.7% [20]. All-perovskite and perovskite-silicon tandem devices currently hold impressive record PCEs of 29.1% and 33.9%, respectively [20]. Whilst these records have solidified perovskites as a significant player in the quest for cheap sustainable energy, there are still challenges that bar their way to large-scale commercial deployment. Although device stability has improved dramatically over recent years [30], long-term stability still needs to be improved for commercial development. Additionally, rigorous stability studies are time-consuming, and there is a pressing need for experimental techniques that can infer the long-term degradation trajectory of a device based on sensitive short-term measurements.

Whilst device architectures are often successfully engineered to maximise PCE, this frequently comes at the expense of reduced stability. It is therefore vital to future development that device degradation can be accurately quantified by standard, and rapid, characterisation experiments that allow quick assessment of strategies to ameliorate degradation. In this work we consider the effect of degradation on the drift-diffusion model of PSCs. Particular attention is paid to current-voltage curves and impedance spectra. The latter are shown to be a remarkably sensitive tool with which to monitor device stability, based solely on visual inspection of the measured Nyquist plot.

To model the slow degradation of the cell, we introduce a time-dependent prefactor, $r(t)$, to the bulk Shockley-Reed-Hall (SRH) recombination rate in the perovskite, *i.e.* Eq. 64 in Ref. [4] is replaced by

$$R(n, p, t) = \underbrace{\beta (np - n_i^2)}_{\text{bi-molecular}} + r(t) \underbrace{\frac{np - n_i^2}{\tau_n p + \tau_p n + (\tau_n + \tau_p) n_i}}_{\text{SRH}}. \quad (1)$$

This prefactor must begin from $r(0) = 1$, representing the ‘pristine’ state of the cell at the beginning of the experiment. For simplicity we consider only the first order Taylor expansion of the degradation factor,

$$r(t) = 1 + \mu t + \dots \quad (2)$$

where $\mu = r'(0) > 0$ is the initial rate of degradation. While a linear increase in recombination rate is unrealistic over ultra-long timescales, it is a reasonable approximation for the small amount of degradation that occurs during a single experiment. Under this degradation mechanism, the decay in PCE can be simulated via a ‘perturb and observe’ method and a simple empirical formula can be used to relate the degradation rate μ (measured in s^{-1}) to the cell’s T_{90} time (measured in hours), the time taken for PCE to drop to 90 % of its pristine value. This formula is

$$T_{90} = \frac{9.99 \times 10^{-3}}{\mu}, \quad (3)$$

and is valid for T_{90} between 0.15 and 1000 hours. This empirical relationship is compared to data from simulated PCE tracking for different values of μ in Figure 1.

In a recent work, Thiesbrummel *et al.* [27] suggest that degradation in PSC performance occurs predominantly as a result of increased screening of the electric field in the perovskite layer, which, in turn, is a consequence of increases in ion vacancy density, rather than increases in recombination in this layer. However, the type of experimentally observed

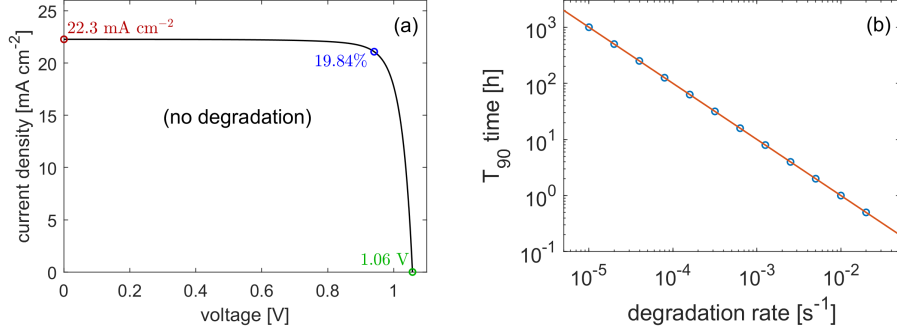


Figure 1: (a) Characterisation of the parameter set in the absence of degradation using a slow (1 mVs^{-1}) voltage scan. (b) The empirical relationship between degradation rate μ and T_{90} time. Circles are from simulated maximum power point tracking using the ‘perturb and observe’ technique and the line is the fit (3).

impedance spectra that we model here cannot be explained solely by increased ion vacancy density as the cell degrades (see Figure S4 in ESI), but are associated with an increased recombination rate in the perovskite layer (see Figure 4). This does not necessarily contradict the Thiesbrummel hypothesis, since a rise in vacancy density is often assumed to be accompanied by increases in recombination rate in the perovskite layer due to the role of vacancies as recombination sites [3, 13, 24].

Simulations presented in this letter were conducted using a single set of material parameters (listed in Table S1). The parameter set is characterised using a slow current-voltage sweep in the absence of degradation in Figure 1. The pristine PCE of the simulated cell is 19.84% at 1 Sun.

The effects of degradation on a current-voltage sweep are difficult to observe as they are blurred by the hysteretic effect caused by ion migration. Simulating two sweeps, before and after the cell has been held at maximum power point under illumination, however, decouples the two. Comparison between the initial and final J - V curves can therefore indicate the level of degradation that has occurred during operation. J - V curves simulated after four hours of operation under different degradation rates are shown in Figure 2. The scan rate (1 Vs^{-1}) was chosen as it is below that at which maximum hysteresis is seen (40 Vs^{-1}) for this parameter set, meaning it gives a reasonable approximation of steady-state behaviour while also being fast enough that the increase in recombination rate over the duration of a single scan is negligible. The effect of increased recombination rate through degradation is a reduction in both short-circuit current and open-circuit voltage, along with an increase in the degree of hysteresis observed. Notably, the J - V curve shows relatively low sensitivity to the increase in recombination. Even after four hours, only curves corresponding to $T_{90} \leq 10$ hours show significant deviation from the pristine example. This corresponds to T_{90} less than 2.5 times the experiment length and a PCE of less than 18.73% after the four hour period, a drop of at least 1.12% from the pristine value of 19.84% (see Figure 2).

Impedance spectroscopy is another powerful tool used to measure device stability. The effects of degradation on impedance spectroscopy in the model can be grouped into two categories: those that occur between successive measurements and those that occur during a single measurement. We begin with the former. Impedance spectra for the parameter set listed in Table S1 were simulated after the cell had been allowed to degrade for 4 hours. For

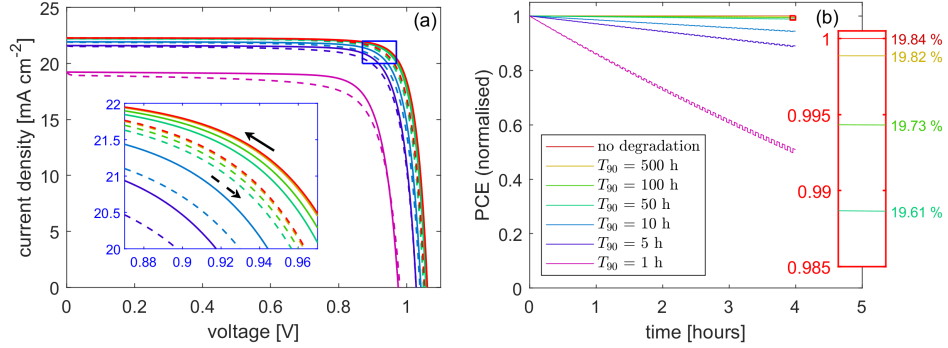


Figure 2: Current-voltage sweeps in the presence of degradation modelled via an increasing bulk SRH recombination rate (1) and computed in IonMonger [4]. Panel (a) compares 1 Vs⁻¹ sweeps after four hours of operation against the pristine case in which degradation is eliminated, for a range of degradation rates. Solid lines are the reverse sweep and dashed the forward. Panel (b) shows simulated MPP tracking for the same device over the four hour period of operation, with final PCEs shown in the inset. Parameter set listed in Table S1.

details of the simulation protocol and the computational methods, see the Methods section below. The results for T_{90} between 50 and 1000 hours are compared to the pristine spectrum in the absence of degradation in Figure 3. The general shape of the Nyquist plot is reasonably

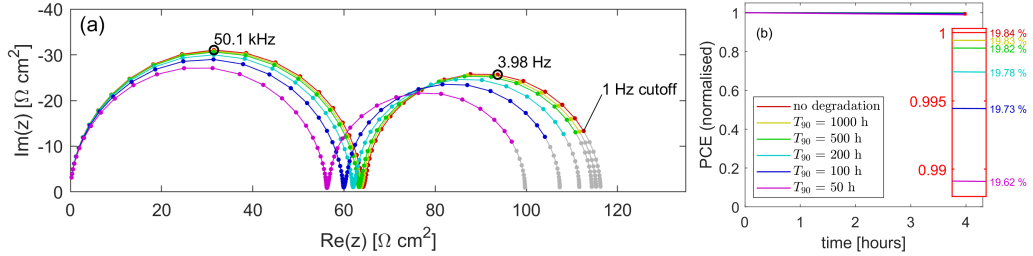


Figure 3: (a) Impedance spectroscopy in the presence of cell degradation via an increasing bulk SRH recombination rate (1) and simulated using Ionmonger [4]. The T_{90} associated with each degradation rate is listed in the legend of panel (b). Grey data show frequencies that lie below the 1 Hz cutoff that is often used experimentally. Parameter set listed in Table S1. Simulated at $V_{\text{DC}} = 0.9$ V under 1 Sun illumination and after a four hour rest from the pristine state. (b) MPP tracking over the four hour rest time for the degradation rates used in (a).

unchanged across these degradation rates, with two clear arcs, both lying above the x axis and the radius of the low-frequency arc slightly smaller than that of the high-frequency. The physical origins of these two arcs are well-described in Ref. [1]. The radii of the two arcs, however, exhibit significant variation depending on the rate of degradation. In the context of the RC-RC equivalent circuit [1, 14, 28, 29], both the high- and low-frequency resistances decrease as the cell degrades. This follows naturally from the work of Bennett *et al.* [1], in which an RC-RC equivalent circuit was systematically derived from the drift-diffusion

equations, identifying both resistances as recombination resistances, inversely proportional to the DC recombination current (j_{rec}),

$$R_{\text{HF}} = \frac{V_T n_{\text{el}}}{j_{\text{rec}}(V_{\text{dc}})}, \quad R_{\text{LF}} = \frac{V_T}{j_{\text{rec}}(V_{\text{dc}})} (n_{\text{ap}}(V_{\text{dc}}) - n_{\text{el}}), \quad ((22)-(23) \text{ from [1]})$$

where n_{el} and n_{ap} are electronic and apparent ideality factors, respectively, and V_T is the thermal voltage. Here the Nyquist plot consists of two semicircular arcs with diameters given by R_{HF} (left arc) and R_{LF} (right arc). Notably, an increase in the recombination rate due to degradation corresponds to a reduction in R_{HF} and R_{LF} and a corresponding decrease in the size of the Nyquist arcs. Accounting for a time-dependent increase in recombination rate, j_{rec} , R_{LF} and R_{HF} all become functions of time. By measuring the evolution of the two resistances over time, one can therefore, in principle, reconstruct the rate at which the recombination rate is increasing, and calculate an estimate of long-term stability.

These simulated spectra suggest that a cell must show remarkably high stability ($T_{90} \geq 500$ h) in order for the degradation-induced change in the spectrum to be unnoticeable after 4 hours. In this example, the effects of degradation are clearly visible when $T_{90} = 200$ h, corresponding to 50 times the experiment length. At this degradation rate, the PCE drop over four hours is just 0.06%. In contrast, the simulated J - V curves discussed above only resolve the effects of degradation over the same four hour window when $T_{90} \leq 10$ h (see Figure 2). This demonstrates the high sensitivity of impedance spectroscopy to degradation rates. A PCE decrease of 0.06% is almost imperceptible in a J - V curve, even in simulations that avoid the limitations of experiment noise, whereas the same degradation is sufficient to very clearly alter the impedance spectrum.

In the simulations described above, the relatively slow rate of degradation has little impact on the cell during the time taken to measure a spectrum, but the cumulative effect over the four hour rest period is significant. We now turn our attention to faster rates of degradation, such that the cell degrades on the timescale of the measurement, warping the observed spectrum. At such rates, we note that the Nyquist plot will depend on the exact measurement protocol adopted. While we have here used a protocol intended to be representative of common practice in the field, the source code for the version of IonMonger used to compute these figures is freely available as a fork of the IonMonger GitHub repository¹ in the hope that readers may use it to investigate results for a variety of lab protocols.

Simulated impedance spectra with varying degradation rates are shown in Figure 4. For relatively stable cells ($T_{90} \geq 10$ h) the degradation that occurs during the experiment time (approx. 8 mins) is not enough to significantly alter the spectrum. Towards the end of the experiment, as the lowest frequencies are measured, the increased recombination acts to decrease the observed resistance, observed as a slight drift toward the origin, but the general shape is unchanged. For faster rates of degradation ($T_{90} \leq 2$ h) the decrease in resistance occurs quickly enough that this drift causes a loop to be formed in the Nyquist plot between the low- and high-frequency arcs. In a stable cell, a plateau typically exists between the high- and low-frequency arcs at which the impedance is real and near-constant. In the presence of degradation, however, the impedance decreases slowly during the measurement of these frequencies, gradually moving toward the origin of the Nyquist plot. The onset of the LF feature therefore closes this loop. Intuitively, the area enclosed by the loop between the low- and high-frequency arcs increases with degradation rate. We note that the minimum degradation rate for which a loop can be observed here corresponds to a T_{90} time of 2 hours,

¹<https://github.com/Will1Clarke25/IonMonger-degradation-modelling>

or approximately 15 times the experiment time. The level of degradation required during an experiment to induce a loop in the Nyquist plot is therefore comparatively small and a loop is observed even though the drop in the cell's PCE over the 8 minute measurement window is only from 19.84% to 19.66%, a difference of 0.18% (see Figure 4b). Once again, by relating the impedance to the recombination current through ((22)-(23) from [1]), one can, in principle, calculate an estimate of long-term stability based on observation of a loop in the impedance spectrum. However, parameterising the decrease in resistance along the path of a single spectrum as a function of time is a significantly more complex challenge than that of comparing multiple spectra measured hours apart. Furthermore, the simulations presented here suggest that a loop is an indicator of poor stability, meaning long-term estimates are of little practical value.

In a similar process, the impedance of a perfectly stable cell will tend toward a constant, real value in the low-frequency limit, while that of a cell with degradation will continue to decrease, drifting slowly toward the origin of the Nyquist plot. This can be observed in the grey data in Figure S3. In practice, however, a 1 Hz cutoff frequency is often adopted [2, 8, 12, 16, 17, 19, 21, 23, 25, 26], meaning this tail may not be observed. Simulated spectra measuring to frequencies as low as 10 mHz can be found in the supplementary information (Figure S3), showing the slow drift toward the origin.

Loops in the Nyquist plots of impedance spectra of PSCs, occurring between the high- and low-frequency features, were recently shown by Clarke *et al.* [6] to be predicted by the standard PSC drift-diffusion model, in the absence of cell degradation, for certain parameter regimes. When one of the perovskite-transport layer band offsets is small, a large density of carriers leaks from the transport layer into the perovskite, and the coupling between the charge carriers introduced into the perovskite and the ion vacancies gives rise to a mid-frequency feature in the spectrum. The sign of this feature depends on the majority carrier in question and the dominant recombination pathway. When the MF feature is negative and the LF feature positive, a loop is formed in the Nyquist plot. In Figure 4c, comparison is made between an ion-induced loop predicted by the theory of Clarke *et al.* [6] and a degradation-induced loop as described above. This comparison highlights a crucial difference between the two mechanisms: ion-induced loops are caused by a negative MF feature, which leads to a semicircle forming below the axis of the Nyquist plot, whereas degradation cannot change the sign of the impedance response, which means that the spectrum always remains above the axis. These apparently similar Nyquist shapes (which have both been observed experimentally, see *e.g.* [9, 11]) therefore originate from very different phenomena and exhibit characteristic properties which enable them to be distinguished from each other. We have previously shown that ion-induced loops in impedance spectra are linked with inverted hysteresis in the current-voltage curve [5, 6], whereas degradation-induced loops are only associated with slow deterioration in JV curves as in Figure 2.

We have studied the effects of degradation on the drift-diffusion model of a perovskite solar cell by introducing a time-dependent degradation factor to the recombination rate. These simulations are the first of their kind and pave the way for sophisticated physics-based modelling of degradation pathways in PSCs, developing techniques to determine long-term stability based only on short-term experiments. Both current-voltage curves and impedance spectra were simulated using this model, enabling investigation of their relative sensitivities as a measure of degradation. By performing both characterisation experiments before and after a four hour period of operation (and degradation), we show that impedance spectroscopy is far more sensitive to device degradation. Observable changes to the impedance spectrum were detected for $T_{90} \leq 200$ h, or 50 times the experiment duration, for which

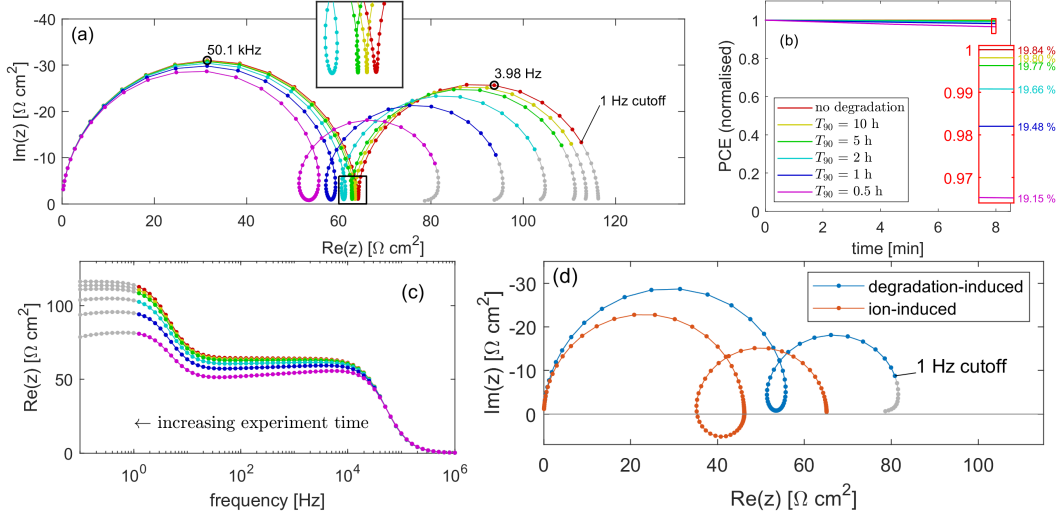


Figure 4: (a) Impedance spectroscopy in the presence of cell degradation modelled via an increasing bulk SRH recombination rate (1) and simulated using Ionmonger [4]. The T_{90} associated with each degradation rate is listed in the legend of panel (b). Grey data show frequencies that lie below the 1 Hz cutoff that is often used experimentally. Parameter set listed in Table S1. Simulated at $V_{\text{DC}} = 0.9$ V under 1 Sun illumination. Panel (b) shows MPP tracking for the same degradation rates over the eight minute window taken to measure the impedance spectra shown in panel (a). The spectra from (a) are shown in (c) with the real part of impedance plotted as a function of frequency. (d) Comparison between loops in simulated Nyquist plots induced by (blue) degradation during measurement and (orange) ion migration coupled with large carrier leakage as described in [6]. The blue spectrum is taken from (a) with degradation corresponding to $T_{90} = 30$ minutes. The orange spectrum was simulated using the parameter set ‘Cell E’ in [6] with no degradation, at $V_{\text{DC}} = 1.0$ V under 1 Sun illumination.

the drop in PCE was only 0.06%. In contrast, similar effects were only seen in the current-voltage curve for $T_{90} \leq 10$ h, or 2.5 times the experiment duration, and the corresponding drop in PCE was 1.12%. This represents a decrease in sensitivity compared to impedance spectroscopy by a factor of approximately 20.

Degradation is observable in the Nyquist plot as a slow drift towards the origin as time progresses. The asymptotic analysis of the drift-diffusion model conducted by Bennett *et al.* [1] identified an inverse proportionality between the recombination current at the DC voltage and the radius of the high- and low-frequency arcs in the Nyquist plot, explaining the smooth reduction in $|Z|$ as the degradation progresses here. When degradation occurs sufficiently quickly, this effect can induce a loop in the Nyquist plot between the high- and low- frequency features. A drop in the cell’s PCE of as little as 0.18% during the 8 minute experiment is sufficient to induce a visible loop, corresponding to a T_{90} time of 2 hours, or 15 times the experiment duration. Importantly, the degradation-induced loops presented here are easily distinguishable from the ion-induced loops, which were simulated from a drift-diffusion model without degradation by Clarke *et al.* [6], by whether or not they cross the real axis. Building on the findings of Clarke *et al.* [6], this work provides researchers with additional tools to interpret the impedance spectra of PSCs from only a visual inspection of the Nyquist plot, without the need to conduct explicit modelling of each dataset.

Computational Methods

Simulations were performed using the open-source PSC simulation software IonMonger, which solves the drift-diffusion model described in Ref [4]. The parameter set used here is representative of a typical cell in which the electron transport layer (ETL) is a metal oxide, the perovskite absorber layer (PAL) is a perovskite in which iodide occupies the X site, the hole transport layer (HTL) is a hole-conducting polymer, and light enters through the ETL. The diffusion coefficient and mean density of the mobile ions in the perovskite are set to $3.5 \times 10^{-10} \text{ cm}^2\text{s}^{-1}$ and $5 \times 10^{17} \text{ cm}^{-3}$, respectively. These values were obtained from Bayesian parameter estimation conducted by McCallum *et al.* [15] for a MAPI-based cell. Recombination is modelled through bi-molecular and Shockley-Read-Hall (SRH) recombination in the perovskite bulk and SRH at the material interfaces between the perovskite and the transport layers. At the DC voltage of 0.9 V employed in Figure 4, surface recombination dominates bulk by approximately one order of magnitude. The full list of material parameters used for simulations can be found in Table S1. As shown in Figure 1, this parameter set gives a relatively high pristine power conversion efficiency of 19.84%.

In IonMonger, the computational cost of simulating impedance spectra is reduced by utilising parallel processing [4]. Once steady state has been achieved at the DC voltage, each frequency measurement is simulated in parallel, beginning from the same initial state. However, this approach is not appropriate when modelling degradation during the experiment, as each frequency measurement must begin from the end state of the preceding measurement. We therefore replace the parallel processing in IonMonger with a simulation protocol in which all measurements are performed sequentially, one after another. This method is validated against the parallel approach in the supplementary information (Figure S1).

Whilst the exact details of experimental impedance protocols vary from lab to lab, we define a representative ‘lab protocol’, on which to base our simulations, that captures the essence of most impedance experiments. This ‘lab protocol’ is defined by impedance

measurements conducted over a range of frequencies beginning with the highest (1 MHz) and ending with the lowest (100 mHz) with a 1 s rest time between each measurement. Frequencies are spaced ‘ten per decade’ between the limits, giving a total of 71. At each frequency the oscillating voltage is applied for a fixed duration, known as the integration time t_{int} (set to 5 s). At high frequencies the integration time is sufficient to perform millions of voltage cycles, ensuring high accuracy of the Fourier fit of current response. For frequencies $f < 2/T_{\text{int}}$, two complete voltage cycles are measured, exceeding the integration time to ensure accuracy of the Fourier fit. This lab protocol is depicted in Figure 5 and has a total duration of less than eight minutes.

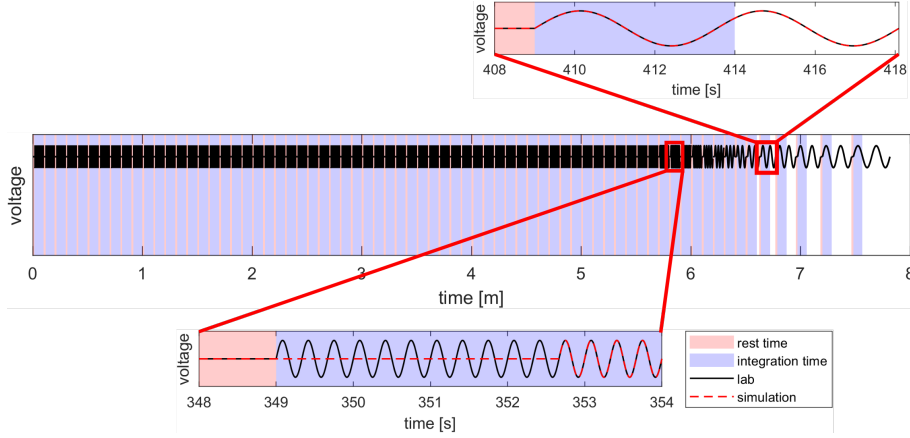


Figure 5: Depiction of the lab protocol for measuring an impedance spectrum. Magnified plots show the simulated protocol used to minimise computation time while occupying the same total experiment time.

In the case of high frequencies, the number of voltage cycles during the integration time may be in the millions, making fully realistic simulations prohibitively expensive. However, the drift-diffusion model typically only requires a few cycles to reach a quasi-equilibrium, meaning only the final few cycles need to be simulated. In our simulation protocol, computational cost is reduced for high frequency measurements by only simulating the final four voltage cycles following a ‘dummy’ period in which time (and degradation) progresses but the voltage is fixed, as shown in Figure 5. One limitation of IonMonger is that only an integer number of voltage cycles can be simulated. In the frequency range $2/T_{\text{int}} < f < 4/T_{\text{int}}$, the lab measurement would take T_{int} but the simulation would exceed this. Consequently the simulation protocol for these frequencies consists of a dummy period followed by two full cycles, such that the measurement duration (and thus degradation incurred) is equal to that of the lab protocol. At frequencies $f < 2/T_{\text{int}}$, two full cycles are simulated with no dummy time, as in the lab protocol. This simulation protocol is designed to reduce computation cost while still measuring each value of impedance at the time (and therefore degradation level) as would occur in the lab protocol. This method is validated against simulations in which many more voltage cycles are explicitly modelled in the supplementary information (Figure S2).

The code to solve this updated version of the charge transport model, including sequential

impedance measurements, is available as a fork of the IonMonger GitHub repository².

Supporting Information Statement

Supporting information: validation of sequential vs. parallel IS simulation, results for ultra-low frequencies, and simulation parameter values.

References

- [1] Laurence J. Bennett, Antonio J. Riquelme, Juan A. Anta, Nicola E. Courtier, and Giles Richardson. Avoiding ionic interference in computing the ideality factor for perovskite solar cells and an analytical theory of their impedance-spectroscopy response. *Physical Review Applied*, 19(1), 2023.
- [2] Qingbin Cai, Yiqiang Zhang, Chao Liang, Pengwei Li, Hao Gu, Xiaotao Liu, Jiefei Wang, Zhexiong Shentu, Jiajie Fan, and Guosheng Shao. Enhancing efficiency of planar structure perovskite solar cells using Sn -doped TiO_2 as electron transport layer at low temperature. *Electrochimica Acta*, 261:227–235, 2018.
- [3] Jiangzhao Chen and Nam-Gyu Park. Causes and solutions of recombination in perovskite solar cells. *Advanced Materials*, 31(47):1803019, 2019.
- [4] Will Clarke, Laurence J. Bennett, Yoana Grudeva, Jamie M. Foster, Giles Richardson, and Nicola E. Courtier. Ionmonger 2.0: software for free, fast and versatile simulation of current, voltage and impedance response of planar perovskite solar cells. *Journal of Computational Electronics*, 2022.
- [5] Will Clarke, Matthew V Cowley, Matthew J Wolf, Petra Cameron, Alison Walker, and Giles Richardson. Inverted hysteresis as a diagnostic tool for perovskite solar cells: Insights from the drift-diffusion model. *Journal of Applied Physics*, 133(9), 2023.
- [6] Will Clarke, Giles Richardson, and Petra Cameron. Understanding the full zoo of perovskite solar cell impedance spectra with the standard drift-diffusion model. *Advanced Energy Materials*, n/a(n/a):2400955.
- [7] Giles E. Eperon, Maximilian T. Hörlantner, and Henry J. Snaith. Metal halide perovskite tandem and multiple-junction photovoltaics. *Nature Reviews Chemistry*, 1(12):0095, 2017.
- [8] Fedros Galatopoulos, Achilleas Savva, Ioannis T Papadas, and Stelios A Choulis. The effect of hole transporting layer in charge accumulation properties of pin perovskite solar cells. *APL Materials*, 5(7), 2017.
- [9] Elnaz Ghahremanirad, Agustín Bou, Saeed Olyaei, and Juan Bisquert. Inductive loop in the impedance response of perovskite solar cells explained by surface polarization model. *The Journal of Physical Chemistry Letters*, 8(7):1402–1406, 2017.
- [10] Martin A. Green, Anita Ho-Baillie, and Henry J. Snaith. The emergence of perovskite solar cells. *Nature Photonics*, 8(7):506–514, 2014.

²<https://github.com/WillClarke25/IonMonger-degradation-modelling>

- [11] Antonio Guerrero, Germà Garcia-Belmonte, Ivan Mora-Sero, Juan Bisquert, Yong Soo Kang, T Jesper Jacobsson, Juan-Pablo Correa-Baena, and Anders Hagfeldt. Properties of contact and bulk impedances in hybrid lead halide perovskite solar cells including inductive loop elements. *The Journal of Physical Chemistry C*, 120(15):8023–8032, 2016.
- [12] Enrique Hernández-Balaguera and Juan Bisquert. Negative transient spikes in halide perovskites. *ACS Energy Letters*, 7(8):2602–2610, 2022.
- [13] Cheng Li, Antonio Guerrero, Sven Huettnner, and Juan Bisquert. Unravelling the role of vacancies in lead halide perovskite through electrical switching of photoluminescence. *Nature communications*, 9(1):5113, 2018.
- [14] Ilaria Matacena, Pierluigi Guerriero, Laura Lancellotti, Brigida Alfano, Antonella De Maria, Vera La Ferrara, Lucia V Mercaldo, Maria Lucia Miglietta, Tiziana Polichetti, Gabriella Rametta, et al. Impedance spectroscopy analysis of perovskite solar cell stability. *Energies*, 16(13):4951, 2023.
- [15] Samuel G McCallum, Oliver Nicholls, Kjeld O Jensen, Matthew V Cowley, James E Lerpinière, and Alison B Walker. Bayesian parameter estimation for characterising mobile ion vacancies in perovskite solar cells. *Journal of Physics: Energy*, 6(1):015005, 2023.
- [16] Govindhasamy Murugadoss, Hiroyuki Kanda, Soichiro Tanaka, Hitoshi Nishino, Seigo Ito, Hiroshi Imahori, and Tomokazu Umeyama. An efficient electron transport material of tin oxide for planar structure perovskite solar cells. *Journal of Power Sources*, 307:891–897, 2016.
- [17] Loreta A Muscarella, Yulia Galagan, Simon Christian Boehme, Elizabeth von Hauff, et al. Trap passivation and suppressed electrochemical dynamics in perovskite solar cells with c60 interlayers. *Electrochimica Acta*, 433:141215, 2022.
- [18] Pabitra K. Nayak, Suhas Mahesh, Henry J. Snaith, and David Cahen. Photovoltaic solar cell technologies: analysing the state of the art. *Nature Reviews Materials*, 4(4):269–285, 2019.
- [19] Ganga R Neupane, Matthew Bamidele, Vishal Yeddu, Do Young Kim, and Parameswar Hari. Negative capacitance and hysteresis in encapsulated mapbi3 and lead–tin (pb–sn) perovskite solar cells. *Journal of Materials Research*, 37(7):1357–1372, 2022.
- [20] NREL. Best research-cell efficiency chart, <https://www.nrel.gov/pv/cell-efficiency.html> (accessed 23/07/2024). <https://www.nrel.gov/pv/cell-efficiency.html>. Accessed 23/07/2024.
- [21] Ik Jae Park, Jae Hyun Park, Su Geun Ji, Min-Ah Park, Ju Hee Jang, and Jin Young Kim. A three-terminal monolithic perovskite/si tandem solar cell characterization platform. *Joule*, 3(3):807–818, 2019.
- [22] Nam-Gyu Park. Perovskite solar cells: an emerging photovoltaic technology. *Materials Today*, 18(2):65–72, 2015.

- [23] Adam Pockett, Giles E Eperon, Timo Peltola, Henry J Snaith, Alison Walker, Laurence M Peter, and Petra J Cameron. Characterization of planar lead halide perovskite solar cells by impedance spectroscopy, open-circuit photovoltage decay, and intensity-modulated photovoltage/photocurrent spectroscopy. *The Journal of Physical Chemistry C*, 119(7):3456–3465, 2015.
- [24] Tejas S Sherkar, Cristina Momblona, Lidon Gil-Escrig, Jorge Avila, Michele Sessolo, Henk J Bolink, and L Jan Anton Koster. Recombination in perovskite solar cells: significance of grain boundaries, interface traps, and defect ions. *ACS energy letters*, 2(5):1214–1222, 2017.
- [25] Jongmoon Shin, Maengsuk Kim, Sujeong Jung, Chang Su Kim, Jucheol Park, Aeran Song, Kwun-Bum Chung, Sung-Ho Jin, Jun Hee Lee, and Myungkwan Song. Enhanced efficiency in lead-free bismuth iodide with post treatment based on a hole-conductor-free perovskite solar cell. *Nano research*, 11:6283–6293, 2018.
- [26] Mohammad Mahdi Tavakoli, Pankaj Yadav, Rouhollah Tavakoli, and Jing Kong. Surface engineering of tio2 etl for highly efficient and hysteresis-less planar perovskite solar cell (21.4%) with enhanced open-circuit voltage and stability. *Advanced Energy Materials*, 8(23):1800794, 2018.
- [27] Jarla Thiesbrummel, Sahil Shah, Emilio Gutierrez-Partida, Fengshuo Zu, Francisco Peña-Camargo, Stefan Zeiske, Jonas Diekmann, Fangyuan Ye, Karol P Peters, Kai O Brinkmann, et al. Ion-induced field screening as a dominant factor in perovskite solar cell operational stability. *Nature Energy*, pages 1–13, 2024.
- [28] Haimang Yi, Dian Wang, Leiping Duan, Faiazul Haque, Cheng Xu, Yu Zhang, Gavin Conibeer, and Ashraf Uddin. Solution-processed wo3 and water-free pedot: Pss composite for hole transport layer in conventional perovskite solar cell. *Electrochimica Acta*, 319:349–358, 2019.
- [29] Jie Zhang and Thierry Pauporté. Effects of oxide contact layer on the preparation and properties of ch3nh3pbi3 for perovskite solar cell application. *The Journal of Physical Chemistry C*, 119(27):14919–14928, 2015.
- [30] Hongwei Zhu, Sam Teale, Muhammad Naufal Lintangpradipto, Suhas Mahesh, Bin Chen, Michael D. McGehee, Edward H. Sargent, and Osman M. Bakr. Long-term operating stability in perovskite photovoltaics. *Nature Reviews Materials*, 8(9):569–586, 2023.